

Cadmium Isotope Variations in the Oceans

A thesis presented for the degree of
Doctor of Philosophy of Imperial College London
April 5, 2012

Zichen Xue

Department of Earth Science and Engineering
South Kensington Campus
Imperial College London
United Kingdom

I certify that this thesis, and the research to which it refers, are the product of my own work, and that any ideas or quotations from the work of other people, published or otherwise, are fully acknowledged in accordance with the standard referencing practices of the discipline.

Zichen Xue

Copyright

Copyright in text of this thesis rests with the Author. Copies (by any process) either in full, or of extracts, may be made **only** in accordance with instructions given by the Author and lodged in the doctorate thesis archive of the college central library. Details may be obtained from the Librarian. This page must form part of any such copies made. Further copies (by any process) of copies made in accordance with such instructions may not be made without the permission (in writing) of the Author.

The ownership of any intellectual property rights which may be described in this thesis is vested in Imperial College, subject to any prior agreement to the contrary, and may not be made available for use by third parties without the written permission of the University, which will prescribe the terms and conditions of any such agreement. Further information on the conditions under which disclosures and exploitation may take place is available from the Imperial College registry.

Abstract

A number of previous studies have identified considerable mass dependent variations in the Cd isotope compositions of both terrestrial and extraterrestrial samples. On Earth, stable isotope effects for Cd are particularly prominent in the oceans, and the largest natural terrestrial Cd isotope fractionations of about 4‰ have been reported for Cd-depleted surface seawater. These effects have generally been attributed to reflect isotope fractionation of Cd that occurs during biological uptake and utilization of dissolved seawater Cd. This finding confirms studies, which identified Cd as an essential marine micronutrient. This was first inferred from the phosphate-like distribution of the metal in the oceans and more recently demonstrated by work, which confirmed that Cd can act as catalytic metal ion in carbonic anhydrase, an enzyme which plays a central role in inorganic carbon acquisition of phytoplankton in the oceans. The marine Cd isotope fractionations are thus of interest, as they can be used to study the cycling of the micronutrient Cd as well as its impact on ocean productivity and the global carbon cycle.

As part of this PhD project, I have developed a new procedure for Cd isotope analyses of seawater, which is suitable for samples as large as 20 L and Cd concentrations as low as 1 pmol/L. The procedure involves use of a ^{111}Cd - ^{113}Cd double spike, co-precipitation of Cd from seawater with $\text{Al}(\text{OH})_3$ Cd purification by column chromatography, and subsequent isotope analysis by MC-ICP-MS (multiple collector inductively coupled plasma mass spectrometry). The methodology can routinely provide $\epsilon^{114/110}\text{Cd}$ data with a precision of about $\pm 0.5\epsilon$ (2sd) when at least 20-30 ng of natural Cd are available for analysis. However, even seawater samples with Cd contents of only 1-3 ng can be analysed with a reproducibility of about ± 3 to $\pm 5\epsilon$.

The new methodology was applied to investigate Cd isotope variations in about 150 seawater samples from the North Atlantic Ocean, the Southern Ocean HNLC (high nutrient low chlorophyll) region, and the Peruvian oxygen minimum zone in the Eastern Pacific Ocean. The samples exhibited variable but highly systematic Cd isotope variations that were comprehensively interpreted in the context of previously published oceanographic and biogeochemical data.

Acknowledgements

First and foremost I would like to thank my supervisors, Professor Dr. Mark Rehkämper and Dr. Tina van de Flierdt, who have guided, supported, guided and encouraged me throughout the completion of the thesis. I also would like to express my gratitude for their generous allowance of time and advice to discuss my work, suggest detailed improvements and corrections for the preparation of our papers and my thesis.

I sincerely appreciate my supervisors for giving me the opportunity and invaluable experience to work in the excellent MAGIC research group at Imperial College London. I acknowledge Rasmus Andreasen, Roz Coggon, Marion Ferrat, Myriam Lambelet, Fiona Larnier, Carl Palk, Dong Shuofei and the other members of the MAGIC group for helpful discussions and contributions. I am grateful to Barry J Coles for his help in keeping the mass spec lab running. I also would like to thank my tutor Saskia Goes for her support and help throughout my PhD studies.

Furthermore, I am grateful to Hein. J. de Baar and Rob Middag for providing the seawater samples from the 2008 IPY GEOTRACES expedition 'Zero & Drake' aboard RV Polarstern (ANT 24-3). Many thanks to Martin Frank and Lothar Stramma for offering me the chance to go to the cruises METEOR M77/3 and M77/4 to collect the seawater samples used in this thesis. We thank all the people who funded and organized this cruise in the context of the Sonderforschungsbereich (SFB-754, 'Climate - Biogeochemistry Interactions in the Tropical Ocean'). Much appreciated for the discussion with Patricia Grasse. I also acknowledge a joint NERC research grant with Prof. Andy Ridgwell and Dr. Mark Rehkämper, which supported this work.

I feel very honored to receive the Lee Family Scholarship to cover my maintenance, tuition fees and some research expenses, such as a travel grant to attend the Goldschmidt meeting in Davos, Switzerland in 2009 and the Ocean Sciences Meeting in Portland, Oregon, USA in 2010. Moreover, I acknowledge a student travel grant by the Geological Society to attend the European Geosciences Union General Assembly (EGU) Vienna in 2011. Finally, I am thankful for obtaining the Goldschmidt' student travel grant to students at EU institutions to attend the Goldschmidt meeting in Knoxville, Tennessee, USA in 2010.

I appreciate my friendship with Rui Li, Veronique Mahue, Jacques Pronchery, Nuno Vieira da Silva, Meng Wang, Fan Zhang to share many unique and special experiences with me.

I am also honoured to thank my parents and grandparents for the continued support. I appreciate the love and support from Orlando Döhring very much.

Zichen Xue

Table of contents

Abstract	4
1 Introduction	19
1.1 Research background	19
1.1.1 Cadmium in the oceans	19
1.1.2 Cd isotopes in the oceans	22
1.1.3 The sources and sinks of Cd in the ocean reservoir	27
1.1.4 Cd isotope analysis by multiple collectors inductively coupled plasma mass spectrometry (MC-ICP-MS)	30
1.1.5 Cd isotope fractionation models for seawater samples	31
1.2 Research motivation and objectives	36
1.2.1 Development of new methodology to enable precise Cd isotope analyses of large-volume Cd-depleted seawater samples	36
1.2.2 Comparison of the marine distribution of Cd in different environments using coupled Cd concentration and isotope data	40
1.2.3 Re-examination of processes that affect the Cd isotope composition of seawater	41
1.3 Outline of this thesis	42
2 A New Methodology for Precise Seawater Cadmium Isotope Analyses	51
2.1 Introduction	52
2.2 Experimental	55
2.2.1 Samples and reference materials	55
2.2.2 Reagents and general laboratory procedures	56
2.2.3 Sample preparation for Cd isotope analysis	57
2.2.4 Cd isotope measurements	61
2.3 Results and discussion	65
2.3.1 Results for the JMC Cd Münster 'zero epsilon' standard	65
2.3.2 Results for other Cd isotope reference materials	66
2.3.3 Results for Solent Strait seawater	70
2.3.4 Results for SAFe D1 seawater	72
2.3.5 Results for the 2008 GEOTRACES Atlantic intercalibration samples	75

2.4	Conclusions	77
2.5	Acknowledgments	78
3	Cadmium Isotope Fractionation in the Southern Ocean	82
3.1	Introduction	84
3.2	Samples	85
3.3	Analytical methods	89
3.4	Background information and results	90
3.4.1	Key water masses	90
3.4.2	Hydrology and nutrient concentrations for zero meridian surface seawater	91
3.4.3	Cd concentration and isotope compositions for zero meridian surface seawater	92
3.4.4	Hydrology and nutrient concentrations for the depth profiles	95
3.4.5	Cd concentrations and isotope compositions for the depth profiles	96
3.5	Discussion	99
3.5.1	Biological Cd isotope fractionation of surface water in the Southern Ocean HNLC region	99
3.5.2	Cd isotope fractionation of seawater samples from depth profiles in the Southern Ocean HNLC region	100
3.5.3	Comparison of Cd isotope variations for the Southern Ocean HNLC region with global oceans	105
3.6	Conclusions	112
3.7	Acknowledgements	113
4	Cd Cycling in the Eastern Equatorial Pacific Ocean (3°S-14°S)	122
4.1	Introduction	124
4.2	Samples and hydrographic background	125
4.2.1	Samples	125
4.2.2	Current System of the Eastern Equatorial Pacific Ocean	125
4.2.3	Water masses of the Eastern Equatorial Pacific Ocean	129
4.2.4	Hydrography of the Peruvian Oxygen Minimum Zone	129
4.3	Analytical methods	131
4.4	Results and discussion	132
4.4.1	Hydrological data	132
4.4.2	Cd concentration and isotope composition profiles and their relationship with oxygen contents	135
4.4.3	Comparison of Cd concentration and isotope composition depth profiles for the OMZ in the EEP with data for other locations	152
4.4.4	Cd isotope fractionation in the Peruvian OMZ	158
4.5	Conclusion	168
4.6	Acknowledgements	169

5	Conclusions and Outlook	174
5.1	Summary and conclusions	174
5.2	Outlook for future work	175
5.2.1	Further investigation of Cd isotope fractionation mechanisms in the ocean	175
5.2.2	Investigation of the sources and sinks of Cd in the oceans	176
5.2.3	Understanding the $\epsilon^{114/110}\text{Cd}$ -[Cd] correlations of the modern ocean as a basis for developing the Cd isotope proxy for past oceans . . .	177
A	List of publications	179
A.1	Published journal papers:	179
A.2	Published conference abstracts:	180
A.3	The following journal paper has been submitted:	181
A.4	The following journal papers are in preparation:	181

List of Tables

2.1	Column chemistry procedures for the isolation of Cd from seawater.	60
2.2	Typical within-day reproducibility of Cd isotope data (reported as $\epsilon^{114/110}\text{Cd}$) for multiple analyses of Cd double spike-natural Cd mixtures at different concentrations and $S/N \approx 1$	63
2.3	Summary of Cd isotope data (as $\epsilon^{114/110}\text{Cd}$) from this study and the literature, for various standards and reported relative to the JMC Cd Münster zero-epsilon isotope reference material.	67
2.4	Cd concentrations and isotope compositions for five sub-samples of Solent Strait Seawater (SSW) that were analyzed with and without the aid of $\text{Al}(\text{OH})_3$ co-precipitation.	68
2.5	Cd concentrations and isotope compositions for seawater reference material SAFe D1 and the GEOTRACES intercalibration samples GDI, GSI, and GPrI	69
3.1	Cd concentrations and isotope compositions for surface seawater samples from Weddell Gyre along the Zero Meridian	86
3.2	Cd concentrations and isotope compositions for seawater samples from three depth profiles collected at Weddell Gyre and Drake Passage	87
4.1	Cd concentrations and isotope compositions of seawater depth profiles in the Peruvian OMZ	156

List of Figures

1.1	Cd and PO_4^{3-} depth profiles for the Atlantic Ocean and Pacific Ocean (from Rehkämper et al. (2011)). Data are from Boyle et al. (1976) and Bruland (1980).	20
1.2	Compilation of published results which shows the correlation of Cd and PO_4^{3-} concentrations. The data were compiled from numerous published studies (Bruland et al., 1978; Bruland, 1980; Danielsson et al., 1985; Martin et al., 1989; Martin, 1990; Martin et al., 1990; Hunter and Ho, 1991; Nolting et al., 1991; Westerlund et al., 1991; Yeats and Westerlund, 1991; Frew and Hunter, 1992, 1995; Saager et al., 1992; de Baar et al., 1994; Löscher et al., 1998; Fitzwater et al., 2000; Lacan et al., 2006).	21
1.3	Cd isotopes and their natural abundances.	26
1.4	Schematic diagram of the Nu Plasma MC-ICP-MS instrument (from Rehkämper et al. (2001)).	38
1.5	Locations of seawater samples analysed as part of this PhD research. Cd data determined in this PhD project are shown in the dots. Cd data from previous studies (Ripperger et al., 2007; Abouchami et al., 2011) are shown in the squares. Cd data from Southern Ocean HNLC region are in red. These data are from Table 3.1 and 3.2 and from a previous study by Abouchami et al. (2011). Cd data for the non-HNLC open ocean areas are from the Arctic, the North Atlantic and the North Pacific Ocean, and are shown in blue. These Cd data are reported in Table 2.3 and previous studies by Ripperger and Rehkämper (2007); Ripperger et al. (2007). Cd data from Peruvian OMZ are reported in table 4.1 and show Cd behavior in a non-HNLC semi-open system OMZ, which are shown in green.	39
2.1	Locations of seawater samples analyzed in this study.	54
2.2	Plot of Cd isotope data (as $\epsilon^{114/110}\text{Cd}$) for mixtures of the Cd double spike with the JMC Cd Münster standard, obtained at various S/N ratios (molar ratio of Cd from spike vs. natural Cd from the standard). The $\epsilon^{114/110}\text{Cd}$ values were determined and calculated relative to a Cd double spike - JMC Cd Münster mixture with S/N = 1. The error bars denote the 2sd uncertainties determined from the results of multiple analyses.	64

2.3	Plot of $\epsilon^{114/110}\text{Cd}$ values vs. Cd concentrations for the five sub-samples of Solent Strait seawater SSW (SSW-A to SSW-E; see Table 2.4.). A significant variability of Cd concentrations is correlated with smaller changes in $\epsilon^{114/110}\text{Cd}$ and the correlation is in accord with Cd isotope fractionation by biological utilization and a fractionation factor of $\alpha = 1.0005 \pm 0.0003$ (red dashed line). The uncertainties are taken from Table 2.4	71
2.4	Depth profiles of Cd concentrations (blue filled squares) and isotope compositions (as $\epsilon^{114/110}\text{Cd}$; red filled dots) for the GEOTRACES intercalibration samples GSI and GDI (surface and deep water, respectively) as well as the GPrI depth profile samples from the BATS station in the North Atlantic (Table 2.5). Together, these samples provide the first full Cd isotope depth profile for the Atlantic Ocean, and this is similar to a published depth profile for the central Pacific (Station 7; (Ripperger et al., 2007)). The Cd concentration of GDI is not plotted, as this deviates significantly from the essentially constant values of the GPrI samples at depths > 1000 m (Table 2.5). This difference presumably reflects that the GDI and GPrI samples are from two different casts.	73
2.5	Cadmium isotope compositions (as $\epsilon^{114/110}\text{Cd}$) vs. Cd concentrations for the GEOTRACES intercalibration samples from the BATS station in the Atlantic Ocean (Table 2.5) and previous data from the literature (Ripperger et al., 2007). The dashed lines denote calculated Rayleigh fractionation trends for fractionation factors of $\alpha \approx 1.0002$ and 1.0006	74
3.1	Locations of seawater samples analyzed in this study. This study includes samples from 3 depth profiles in the Drake Passage (Station 249, in purple), and the northwestern Weddell Sea (Station 216, in yellow) & central Weddell Sea (Station 198, in green) as well as 13 surface waters from the Zero Meridian between 62° and 69°S (in orange). The black dots represent the data reported in a previous study (Abouchami et al., 2011). The boundary of Weddell Gyre is shown by red dash circle. WG = Weddell Gyre, ACC = Antarctic Circumpolar Current, SAZ = Sub Antarctic Zone, PFZ = Polar Frontal Zone, and AAZ = Antarctic Zone.	88
3.2	The variations of Cd concentration and isotopic composition, hydrologic and nutrient CTD data for the Zero Meridian surface water samples. The samples analyzed in this study are in orange filled dots and the black dots depict the data from a previous study (Abouchami et al., 2011). ACC = Antarctic Circumpolar Current, SAZ = Sub Antarctic Zone, PFZ = Polar Frontal Zone, and AAZ = Antarctic Zone.	93
3.3	Depth distribution of hydrological parameters and nutrient data for Station 249, 216 and 198. Station 249 is in the Drake Passage (in purple), Station 216 is in the Scotia Sea (in yellow) and Station 198 is in the Weddell Gyre (in green).	94

- 3.4 Depth profiles of Cd concentrations and isotope compositions for Station 249, 216 and 198. Cd concentration data are shown by dark blue dots and isotope composition data are shown by red dots. 97
- 3.5 Correlation of Cd isotope compositions and concentrations for surface water samples from the ACC and Weddell Gyre along the Zero Meridian. The Cd data from the Weddell Gyre obtained in this study are listed in Table 3.1 and shown in orange dots. The data from the ACC and Weddell Gyre in a previous study (Abouchami et al., 2011) are shown by the black and white dots, respectively. The dashed lines denote calculated Rayleigh fractionation trends for fractionation factors of $\alpha \approx 1.0002$ and 1.0006 98
- 3.6 Plots of $\epsilon^{114/110}\text{Cd}$ vs. $[\text{Cd}]$ for the seawater samples from depth profiles in the Southern Ocean HNLC region. The Cd data from three depth profiles at Station 249, 216 and 198 are plotted in purple, yellow and green (Table 3.2). The light to dark shading represents water samples from ≤ 100 m, 100-500 m and ≥ 500 m. Surface water samples from the Weddell Gyre along the Zero Meridian (data in this study in Table 3.1 and previous data from Abouchami et al. (2011)) are shown in white dots. The light blue dots present the Zero Meridian Surface water samples from the ACC. The red dashed line denotes calculated Rayleigh fractionation trends for fractionation factors of $\alpha \approx 1.0005$. The blue line demonstrates mixing of surface water from the Weddell Gyre with remineralized biomass with a negative $\epsilon^{114/110}\text{Cd}$ values of about -1.5. The green line illustrates the Rayleigh fractionation trends, which were calculated for the isotope composition of an accumulated biomass preferentially incorporating light Cd with fractionation factor of $\alpha \approx 1.0005$ 101
- 3.7 Plots of $\epsilon^{114/110}\text{Cd}$ vs. $1/[\text{Cd}]$ for the seawater samples from depth profiles in the Southern Ocean HNLC region. The Cd data from three depth profiles at Station 249, 216 and 198 are plotted in purple, yellow and green (Table 3.2). The shading from light to dark represents water samples from ≤ 100 m, 100-500 m and ≥ 500 m. Surface water samples from the Weddell Gyre along the Zero Meridian (data in this study in Table 3.1 and previous data from Abouchami et al. (2011)) are shown in white dots. The light blue dots show the Zero Meridian Surface water samples from the ACC. The blue line demonstrates mixing of surface water from the Weddell Gyre with remineralized biomass with a negative $\epsilon^{114/110}\text{Cd}$ value of about -1.5. The correlation of Cd isotope compositions and $1/[\text{Cd}]$ clearly illustrates that the mixing of surface waters (from Zero Meridian and depth profiles) with biogenic particles drives the Cd isotope composition with the value of $\epsilon^{114/110}\text{Cd} = +1$ at the intermediate depth (100-500m) in the Weddell Gyre. 103

- 3.8 The correlation of potential temperature and salinity for the seawater samples from 3 vertical profile stations and the surface water samples along Zero Meridians. The potential temperature and salinity data are from CTD values. The data from Station 198 (in green), 216 (in yellow), 249 (in purple) and the surface water samples from Weddell Gyre (in orange) and ACC (in black) which were discussed in this study and a previous study (Abouchami et al., 2011), are plotted in this figure, along with the CTD data from other stations collected on the same cruise. AAIW = Antarctic Intermediate Water, LCDW = Lower Circumpolar Deep Water, UCDW= Upper Circumpolar Deep Water, AABW = Antarctic Bottom Water, AASW = Antarctic Surface Water. 107
- 3.9 Plots of Cd isotope compositions vs. concentrations for the samples from Southern Ocean HNLC region and non-HNLC open ocean area. The data plotted in this figure are from this study (Table 3.1, 3.2) and previous studies (Ripperger and Rehkämper, 2007; Ripperger et al., 2007; Xue et al., 2012). The samples from upper 200m are shown in orange and blue, respectively, whilst below 200m in grey. The dashed lines are calculated Rayleigh fractionation trends $\alpha \approx 1.0002$ and 1.0005. 108
- 3.10 The correlation of Cd versus PO_4^{3-} concentrations in the Southern Ocean HNLC region. The grey dots show the Cd and PO_4^{3-} concentrations from a number of previous studies (Bruland et al., 1978; Bruland, 1980; Jones and Murray, 1984; Danielsson et al., 1985; Martin et al., 1989; Martin, 1990; Martin et al., 1990b; Hunter and Ho, 1991; Nolting et al., 1991; Westerlund et al., 1991; Yeats and Westerlund, 1991; Saager et al., 1992; Frew and Hunter, 1992, 1995; de Baar et al., 1994; Löscher et al., 1998; Fitzwater et al., 2000; Lacan et al., 2006). The data (in blue) from the North Pacific (square), the North Atlantic (diamond) and the Arctic Oceans (triangle) plotted in this figure are from Ripperger and Rehkämper (2007). All the data from this study and (Abouchami et al., 2011) show a linear correlation with slope = 0.64 ($R^2 = 0.93, n = 66$). 109
- 3.11 Cadmium isotope compositions vs. the ratio of $[\text{Cd}]/[\text{PO}_4^{3-}]$ of the water samples from the Southern Ocean. The three depth profiles at Station 249 (in purple), Station 216 (in yellow) and Station 198 (in green) as well as the surface water samples from Weddell Gyre (in orange) and ACC (in black) along the Zero Meridian from this study together with the data from (Abouchami et al., 2011) are shown. 110

4.1	Locations of seawater samples analyzed in this study. Cd concentrations and isotope compositions were determined for 74 seawater samples from the oxygen minimum zone (OMZ) in the Eastern Equatorial Pacific Ocean (EEP) off the coast of Peru during the research cruise METEOR M77/3 and M77/4. The samples are from 9 depth profiles located at about 3°S-14°S and 77°W - 86°W. These profiles cover: (A) two meridional (north-south) sections - (1) at 85.83°W (offshore Stations 109, 134, 97, 93; in blue colors) and (2) between 77.06°W and 82.02°W (nearshore Stations 117, 124, 11, 78; in red colors); (B) one zonal (west-east) section at 14°S (Stations 93, 86, and 78; in blue, purple and red, respectively).	126
4.2	Sample locations and water masses	128
4.3	The depth variations of salinity, temperature and oxygen CTD data for the 9 stations in this study.	140
4.4	Temperature versus salinity for seawater samples from the 9 vertical profiles. ESW = Equatorial Surface Water, STSW = Subtropical Surface Water, SAAW = Subantarctic Intermediate Water, ESPIW = Eastern South Pacific Intermediate Water, AAIW = Antarctic Intermediate Water, LCDW = Lower Circumpolar Deep Water.	141
4.5	The hydrology section profiles of the W-E transects and N-S transects in the upper 500m.	148
4.6	Cd concentrations and isotope compositions for 9 stations.	149
4.7	Vertical profiles of Cd concentration, Cd isotope compositions and oxygen contents in the nearshore and offshore N-S sections. Cd concentration data are shown in dark blue squares; Cd isotope composition data are shown in red dots; oxygen concentrations are shown in the green solid line.	151
4.8	Profiles of Cd concentration, Cd isotope compositions and oxygen contents in the W-E section at 14°S. Cd concentration data are shown in dark blue squares; Cd isotope composition data are shown in red dots; oxygen concentrations are shown in the green solid line.	153
4.9	Comparison of vertical profiles of Cd concentrations and isotope compositions from the Weddle Sea, the North Atlantic Ocean and the Eastern Equatorial Pacific Ocean. Cd concentration data are shown in dark blue squares and isotope composition data are shown in red dots.	155

- 4.10 Correlation of Cd isotope compositions and Cd concentrations for water samples from the OMZ in the Eastern Equatorial Pacific Ocean, the Southern Ocean HNLC region, and non-HNLC open ocean areas. The data plotted in this figure are from this study (Table 4.1) and previous studies ((Ripperger and Rehkämper, 2007; Abouchami et al., 2011; Xue et al., 2012); Chapter 3 - Table 3.1, 3.2). The samples from the OMZ in the Eastern Equatorial Pacific Ocean and the Southern Ocean HNLC region are shown in the green squares and orange dots. The Cd data presented for non-HNLC open ocean areas are from the Arctic, the North Atlantic and the North Pacific Ocean, which are shown in blue triangles, diamonds and squares, respectively. The dashed lines denote the calculated Rayleigh fractionation trends for closed system fractionation factors of $\alpha \approx 1.0002$ and 1.0005 with deep water $[Cd] = 0.77\text{nM}$ and $\epsilon^{114/110}\text{Cd} = 2.5$ 163
- 4.11 Steady state model for Cd isotope fractionation of seawater from the upper 50 m in the Peruvian OMZ. Cd data (Table 4.1) from the offshore and nearshore stations are shown in diamonds and dots, respectively. In this steady state model, the initial Cd concentration and isotope compositions of the upwelled water masses are applied with $[Cd] = 0.7 - 0.9 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +4.5 - 6.5$, which are the values from seawater at 100-300m in the Peruvian OMZ. The Cd concentrations and isotope compositions of the seawater from upper 50m in the Peruvian OMZ analyzed in this study, fall along the calculated Cd isotope fractionation trends with steady state model and fractionation factor α between 1.0001 and 1.0003. . . 164
- 4.12 Cd isotope fractionations of seawater at the intermediate depth (200-1500m) in the Peruvian OMZ. Cd data (Table 4.1) from the offshore and nearshore stations are shown in diamonds and dots, respectively. Assuming that water mass upwell from 1500m, the blue dashed lines represent the open system Cd isotope fractionation trend, which is calculated using steady state model with fractionation factor $\alpha \approx 1.0006$. If Cd isotope variations in the seawater at the intermediate depth happen in the closed system, the green dashed line indicates the Cd isotope fractionation trend calculated using Rayleigh fractionation model with fractionation factor of $\alpha \approx 1.0005$. The water mass from 1500m has the average value of $[Cd] = 1.0 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +4$. The steady state model and Rayleigh fractionation model have been discussed in section 1.1.5. 165
- 4.13 Water masses mixing trend for Cd isotope fractionation at the intermediate depths. Cd data (Table 4.1) from the offshore and nearshore stations are shown in diamonds and dots, respectively. The purple line shows the water masses mixing at the intermediate depth, which is calculated using the water masses mixing model with water mass from 1500m having average value of $[Cd] = 1.0 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +4$ and water mass from 100-300m having $[Cd] = 0.7 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +6$. The water masses mixing model has been discussed in section 1.1.5. 166

- 4.14 Cd isotope fractionation trend at intermediate depth associated with organic material remineralization. Cd data (Table 4.1) from the offshore and nearshore stations are shown in diamonds and dots, respectively. The water mass from 100-300m with $[Cd] = 0.7 \text{ nmol/kg}$ and $\epsilon^{114/110}Cd = +6$ is applied as the initial Cd value to the organic material remineralization model. The calculated trend demonstrates Cd isotope variations at the intermediate depth in association with a continued release of Cd from organic material remineralization. 167

Chapter 1

Introduction

1.1 Research background

1.1.1 Cadmium in the oceans

The Cd concentrations in seawater show a nutrient-like distribution, which is very similar to the distribution of phosphate, a marine macronutrient (Boyle et al., 1976; Bruland, 1980), Fig. 1.1. Both Cd and PO_4^{3-} display low concentrations in surface waters due to marine biological utilization. When organisms cease, the organic material sinks through the water column and is subsequently decomposed at depth. Hence, Cd and PO_4^{3-} are remineralized into the dissolved form (Boyle et al., 1976; Bruland, 1980). However, a number of previous investigations also state that Cd may be passively adsorbed onto organic matter (Collier and Edmond, 1984; Yee and Fein, 2001; Dixon et al., 2006), which might also result in a nutrient-like distribution of dissolved Cd in seawater.

Recent studies suggest that Cd, as a marine micronutrient, plays an important role in marine biological processes. In particular, it has been shown that Cd can substitute for Zn in the enzyme carbonic anhydrase, which plays an important role in the process of inorganic carbon acquisition (Price and Morel, 1990; Cullen et al., 1999; Sunda and Huntsman, 2000; Lane et al., 2005; Xu et al., 2008). The substitution of Zn by Cd was also suggested for other Zn-metalloenzymes, such as alkaline phosphatase, which allows phytoplankton

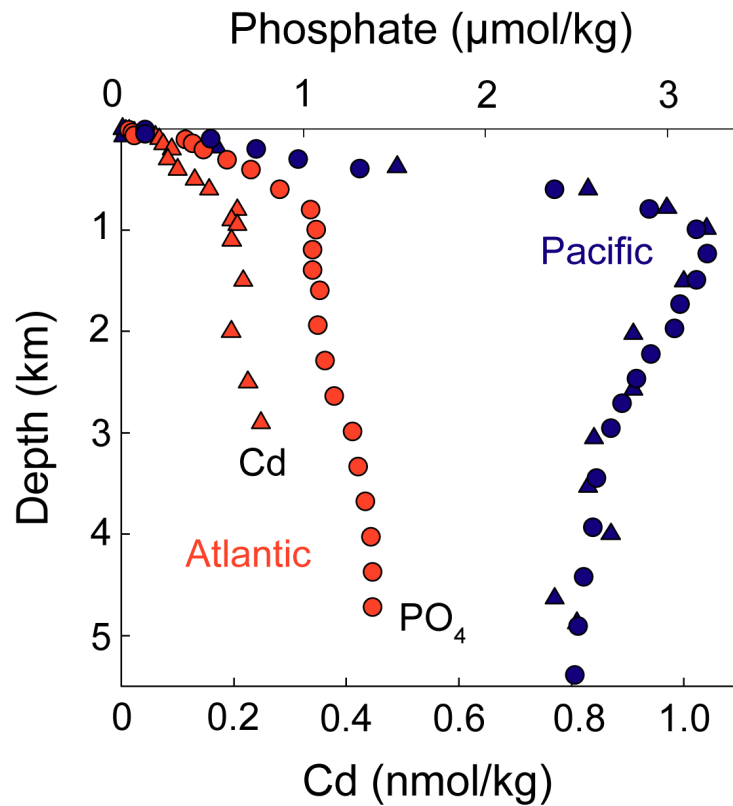


Figure 1.1: Cd and PO_4^{3-} depth profiles for the Atlantic Ocean and Pacific Ocean (from Rehkämper et al. (2011)). Data are from Boyle et al. (1976) and Bruland (1980).

to acquire phosphate from organic compounds (Morel and Price, 2003). These results indicate that the behavior of Cd, as a micronutrient, in the oceans is probably a consequence of true biological demand for Cd during growth of marine phytoplankton.

The vertical distributions of Cd and phosphate are further modified by oceanic circulation, which creates water masses with distinct chemical signatures. A key feature is that the concentrations of Cd and phosphate are significantly higher in the deep-water of the Pacific Ocean than in Atlantic Ocean deep-water. This difference reflects the progressive accumulation of remineralized nutrients, as deep-water masses pass from the Atlantic Ocean

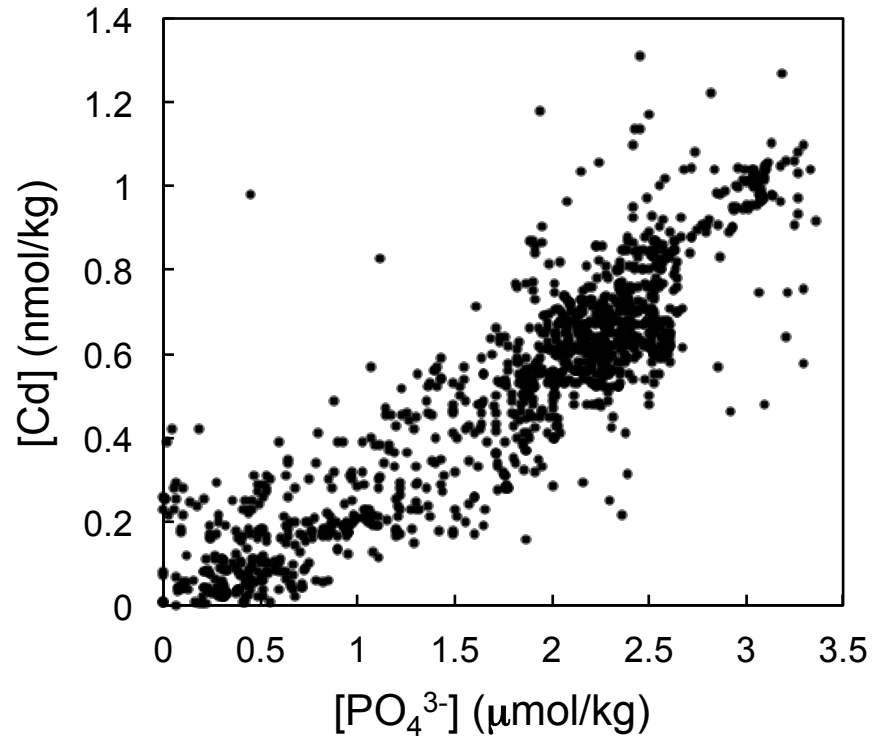


Figure 1.2: Compilation of published results which shows the correlation of Cd and PO_4^{3-} concentrations. The data were compiled from numerous published studies (Bruland et al., 1978; Bruland, 1980; Danielsson et al., 1985; Martin et al., 1989; Martin, 1990; Martin et al., 1990; Hunter and Ho, 1991; Nolting et al., 1991; Westerlund et al., 1991; Yeats and Westerlund, 1991; Frew and Hunter, 1992, 1995; Saager et al., 1992; de Baar et al., 1994; Löscher et al., 1998; Fitzwater et al., 2000; Lacan et al., 2006).

through the Southern Ocean to the Pacific Ocean (Donat and Bruland, 1995). Hence, deep water masses with older ventilation ages have higher nutrient (and Cd) contents.

The main input of Cd into the ocean is from rivers, the deposition of atmospheric dust particles in surface waters and hydrothermal fluids. Moreover, Cd is involved in many internal cycles, such as biological utilization and remineralisation, prior to being incorporated into marine sediments (Collier and Edmond, 1984; Rosenthal et al., 1995). As a

consequence of these processes, Cd displays an intermediate residence time in the ocean of about 10 to 100 kyr, which is similar to that of phosphorus (Bewers and Yeats, 1977; Martin and Whitfield, 1983; Ruttenberg, 2003). The geochemistry of Cd in the oceans has attracted significant scientific interest for more than 30 years (Rehkämper et al., 2011). The interest is primarily based on the approximately linear correlation of Cd and phosphate concentrations in seawater, which is modified by a pronounced 'kink' at intermediate Cd and phosphate abundances (Fig. 1.2). A number of previous studies have investigated the origin of the $[\text{Cd}]-[\text{PO}_4^{3-}]$ correlation and, in particular, the processes that may be responsible for the conspicuous 'kink' (Frew and Hunter, 1992; de Baar et al., 1994; Elderfield and Rickaby, 2000; Cullen, 2006). For example, this 'kink' has been described as an artefact of a $[\text{Cd}]-[\text{PO}_4^{3-}]$ fractionation trend, which is not linear but slightly curved, due to preferential biological uptake of Cd relative to phosphate (Elderfield and Rickaby, 2000).

Moreover, Cd has also been applied as a paleoclimate proxy. This application is based on the observation that Cd is incorporated into the tests of foraminifera in proportion to the Cd (and hence phosphate) concentration of the ambient seawater (Boyle, 1981, 1992; Rickaby and Elderfield, 1999; Ripperger et al., 2008). Hence, the Cd/Ca data of foraminifera have been used as an important tool in paleoceanography, to trace water masses and past marine nutrient utilization (Henderson, 2002; Lynch-Stieglitz, 2006).

1.1.2 Cd isotopes in the oceans

Isotopic analyses have previously provided a wealth of information on the marine cycling of nutrient elements, such as nitrogen (Sigman et al., 1999), silicon (De La Rocha et al., 1998; Reynolds et al., 2006) and others. Therefore, further insight into the processes governing the marine distribution of Cd, may be provided by Cd isotope measurements.

At the time when this research project began, the published Cd isotope database for seawater samples was limited to the results for only 50 samples in total from two studies (Lacan et al., 2006; Ripperger and Rehkämper, 2007). During this PhD study, another study was published, in which Cd isotope composition for another 20 surface seawater samples

were reported (Abouchami et al., 2011). Nevertheless, the published research on Cd isotope fractionations in the seawater is still very limited.

The first investigation of Cd isotopes in seawater was published by Lacan et al. (2006). The technique of external normalization to the added Ag was used in this study for the instrumental mass bias correction of the Cd isotope data, a method that was first applied by Wombacher et al. (2003). With this technique, Cd isotope compositions for 28 seawater samples from two depth profiles in the northwest Pacific Ocean and the Mediterranean Sea were determined by MC-ICP-MS. However, these samples displayed only a limited variability in Cd concentrations and isotope compositions, with $\epsilon^{114/110}\text{Cd}$ values between about -4 and +2 ($\epsilon^{114/110}$ denotes variations of $^{114}\text{Cd}/^{110}\text{Cd}$ relative to a standard in part per 10,000; relative to NIST SRM 3108 Cd standard).

Due to the relatively large uncertainty of these measurements of about $\pm 3\epsilon$ (2sd), the study was unable to clearly determine Cd isotope variations in seawater. However, despite the limited variation, the samples exhibited a statistically significant correlation between Cd isotope compositions and concentrations, from which an isotope fractionation factor of 1.0014 ± 0.0006 (2sd) was inferred. This result was further supported by a culture experiment, which yielded organisms (freshwater phytoplankton) systematically enriched in isotopically light Cd. This result was interpreted to reflect kinetic isotope fractionation that was produced during biological uptake and utilization of dissolved Cd.

To improve the precision of Cd isotope analysis, Ripperger and Rehkämper (2007) developed a more precise and accurate double spike procedure for the determination of Cd isotope compositions. With this method, they were able to achieve precisions of about $\pm 1\epsilon$ for the determination of $\epsilon^{114/110}\text{Cd}$. This is about a factor of 3 to 5 more precise compared to the external normalisation technique of Wombacher et al. (2003). The subsequent study of Ripperger et al. (2007) provided the first comprehensive Cd isotope dataset for seawater. Results were presented for 22 samples, representing both surface waters and depth profiles, from 8 locations in the Arctic Ocean, the Atlantic Ocean, the Pacific Ocean and the Southern Ocean. The most important conclusions of this study can be summarized as

follows:

- (A) Large variations in Cd isotope compositions with values of $\epsilon^{114/110}\text{Cd}$ from 0 to $+38 \pm 6$ (relative to NIST SRM 3108 Cd standard) were observed in this study and the majority of the samples defined an inverse relationship between dissolved Cd contents and isotope compositions. The large Cd isotope variations observed in the upper water column were thought to be due to biological utilization of Cd. This was supported by the fact that the Cd data are in accord with closed system Rayleigh fractionation trends with fractionation factors $\alpha \approx 1.0002$ to 1.0006 . These results broadly agree with the conclusion of the previous study (Lacan et al., 2006), which obtained an isotope fractionation factor of about 1.0014 ± 0.0006 (2sd) for utilization of Cd by cultured phytoplankton. The minor difference between the fractionation factors inferred from seawater and the culturing experiments may reflect additional marine processes.
- (B) A few samples did not follow the broad Rayleigh fractionation trend but exhibited both low Cd contents and Cd isotope compositions with $\epsilon^{114/110}\text{Cd}$ of about 0 to +5 (relative to NIST SRM 3108 Cd standard). These results were thought to be caused by mixing processes. In particular, it was shown that mixing of Cd-rich water masses with Cd-depleted water could generate large deviations from the main fractionation trend.
- (C) The Cd-rich deep waters ($\geq 900\text{m}$ depth) from the Arctic Ocean, Atlantic Ocean, Southern Ocean and Pacific Ocean were observed to have nearly constant and unfractionated Cd isotope composition with an average value of $\epsilon^{114/110}\text{Cd} = +2.9 \pm 1.0$ (2sd; relative to NIST SRM 3108 Cd standard). This result also agrees with the previous observation that the average Cd isotope composition of 7 deep-water samples from depths $\geq 1\text{ km}$ in the Pacific Ocean is $+0.7 \pm 1.4\epsilon$ (Lacan et al., 2006). Note that the individual data from the latter study (Lacan et al., 2006) have a large uncertainty of about $\pm 3\epsilon$. However, the Cd concentrations of the deep-water samples increase systematically along the global deep-water pathway, with values of $0.20 - 0.30\text{ nM}$ in the Arctic and Atlantic Ocean to $0.80 - 1.0\text{ nM}$ in the Pacific Ocean.

At present, most laboratories use the technique of MC-ICP-MS for Cd isotope analyses. However, Abouchami et al. (2011) carried out Cd isotope measurements for 20 surface water samples from the Southern Ocean High Nutrient Low Chlorophyll (HNLC) region using Thermal Ionization Mass Spectrometry (TIMS, ThermoFisher Triton). The isotope fractionation and instrumental bias were quantified with the aid of a ^{106}Cd - ^{108}Cd double spike, which featured a composition that was optimized using numerical methods (Galer, 2007; Schmitt et al., 2009a). Abouchami et al. (2011) found that their Southern Ocean samples defined two distinct correlations in a plot of Cd isotope composition versus concentration, which were consistent with different Rayleigh fractionation factors. The two groups of samples, furthermore, roughly corresponded to differences in the location of sampling sites, which were either within the Weddell Gyre (WG) or the Antarctic Circumpolar Current (ACC). Based on this, the distinct Cd isotope fractionation trends were inferred to be caused by differences in phytoplankton biomass, community composition, and their physiological uptake mechanisms in the WG and the ACC. Hence, Abouchami et al. (2011) concluded that Cd isotopes can be used as a paleoclimate proxy to study marine primary productivity and the global carbon cycle.

In summary, the published Cd isotope data for seawater suggest that Cd isotopes may potentially have important applications in marine research: (I) Cd isotope compositions could provide new insights into the biogeochemical processes, which govern the cycling of Cd and possibly other micro- and macronutrients in the oceans; (II) The $\epsilon^{114/110}\text{Cd}$ -[Cd] correlation observed for seawater suggests that Cd isotopes could be used in paleoceanography as a proxy of nutrient utilization.

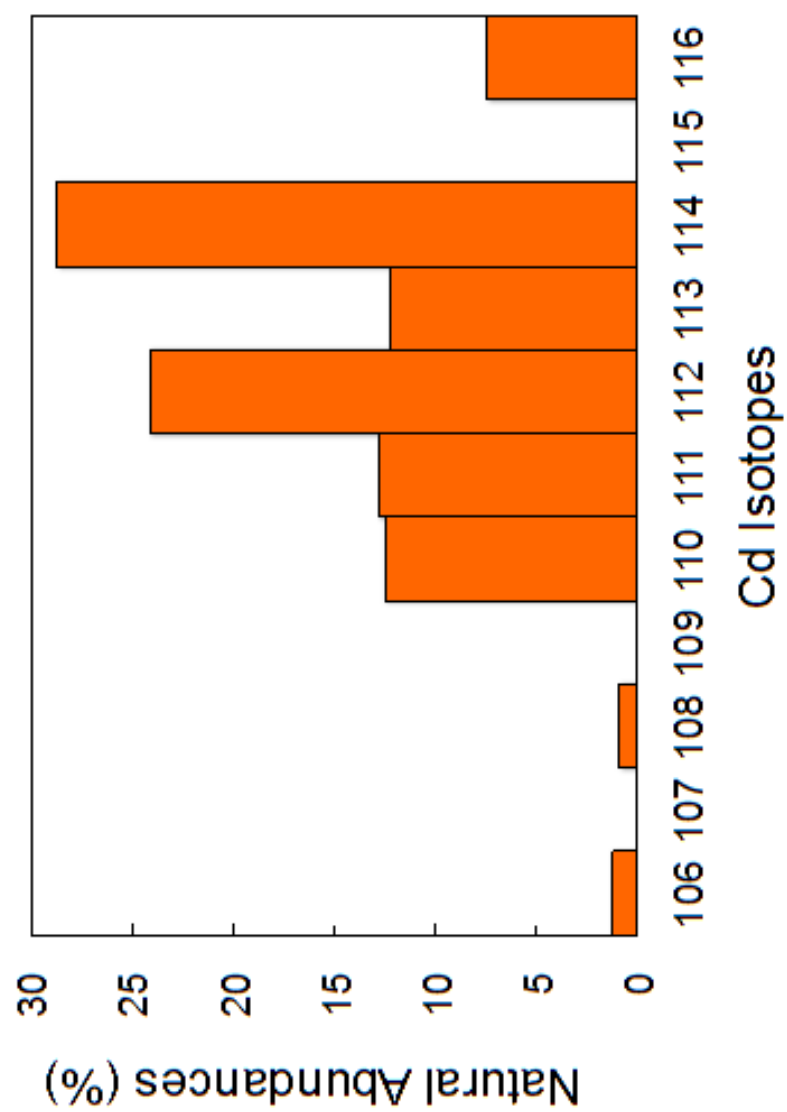


Figure 1.3: Cd isotopes and their natural abundances.

1.1.3 The sources and sinks of Cd in the ocean reservoir

The major natural sources of Cd are injected into the ocean by atmospheric deposition to all regions of the surface ocean, rivers through estuarine systems at the land-sea boundaries and hydrothermal activity to deep and intermediate waters above the sea floor (Chester, 2003). In the oceans, Cd joins many internal cycles of assimilation into biogenic matter and remineralisation, and is finally incorporated into marine sediments, which are the primary Cd sink (Collier and Edmond, 1984; Rosenthal et al., 1995).

Cd input from the atmosphere

Cd in the atmosphere has a relatively short lifetime (European Commission, 2001). The major natural source for Cd mobilization into the atmosphere is from the continental crust, mainly by low-temperature weathering processes and high-temperature volcanic activity. In addition, anthropogenic processes also emit Cd into the air. Rehkämper et al. (2011) summarized the Cd contents and isotope compositions in various anthropogenic samples and rocks and minerals of the continental crust. The data reveal Cd isotope variation of between $-14\epsilon^{114/110}\text{Cd}$ and $+5\epsilon^{114/110}\text{Cd}$ in the anthropogenic samples. In the continental crustal rocks, Cd concentration varies from 50 to 200 ng/g, whilst the Cd isotope composition ranges from $\epsilon^{114/110}\text{Cd}$ values of -4 to +4.

The low temperature mechanical mobilization of surface deposits by wind erosion or weathering produces an important component of Cd in marine aerosols. Cd can also be volatilised by high temperature processes and emitted as a vapour, since Cd and its compounds are relatively volatile. Cd vapours quickly condense on aerosols and then enter the atmosphere (European Commission, 2001). Most Cd in the atmosphere is bound to small size particulate matter (below 1 μm) (United Nations Environment Programme Chemicals Branch (UNEPCB), 2010). Cd emissions can be transported by airflows over hundreds or even thousands of kilometers away from the emission source.

Duce et al. (1991) estimated the gross fluxes of Cd and other trace metal elements from the atmosphere to the oceans, using elemental ratio calculations relative to lead (Pb) and Pb

fluxes determined for aerosol and precipitation samples from a wide range of environments. The global Cd inputs to the ocean from atmospheric deposition were estimated at $1.9\text{--}3.3 \times 10^9 \text{ g}\cdot\text{yr}^{-1}$ from the dissolved phase and $0.4\text{--}0.7 \times 10^9 \text{ g}\cdot\text{yr}^{-1}$ from the particulate phase, respectively. In addition, the total atmospheric fluxes of Cd to the North Sea, Baltic Sea and Mediterranean Sea were calculated to be 0.1-0.5, 0.14 and $1 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively (Duce et al., 1991). Cd isotope fractionation during the transportation processes in the atmosphere has not been discussed in the previous studies and isotopic data are currently not available for any aerosols. However, several samples of loess have been analyzed, which were found to have a mean $\epsilon^{114/110}\text{Cd}$ value of -0.1 ± 0.4 (1sd; (Schmitt et al., 2009b)).

Cd input from rivers

Previous studies showed that rivers transport large quantities of Cd to the oceans (Duce et al., 1991). The concentration of Cd and other dissolved trace elements in the river waters are influenced by several factors, such as the weathering and erosion processes of the earth's crust in the river catchment, anthropogenic inputs, and chemical processes within the aqueous system (Chester, 2003). Cd concentrations in river water are between < 1 and 13.5 ng/L (United Nations Environment Programme Chemicals Branch (UNEP/CB), 2010). Duce et al. (1991) summarized that the global deposition of Cd from rivers to the ocean are $0.3 \times 10^9 \text{ g}\cdot\text{yr}^{-1}$ in the dissolved form and $15 \times 10^9 \text{ g}\cdot\text{yr}^{-1}$ in the particulate form. At present, Cd isotope data are not available in the literature for any samples of river water.

Cd input from hydrothermal activity

Hydrothermal activity is also a natural source of Cd to the oceans. Most hydrothermal activity is associated with high-temperature processes at spreading ridge centres, where cold seawater circulates through hot newly formed basaltic crust (Bruland and Lohan, 2004). However, basalt-sea water reactions take place over a variety of temperatures and rock/water ratios, which can be distinguished as 4 different types (Thompson, 1983).

- I) Away from the spreading centres, with surface basement rocks, at low temperature,

high water/rock ratios, over long time periods.

- II) Away from the spreading centres, with deeper basement rocks, at low temperature, low water/rock ratios, over short time periods.
- III) At the mid-ocean ridge flanks, with hydrothermal circulation, at medium temperature, medium water/rock ratios, during passive circulation phase.
- IV) At mid-ocean ridge axes, with the dramatic venting of hydrothermal solutions at the spreading centers, at high temperature, low water/rock ratios, during the active phase of hydrothermal activity.

All these reaction types can provide hydrothermal fluxes. The high temperature axial hydrothermal flux of Cd in the East Pacific Rise at 21°N was estimated to be $2.3 - 26 \times 10^6$ mol yr⁻¹ (Damm et al., 1985).

Recent studies of Cd contents and isotope composition were carrying out on samples related to sub-seafloor hydrothermal activity at spreading centers (Schmitt et al., 2009b). The Cd isotopes in the black smoker sulfides record the isotope composition of the pristine hydrothermal fluids, with $\epsilon^{114/110}\text{Cd} \approx 0.5$ (Schmitt et al., 2009b), which is similar to that in the bulk silicate Earth with $\epsilon^{114/110}\text{Cd} \approx -0.3$ (Schmitt et al., 2009b). This result demonstrates that the Cd signature in pristine hydrothermal fluids is derived from the basaltic ocean crust without significant isotope fractionation in the process of leaching (Rehkämper et al., 2011). However, the grey smoker sulfides showed $\epsilon^{114/110}\text{Cd}$ values between -4.5 and 3.9 with $[\text{Cd}] = 100\text{-}400 \mu\text{g/g}$, which is the largest Cd isotope variations of the hydrothermal deposits. These variations were thought to be a consequence of isotope fractionation during sulfide precipitation in the vent system (Schmitt et al., 2009b).

Cd in the marine sediments

Marine sediments are the primary sink of Cd in the oceans (Collier and Edmond, 1984; Rosenthal et al., 1995). Marine sediments are deposited under a wide variety of depositional environments. In general, nearshore and deep-sea deposits are two distinctive

oceanic depositional regimes. Nearshore sediments are deposited mainly on the shelf regions under a wide variety of regimes that are strongly influenced by adjacent land masses. As a result, physical, chemical and biological conditions in nearshore areas are much more variable than in deep-sea regions. Deep-sea sediments are usually deposited in depths of water below 500m. Sediment deposition in deep-sea environment is affected by various factors, such as remoteness from the land-mass sources, reactivity between particulate and dissolved components within the oceanic water column, and the presence of a distinctive biomass (Chester, 2003).

Previous studies show that Cd is released to pore waters during the process of organic material diagenesis. In the Mn depleted sediments, Cd is enriched authigenically (Gobeil et al., 1997). The accumulation of Cd in sediments is through the process of insoluble sulfide precipitation (Framson and Leckie, 1978; Rosenthal et al., 1995) or adsorption to the freshly precipitated Fe oxides (McCorkle and Klinkhammer, 1991). van Geen et al. (1995) estimate an accumulation rate for Cd in the marine sediments of $0.58 \text{ ng cm}^{-1} \text{ yr}^{-1}$ and they argue that suboxic sediments appear to be the major sink of Cd in the oceans.

1.1.4 Cd isotope analysis by multiple collectors inductively coupled plasma mass spectrometry (MC-ICP-MS)

Cadmium has eight stable isotopes (^{106}Cd , ^{108}Cd , ^{110}Cd , ^{111}Cd , ^{112}Cd , ^{113}Cd , ^{114}Cd , ^{116}Cd) with relative abundances varying from 0.89% (^{108}Cd) to 28.73% (^{114}Cd) (Fig. 1.3). Wombacher et al. (2003) were the first to carry out analysis of Cd stable isotope compositions in terrestrial samples using MC-ICP-MS (Fig. 1.4). The success of this investigation established MC-ICP-MS as the dominant instrumental technique for Cd stable isotope measurements. At present, the majority of the published MC-ICP-MS Cd isotope data were obtained utilizing external normalization to admixed Ag (and, in some cases Sb) for the mass fractionation correction (Rehkämper et al., 2011). Using this method, Wombacher et al. (2003) obtained Cd isotope data with reproducibilities of about ± 0.2 to $\pm 1.0 \text{ ‰}$ for analyses of pure Cd standards and geological samples. They also tested the method of standard sample bracketing for mass bias correction and found that this is clearly more

susceptible to matrix effects, which result in inaccurate isotopic data for natural samples, than the various techniques of external normalization (Lacan et al., 2006; Shiel et al., 2009; Wombacher et al., 2003).

Ripperger and Rehkämper (2007) developed a new ^{110}Cd - ^{111}Cd double spike approach for the mass bias correction of MC-ICP-MS Cd isotope measurements. This procedure effectively avoids matrix effects and was shown to be suitable for accurate and precise Cd isotope analyses of seawater. With the application of the Cd double spike, it was shown that reproducibilities (2sd) of about 0.2-0.3 ϵ/amu could be achieved for Cd isotope analyses of both pure standard solutions and samples, if 40-60 ng of natural Cd are available for measurement.

1.1.5 Cd isotope fractionation models for seawater samples

Typically, organisms prefer to utilize the lighter isotopes and biological reactions, hence, often generate significant isotope fractionations between the substrate and the biologically mediated product, whereby the latter features a lighter isotope composition. Biological processes are generally unidirectional and hence, the isotope fractionations are typically of kinetic origin. The intensity of kinetic isotopic fractionations in biological processes is affected by numerous factors, including the nature of the reaction, reaction rates, the concentrations of products and reactants, environmental conditions, and species of the organism (Kendall and McDonnell, 1998). This interpretation is in accord with previous studies on isotope variations of the marine nutrient elements N, Si and Cd in seawater samples (De La Rocha et al., 1998; Sigman et al., 1999; Reynolds et al., 2006; Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011).

Previous studies show that if the substrate concentration is large enough, such that the isotopic composition of the reservoir is insignificantly changed by the reaction (O'Leary, 1981), or if the isotopic ratio of the product is measured within an infinitely short time period (Mariotti et al., 1981), the fractionation factor can be defined using an open system model. For unidirectional reactions, the change in the isotope ratio of the substrate rela-

tive to the fraction of the unreacted substrate can be described by the Rayleigh equation (Kendall and McDonnell, 1998). The isotope fractionation of Cd in the seawater is primarily governed by unidirectional biological uptake and it can be described with the models discussed below (Mariotti et al., 1981):

(A) Rayleigh fractionation model

The Cd isotope variations determined for seawater can be described as:

$$R_{sw} = R_{sw,0} \times F^{(\frac{1}{\alpha}-1)} \quad (1.1)$$

where R_{sw} and $R_{sw,0}$ denote $^{114}\text{Cd}/^{110}\text{Cd}$ isotope ratio of the remaining and initial seawater, respectively. Values c and c_0 denote the residual and initial seawater Cd concentration, respectively; hence, the fraction of remaining dissolved seawater Cd is represented by $F = c/c_0$. The fractionation factor α is defined as $\alpha = R_{sw}/R_{BIO}$, where R_{BIO} denote the $^{114}\text{Cd}/^{110}\text{Cd}$ isotope ratios of biomass. Natural Cd variations in the isotopic composition are expressed relative to a standard with an epsilon notation.

$$\epsilon = \left(\frac{R}{R_{std}} - 1 \right) \times 10000 \quad (1.2)$$

where R and R_{std} denote the $^{114}\text{Cd}/^{110}\text{Cd}$ isotope ratio of the sample and Cd standard, respectively. Change the format of equation 1.2 to obtain:

$$\frac{R}{R_{std}} = 10^{-4}\epsilon + 1 \quad (1.3)$$

Then, equation 1.1 can be written with the epsilon notation as:

$$\left(\frac{1}{\alpha} - 1\right) \times \ln(F) = \ln\left(\frac{R_{sw}}{R_{sw,0}}\right) = \ln\left(\frac{10^{-4}\epsilon_{sw} + 1}{10^{-4}\epsilon_{sw,0} + 1}\right) \quad (1.4)$$

Given $\ln\left(\frac{1+u}{1+v}\right) \approx u - v$ when u and v are small relative to 1, equation 1.4 can be written in the epsilon notation as:

$$\left(\frac{1}{\alpha} - 1\right) \times \ln(F) = 10^{-4}\epsilon_{sw} - 10^{-4}\epsilon_{sw,0} \quad (1.5)$$

Hence, the Cd isotope composition in the seawater can be written as

$$\epsilon_{sw} = \epsilon_{sw,0} + 10000 \times \left(\frac{1}{\alpha} - 1\right) \times \ln(F) \quad (1.6)$$

or

$$\epsilon_{sw} = \epsilon_{sw,0} + 10000 \times \left(\frac{1}{\alpha} - 1\right) \times [\ln(c) - \ln(c_0)] \quad (1.7)$$

where ϵ_{sw} and $\epsilon_{sw,0}$ denote the Cd isotope composition of the remaining and the initial seawater, respectively, and c and c_0 denote the residual and initial seawater Cd concentration, respectively. Hence, the fraction of remaining dissolved seawater Cd is given by $F = c/c_0$. The fractionation factor α is defined as $\alpha = R_{sw}/R_{BIO}$, where R_{BIO} denotes the $^{114}\text{Cd}/^{110}\text{Cd}$ isotope ratios of biomass.

From equation 1.6 or 1.7, it can be seen that (1) the Cd isotope composition of the seawater will display a logarithmic correlation with the Cd concentration and (2) that more positive $\epsilon^{114/110}\text{Cd}_{sw}$ values reflect increased utilization of Cd in the seawater. The data of Cd concentration and isotope variations observed for surface seawater

samples in previous studies (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011) follow such a kinetic isotope fractionation trend of biological uptake of Cd. This strengthens the interpretation that the Cd cycling and isotope fractionation is primarily governed by biological uptake. Given the isotopic mass balance in a closed system requires that (Mariotti et al., 1981):

$$F \times R_{sw} + (1 - F) \times R_{bio,acc} = R_{sw,0} \quad (1.8)$$

where R_{sw} and $R_{sw,0}$ denote the $^{114}\text{Cd}/^{110}\text{Cd}$ isotope ratio of the remaining and initial seawater; $R_{bio,acc}$ is the $^{114}\text{Cd}/^{110}\text{Cd}$ isotope ratio of the accumulated biomass; F is the fraction of remaining dissolved seawater Cd.

The format of equation 1.8 can be changed to obtain:

$$\frac{R_{sw}}{R_{std}} = \frac{1}{F} \left[\frac{R_{sw,0}}{R_{std}} - (1 - F) \frac{R_{bio,acc}}{R_{std}} \right] \quad (1.9)$$

Substituting equation 1.3 into equation 1.9, we can rewrite this in the epsilon notation that:

$$10^{-4}\epsilon_{sw} + 1 = \frac{1}{F} \left[10^{-4}\epsilon_{sw,0} + 1 - (1 - F) \cdot (10^{-4}\epsilon_{bio,acc} + 1) \right] \quad (1.10)$$

Inserting ϵ_{sw} from equation in 1.6, we obtain:

$$\epsilon_{bio,acc} = \epsilon_{sw,0} - 10000 \times \left(\frac{1}{\alpha} - 1 \right) \times \frac{F \times \ln(F)}{1 - F} \quad (1.11)$$

where $\epsilon_{bio,acc}$ denotes the isotopic composition of the accumulated biomass.

Hence, equation 1.11 describes how that the Cd isotope composition of the accumulated biomass is related with the increased utilization of dissolved seawater Cd.

(B) Open system at steady state

For the kinetic fractionations in the biological process, an open system implies that the supply of substrate is infinite (Kendall and McDonnell, 1998). Hence, in the surface water reservoir, the input of Cd contents from all the sources are balanced by the output of Cd mainly via biomass production and lateral outflow of water. The isotopic composition ϵ_{sw} of this reservoir can be presented as:

$$\epsilon_{sw} = \epsilon_{sw,0} - 10000 \times \left(\frac{1}{\alpha} - 1 \right) \times (1 - f_{net}) \quad (1.12)$$

where ϵ_{sw} and $\epsilon_{sw,0}$ denote the isotopic compositions of the net and initial Cd input; the fractionation factor α is defined as $\alpha = R_{sw}/R_{BIO}$, where v and R_{BIO} denote the $^{114}\text{Cd}/^{110}\text{Cd}$ isotope ratios of the remaining seawater and biomass, respectively; f_{net} describes the fraction of the net Cd input into the surface seawater, which is represented by $f_{net} = c/c_0$ (Hayes, 2004), where c and c_0 denote the Cd contents in the remaining surface waters and the initial input of Cd contents, respectively. Hence, the equation 1.12 can be written as:

$$\epsilon_{sw} = \epsilon_{sw,0} - 10000 \times \left(\frac{1}{\alpha} - 1 \right) \times \left(1 - \frac{c}{c_0} \right) \quad (1.13)$$

Therefore, equation 1.13 shows that (1) the Cd isotope composition of the remaining seawater has a linear correlation with the Cd contents and (2) that more positive $\epsilon^{114/110}\text{Cd}_{sw}$ values reflect lower seawater Cd content.

In addition, Cd isotope variations in seawater can also be affected by water masses mixing. According to Mariotti et al. (1981), the isotope composition of a mixture of

two components A and B can be calculated by:

$$\epsilon_M = \frac{c_A \times f \times \epsilon_A + c_B \times (1 - f) \times \epsilon_B}{c_M} \quad (1.14)$$

where c denotes Cd concentrations in the water masses and ϵ represents the isotope compositions of the components A and B. The mixing ratio f is given by $f = m_A / (m_A + m_B)$, where m_A and m_B correspond to the masses of component A and B, respectively.

1.2 Research motivation and objectives

It has long been known that the biological activity of the oceans is regulated by the availability of the major nutrients phosphate, nitrate, and silicate. More recently, however, it has been recognized that micronutrient trace elements, such as Cd, also play an important role in limiting marine productivity. As biological activity draws down CO_2 from the atmosphere, micronutrients play a significant role in regulating the Earth's carbon cycle and climate. In this PhD research project, Cd stable isotope fractionations in the oceans were further investigated to improve the understanding of the marine cycling of Cd. The following aspects were investigated in particular:

1.2.1 Development of new methodology to enable precise Cd isotope analyses of large-volume Cd-depleted seawater samples

A number of recent studies have applied a double spike technique for more accurate Cd stable isotope analysis using either MC-ICP-MS or TIMS instruments. However, the quality of the data generated with the double spike methodology is critically dependent on the application of an optimized spike composition and spike sample ratio. Another key factor for obtaining high-quality Cd isotope data is an appropriate separation procedure that achieves both high yields and purified Cd samples that are free of contaminants, which generate matrix effects or spectral interferences.

Previous studies have shown that biological uptake of Cd from seawater is associated with considerable isotope fractionation (Lacan et al., 2006; Ripperger et al., 2007). The most fractionated isotope compositions were determined for nutrient-depleted surface waters. The low Cd concentrations (<10 pmol/L) that are commonly encountered in nutrient-depleted surface seawater, however, pose a particular challenge for precise Cd isotope analyses. This implies that Cd must be isolated from a large volume of seawater to obtain a sufficient quantity (ideally, more than 10-20 ng) for precise Cd isotope analyses. However, the published methods are not suitable for the isolation of Cd at high yield and the efficient purification of Cd from seawater samples larger than 2 L. To cope with this shortcoming, a new method that is suitable for the processing of seawater samples with volumes as large as 10 to 20 L and Cd concentrations as low as 1 pmol/L was developed. In addition, a new double spike composition was also selected, in accord with the results of model calculations, which evaluated analytical uncertainties.

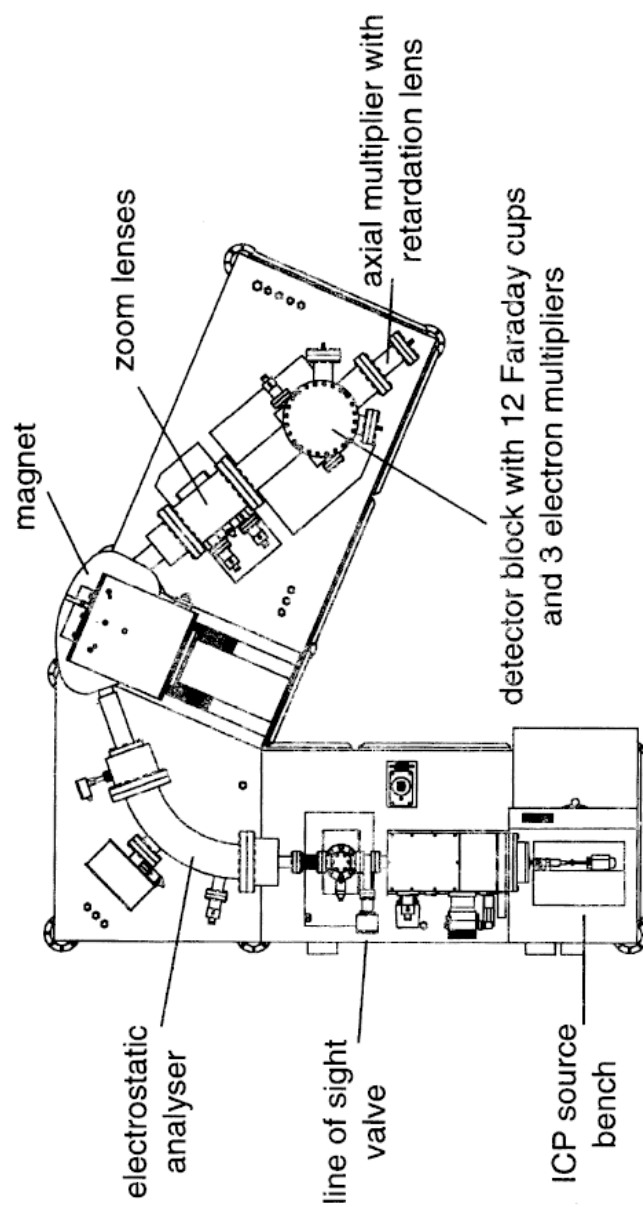


Figure 1.4: Schematic diagram of the Nu Plasma MC-ICP-MS instrument (from Rehkämper et al. (2001)).

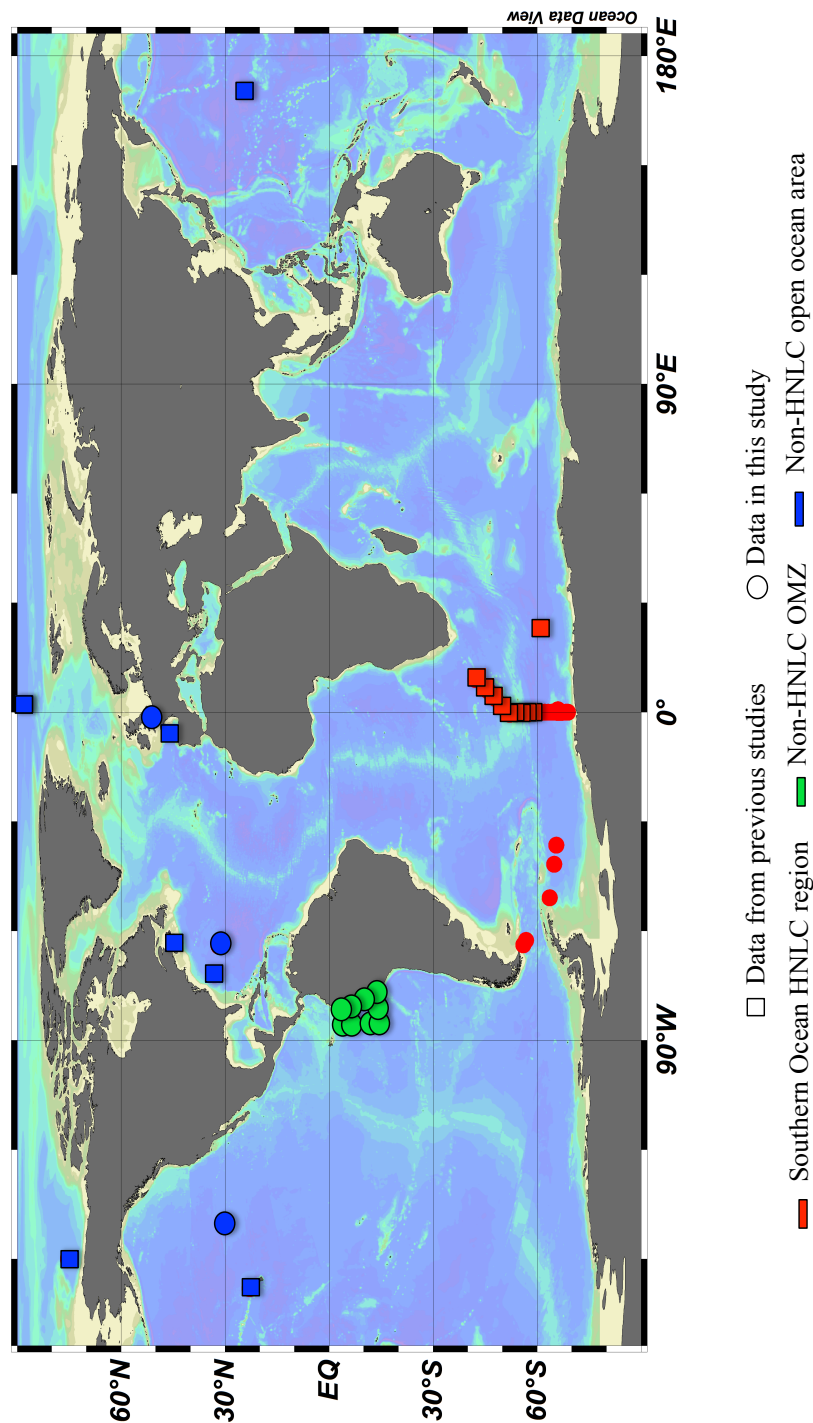


Figure 1.5: Locations of seawater samples analysed as part of this PhD research. Cd data determined in this PhD project are shown in the dots. Cd data from previous studies (Ripperger et al., 2007; Abouchami et al., 2011) are shown in the squares. Cd data from Southern Ocean HNLC region are in red. These data are from Table 3.1 and 3.2 and from a previous study by Abouchami et al. (2011). Cd data for the non-HNLC open ocean areas are from the Arctic, the North Atlantic and the North Pacific Ocean, and are shown in blue. These Cd data are reported in Table 2.3 and previous studies by Ripperger and Rehkämper (2007); Ripperger et al. (2007). Cd data from Peruvian OMZ are reported in table 4.1 and show Cd behavior in a non-HNLC semi-open system OMZ, which are shown in green.

1.2.2 Comparison of the marine distribution of Cd in different environments using coupled Cd concentration and isotope data

The initial studies of Cd isotopes in seawater obtained novel and promising results, which suggested that further investigations are necessary (Lacan et al., 2006; Ripperger et al., 2007). At present, the published Cd isotope database for seawater presents results for only about 70 samples from 11 locations (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011). Furthermore, no systematic research has been carried out to investigate the behavior of Cd in different marine environments.

Therefore, in this PhD project, the marine distribution and behavior of Cd was studied systematically using samples from (i) the Southern Ocean HNLC region, (ii) the oligotrophic North Atlantic Ocean and (iii) the oxygen minimum zone (OMZ) of the Eastern Equatorial Pacific Ocean (EEP) (Fig. 1.5). These investigations involved Cd concentration and isotope composition measurements for numerous surface water samples and vertical profiles.

In the Southern Ocean HNLC (High Nutrient Low Chlorophyll) region, biological productivity and biological uptake of macronutrients are considered to be limited by the lack of the micronutrient Fe. At present, Cd isotope data for the Southern Ocean is still limited to results for only 20 surface water samples and a single deep-water sample (Ripperger et al., 2007; Abouchami et al., 2011). Hence, this thesis encompasses the first comprehensive investigation of the behavior of Cd in the Southern Ocean HNLC region. This study presents both Cd concentration and stable isotope composition data for surface waters and full depth profiles from three sampling stations.

Previous research on the Cd isotopic composition of seawater in the North Atlantic Ocean was also limited to analyses of only a few surface and deep-water samples (Ripperger et al., 2007). In this study, the first comprehensive depth profile for Cd and Cd isotope compositions was determined from the oligotrophic North Atlantic Ocean.

As part of this PhD project, the Cd distribution and isotope composition of seawater from the oxygen minimum zones (OMZ) in the south Eastern Equatorial Pacific Ocean (EEP) were explored. Off the coast of Chile and Peru, one of the most extensive OMZs in the world oceans is located in the EEP. This region is characterized by the combination of intense upwelling, high primary productivity and an extensive shallow OMZ. The distinct marine environment of OMZ is likely to have a unique impact on marine micronutrient cycling. Therefore, the first detailed study that investigates the distribution and cycling of Cd in the OMZ has been carried out in this PhD project, using the combined Cd concentration and stable isotope data in the seawater samples from the OMZ in the EEP.

1.2.3 Re-examination of processes that affect the Cd isotope composition of seawater

Previous studies (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011) of Cd concentrations and isotope compositions in the oceans demonstrate that the Cd isotope fractionation, which is associated with biological utilization, generates closed system Rayleigh fractionation trends. These trends are manifested as logarithmic correlations in plots of Cd isotope compositions versus Cd concentrations. The slopes of these correlations are furthermore indicative of isotope fractionation factors α with values of about 1.0002 to 1.0006. Consequently, it has been suggested that the $\epsilon^{114/110}\text{Cd}-[\text{Cd}]$ correlation underpins the application of Cd isotopes as a paleoceanographic proxy for the studies of marine nutrient utilization. This conclusion is further examined in this thesis, using the much larger Cd isotope dataset that was produced in this PhD project based on analyses of seawater samples from the Southern, the North Atlantic and the Eastern Equatorial Pacific Oceans.

Abouchami et al. (2011) presented Cd isotope and concentration data for 20 surface water samples from the Southern Ocean HNLC region. In their study, it also was concluded that the Southern Ocean samples defined two distinct $\epsilon^{114/110}\text{Cd}-[\text{Cd}]$ trends and these were interpreted to reflect different conditions of biological utilization in the ACC and the Weddell Gyre. This observation and interpretation is revisited here, based on data acquired for 47 seawater samples, including three full depth profiles and 13 surface water

samples.

Ripperger et al. (2007) pointed out that coupled $\epsilon^{114/110}\text{Cd}$ and $[\text{Cd}]$ data for seawater can be used to distinguish the effects that water mass mixing and biological utilization have on the marine cycling and distribution of Cd. This hypothesis is also tested in this study, based on the Cd data that were obtained for samples from the Peruvian OMZ in the south EEP.

1.3 Outline of this thesis

- **Chapter 2** describes a new methodology that was developed for precise and accurate Cd isotope analyses of seawater with MC-ICP-MS. The method is suitable for samples as large as 20 L and Cd concentrations as low as 1 pmol/L. The procedure involves the application of a new ^{111}Cd - ^{113}Cd double spike and a new $\text{Al}(\text{OH})_3$ coprecipitation method to separate and purify Cd from seawater. The overall Cd yield of the procedure is consistently better than 85% and the methodology can routinely provide Cd isotope data with a precision of about $\pm 0.5\epsilon$ (2sd) for $\epsilon^{114/110}\text{Cd}$, when at least 20-30 ng of natural Cd are available for analysis. Furthermore, the Cd concentrations and isotope compositions of 21 seawater samples from the English Channel (50.9°N, 1.4°W), the western Pacific Ocean (30°N, 140°W) and the Atlantic Ocean (31.8°N, 64.1°W) were analyzed to test the new technique. Importantly, these analyses provide the first comprehensive Cd isotope depth profile for the Atlantic Ocean. A number of different Cd isotope standards, such as JMC Cd Münster, Münster Cd, Alfa Cd Zurich, BAM-I012, and NIST SRM 3108 were also analyzed, to test the performance of the new ^{111}Cd - ^{113}Cd double spike and to better characterize the small isotopic offsets between these materials.
- **Chapter 3** presents the results of Cd concentration and isotope composition measurements that were carried out for 47 seawater samples from the 2008 GEOTRACES expedition ANT 24-3 aboard RV Polarstern. This includes samples from 3 depth profiles (in the Drake Passage, and the northwestern and central Weddell Sea) as well as

13 surface waters from the Zero Meridian between 62° and 69°S. These results are then discussed and interpreted to obtain improved constraints on the cycling and isotope fractionation of Cd within in the Southern Ocean HNLC region. In addition, the distinct $\epsilon^{114/110}\text{Cd}$ -[Cd] correlation that is found for the samples from the Southern Ocean HNLC region, is compared with the results obtained for samples from other non-HNLC open ocean regions.

- **Chapter 4** presents the results of Cd concentration and isotope composition analyses for 74 seawater samples from the Peruvian OMZ in the EEP. These samples encompass 9 full depth profiles that were obtained between 3°S and 14°S at both near-shore locations that feature strong upwelling and offshore localities where upwelling is significantly weaker. The results are interpreted to provide an improved understanding of the cycling and isotope fractionation of Cd in the environment of an OMZ.
- **Chapter 5** presents a brief summary and the main conclusions of this thesis. In addition, future research plans are also discussed in this chapter.

References

- Abouchami, W., Galer, S., de Baar, H., Alderkamp, A., Middag, R., Laan, P., Feldmann, H., Andreae, M., 2011. Modulation of the Southern Ocean cadmium isotope signature by ocean circulation and primary productivity. *Earth and Planetary Science Letters* 305, 83 – 91.
- de Baar, H.J., Saager, P.M., Nolting, R.F., van der Meer, J., 1994. Cadmium versus phosphate in the world ocean. *Marine Chemistry* 46, 261 – 281.
- Bewers, J.M., Yeats, P.A., 1977. Oceanic residence times of trace metals. *Nature* 268, 595–598.
- Boyle, E., 1981. Cadmium, zinc, copper, and barium in foraminifera tests. *Earth and Planetary Science Letters* 53, 11–35.
- Boyle, E., 1992. Cadmium and $\delta^{13}\text{C}$ Paleochemical Ocean Distributions during the Stage 2 Glacial Maximum. *Annual Review of Earth and Planetary Sciences* 20, 245–287.
- Boyle, E., Sclater, F., Edmond, J., 1976. On the marine geochemistry of cadmium. *Nature* 263, 42–44.
- Bruland, K., Lohan, M., 2004. Controls of trace metals in seawater. *The oceans and marine geochemistry*. Elsevier , 23–47.
- Bruland, K.W., 1980. Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth and Planetary Science Letters* 47, 176–198.
- Bruland, K.W., Knauer, G.A., Martin, J.H., 1978. Cadmium in Northeast Pacific Waters. *Limnology and Oceanography* 23, 618–625.

- Chester, R., 2003. Marine geochemistry. Wiley-Blackwell.
- Collier, R., Edmond, J., 1984. The trace element geochemistry of marine biogenic particulate matter. *Progress In Oceanography* 13, 113 – 199.
- Cullen, J., Lane, T., Morel, F., Sherrell, R., 1999. Modulation of cadmium uptake in phytoplankton by seawater CO₂ concentration. *Nature* 402, 165–166.
- Cullen, J.T., 2006. On the Nonlinear Relationship between Dissolved Cadmium and Phosphate in the Modern Global Ocean: Could Chronic Iron Limitation of Phytoplankton Growth Cause the Kink? *Limnology and Oceanography* 51, 1369–1380.
- Damm, K.V., Edmond, J., Grant, B., Measures, C., Walden, B., Weiss, R., 1985. Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochimica et Cosmochimica Acta* 49, 2197 – 2220.
- Danielsson, L., Magnusson, B., Westerlund, S., 1985. Cadmium, copper, iron, nickel and zinc in the north-east Atlantic Ocean. *Marine Chemistry* 17, 23–41.
- De La Rocha, C., Brzezinski, M., DeNiro, M., Shemesh, A., 1998. Silicon-isotope composition of diatoms as an indicator of past oceanic change. *Nature* 395, 680–683.
- Dixon, J., Statham, P., Widdicombe, C., Jones, R., Barquero-Molina, S., Dickie, B., Nimmo, M., Turley, C., 2006. Cadmium uptake by marine micro-organisms in the English Channel and Celtic Sea. *Aquatic microbial ecology* 44, 31–43.
- Donat, J., Bruland, K., 1995. Trace elements in the oceans. Trace elements in natural waters. CRC , 247–281.
- Duce, R., Liss, P., Merrill, J., Atlas, E., Buat-Menard, P., Hicks, B., Miller, J., Prospero, J., Arimoto, R., Church, T., Ellis, W., Galloway, J., Hansen, L., Jickells, T., Knap, A.H., Reinhardt, K., Schneider, B., Soudine, A., Tokos, J., Tsunogai, S., Wollast, R., Zhou, M., 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochem. Cycles* 5, 193–259.

- Elderfield, H., Rickaby, R., 2000. Oceanic Cd/P ratio and nutrient utilization in the glacial Southern Ocean. *Nature* 405, 305–310.
- European Commission, 2001. Ambient air pollution by AS, CD, and NI compounds.
- Fitzwater, S., Johnson, K., Gordon, R., Coale, K., Smith, W., et al., 2000. Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. *Deep Sea Research Part II: Topical Studies in Oceanography* 47, 3159–3179.
- Framson, P.E., Leckie, J.O., 1978. Limits of coprecipitation of cadmium and ferrous sulfides. *Environmental Science and Technology* 12, 465–469.
- Frew, R., Hunter, K., 1992. Influence of Southern Ocean waters on the cadmium–phosphate properties of the global ocean. *Nature* 360, 144–146.
- Frew, R., Hunter, K., 1995. Cadmium-phosphorus cycling at the subtropical convergence south of New Zealand. *Marine chemistry* 51, 223–237.
- Galer, S., 2007. The double-spike cookbook, in: Goldschmidt Conference, p. A303.
- van Geen, A., McCorkle, D., Klinkhammer, G., 1995. Sensitivity of the phosphate-cadmium-carbon isotope relation in the ocean to cadmium removal by suboxic sediments. *Paleoceanography* 10, 159–169.
- Gobeil, C., Macdonald, R.W., Sundby, B., 1997. Diagenetic separation of cadmium and manganese in suboxic continental margin sediments. *Geochimica et Cosmochimica Acta* 61, 4647 – 4654.
- Hayes, J., 2004. An introduction to isotopic calculations. Woods Hole Oceanographic Institute, Woods Hole, MA .
- Henderson, G., 2002. New oceanic proxies for paleoclimate. *Earth and Planetary Science Letters* 203, 1–13.
- Hunter, K., Ho, F., 1991. Phosphorus-cadmium cycling in the northeast Tasman Sea, 35–40°S. *Marine chemistry* 33, 279–298.

- Kendall, C., McDonnell, J., 1998. Isotope tracers in catchment hydrology. Elsevier Science.
- Lacan, F., Francois, R., Ji, Y., Sherrell, R., 2006. Cadmium isotopic composition in the ocean. *Geochimica et Cosmochimica Acta* 70, 5104–5118.
- Lane, T., Saito, M., George, G., Pickering, I., Prince, R., Morel, F., 2005. Biochemistry: a cadmium enzyme from a marine diatom. *Nature* 435, 42–42.
- Löscher, B., De Jong, J., De Baar, H., 1998. The distribution and preferential biological uptake of cadmium at 6°W in the Southern Ocean. *Marine chemistry* 62, 259–286.
- Lynch-Stieglitz, J., 2006. Tracers of past ocean circulation. *The oceans and marine geochemistry* 6, 433.
- Mariotti, A., Germon, J., Hubert, P., Kaiser, P., Letolle, R., Tardieux, A., Tardieux, P., 1981. Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes. *Plant and Soil* 62, 413–430.
- Martin, J., 1990. Glacial-interglacial CO₂ change: The iron hypothesis. *Paleoceanography* 5, 1–13.
- Martin, J., Gordon, R., Fitzwater, S., 1990. Iron in Antarctic waters. *Nature* 345, 156–158.
- Martin, J., Gordon, R., Fitzwater, S., Broenkow, W., 1989. VERTEX: phytoplankton/iron studies in the Gulf of Alaska. *Deep Sea Research Part A. Oceanographic Research Papers* 36, 649–680.
- Martin, J., Whitfield, M., 1983. The significance of the river input of chemical elements to the ocean. *Trace metals in sea water*, 265–296.
- McCorkle, D.C., Klinkhammer, G.P., 1991. Porewater cadmium geochemistry and the porewater cadmium: $\delta^{13}\text{C}$ relationship. *Geochimica et Cosmochimica Acta* 55, 161 – 168.
- Morel, F., Price, N., 2003. The biogeochemical cycles of trace metals in the oceans. *Science* 300, 944–947.

- Nolting, R., De Baar, H., Van Bennekom, A., Masson, A., 1991. Cadmium, copper and iron in the Scotia Sea, Weddell Sea and Weddell/Scotia Confluence (Antarctica). *Marine chemistry* 35, 219–243.
- O’Leary, M.H., 1981. Carbon isotope fractionation in plants. *Phytochemistry* 20, 553 – 567.
- Price, N., Morel, F., 1990. Cadmium and cobalt substitution for zinc in a marine diatom. *Nature* 344, 658–660.
- Rehkämper, M., Schönbächler, M., Stirling, C., 2001. Multiple Collector ICP-MS: Introduction to Instrumentation, Measurement Techniques and Analytical Capabilities. *Geo-standards Newsletter* 25, 23–40.
- Rehkämper, M., Wombacher, F., Horner, T., Xue, Z., 2011. Natural and anthropogenic Cd isotope variations. *Handbook of Environmental Isotope Geochemistry* , 125–154.
- Reynolds, B., Frank, M., Halliday, A., 2006. Silicon isotope fractionation during nutrient utilization in the North Pacific. *Earth and Planetary Science Letters* 244, 431–443.
- Rickaby, R., Elderfield, H., 1999. Planktonic foraminiferal Cd/Ca: paleonutrients or paleotemperature. *Paleoceanography* 14, 293–303.
- Ripperger, S., Rehkämper, M., 2007. Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS. *Geochimica et cosmochimica acta* 71, 631–642.
- Ripperger, S., Rehkämper, M., Porcelli, D., Halliday, A., 2007. Cadmium isotope fractionation in seawater—A signature of biological activity. *Earth and Planetary Science Letters* 261, 670–684.
- Ripperger, S., Schiebel, R., Rehkämper, M., Halliday, A., 2008. Cd/Ca ratios of in situ collected planktonic foraminiferal tests. *Paleoceanography* 23, PA3209.
- Rosenthal, Y., Lam, P., Boyle, E., Thomson, J., 1995. Authigenic cadmium enrichments in suboxic sediments: Precipitation and postdepositional mobility. *Earth and Planetary Science Letters* 132, 99–111.

- Ruttenberg, K., 2003. The global phosphorus cycle. *Treatise on geochemistry* 8, 585–643.
- Saager, P., De Baar, H., Howland, R., 1992. Cd, Zn, Ni and Cu in the Indian Ocean. *Deep Sea Research Part A. Oceanographic Research Papers* 39, 9–35.
- Schmitt, A., Galer, S., Abouchami, W., 2009a. High-precision cadmium stable isotope measurements by double spike thermal ionisation mass spectrometry. *Journal Analytical Atomic Spectrometry* 24, 1079–1088.
- Schmitt, A., Galer, S., Abouchami, W., 2009b. Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. *Earth and Planetary Science Letters* 277, 262–272.
- Shiel, A., Barling, J., Orians, K., Weis, D., 2009. Matrix effects on the multi-collector inductively coupled plasma mass spectrometric analysis of high-precision cadmium and zinc isotope ratios. *Analytica Chimica Acta* 633, 29–37.
- Sigman, D., Altabet, M., McCorkle, D., Francois, R., Fischer, G., 1999. The d15N of nitrate in the Southern Ocean: Consumption of nitrate in surface waters. *Global Biogeochem. Cycles* 13, 1149–1166.
- Sunda, W.G., Huntsman, S.A., 2000. Effect of Zn, Mn, and Fe on Cd Accumulation in Phytoplankton: Implications for Oceanic Cd Cycling. *Limnology and Oceanography* 45, 1501–1516.
- Thompson, G., 1983. Hydrothermal fluxes in the ocean. *Chemical Oceanography* 8, 271–337.
- United Nations Environment Programme Chemicals Branch (UNEPCB), 2010. Final review of scientific information on cadmium.
- Westerlund, S., et al., 1991. Cadmium, copper, cobalt, nickel, lead, and zinc in the water column of the Weddell Sea, Antarctica. *Geochimica et Cosmochimica Acta* 55, 2127–2146.

- Wombacher, F., Rehkämper, M., Mezger, K., Münker, C., 2003. Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS. *Geochimica et Cosmochimica Acta* 67, 4639–4654.
- Xu, Y., Feng, L., Jeffrey, P., Shi, Y., Morel, F., 2008. Structure and metal exchange in the cadmium carbonic anhydrase of marine diatoms. *Nature* 452, 56–61.
- Yeats, P., Westerlund, S., 1991. Trace metal distributions at an Arctic Ocean ice island. *Marine chemistry* 33, 261–277.
- Yee, N., Fein, J., 2001. Cd adsorption onto bacterial surfaces: A universal adsorption edge? *Geochimica et Cosmochimica Acta* 65, 2037–2042.

Chapter 2

A New Methodology for Precise Seawater Cadmium Isotope Analyses

This chapter has been published as: Xue, Z., Rehkämper, M., Schönbächler, M., Statham, P.J., and Coles, B.J., 2012 A new methodology for precise cadmium isotope analyses of seawater. *Analytical and Bioanalytical Chemistry* 402: 883-893, DOI: 10.1007/s00216-011-5487-0

Abstract:

Previous studies have revealed considerable Cd isotope variations in seawater, which can be used to study the marine cycling of this micronutrient element. The low Cd concentrations that are commonly encountered in nutrient-depleted surface seawater, however, pose a particular challenge for precise Cd stable isotope analyses. In this study, we have developed a new procedure for Cd isotope analyses of seawater, which is suitable for samples as large as 20 L and Cd concentrations as low as 1 pmol/L. The procedure involves the use of a ^{111}Cd - ^{113}Cd double spike, co-precipitation of Cd from seawater using $\text{Al}(\text{OH})_3$, and subsequent Cd purification by column chromatography. To save time, seawater samples with higher Cd contents can be processed without co-precipitation. The Cd isotope analyses are carried out by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The performance of this technique was verified by analyzing multiple aliquots of a large seawater sample that was collected from the English Channel, the SAFe D1 seawater reference material, and several samples from the GEOTRACES Atlantic intercalibration exercise. The overall Cd yield of the procedure is consistently better than 85% and the methodology can routinely provide $\epsilon^{114/110}\text{Cd}$ data with a precision of about $\pm 0.5\epsilon$ (2sd, standard deviation) when at least 20-30 ng of natural Cd is available for analysis. However, even seawater samples with Cd contents of only 1-3 ng can be analyzed with a reproducibility of about ± 3 to $\pm 5\epsilon$. A number of experiments were furthermore conducted to verify that the isotopic results are accurate to within the quoted uncertainty.

2.1 Introduction

A number of previous studies have identified considerable mass dependent variations in the Cd isotope compositions of both terrestrial and extraterrestrial samples (Rehkämper et al., 2011; Wombacher et al., 2008). On Earth, stable isotope effects for Cd are particularly prominent in the oceans, and the largest natural terrestrial Cd isotope fractionations of about 4‰ have been reported for Cd-depleted surface seawater (Abouchami et al., 2011; Lacan et al., 2006; Ripperger et al., 2007). These effects have generally been attributed to reflect isotope fractionation of Cd that occurs during biological uptake and utilization of dissolved seawater Cd. This finding confirms studies, which identified Cd as an essential

marine micronutrient. This was first inferred from the phosphate-like distribution of the metal in the oceans (Boyle et al., 1976) and more recently demonstrated by work, which confirmed that Cd can act as catalytic metal ion in carbonic anhydrase, an enzyme which plays a central role in inorganic carbon acquisition by phytoplankton in the oceans (Cullen et al., 1999; Xu et al., 2008). Therefore, the marine Cd isotope fractionations are of interest, as they can be used to study the cycling of the micronutrient Cd as well as its impact on ocean productivity and the global carbon cycle.

Recent studies have applied a double spike technique in combination with either MC-ICP-MS (multiple collector inductively coupled plasma mass spectrometry) (Ripperger and Rehkämper, 2007) or TIMS (thermal ionization mass spectrometry) (Schmitt et al., 2009a) for Cd stable isotope measurements, as this procedure can provide more accurate results that are less prone to analytical artifacts from matrix effects than analyses, which utilize other methods of instrumental mass bias correction, such as standard-sample bracketing or 'external normalization' of the Cd isotope data to the $^{107}\text{Ag}/^{109}\text{Ag}$ ratio of admixed Ag (Lacan et al., 2006; Cloquet et al., 2005; Shiel et al., 2009; Wombacher et al., 2003). The data quality that is generated with a double spike methodology is, however, critically dependent on the application of an optimized spike composition and spike sample ratio (Rehkämper et al., 2011).

Another key factor for obtaining high-quality Cd isotope data is the use of an appropriate separation procedure, which can achieve both high yields and purified Cd samples that are free from contaminants that generate matrix effects or spectral interferences. A suitable and efficient pre-concentration technique is particularly critical for seawater Cd isotope analyses, because Cd contents of less than 0.05 nmol/L are common in the surface ocean. This implies that Cd must be isolated from several liters of seawater, in order to obtain a sufficient quantity of the element (ideally, more than 10 - 20 ng) for precise isotopic analyses. The presently published methods, however, are not suitable or untested for the isolation of Cd at high yield from seawater samples larger than about 2 L and at a purity that is sufficient for accurate isotopic measurements.

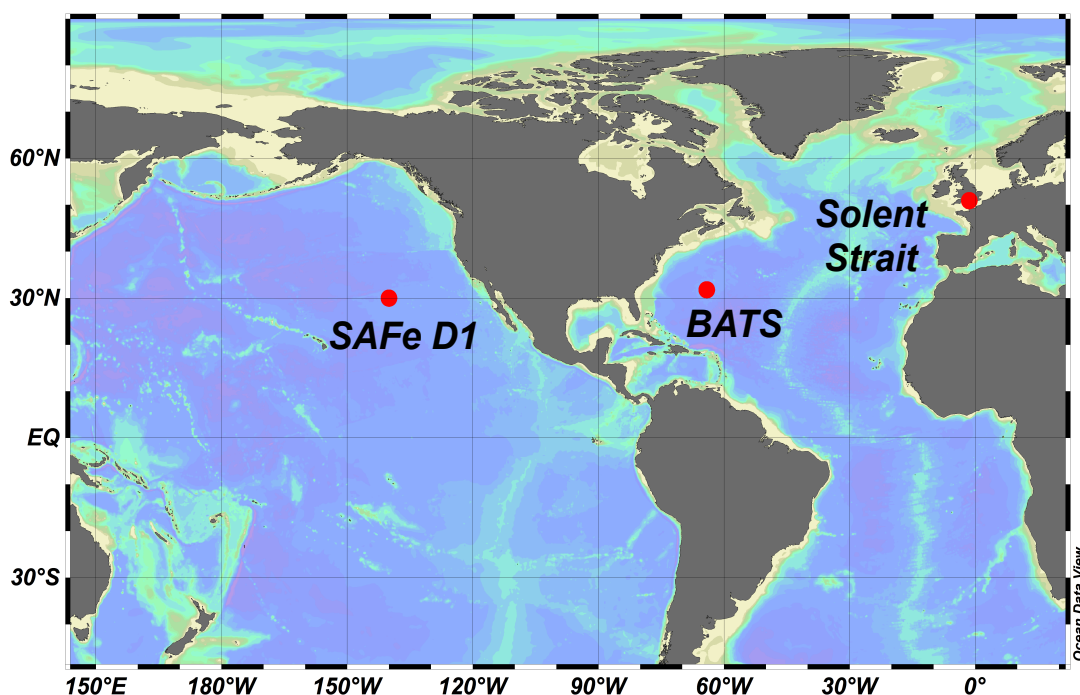


Figure 2.1: Locations of seawater samples analyzed in this study.

The present study addresses these shortcomings, through the development and validation of a novel technique for the isolation of Cd from seawater samples as large as 20 L, prior to stable isotope analysis. The methodology is able to process large samples by coprecipitation of Cd with $\text{Al}(\text{OH})_3$, and achieves excellent yields and high elemental purity for Cd. The isotopic analyses of Cd were carried out using a double spike technique in conjunction with MC-ICP-MS. A new ^{111}Cd - ^{113}Cd double spike was used, which is more suitable than other previously employed double spikes for MC-ICP-MS analyses, as it is less subject to spectral interferences whilst providing isotopic and concentration data of excellent precision and accuracy.

2.2 Experimental

2.2.1 Samples and reference materials

The method development required access to a large volume of seawater and hence a 180 L sample was collected from onboard the R/V Bill Conway in the Solent Strait of the English Channel (at 50.9°N, 1.4°W) in February 2008 (Fig. 2.1). The water was obtained with a trace metal clean pumping system that utilized a boom to allow sampling at a distance of about 3 m from the boat to minimize contamination from the ship. The seawater was initially stored in pre-cleaned low density polyethylene (LDPE) vessels, then transported to Imperial College London and filtered through 0.45 m Millipore cellulose filters with the aid of a peristaltic pump into cleaned 10 L and 20 L LDPE containers. For storage, the samples were subsequently acidified with distilled 6 M HCl to pH 2. Growth of plankton was observed in all vessels holding Solent Strait seawater prior to filtration. The filtration (and thereby removal of plankton) was a slow process that was only completed after 5 days for the 180 L sample, as a result of frequent clogging of the filters by organic material. To distinguish between seawater that was filtered at different times (and which hence supported plankton growth for different time periods), the various 10 to 20 L sub-samples of filtered Solent Strait seawater (SSW) are denoted by distinct letters, whereby SSW-A was filtered within 24 h of collection, whilst SSW-E was treated last (about 4 days later).

Various other seawater reference samples were analyzed to validate and document the performance of the new analytical method. This includes aliquots of SAFe D1 seawater and a number of samples from the 2008 GEOTRACES Atlantic intercalibration exercise. The SAFe D1 seawater was collected in the western Pacific Ocean (30°N, 140°W) at 1000 m depth during the Sampling and Analysis of Fe (SAFe) research cruise in October/November, 2004 (Johnson et al., 2007) (Fig. 2.1). Following collection, this water was filtered using 0.2m Poretics cartridge filters, homogenized, acidified to pH 1.8 using distilled HCl, and filled into 500 ml LDPE bottles (Johnson et al., 2007).

The 2008 GEOTRACES Atlantic Intercalibration cruise obtained seawater from the

BATS (Bermuda Atlantic Time Series) station at 31.8°N, 64.1°W (Fig. 2.1). The seawater samples, which were transferred to and stored in pre-cleaned LDPE containers following collection, are (i) GSI (GEOTRACES Surface Intercalibration) collected from near the surface by a towed underway fish; (ii) GDI (GEOTRACES Deep Intercalibration) obtained at 2000 m depth by multiple casts of the GEOTRACES Go-Flo Rosette; and (iii) an intercalibration depth profile (GPrI) covering 75-3000 m that was collected with the same device.

A number of different Cd isotope standards, for which previously published reference values are available, were analyzed to test the performance of the new ^{111}Cd - ^{113}Cd double spike. These included JMC Cd Münster, Münster Cd, Alfa Cd Zurich, BAM-I012 Cd (from the German Bundesanstalt für Materialwissenschaft und -prüfung) and NIST SRM 3108, which is a new proposed Cd isotope reference material (Wombacher and Rehkämper, 2004; Rehkämper et al., 2011).

2.2.2 Reagents and general laboratory procedures

All critical sample preparation work was carried out in Class 10 laminar flow workbenches within the Class 1,000 MAGIC clean room facility at Imperial College London. Mineral acids were purified once by sub-boiling distillation in either quartz (6 M HCl, 15 M HNO₃) or Teflon (12 M HCl) stills. A purified about 8 M NH₃ solution was prepared by isopiestic distillation of commercially available 28% NH₃ solution in a Savillex Teflon elbow. All water used was of better than 18 MΩ grade from a Millipore purification system. The HNO₃ - HBr mixture that is required for the anion-exchange chemistry was prepared freshly on the day of use.

Two different ^{111}Cd - ^{113}Cd double spike solutions with Cd concentrations of approximately 100 ng/g in 0.7 M HCl were used during the course of this work. Both featured $^{111}\text{Cd}/^{113}\text{Cd} \approx 1.5$ to 2.0, in accord with error propagation models, which suggest that a spike with $^{111}\text{Cd}/^{113}\text{Cd}$ ratio of 1.56 is the best composition for precise double spike stable Cd isotope analyses that do not require measurement of ^{106}Cd , ^{108}Cd , ^{110}Cd and ^{116}Cd

(Rudge et al., 2009). These isotopes were avoided for the MC-ICP-MS analyses, as they may involve the monitoring of ion beams that have an unsuitably large mass dispersion or feature problematic spectral interferences, particularly from Pd and Sn. In comparison with a previously used ^{110}Cd - ^{111}Cd double spike, the new spike composition is thus superior as provides more favorable error propagation (Rudge et al., 2009) and does not suffer from Pd interferences, which are not straightforward to correct (Ripperger and Rehkämper, 2007). The preparation and calibration of both double spike solutions followed techniques previously outlined (Ripperger and Rehkämper, 2007).

A purified, Cd-free solution of Al at a concentration of about 0.23 mol/L (or 0.63% w/v) in 0.7 M HCl (which yields the stoichiometry of AlCl_3) was used to produce insoluble $\text{Al}(\text{OH})_3$ for the co-precipitation of Cd. This Al solution was prepared as follows. About 0.5 g of Al slug (99.9999% purity; Alfa Aesar Puratronic) was dissolved in 15 ml 6 M HCl at 90°C on a hotplate. Following digestion of the metal, the solution was diluted with Milli-Q water to obtain 0.7 M HCl. Purification of the Al solution (particularly for the removal of Cd) was then achieved by anion-exchange chromatography, using a variant of the procedure that is applied for Cd separation from seawater (see below).

2.2.3 Sample preparation for Cd isotope analysis

Rationale

A commonly employed procedure for the separation of Cd and other trace metals from seawater for concentration analyses involves co-precipitation with $\text{Mg}(\text{OH})_2$, which forms on addition of aqueous NH_3 to seawater (Hendry et al., 2008; Wu and Boyle, 1997). In principle, such a technique is also adaptable to the much larger seawater volumes that are needed for Cd isotopic measurements, but there are a number of drawbacks. These include the relatively large volumes of aqueous NH_3 needed to precipitate Mg hydroxide, poor Cd yields and co-precipitation of other elements (such as Mo, Sn), which can introduce problematic spectral interferences. The results of this study demonstrate that the disadvantages of $\text{Mg}(\text{OH})_2$ can be avoided, if Cd is precipitated from seawater using $\text{Al}(\text{OH})_3$. Following

this, the samples are further purified by column chromatography prior to isotopic analysis. For the seawater samples with volumes of less than 1-2 L and Cd contents approximately greater than 0.05 nmol/kg, $\text{Al}(\text{OH})_3$ co-precipitation procedure is not necessary; hence, the double spiked seawater samples can be processed directly with the column chemistry (Ripperger and Rehkämper, 2007).

Preliminary Cd concentration measurements

Prior to preparing seawater samples for Cd isotope analyses, it is helpful if the Cd concentrations are known to within a factor of 2-5, or better. This is to (i) determine whether use of the co-precipitation technique is necessary for the processing of samples with low Cd contents ($[\text{Cd}] < 0.05 \text{ nmol/kg}$) and (ii) achieve optimum spiking of samples with a (molar) ratio of spike-derived Cd to natural Cd (S/N ratio) of about 1, relevant for our particular double spike composition (Rudge et al., 2009).

If the Cd concentration of a sample is not known or cannot be estimated to the desired level of accuracy (e.g., based on published phosphate data), it is useful to carry out a preliminary concentration analysis using a small aliquot of the available sample. Such measurements can utilize published techniques that employ either quadrupole or high resolution ICP-MS (Hendry et al., 2008; Wu and Boyle, 1997). In this study, we used an abbreviated version of the methodology that is applied for the Cd isotope analyses. To this end, a small aliquot (about 50-100 ml) of the seawater sample was taken, spiked with a suitable amount of the Cd double spike solution, and acidified to 0.7 M HCl. Then, the Cd was separated from the matrix with a simplified version of the column chemistry described below (this involved use of only the 1st stage anion exchange and the 3rd stage Eichrom TRU-spec resin columns (Ripperger and Rehkämper, 2007)). Finally, the Cd concentration was determined by isotope dilution analysis with the MC-ICP-MS, in a manner similar to that employed for the stable isotope measurements. It is conceivable that a simpler procedure, using only the 1st stage anion exchange columns with or even without double spiking, could also be used for the preliminary concentration measurements by MC-ICP-MS, but this was not tested during the course of this study.

Weighing and spiking of samples

The Cd isotope analyses of this study utilized seawater samples with volumes of about 0.25 to 20 L. These samples were first weighed and then a suitable volume of ^{111}Cd - ^{113}Cd double spike solution was weighed into a 15 ml Savillex Teflon beaker for each samples, to obtain an optimal S/N ratio of about 1. Large seawater samples (volume > 2 L), which required Cd co-precipitation, were checked to have $\text{pH} < 1.6$, prior to the addition of the Cd double spike. For smaller samples, which were processed without co-precipitation, the double spike solution was added directly and the double spiked samples were then made up to be in 0.7 M HCl by addition of 6 M HCl. All samples were then left to stand for at least three days (Ripperger and Rehkämper, 2007) prior to further processing.

Co-precipitation of Cd with Al-hydroxide

Following spike-sample equilibration, a suitable volume of the about 0.23 M AlCl_3 solution was added to the seawater samples, to obtain an Al^{3+} concentration of 50 mg/l. The solutions were first left to stand for 48h and $\text{Al}(\text{OH})_3$ was then precipitated by addition of aqueous NH_3 solution, to obtain a final pH of 8.5. The samples were thoroughly shaken and left to stand for at least 3 days to allow the precipitate to fully form, coagulate and sink to the bottom of the containers. Next, the supernatant was decanted as far as possible in several careful steps. In general, 90%-95% of the supernatant could be decanted without significant entrainment of precipitate. Subsequently, the precipitate was dissolved in 6 M HCl and the volume of acid added was adjusted, on the basis of the volume of (i) NH_3 used and (ii) remaining sample solution, to obtain a final HCl molarity of about 0.7 M. This solution was left to stand for at least 24 hr, following which it was ready for the separation of Cd by column chromatography.

Cd separation by column chromatography

The three-stage column chemistry procedure that was used for the purification of Cd is essentially identical to that previously employed (Ripperger and Rehkämper, 2007) and hence, this is only briefly summarized here along with the modifications (Table 2.1). The

Table 2.1: Column chemistry procedures for the isolation of Cd from seawater.

	First Stage Column Chemistry		Second Stage Column Chemistry		Third Stage Column Chemistry	
Column Cleaning	large quartz glass columns with 100 ml reservoirs and 1.5 ml resin beds		small shrink-fit Teflon columns with 1.4 ml reservoirs and 100 μ l resin beds		small shrink-fit Teflon columns with 1.4 ml reservoirs and 100 μ l resin beds	
	4M HNO ₃		4M HNO ₃		6M HCl	
	0.4M HBr		0.4M HBr			
	6M HCl		6M HCl			
	Milli-Q		Milli-Q		Milli-Q	
0.1M HCl		0.1M HCl				
Resin Loading	Biorad AG 1X8 anion exchange resin, 100-200 mesh, 1.5ml		Biorad AG 1X8 anion exchange resin, 200-400 mesh, 100ul		Eichrom TRU Spec resin, 100 ul	
Resin Cleaning	11 ml 2M HNO ₃	Resin cleaning	750 ul 2M HNO ₃	Resin cleaning	10 ml 6M HCl	Cleaning & equilibration
	0.5 ml H ₂ O		50 ul H ₂ O			
	25 ml 6M HCl	Conversion to Cl ⁻ form	1000 ul 8M HCl	Conversion to Cl ⁻ form		
	11 ml 0.7M HCl	Resin equilibration	800 ul 0.7M HCl	Resin equilibration		
Sample Loading & Chemical Elution	Up to ~4L seawater, 0.7M in HCl	Sample loading	1400 ul sample solution in 0.7M HCl	Sample loading	200 ul sample solution in 8M HCl	Sample loading & collect Cd
	23 ml 0.7M HCl	Matrix elution	1000 ul 0.7M HCl	Matrix elution	200 ul 8M HCl	Collect Cd
	10 ml 1M HCl		650 ul 1M HCl			
	10 ml 2M HCl		650 ul 2M HCl			
	10 ml 8M HCl	Elution of Ag	650 ul 8M HCl	Elution of Ag	1.4 ml 6M HCl	
	10 ml 0.5M HNO ₃ -0.1M HBr	Elution of Zn	650 ul 0.5M HNO ₃ -0.1M HBr	Elution of Zn		
	2 ml 2M HNO ₃		130 ul 2M HNO ₃			
	10 ml 2M HNO ₃	Collect Cd	700 ul 2M HNO ₃	Collect Cd		

first separation stage employed 1.5 ml anion exchange resin in large quartz glass columns with 100 ml reservoirs and two modifications were made in comparison to the methods employed (Ripperger and Rehkämper, 2007): (i) Biorad AG 1X8 100-200 mesh anion exchange resin was employed in this study (instead of AG 1X8 with 200-400 mesh beads), because this provides higher elution rates; and (ii) the initial conversion of the resin to the Cl⁻ form was accomplished using 25 ml 6M HCl instead of 16 ml 8M HCl. The remaining two stages of the separation chemistry were identical to those described by Ripperger and Rehkämper (2007). Both were carried out in small shrink-fit Teflon columns that featured 100 μ l beds of (i) Biorad AG 1X8 200-400 mesh anion exchange resin (2nd stage) and (ii) Eichrom TRU Spec resin (3rd stage), respectively.

Following separation, the purified Cd fractions were evaporated to dryness, dried twice with a drop (about 30 μl) of 15M HNO_3 and a further drop of 15M HNO_3 was then added for sample storage. Prior to Cd isotope analysis, these solutions were evaporated to near complete dryness, redissolved in an appropriate volume of 0.1M HNO_3 to obtain the desired Cd concentration and ultra-sonicated for 5-15 min to ensure complete dissolution.

2.2.4 Cd isotope measurements

Mass spectrometry

The double spike isotope measurements were carried out with a Nu Instruments Nu Plasma MC-ICP-MS at the MAGIC Laboratories, Imperial College London. The instrument was operated using an acceleration potential of 6 kV and is fitted with a large capacity (80 l/min) rotary pump for evacuation of the expansion chamber. Sample introduction was achieved with a Nu Instrument DSN desolvator and Micromist glass nebulizers with flow rates of about 100-120 $\mu\text{l}/\text{min}$. For the isotopic analyses, the ion currents at masses 111 (Cd), 112 (Cd + Sn), 113 (Cd + In), 114 (Cd + Sn), 115 (In), and 117 (Sn) were measured simultaneously with Faraday cups, which are equipped with $10^{11} \Omega$ resistors. The ion beams of ^{115}In and ^{117}Sn were monitored to achieve precise interference corrections. The measurement and washout procedures are otherwise identical to those described in the previous study (Ripperger and Rehkämper, 2007). Most seawater samples were analyzed as solutions with total Cd concentrations of about 40-60 ng/ml and typically, these samples were spiked to obtain a S/N ratio of about 1, such that each analysis consumed only about 20-30 ng of natural (seawater-derived) Cd. In general, these measurements were carried out at sensitivities of about 250 to 350 V/ppm, equivalent to a transmission efficiency of up to about 0.25%.

Data reduction and reporting

The Cd isotope data collected during the mass spectrometric analyses were further processed, to calculate the 'true' isotope compositions of the unspiked samples that were cor-

rected for both instrumental mass bias and isobaric interferences. These data were then used to determine the reported $\epsilon^{114/110}\text{Cd}$ values of the samples relative to an isotopic standard (std):

$$\epsilon^{114/110}\text{Cd} = \left[\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{sample}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{std}}} - 1 \right] \times 10,000$$

In this study, $\epsilon^{114/110}\text{Cd}$ are reported relative to the JMC Cd Münster solution, which has been used in a number of previous investigations (Rehkämper et al., 2011; Wombacher and Rehkämper, 2004). The reduction of the isotopic data was carried out offline, using a modified version of the spreadsheet-based methods (Ripperger and Rehkämper, 2007). In brief, our calculations utilized the measured $^{112}\text{Cd}/^{111}\text{Cd}$, $^{113}\text{Cd}/^{111}\text{Cd}$ and $^{114}\text{Cd}/^{111}\text{Cd}$ isotope ratios. These were first corrected for isobaric interferences and the double spike equations were then solved to determine $\epsilon^{114/113}\text{Cd}$ values relative to the JMC Cd Münster standard. These calculations utilized the iterative procedure of (Siebert et al., 2001), which was modified to allow use of the general power law (Maréchal et al., 1999), as this permits mass fractionation effects to be described by any desired non-linear function. In this study, the instrumental and natural mass fractionation was assumed to follow the general power law with an exponent of $n \approx 0.2$ (Wombacher and Rehkämper, 2003) and the exponential law, respectively. Finally, the $\epsilon^{114/113}\text{Cd}$ data were translated into $\epsilon^{114/110}\text{Cd}$ using the relationship:

$$\epsilon^{k/m} = \left[(\epsilon^{l/m}\text{Cd}/10,000 + 1)^\beta - 1 \right] \times 10,000$$

For the kinetic law, β is defined as:

$$\beta = \ln(m_k/m_m) / \ln(m_l/m_m)$$

where m_k , m_l and m_m refer to the exact atomic masses of the Cd isotopes k , l , and m (Rehkämper et al., 2011; Wombacher and Rehkämper, 2004).

As a by-product, the Cd double spike isotope measurements also yield precise Cd concentration data. To this end, the mass-bias-corrected $^{114}\text{Cd}/^{111}\text{Cd}$ isotope ratios of the

Chapter 2. A New Methodology for Precise Seawater Cadmium Isotope Analyses 63

Table 2.2: Typical within-day reproducibility of Cd isotope data (reported as $\epsilon^{114/110}\text{Cd}$) for multiple analyses of Cd double spike-natural Cd mixtures at different concentrations and $S/N \approx 1$.

Total Cd concentration of spike + std. solution (ppb)	$\pm 2\text{sd}$ uncertainty for $\epsilon^{114/110}\text{Cd}$	Natural Cd consumed per analysis (ng)
120	0.4-0.7	~60
60	0.4-0.7	~30
40	0.5-0.8	~20
20	1.0-1.4	~10
3	~2-3	~1.5
1	~5	~0.5

spiked samples were evaluated using a conventional isotope dilution equation. All concentration data were corrected for blanks of about 20 - 30 pg Cd, which determined by processing total procedural blanks alongside each batch of 6 - 12 samples. No blank correction were applied to the $\epsilon^{114/110}\text{Cd}$ results, as the blank raised the natural Cd concentrations for the most Cd depleted samples (from the GEOTRACES Intercalibration cruise) by only about 1.0 - 1.5% and amounted to the less than 0.25% of the indigenous Cd for the remainder of the seawater samples.

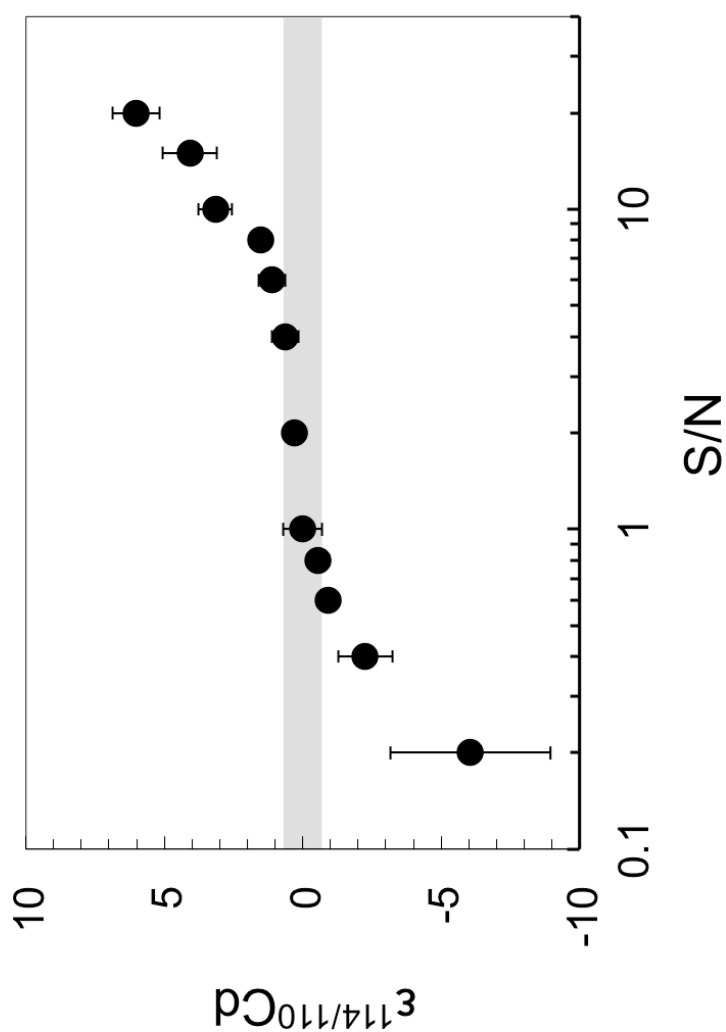


Figure 2.2: Plot of Cd isotope data (as $\epsilon^{114/110}\text{Cd}$) for mixtures of the Cd double spike with the JMC Cd Münster standard, obtained at various S/N ratios (molar ratio of Cd from spike vs. natural Cd from the standard). The $\epsilon^{114/110}\text{Cd}$ values were determined and calculated relative to a Cd double spike - JMC Cd Münster mixture with $S/N = 1$. The error bars denote the 2sd uncertainties determined from the results of multiple analyses.

2.3 Results and discussion

2.3.1 Results for the JMC Cd Münster 'zero epsilon' standard

Mixtures of the ^{111}Cd - ^{113}Cd double spike and the zero-epsilon standard with a near-optimal S/N ratio of about 1 were analyzed at least 5-7 times during each measurement session. Such analyses typically achieved within-day reproducibilities (2sd) of about $\pm 0.5 \epsilon^{114/110}\text{Cd}$, when spiked Cd standard solutions with total Cd concentrations of about 60 ng/ml were used for the analysis (Table 2.2). Higher total Cd contents of up to 120 ng/ml did not significantly improve the precision, presumably because this is the primarily limited by uncertainties of the data reduction scheme rather than counting statistics. These analyses consumed about 30 to 60 ng of natural Cd, but smaller samples can also be analyzed with good precision (Table 2.2). For example, the measurements of spiked Cd solutions with concentrations of 40 ng/ml and 20 ng/ml showed within-day reproducibilities of about ± 0.7 and $\pm 1.4 \epsilon^{114/110}\text{Cd}$, respectively. Even isotopic measurement of only 0.5-1.5 ng of natural Cd are possible, as solutions with total Cd at 1-3 ng/ml, but such analyses typically feature uncertainties of ± 2 to $4 \pm 5 \epsilon$ (Table 2.2). In summary, this demonstrates that sample analyses with solutions containing 60 ng/ml Cd are ideal and these only require 30 ng of natural Cd for a solution volume of 1 ml. Importantly, no deviations in $\epsilon^{114/110}\text{Cd}$ values were found when solutions with Cd concentrations of between 20 to 120 ng/ml were analyzed relative to one another.

As in a previous Cd isotope investigation (Ripperger and Rehkämper, 2007), which utilized a ^{110}Cd - ^{111}Cd double spike, our analyses of double spike - zero-epsilon standard mixtures generally yielded small but non-negligible offsets (typically ± 0.5 to $\pm 3 \epsilon^{114/110}\text{Cd}$) from the correct result of $\epsilon^{114/110}\text{Cd} = 0$. These deviations are interpreted to reflect day-to-day variations in the mass bias behavior of the instrument and sample introduction system (Ripperger and Rehkämper, 2007). To account for this variability, the $\epsilon^{114/110}\text{Cd}$ data of samples are given relative to the mean result obtained for multiple analyses of double spike - zero-epsilon standard mixtures on the same measurement session, an approach that was previously shown to be reliable (Ripperger and Rehkämper, 2007).

Analyses were also carried out to ascertain that the ^{111}Cd - ^{113}Cd double spike can provide accurate results over a wide range of spike to sample (S/N) ratios. In these experiments, the $\epsilon^{114/110}\text{Cd}$ values of double spike - zero-epsilon standard mixtures characterized by S/N ratios of between 0.2 and 20 were analyzed relative to a mixture with S/N = 1 (Fig. 2.2). These measurements showed that accurate results, with $\epsilon^{114/110}\text{Cd}$ values that are identical within uncertainty to $\epsilon^{114/110}\text{Cd} = 0$, were obtained over a relatively wide range of S/N, from about 0.6 to 6 (Fig. 2.1). Despite this excellent dynamic range, the actual seawater analyses were typically carried out relative to double spike - standard mixtures, which had S/N ratios and total Cd contents that were matched to within better than a factor of 2. This procedure was adopted to optimize the accuracy of the results and ensure that the uncertainty of the sample data could be determined from multiple analyses of a comparable standard solution.

2.3.2 Results for other Cd isotope reference materials

A number of different Cd isotope reference materials, which have been used in previous studies, were analyzed as part of this study (Table 2.3). Such analyses are vital, (i) to document the accuracy of the data and (ii) to facilitate the comparison of Cd isotope results acquired in different laboratories, with different zero epsilon standards. The data summarized in Table 2.3. show that the analyses with the new ^{111}Cd - ^{113}Cd double spike yielded results that are identical, within uncertainty, to previously published data. Of particular importance in this regard are the fractionated BAM-I012 and Münster Cd reference materials, as data are available for these samples from a large number of different laboratories and studies. The results acquired for the SRM NIST 3108 Cd solution, which is only marginally fractionated relative to the JMC Cd Münster solution with $\epsilon^{114/110}\text{Cd} = 1.0 \pm 0.3$, are of interest because this material has been proposed as a possible international zero-epsilon standard for future Cd isotope studies (Abouchami et al., 2011; Rehkämper et al., 2011).

Table 2.3: Summary of Cd isotope data (as $\epsilon^{114/110}\text{Cd}$) from this study and the literature, for various standards and reported relative to the JMC Cd Münster zero-epsilon isotope reference material.

Cd Standard	Method	Alfa Cd Zurich	BAM-1012 Cd	Münster Cd	NIST 3108 Cd
This study	^{111}Cd - ^{113}Cd DS, MC-ICP-MS	0.5 ± 0.3	-12.4 ± 0.8	46.2 ± 0.5	1.0 ± 0.3
Wombacher and Rehkämper (2004)	Ag norm, MC-ICP-MS		-10.8 ± 1.5	46.5 ± 0.5	
Ripperger and Rehkämper (2007)	^{110}Cd - ^{111}Cd DS, MC-ICP-MS	0.0 ± 0.5	-12.4 ± 1.1	46.4 ± 1.2	
Ripperger and Rehkämper (2007)	Ag norm, MC-ICP-MS		-11.4 ± 1.5	46.0 ± 1.5	
Schmitt et al. (2009)	^{106}Cd - ^{108}Cd DS, TIMS		-12.3 ± 0.3	44.8 ± 0.2	
Gao et al. (2008)	SSB, MC-ICP-MS		-12.0 ± 1.2	45.9 ± 1.2	
Shiel et al. (2009)	Ag norm, MC-ICP-MS		-13.7 ± 2.5	45.0 ± 0.3	

All results are reported with $\pm 2\text{sd}$ uncertainties. For the data of this study, the uncertainties are based on the results of multiple sample analyses except for Münster Cd, where the uncertainty is based on multiple analyses of a matching standard. For the published results, the uncertainties are reported as given. Ag norm = external normalization using admixed Ag; DS = double spike; SSB = sample-standard bracketing of measured ratios

Table 2.4: Cd concentrations and isotope compositions for five sub-samples of Solent Strait Seawater (SSW) that were analyzed with and without the aid of $\text{Al}(\text{OH})_3$ co-precipitation.

Sub-sample	Aliquot	Sample Weight (g)	Co-precipitation	Cd Concentration (pmol/kg)	$\epsilon^{114/110}\text{Cd} \pm 2\text{sd}^b$
SSW-A	1	932	-	196.7	2.5 ± 0.6
	2	926	-	195.1	2.0 ± 0.6
	3	928	Yes	195.8	1.9 ± 0.6
	4	928	Yes	195.8	2.6 ± 0.6
	Average SSW-A ^a			195.8 ± 0.9	2.3 ± 0.4
SSW-B	1	931	-	158.6	3.1 ± 0.9
SSW-C	1	931	-	149.7	4.2 ± 0.7
SSW-D	1	906	-	148.5	5.2 ± 0.8
	2	3624	-	148.6	3.3 ± 1.4
	3	3624	Yes	148.6	4.2 ± 0.7
	Average SSW-D ^a			148.6 ± 0.1	4.2 ± 1.0
SSW-E	1	914	-	147.1	3.7 ± 0.8
	2	3655	-	147.2	3.7 ± 1.4
	3	3655	Yes	147.2	3.3 ± 0.7
	Average SSW-E ^a			147.2 ± 0.1	3.6 ± 0.3

^a To account for the small number of replicates, the uncertainties given for average values encompass the total range of the data.

^b The uncertainties of the individual sample analyses are based on the 2sd uncertainties of the $\epsilon^{114/110}\text{Cd}$ values obtained for matching standard solutions that were analyzed before and after sample measurements.

Table 2.5: Cd concentrations and isotope compositions for seawater reference material SAFe D1 and the GEOTRACES inter-calibration samples GDI, GSI, and GPrI

Sample	Aliquot/Bottle	Water Depth (m)	Sample Weight (g)	Co- precipitation	Cd Concentration (pmol/kg)	$\epsilon^{114/110}\text{Cd} \pm 2\text{sd}^b$
SAFe D1	256-1	2000	255	-	1011	4.2 ± 1.1
	256-2	2000	252	-	1014	4.1 ± 0.5
	257-1	2000	256	-	1012	4.3 ± 0.5
	255-2, 257-2, 258	2000	1025	Yes	1010	4.2 ± 0.5
	Average SAFe D1 ^a				1012 ± 2	4.2 ± 0.1
GDI	49	2000	931	-	270.6	6.1 ± 0.4
	50	2000	931	-	272.1	6.0 ± 0.4
	51	2000	938	-	270.8	5.5 ± 0.4
	Average GDI ^a				271.2 ± 0.9	5.8 ± 0.3
GSI	74, 75	5	20393	Yes	1.2	23.1 ± 5.3
GPrI	49	75	8859	Yes	2.2	14.5 ± 5.3
GPrI	41	125	7932	Yes	1.7	12.8 ± 5.3
GPrI	33	250	150	-	34.8	- ^c
GPrI	27	500	927	-	138.4	6.7 ± 0.6
GPrI	21	1000	937	-	293.8	6.6 ± 0.6
GPrI	9	2500	931	-	293.1	5.2 ± 0.6
GPrI	4	3500	934	-	295.1	5.5 ± 0.6

^a To account for the small number of replicates, the uncertainties given for mean values encompass the total range of the data.^b The uncertainties quoted for the samples are based on the 2sd uncertainties determined for multiple analyses of matching standard solutions that were analyzed before and after each sample measurement. ^c Insufficient sample volume available for an isotopic measurement of comparable precision.

2.3.3 Results for Solent Strait seawater

Five different sub-samples of Solent Strait seawater from separate containers, denoted SSW-A through SSW-E, were analyzed (Table 2.5). Initial co-precipitation experiments with SSW-A3 and SSW-A4 utilized additions of 40 and 100 mg/L Al^{3+} , respectively, and both experiments provided essentially identical Cd yields of about 90%. Based on this, the co-precipitation experiments for SSW-D3 and SSW-E3 (and all other samples; see Table 2.5) utilized Al^{3+} additions of 50 mg/L and Cd yields of better than 85% were achieved in all cases. Similar measurements were carried out for samples that only utilized column chromatography for the Cd separation, and these also consistently showed yields of greater than 90%. Overall, these results demonstrate that the present methods can provide nearly quantitative Cd separation yields on a routine basis.

Three of the SSW sub-samples, SSW-A, SSW-D and SSW-E, were analyzed multiple times, with and without the application of co-precipitation for Cd separation (Table 2.4.). Importantly, the different separation methods provide data that are identical, within uncertainty, for all analyzed aliquots. This suggests that the Cd separation and data acquisition are robust and can routinely provide reliable results. The uncertainties quoted for the individual SSW aliquots (Table 2.4.) are based on the reproducibility of the matching double spike - zero-epsilon standard analyses, which is typically about 0.5 - 1.0 ‰ ($\pm 2\text{sd}$, Table 2.4.). For a few samples, the uncertainties are larger, as a result of instabilities in the instrumental mass bias that were tolerated during the early stages of method validation.

For the Cd concentration data, the results obtained for individual aliquots deviate from the mean value by less than $\pm 0.1\%$ for sub-samples SSW-D and SSW-E, whilst larger deviations of up to about $\pm 0.5\%$ were observed for SSW-A (Table 2.4.). Based on these results, the Cd concentrations are estimated to have an accuracy and precision of better than 0.5% ($\pm 2\text{sd}$), in accordance with the data of a study that utilized similar methods (Ripperger and Rehkämper, 2007).

Of interest is the observation that the five SSW sub-samples (A-E) display resolvable

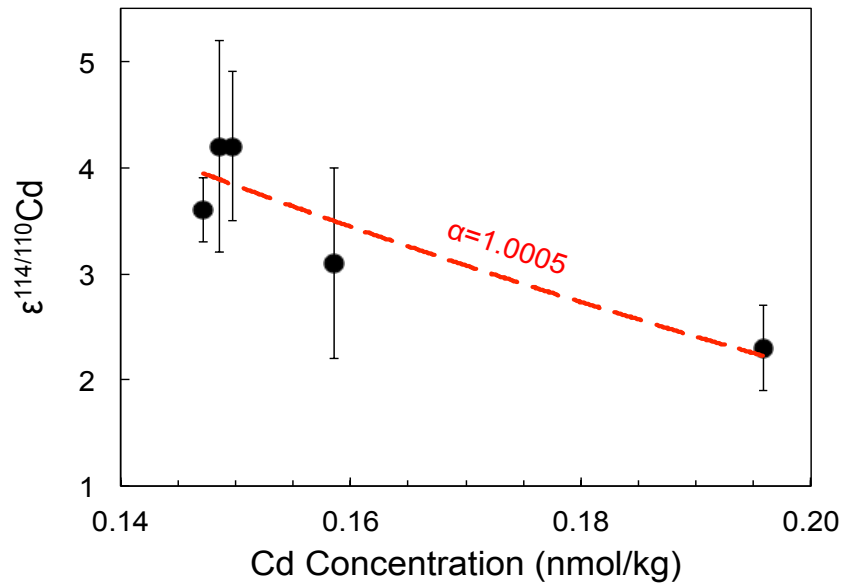


Figure 2.3: Plot of $\epsilon^{114/110}\text{Cd}$ values vs. Cd concentrations for the five sub-samples of Solent Strait seawater SSW (SSW-A to SSW-E; see Table 2.4.). A significant variability of Cd concentrations is correlated with smaller changes in $\epsilon^{114/110}\text{Cd}$ and the correlation is in accord with Cd isotope fractionation by biological utilization and a fractionation factor of $\alpha = 1.0005 \pm 0.0003$ (red dashed line). The uncertainties are taken from Table 2.4

and systematic variations in Cd concentrations from 147.2 to 195.8 pmol/kg. This variability is unlikely to reflect original differences in the Cd content of the sampled seawater, because all bottles were filled at the same location within a time span of 1.5 hr. Rather, it is more plausible that the differences in dissolved Cd contents are due to biological uptake within the bottles prior to filtration and subsequent acidification. This interpretation is reasonable, because the time period between collection and filtration varied from about 3h for SSW-A to about 96 hr for SSW-E.

Further support for this explanation is provided by the observation that the SSW data are in accordance with a logarithmic trend in a diagram of $\epsilon^{114/110}\text{Cd}$ vs. Cd content (Fig. 2.3), equivalent to a linear trend in a plot of $\epsilon^{114/110}\text{Cd}$ vs. $\ln[\text{Cd}]$. The slope of the lat-

ter correlation (m) was used to determine the isotope fractionation factor α for biological uptake and utilization of Cd (Ripperger et al., 2007):

$$\alpha = \left(\frac{m}{10,000} + 1 \right)^{-1}$$

The observed slope of $m = -5.0 \pm 2.7$, determined with software package Isoplot (Ludwig, 2003), thus yields a fractionation factor of $\alpha \approx 1.0005 \pm 0.0003$. This value is identical to the fractionation factors of $\alpha \approx 1.0002 - 1.0006$ that were previously inferred to characterize biological Cd isotope fractionation in the oceans (Abouchami et al., 2011; Lacan et al., 2006; Ripperger et al., 2007). The agreement thus supports the conclusion that the observed variations in Cd concentration amongst different sub-samples of SSW (Table 3) reflect in situ uptake of Cd by plankton prior to filtration.

2.3.4 Results for SAFe D1 seawater

A 1 L aliquot of SAFe D1 was analyzed using co-precipitation for the pre-concentration of Cd, whilst three further analyses utilized only the column chemistry for the isolation of Cd (Table 2.5). Notably, the Cd concentrations and $\epsilon^{114/110}\text{Cd}$ values of these four analyses deviate from the mean by less than 0.2% and 0.1 ϵ . The lack of any systematic offset between the results obtained with and without co-precipitation furthermore underlines the accuracy of the results. This conclusion is reinforced by the observation that SAFe D1, which was collected in the Pacific Ocean at 1000 m depth (Johnson et al., 2007), has an isotope composition of $\epsilon^{114/110}\text{Cd} = 4.2 \pm 0.1$ (Table 2.5), which is in accord with previous results for Pacific seawater from depths ≥ 1500 m and the relatively constant $\epsilon^{114/110}\text{Cd}$ of $+3.8 \pm 0.5$ inferred for global deepwater (corrected for a 0.5 ϵ offset between JMC Cd Münster and Alfa Cd Zürich; Table 2.3) (Abouchami et al., 2011; Ripperger et al., 2007).

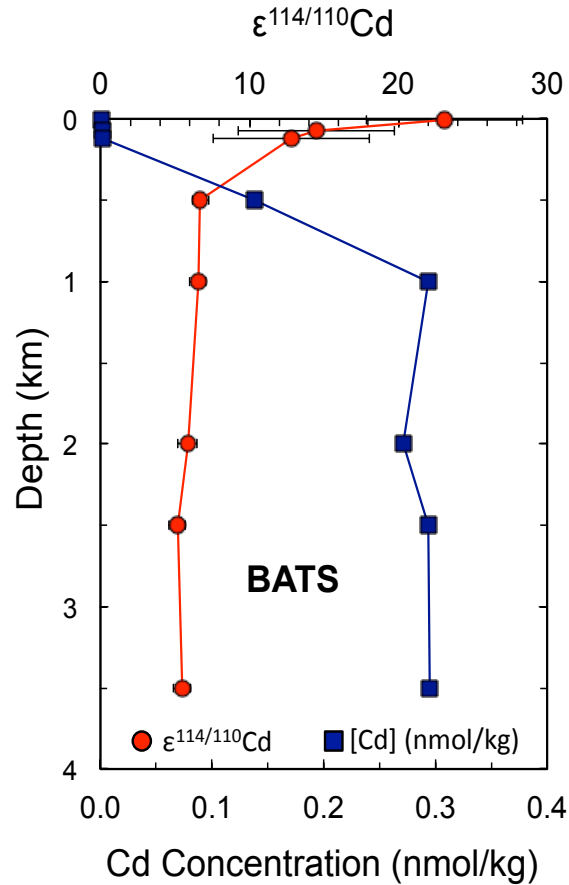


Figure 2.4: Depth profiles of Cd concentrations (blue filled squares) and isotope compositions (as $\epsilon^{114/110}\text{Cd}$; red filled dots) for the GEOTRACES intercalibration samples GSI and GDI (surface and deep water, respectively) as well as the GPrI depth profile samples from the BATS station in the North Atlantic (Table 2.5). Together, these samples provide the first full Cd isotope depth profile for the Atlantic Ocean, and this is similar to a published depth profile for the central Pacific (Station 7; (Ripperger et al., 2007)). The Cd concentration of GDI is not plotted, as this deviates significantly from the essentially constant values of the GPrI samples at depths > 1000 m (Table 2.5). This difference presumably reflects that the GDI and GPrI samples are from two different casts.

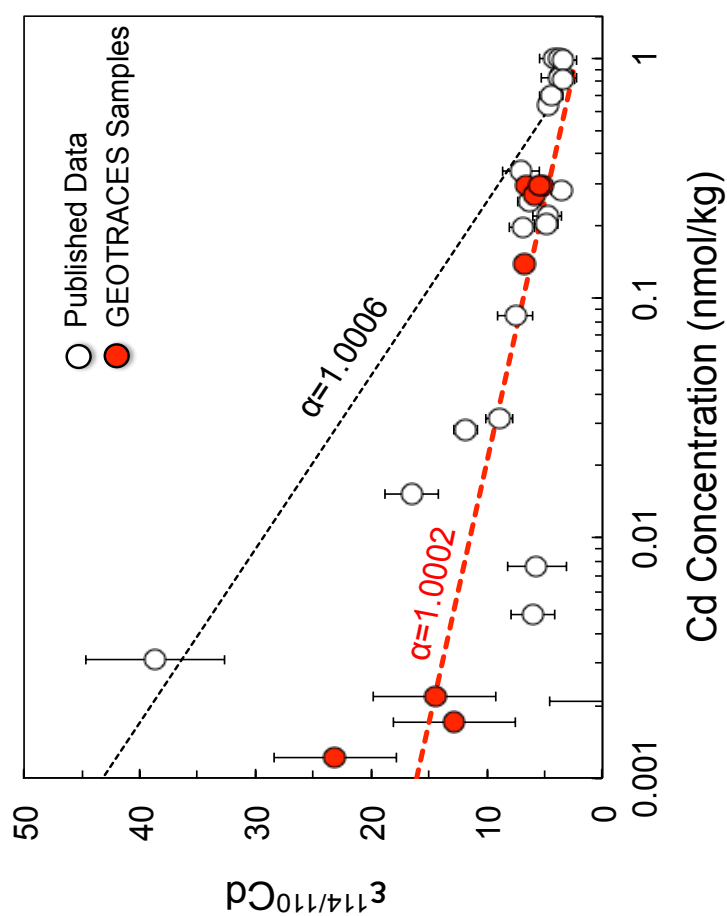


Figure 2.5: Cadmium isotope compositions (as $\epsilon^{114/110}\text{Cd}$) vs. Cd concentrations for the GEOTRACES intercalibration samples from the BATS station in the Atlantic Ocean (Table 2.5) and previous data from the literature (Ripperger et al., 2007). The dashed lines denote calculated Rayleigh fractionation trends for fractionation factors of $\alpha \approx 1.0002$ and 1.0006 .

2.3.5 Results for the 2008 GEOTRACES Atlantic intercalibration samples

Three of the GEOTRACES intercalibration samples, GSI and the GPrI samples from 75 m and 125 m depth, have Cd contents of only about 1-2 pmol/kg (Table 2.5). For the isotope analyses, it was therefore necessary to isolate Cd from large seawater volumes of about 10-20 L by co-precipitation with $\text{Al}(\text{OH})_3$ (Table 2.5). However, despite the large sample volumes, less than 2.5 ng of natural Cd was available for the isotopic analyses. Nonetheless, the measurements achieved reasonable uncertainties of about $\pm 5\epsilon$, and this was sufficient to identify and characterize the isotopic composition of these samples (Table 2.5; Figs. 2.4, 2.5)

The remaining GEOTRACES samples (with exception of GPrI from 250 m depth, which was only analyzed for Cd content; Table 2.5) had Cd concentrations of greater than 0.1 nmol/kg, and the sample preparation thus required only column chemistry (Table 2.5). For these samples, about 10-30 ng of natural Cd was available and the analyses achieved uncertainties (2sd), based on multiple analyses of matching standards, of about $\pm 0.5 \epsilon^{114/110}\text{Cd}$. Furthermore, three separate 1 L aliquots of the deepwater sample GDI were analyzed, and the individual results deviate from the mean value by less than $\pm 0.5 \%$ for the Cd concentration and by less than $\pm 0.3\epsilon$ for the isotope composition (Table 2.5). This indicates that the new analytical procedures can produce Cd isotope data with reproducibilities that approach those of the best double spike TIMS results (Abouchami et al., 2011; Schmitt et al., 2009a,b).

An important feature of the GEOTRACES intercalibration data is that they combine to provide the first comprehensive Cd isotope depth profile for the Atlantic Ocean (Fig. 2.4). Importantly, this isotopic profile is in accord with published seawater results, in that large isotope fractionations, with $\epsilon^{114/110}\text{Cd}$ values of greater than +10, are only found in Cd-depleted samples from depths of less than 250 m (Ripperger et al., 2007). In contrast, the GPrI samples from ≥ 1000 m exhibit almost identical Cd concentrations of about 0.29 nmol/kg and only very limited variability in $\epsilon^{114/110}\text{Cd}$, with values of between about +5.2 and +6.7 (Table 2.5, Fig. 2.4). However, the mean Cd content of GDI is slightly but signifi-

cantly lower compared to the deeper GPrI samples from depths of 1000-3500m. The origin of this difference is unclear but may reflect that the GDI and GPrI samples were collected from separate casts.

The observation that the GEOTRACES deepwater samples have a relatively constant $\epsilon^{114/110}\text{Cd}$ of approximately +5.5 (Table 2.5; Fig. 2.4) is significant, because previous analyses of deepwater from the Southern, Pacific and Arctic Oceans defined an essentially constant isotope composition of $\epsilon^{114/110}\text{Cd} = +3.8 \pm 0.5$ (1sd, $n = 7$; [5]). It is conceivable, that the marginally more positive value determined here for the deep Atlantic Ocean reflects the young ventilation age of this water mass. This tentative interpretation is interesting, as it implies that Cd isotope data can be used for isotopic tracing of water masses, but will need to be confirmed by additional analyses of further suitable samples.

In a diagram of $\epsilon^{114/110}\text{Cd}$ vs. Cd concentrations, the GEOTRACES samples define a positive correlation, albeit with significant scatter (Fig. 2.5). This observation supports the interpretation that the positive $\epsilon^{114/110}\text{Cd}$ values of the surface and near-surface water samples are generated by isotope fractionation from biological utilization. In fact, all data are in accord with a single, closed system Rayleigh fractionation trend characterized by a fractionation factor of $\alpha = 1.0002$ (Fig. 2.5). This result is in general agreement with previous Cd isotope analyses of seawater, which suggested that marine biological utilization of Cd is associated with isotope fractionation factors of about 1.0002 to 1.0006 (Abouchami et al., 2011; Lacan et al., 2006; Ripperger et al., 2007). However, the fractionations seen here for the most Cd-depleted samples are more moderate than the maximum effect, of $\epsilon^{114/110}\text{Cd} \approx +40$, that was previously determined for Pacific Ocean surface water. Hence, it is conceivable that the trend seen in Fig. 2.5 not only presents biological isotope fractionation during Cd uptake, but also reflects at least in part, mixing of surface water with water masses that feature more moderate $\epsilon^{114/110}\text{Cd}$ values combined with higher Cd contents (Ripperger et al., 2007).

2.4 Conclusions

A new technique has been developed for Cd isotope analyses of seawater. The methodology employs a new ^{111}Cd - ^{113}Cd double spike, co-precipitation of Cd with $\text{Al}(\text{OH})_3$, Cd purification by column chromatography, and isotopic analysis by MC-ICP-MS. The method can routinely achieve Cd yields of better than 85%, whilst the co-precipitation step allows isolation of Cd from seawater samples with volumes of up to 20 L. Together, this enables isotopic analyses of highly nutrient-depleted seawater with dissolved Cd contents of less than 5 pmol/kg. Co-precipitation is not required, however, for samples with Cd concentrations that exceed 50-100 pmol/kg. In this case, the separation of Cd is best accomplished using column chromatography only.

The performance of the procedure was evaluated by multiple analyses of several Cd isotope reference materials and various seawater samples. The results of these measurements demonstrate that the Cd isotope composition of seawater can be determined with an accuracy and precision ($\pm 2\text{sd}$) of 0.4-0.6 $\epsilon^{114/110}\text{Cd}$ at optimal analytical conditions, which require at least about 20 ng of natural Cd.

The methods were furthermore employed to obtain the first Cd isotope depth profile for the Atlantic Ocean. These measurements revealed extremely low Cd contents of 1-2 pmol/kg in the upper water column (0-125 m depth), and highly fractionated Cd isotope compositions with $\epsilon^{114/110}\text{Cd}$ values of up to about +20. The highly positive $\epsilon^{114/110}\text{Cd}$ data of the samples are in accord with previous results obtained for nutrient depleted surface seawater from the Pacific Ocean, and are thus likely to reflect isotope fractionation from biological utilization of Cd. The samples from depths ≥ 2000 m feature an essentially constant Cd isotope composition of $\epsilon^{114/110}\text{Cd} \approx +5.5$ that is slightly more positive than the previously inferred global Cd isotope deepwater value of $+3.8 \pm 0.5$, which is based primarily on results for Pacific, Southern and Arctic Ocean samples (Ripperger et al., 2007). It is conceivable, that this small difference in $\epsilon^{114/110}\text{Cd}$ reflects the relatively young ventilation age of Atlantic deepwater.

2.5 Acknowledgments

A huge thanks goes to Corey Archer and Derek Vance for sharing the idea to use Al-hydroxide for co-precipitation of Cd and for making an initial recipe available. We are grateful to Ken Bruland and Geoffrey Smith for providing the SAFe reference samples. The collection of the GEOTRACES intercalibration samples for trace metal isotope analyses was organized by Ed Boyle and carried out by Ed with assistance from Seth John using the GOFlo rosette that was put together and is maintained by Greg Cutter. Geoff Smith homogenized the GDI sample and his equipment was also used for filling the bottles. The GEOTRACES intercalibration cruise was sponsored by the US National Science Foundation and adeptly supported by the officers and crew of the R/V Knorr. The authors furthermore thank Rasmus Andreasen, Roz Coggon, Katharina Kreissig and the other members of the MAGIC team for their help in keeping the mass spec running and the clean lab organized. Comments by two anonymous referees and editor K. Heumann helped to shape an improved version of the manuscript. This research was made possible by funding from a NERC research grant to MR, ZX and Andy Ridgwell (Bristol).

References

- Abouchami, W., Galer, S., de Baar, H., Alderkamp, A., Middag, R., Laan, P., Feldmann, H., Andreae, M., 2011. Modulation of the Southern Ocean cadmium isotope signature by ocean circulation and primary productivity. *Earth and Planetary Science Letters* 305, 83 – 91.
- Boyle, E., Sclater, F., Edmond, J., 1976. On the marine geochemistry of cadmium. *Nature* 263, 42–44.
- Cloquet, C., Rouxel, O., Carignan, J., Libourel, G., 2005. Natural Cadmium Isotopic Variations in Eight Geological Reference Materials (NIST SRM 2711, BCR 176, GSS-1, GXR-1, GXR-2, GSD-12, Nod-P-1, Nod-A-1) and Anthropogenic Samples, Measured by MC-ICP-MS. *Geostandards and Geoanalytical Research* 29, 95–106.
- Cullen, J., Lane, T., Morel, F., Sherrell, R., 1999. Modulation of cadmium uptake in phytoplankton by seawater CO₂ concentration. *Nature* 402, 165–166.
- Hendry, K., Rickaby, R., de Hoog, J., Weston, K., Rehkämper, M., 2008. Cadmium and phosphate in coastal Antarctic seawater: Implications for Southern Ocean nutrient cycling. *Marine Chemistry* 112, 149–157.
- Johnson, K., Boyle, E., Bruland, K., Coale, K., Moffett, J., Aguilar-Islas, A., Barbeau, K., Bergquist, B., Bowie, A., Buck, K., et al., 2007. Developing standards for dissolved iron in seawater. *Eos* 88, 131–132.
- Lacan, F., Francois, R., Ji, Y., Sherrell, R., 2006. Cadmium isotopic composition in the ocean. *Geochimica et Cosmochimica Acta* 70, 5104–5118.

- Ludwig, K., 2003. ISOPLOT 3.00: a geochronology toolkit for Microsoft Excel. Berkeley Geochronological Center Special Publication, Berkeley .
- Maréchal, C., Telouk, P., Albarede, F., 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology* 156, 251–273.
- Rehkämper, M., Wombacher, F., Horner, T., Xue, Z., 2011. Natural and anthropogenic Cd isotope variations. *Handbook of Environmental Isotope Geochemistry* , 125–154.
- Ripperger, S., Rehkämper, M., 2007. Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS. *Geochimica et cosmochimica acta* 71, 631–642.
- Ripperger, S., Rehkämper, M., Porcelli, D., Halliday, A., 2007. Cadmium isotope fractionation in seawater—A signature of biological activity. *Earth and Planetary Science Letters* 261, 670–684.
- Rudge, J., Reynolds, B., Bourdon, B., 2009. The double spike toolbox. *Chemical Geology* 265, 420–431.
- Schmitt, A., Galer, S., Abouchami, W., 2009a. High-precision cadmium stable isotope measurements by double spike thermal ionisation mass spectrometry. *Journal Analytical Atomic Spectrometry* 24, 1079–1088.
- Schmitt, A., Galer, S., Abouchami, W., 2009b. Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. *Earth and Planetary Science Letters* 277, 262–272.
- Shiel, A., Barling, J., Oriens, K., Weis, D., 2009. Matrix effects on the multi-collector inductively coupled plasma mass spectrometric analysis of high-precision cadmium and zinc isotope ratios. *Analytica Chimica Acta* 633, 29–37.
- Siebert, C., Nägler, T., Kramers, J., 2001. Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry. *Geochem. Geophys. Geosyst* 2, 1032.

- Wombacher, F., Rehkämper, M., 2003. Investigation of the mass discrimination of multiple collector ICP-MS using neodymium isotopes and the generalised power law. *Journal of Analytical Atomic Spectrometry* 18, 1371–1375.
- Wombacher, F., Rehkämper, M., 2004. Problems and suggestions concerning the notation of cadmium stable isotope compositions and the use of reference materials. *Geostandards and Geoanalytical Research* 28, 173–178.
- Wombacher, F., Rehkämper, M., Mezger, K., Bischoff, A., Münker, C., 2008. Cadmium stable isotope cosmochemistry. *Geochimica et Cosmochimica Acta* 72, 646–667.
- Wombacher, F., Rehkämper, M., Mezger, K., Münker, C., 2003. Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS. *Geochimica et Cosmochimica Acta* 67, 4639–4654.
- Wu, J., Boyle, E., 1997. Low blank preconcentration technique for the determination of lead, copper, and cadmium in small-volume seawater samples by isotope dilution ICPMS. *Analytical Chemistry* 69, 2464–2470.
- Xu, Y., Feng, L., Jeffrey, P., Shi, Y., Morel, F., 2008. Structure and metal exchange in the cadmium carbonic anhydrase of marine diatoms. *Nature* 452, 56–61.

Chapter 3

Cadmium Isotope Fractionation in the Southern Ocean

The study discussed in this chapter has been prepared for submission to EPSL.

Abstract:

Cadmium concentrations and isotope compositions were determined for 47 seawater samples from the high nutrient low chlorophyll (HNLC) zone of the Atlantic sector of the Southern Ocean. The samples comprise 13 surface waters from the Weddell Gyre and 3 depth profiles from the Weddell Sea and Drake Passage. The surface waters feature relatively high Cd concentrations of 0.25 to 0.46 nmol/kg coupled with only moderately fractionated Cd isotope compositions of $\epsilon^{114/110}\text{Cd} = +4.5$ to $+7.5$. The Cd data for the HNLC surface water samples analyzed here and by previous workers furthermore combine to define a single closed-system Rayleigh fractionation trend with a fractionation factor of $\alpha \approx 1.0005$. In contrast, most surface waters from non-HNLC regimes suggest a significantly lower fractionation factor of $\alpha \approx 1.0002$. The reason for this apparent difference in fractionation behavior is unclear but may reflect that different mechanisms are responsible for the uptake of Cd by plankton or its sequestration within cells at high and low dissolved seawater Cd concentrations.

The depth profile samples from below 1000 m have an average $\epsilon^{114/110}\text{Cd}$ of $+2.5 \pm 0.75$ (2sd, $n = 13$), in accord with previous observations that deep waters from the Southern and Pacific Ocean feature a nearly constant $\epsilon^{114/110}\text{Cd}$ value of about $+2.5$. In contrast, significant isotopic variability was observed at intermediate depths of between 200 and 750 m. Samples from depths of 200 m to 400 m from Weddell Sea show high Cd concentrations and light Cd isotope compositions of $\epsilon^{114/110}\text{Cd} \approx +1$ as a result of remineralization of Cd from biomass that records incomplete nutrient utilization at the surface. Moreover, the samples from 200 to 750 m in the Drake Passage feature $\epsilon^{114/110}\text{Cd}$ values of about $+4$, similar to the surface water of the Weddell Sea. This presumably traces the presence of Subantarctic Mode Water and/or Antarctic Intermediate Water, which both have young ventilation ages, thereby carrying a fractionated Cd isotope surface signature. Taken together, the results thus demonstrate that Cd isotope data can provide useful constraints on the mechanisms of nutrient cycling and potentially be applied for water mass tracing.

3.1 Introduction

The Southern Ocean is one of the three major HNLC (High Nutrient Low Chlorophyll) regions with the others being the equatorial Pacific Ocean and the subarctic Pacific Ocean. HNLC regions are distinguished by having a relatively low and constant amount of biomass in spite of high concentrations of the macronutrients nitrate, phosphate and silicate being available for phytoplankton growth (Nelson and Smith, 1991). Previous studies have suggested that the nutrient utilization in the Southern Ocean HNLC region is limited by the low iron concentration (Martin et al., 1990a; de Baar et al., 1995).

Cadmium is a micronutrient element with a marine distribution similar to that of dissolved phosphate (PO_4^{3-}), which suggests that Cd is also controlled by phytoplankton uptake in surface waters and the sinking and remineralization of organic matter at depth (Boyle et al., 1976; Bruland, 1980; de Baar et al., 1994). Considerable Cd isotope fractionations in seawater have been revealed in the recent studies, which can be used to study the marine cycling of this micronutrient element (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011; Xue et al., 2012). Cadmium depleted surface waters exhibit $\epsilon^{114/110}\text{Cd}$ values as high as +20 to +40 (Ripperger et al., 2007), presumably as a result of isotope fractionation during biological utilization with a fractionation factor of about 1.0002 to 1.0006 (Ripperger et al., 2007; Abouchami et al., 2011; Xue et al., 2012). In contrast, the deep ocean appears to be characterized by a relatively constant $\epsilon^{114/110}\text{Cd}$ value of +2.5, relative to the NIST 3108 Cd standard (Ripperger et al., 2007; Abouchami et al., 2011; Horner et al., 2011; Xue et al., 2012; Gault-Ringold and Stirling, 2012).

A previous Cd isotope study of water samples from the Southern Ocean identified two different biogeochemical oceanic provinces, the Antarctic Circumpolar Current and the Weddell Gyre (Abouchami et al., 2011). These authors found that each province defined a distinct relationship between $\epsilon^{114/110}\text{Cd}$ and $\ln[\text{Cd}]$, which implies that Cd uptake is associated with different fractionation factors.

The present investigation follows up on the findings of Abouchami et al. (2011), with

coupled Cd isotope and concentration analyses for almost 50 seawater samples from the Southern Ocean. These waters were collected on the same cruise as the samples of Abouchami et al. (2011) and they include 13 surface waters from the Weddell Gyre and three depth profiles from the Weddell Sea and the Drake Passage. Our results, therefore, significantly enlarge the very limited Cd isotope dataset that is currently available for the Southern Ocean HNLC region.

3.2 Samples

The seawater analyzed in this study was collected during the 2008 GEOTRACES expedition ANT XXIV/3 aboard the RV Polarstern, also termed the 'Zero & Drake' cruise in the following. In total, Cd concentrations and isotope compositions were determined for 47 seawater samples. These include 13 surface waters that were collected along Zero Meridian between 62°S and 69°S in the Weddell Gyre (Fig. 3.1, Table 3.1). In addition, 34 samples from three vertical profiles in the Weddell Gyre (Station 198), the Scotia Sea (Station 216) and the northern Drake Passage (Station 249) were analyzed (Fig. 3.1, Table 3.2). The vertical profiles samples were collected with an ultraclean CTD system, whilst the Zero Meridian surface waters were obtained with an IFISH torpedo and pumpline system. After collection, all the samples were filtered through a 0.2 μm nominal size cutoff filter cartridges into pre-cleaned bottles and then acidified to pH 2 with distilled 6 M HCl. Further details of the sampling techniques are available in Middag et al. (2011a). A summary of the circulation system and water masses present in the Atlantic sector of the Southern Ocean is available in a number of recent publications (Baars and Croot, 2011; Barre et al., 2011; Behrendt et al., 2011; Bluhm et al., 2011; Croot et al., 2011; Fahrbach et al., 2011a,b; Klunder et al., 2011; Middag et al., 2011a,b; Neven et al., 2011; Provost et al., 2011; Renault et al., 2011; van der Loeff et al., 2011; Sudre et al., 2011; Thuroczy et al., 2011; van Heuven et al., 2011; Venchiarutti et al., 2011).

Table 3.1: Cd concentrations and isotope compositions for surface seawater samples from Weddell Gyre along the Zero Meridian

Sample Station	Date	Latitude	Longitude	Salinity	Potential Temperature (°C)	[PO ₄ ³⁻] (μmol/kg)	[Si] (μmol/kg)	[NO ₃ ⁻] (μmol/kg)	[NO ₂ ⁻] (μmol/kg)	[NO ₃ ⁻] (μmol/kg)	[Si*] (μmol/kg)	[Cd] (nmol/kg)	ε ^{114/110} Cd	2 s.d.
142	27/02/2008	62.23°S	0.00	33.95	0.44	1.69	57.76	23.69	0.16	23.53	34.23	0.27	6.76	0.50
145	28/02/2008	63.25°S	0.00	33.91	0.59	1.61	53.83	23.31	0.16	23.15	30.68	0.26	7.31	0.50
148	29/02/2008	64.21°S	0.01	33.94	0.60	1.60	46.87	22.91	0.15	22.76	24.11	0.25	7.38	0.50
151	29/02/2008	65.24°S	0.00	33.95	-0.24	1.62	62.49	25.35	0.22	25.14	37.36	0.38	5.39	0.50
153A	29/02/2008	66.00°S	0.73	33.85	-0.21	1.61	61.97	25.74	0.23	25.52	36.46	0.37	6.34	0.50
156	07/03/2008	66.52°S	0.01	33.8	-0.76	1.64	59.23	25.45	0.21	25.25	33.99	0.38	5.76	0.50
160	08/03/2008	66.03°S	0.07°W	34.09	-0.41	1.63	58.70	25.68	0.27	25.41	33.29	0.26	7.48	0.68
162	09/03/2008	66.56°S	0.00	33.84	-0.76	1.67	58.26	25.53	0.21	25.32	32.94	0.39	5.66	0.50
164	09/03/2008	67.02°S	0.01°W	33.94	-0.73	1.77	65.49	27.00	0.23	26.77	38.72	0.43	4.75	0.70
166	10/03/2008	67.58°S	0.00	33.93	-0.76	1.84	67.56	27.50	0.25	27.25	40.32	0.46	4.54	0.70
168	10/03/2008	68.29°S	0.00	33.97	-0.74	1.78	62.87	26.68	0.28	26.4	36.47	0.41	4.83	0.71
170	10/03/2008	68.65°S	0.00	33.93	-0.78	1.74	60.58	25.94	0.27	25.67	34.91	0.38	4.99	0.70
172	10/03/2008	68.96°S	0.00	33.92	-1.02	1.75	60.50	25.93	0.27	25.66	34.84	0.39	5.00	0.50

^a The uncertainties quoted for the samples are based on the 2sd uncertainties determined for multiple analyses of matching standard solutions that were analyzed before and after each sample measurement. ^b Cd concentration and isotope composition data were analyzed at MAGIC team, Imperial College London. ^c The rest of the data in this table are all from CTD data, which is from the 2008 GEOTRACES expedition ANT-XXIV/3 aboard the RV Polarstern. ^d [Si*] value is calculated by [Si*] = [Si(OH)₄] - [NO₃⁻]. ^e The surface water samples were collected with the clean IFISH torpedo and pump line system at 0-5m depth.

Table 3.2: Cd concentrations and isotope compositions for seawater samples from three depth profiles collected at Weddell Gyre and Drake Passage

Sample Station	Date	Latitude	Longitude	Water Depth (m)	Salinity	Potential Temperature (°C)	[Oxygen] (μmol/kg)	[PO ₄ ³⁻] (μmol/kg)	[Si] (μmol/kg)	[NO ₃ ⁻] (μmol/kg)	[NO ₂ ⁻] (μmol/kg)	[NO ₃ ⁻] (μmol/kg)	[Si*] (μmol/kg)	[Cd] (nmol/kg)	ε ^{114/110} Cd	2 s.d.
198	2003/2004	65.61°S	36.40°W	25	34.16	-1.45	334.38	1.88	73.33	27.85	0.26	27.59	45.74	0.55	4.04	0.63
198	2003/2004	65.61°S	36.40°W	100	34.51	-1.73	291.98	2.11	83.56	30.68	0.09	30.59	52.97	0.72	2.59	0.35
198	2003/2004	65.61°S	36.40°W	200	34.67	0.25	196.24	2.36	112.35	34.19	0.02	34.17	78.18	0.89	1.68	0.39
198	2003/2004	65.61°S	36.40°W	300	34.67	0.24	196.16	2.38	120.64	34.45	0.02	34.43	86.21	0.89	1.35	0.35
198	2003/2004	65.61°S	36.40°W	400	34.68	0.39	191.00	2.39	118.49	34.43	0.02	34.41	84.08	0.88	0.98	0.35
198	2003/2004	65.61°S	36.40°W	500	34.69	0.43	191.38	2.39	121.52	34.40	0.02	34.39	87.14	0.86	2.48	0.23
198	2003/2004	65.61°S	36.40°W	1000	34.68	0.18	207.62	2.36	126.11	33.96	0.02	33.94	92.17	0.81	2.56	0.26
198	2003/2004	65.61°S	36.40°W	2000	34.66	-0.15	225.64	2.31	125.91	33.20	0.02	33.19	92.73	0.79	2.30	0.35
198	2003/2004	65.61°S	36.40°W	3000	34.66	-0.30	236.17	2.28	124.55	32.70	0.02	32.69	91.87	0.78	2.94	0.65
198	2003/2004	65.61°S	36.40°W	4000	34.65	-0.38	243.14	2.28	124.94	32.69	0.02	32.67	92.27	0.76	2.55	0.65
198	2003/2004	65.61°S	36.40°W	4759	34.64	-0.51	250.41	2.27	115.96	32.54	0.02	32.52	83.44	0.75	1.69	0.65
216	2603/2004	63.70°S	50.84°W	25	34.14	-1.85	305.96	2.05	73.04	28.92	0.12	28.80	44.24	0.65	4.65	0.82
216	2603/2004	63.70°S	50.84°W	100	34.43	-1.81	278.14	2.14	76.25	30.80	0.09	30.71	45.54	0.71	3.29	0.81
216	2603/2004	63.70°S	50.84°W	150	34.44	-1.80	275.83	2.14	77.03	30.81	0.03	30.78	46.25	0.74	2.41	0.23
216	2603/2004	63.70°S	50.84°W	200	34.46	-1.47	271.91	2.17	79.17	31.04	0.03	31.01	48.16	0.77	2.01	0.49
216	2603/2004	63.70°S	50.84°W	400	34.65	0.43	211.87	2.26	99.37	32.38	0.02	32.36	67.01	0.79	2.49	0.23
216	2603/2004	63.70°S	50.84°W	500	34.67	0.49	208.51	2.26	104.25	32.40	0.03	32.37	71.88	0.79	1.97	0.76
216	2603/2004	63.70°S	50.84°W	1000	34.68	0.38	211.33	2.29	115.96	32.89	0.02	32.87	83.09	0.78	2.23	0.49
216	2603/2004	63.70°S	50.84°W	1500	34.67	0.10	219.23	2.30	121.81	33.04	0.02	33.02	88.79	0.78	2.49	0.76
216	2603/2004	63.70°S	50.84°W	2000	34.66	-0.19	231.79	2.27	118.89	32.56	0.03	32.53	86.36	0.77	1.93	0.76
216	2603/2004	63.70°S	50.84°W	2486	34.61	-1.14	279.92	2.18	84.43	31.32	0.01	31.31	53.12	0.74	2.99	0.33
249	09/04/2004	56.12°S	63.76°W	10	33.87	4.56	304.64	1.66	5.23	24.14	0.27	23.87	-18.64	0.40	6.68	0.63
249	09/04/2004	56.12°S	63.76°W	25	33.87	4.56	305.13	1.67	5.24	24.34	0.26	24.08	-18.84	0.40	7.02	0.63
249	09/04/2004	56.12°S	63.76°W	75	33.88	4.47	310.15	1.70	5.87	24.38	0.27	24.11	-18.24	0.41	6.72	0.63
249	09/04/2004	56.12°S	63.76°W	150	33.99	2.89	302.15	1.87	15.21	27.06	0.07	26.99	-11.78	0.65	3.42	0.63
249	09/04/2004	56.12°S	63.76°W	250	34.03	2.33	300.80	1.96	20.57	28.28	0.03	28.25	-7.68	0.64	4.01	0.63
249	09/04/2004	56.12°S	63.76°W	400	34.16	2.52	254.70	2.11	31.22	30.49	0.02	30.47	0.75	0.70	3.27	0.63
249	09/04/2004	56.12°S	63.76°W	750	34.43	2.57	180.40	2.30	79.43	33.18	0.02	33.16	46.27	0.81	2.46	0.35
249	09/04/2004	56.12°S	63.76°W	1250	34.64	2.26	163.92	2.24	93.43	32.26	0.01	32.25	61.18	0.76	2.81	0.58
249	09/04/2004	56.12°S	63.76°W	1750	34.71	1.90	170.40	2.24	104.12	31.91	0.02	31.89	72.23	0.74	2.40	0.58
249	09/04/2004	56.12°S	63.76°W	2500	34.73	1.48	186.88	2.21	115.20	32.14	0.02	32.12	83.08	0.76	2.71	0.58
249	09/04/2004	56.12°S	63.76°W	3000	34.72	1.10	195.36	2.22	115.20	32.14	0.02	32.12	83.08	0.76	2.71	0.58
249	09/04/2004	56.12°S	63.76°W	4000	34.69	0.67	210.89	2.24	120.37	32.47	0.03	32.44	87.93	0.76	2.50	0.58
249	09/04/2004	56.12°S	63.76°W	4250	34.69	0.68	211.56	2.25	116.98	32.44	0.03	32.41	84.57	0.77	2.83	0.58
202	21/03/2004	64.95°S	41.67°W	400	34.68	0.36	194.25	2.38	118.01	34.35	0.04	34.31	83.70	0.89	3.23	0.16
245	08/04/2004	56.88°S	62.52°W	0	-	-	-	-	-	-	-	-	-	0.37	6.81	0.82

^a The uncertainties quoted for the samples are based on the 2σ uncertainties determined for multiple analyses of matching standard solutions that were analyzed before and after each sample measurement. ^b Cd concentration and isotope composition data were analyzed at MAGIC, Imperial College London. ^c The rest of the data in this table are all CTD data, which are from the 2008 GEOTRACES expedition ANT XXIV/3 aboard the RV Polarstern. ^d [Si*] value is calculated by [Si*]=[Si(OH)₄-[NO₃]].

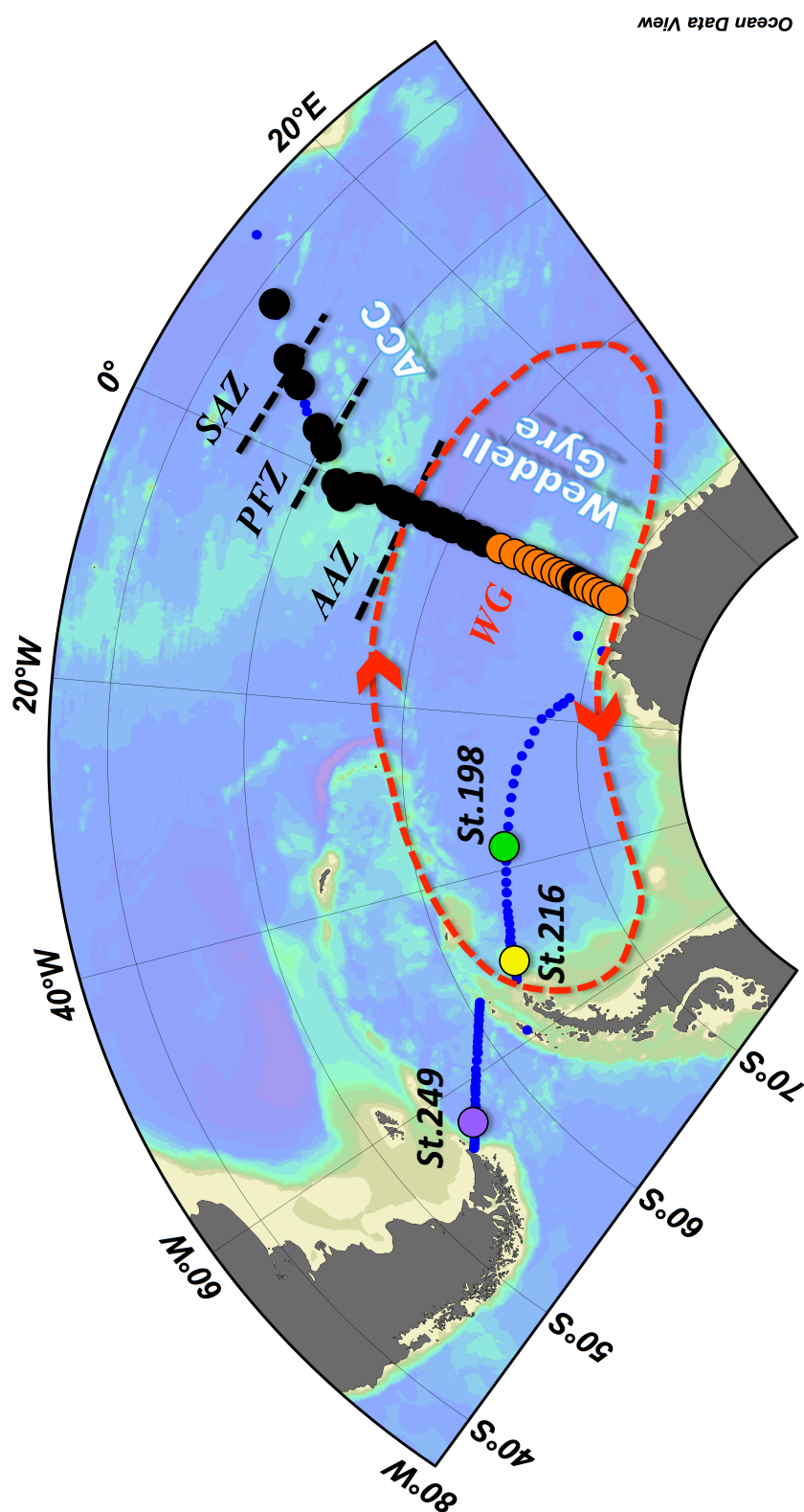


Figure 3.1: Locations of seawater samples analyzed in this study. This study includes samples from 3 depth profiles in the Drake Passage (Station 249, in purple), and the northwestern Weddell Sea (Station 216, in yellow) & central Weddell Sea (Station 198, in green) as well as 13 surface waters from the Zero Meridian between 62° and 69°S (in orange). The black dots represent the data reported in a previous study (Abouchami et al., 2011). The boundary of Weddell Gyre is shown by red dash circle. WG = Weddell Gyre, ACC = Antarctic Circumpolar Current, SAZ = Sub Antarctic Zone, PFZ = Polar Frontal Zone, and AAZ = Antarctic Zone.

3.3 Analytical methods

A recent publication provides a detailed description of the analytical techniques that were used during the course of this study ((Xue et al., 2012); Chapter 2). Thus, only a brief summary of the methods is provided here.

The first step of the procedure encompasses a preliminary determination of the seawater Cd concentrations. These analyses were carried out on small aliquots, such that an optimal amount of the Cd double spike could subsequently be added to the main sample mass to enable accurate and precise Cd stable isotope measurements. To this end, seawater aliquots of about 50 ml were spiked with ^{111}Cd - ^{113}Cd double spike solution, the Cd was separated from the seawater matrix with a simplified version of the column chemistry and the Cd concentrations were then determined with the isotope dilution technique (Xue et al., 2012).

Based on the results of these preliminary analyses, about 0.3 to 1.1 L of seawater were accurately weighed to obtain approximately 30 ng natural Cd and a suitable volume of the ^{111}Cd - ^{113}Cd double spike was then added to achieve spike-sample ratios of $S/N \approx 1$. An appropriate volume of 6 M HCl was then added to the spiked seawater to acidify the samples to 0.7 M HCl. All samples were then left to stand for at least three days prior to the three-stage column chemistry procedure that was used for the purification of Cd (Xue et al., 2012). The chemical separation method typically achieved yields of better than 90% and was associated with a procedural blank of about 20 pg Cd. Hence, the blank was equivalent to less than 0.07% of the indigenous Cd present in the samples and thus had only a negligible effect on the measured isotope compositions. A correction was therefore only applied to the concentration results.

The Cd double spike stable isotope measurements were carried out with a Nu Plasma HR MC-ICP-MS (multiple collector inductively coupled plasma mass spectrometer) using previously described techniques (Xue et al., 2012). After data acquisition, all results were further processed offline to calculate the 'true' isotope compositions of the unspiked samples, following correction for both instrumental mass bias and isobaric interferences. These

data were then used to determine the reported $\epsilon^{114/110}\text{Cd}$ values of the samples relative to an isotopic standard (std):

$$\epsilon^{114/110}\text{Cd} = \left[\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{sample}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{std}}} - 1 \right] \times 10,000$$

In this study, $\epsilon^{114/110}\text{Cd}$ data are reported relative to the NIST SRM 3108 reference material (Rehkämper et al. 2011; Xue et al., 2012). Additional analyses of the secondary Cd isotope standards JMC Cd Münster, BAM-I012 Cd and Zurich Cd Alfa were carried out during each measurement session to monitor data quality and all results were found to be within accepted limits (Ripperger and Rehkämper, 2007; Rehkämper et al., 2011; Xue et al., 2012).

3.4 Background information and results

3.4.1 Key water masses

Previous studies (Orsi et al., 1995, 1999, 2002; Stramma and England, 1999; Stichel et al., 2012) show that the eastward flowing Antarctic Circumpolar Current (ACC) governs the circulation in the Southern Ocean. The major part of the ACC ranges from the sea surface to depths of 2-4 km and can be as wide as 2000 km (Klinck and Nowlin Jr, 2001). The ACC passes through 3 oceanic frontal systems, the Subantarctic Zone (SAZ), the Polar Frontal Zone (PFZ) and the Antarctic Zone (AAZ), from the north to south (Fig. 3.1). The Circumpolar Deep Water (CDW) of the ACC is divided into Upper Circumpolar Deep Water (UCDW) and Lower Circumpolar Deep Water (LCDW) by neutral densities (Stichel et al., 2012).

The Weddell Gyre (WG) is a cyclonic circulation system in the Southern Ocean and it is located in the Weddell Sea between the southern ACC boundary and the Antarctic continental shelf. The two main water masses in the WG are Warm Deep Water (WDW) and Weddell Sea Deep Water (WSDW). The WDW is derived from Circumpolar Deep Water (CDW) of the ACC. On the shelves and slopes of the western and southwestern Weddell

Sea, the mixing of dense shelf waters with variants of WDW forms the Weddell Sea Deep Water (WSDW) (Foster and Carmack, 1976; Whitworth III et al., 1994; Meredith et al., 2008). WSDW is an essential component of the Antarctic Bottom Water (AABW), which forms the bottom layers in most of the world's oceans (Heywood and King, 2002; Klatt et al., 2005; Orsi et al., 1999, 2002; Meredith et al., 2008; Stichel et al., 2012). Antarctic Surface Water (AASW) is a cold and fresh water mass, which flows in the upper 200m at south of the PFZ. AAIW is a unique water mass, which forms from the cold surface waters at depths of above 75 m in the Weddell Gyre and then subducted to depths of below 100 m at north of the PFZ in the Drake Passage (Sievers and Nowlin Jr, 1984; Naveira Garabato et al., 2009).

3.4.2 Hydrology and nutrient concentrations for zero meridian surface seawater

The hydrographic and nutrient concentration data that were obtained for 13 surface water samples collected close to the Zero Meridian are shown in Fig. 3.2 and Table 3.1. Also shown in this figure for comparison are previously published results (Abouchami et al., 2011) for additional surface water samples that were collected during the same cruise but further to the north (Fig. 3.2). Whilst the samples analyzed in this study (orange dots) are from 62.2°S to 69.0°S in the Weddell Gyre region, the previously analyzed surface seawater (black dots) was obtained at between 42.0°S and 61.2°S (Figs. 3.1, 3.2).

For the samples analyzed in the present study, the potential temperature transect reveals two groups of samples (Fig. 3.2). At 62.2°S to 64.2°S, the potential temperature of the surface water samples increased modestly from 0.4°C to 0.6°C, and these values are in the same range as the data (0.1°C to 0.6°C) obtained for Weddell Sea surface seawater further to the north (Fig. 3.2; (Abouchami et al., 2011)). However, at 65.2°S to 69.0°S, the potential temperature decreases continuously from -0.2°C to -1°C. It is likely that this variation of potential temperature at about 65°S reflects a change in water mass or marine environment.

The latter interpretation is reinforced by the nutrient (PO_4^{3-} , Si and NO_3^-) data, which also fall into two groups at the same latitudes (Fig. 3.2). At 62.2°S to 64.2°S, PO_4^{3-} , Si and NO_3^- decrease continuously, but centered around 67.6°S these parameters define a noticeable kink with first increasing then decreasing concentrations in a southward direction.

3.4.3 Cd concentration and isotope compositions for zero meridian surface seawater

The Cd concentration and isotope composition of the surface seawater samples from the Zero Meridian transect are also shown in Fig. 3.2. Again, the data obtained in the present investigation are combined with the previously published results of Abouchami et al. (2011). A key observation is that the Cd concentration and isotope data obtained in both investigations match up perfectly, with no apparent systematic difference. This conclusion is in accord with the excellent correspondence that was observed for Cd concentration and isotope composition data that was produced by the same laboratories for various standard reference materials (Abouchami et al., 2012) and the GEOTRACES GSI seawater intercomparison sample from the North Atlantic (Boyle et al., 2012). This excellent correspondence is furthermore important because it allows both datasets to be used and interpreted in unison, without the need to correct for systematic differences.

Focusing on the samples analyzed in this investigation, the surface waters sampled from the Weddell Sea transect show Cd concentrations of about 0.25 nmol/kg to 0.46 nmol/kg, and $\epsilon^{114/110}\text{Cd}$ values of between $+4.5 \pm 0.7$ and $+7.5 \pm 0.7$ (Fig. 3.2, Table 3.1.). In addition, the Cd concentration and isotope composition data along the transect again fall into two groups. These groups, from 62.2°S - 64.2°S and 65.2°S - 69.0°S, coincide with the sample groups that were previously identified based on potential temperature and macronutrient concentrations (Fig. 3.2).

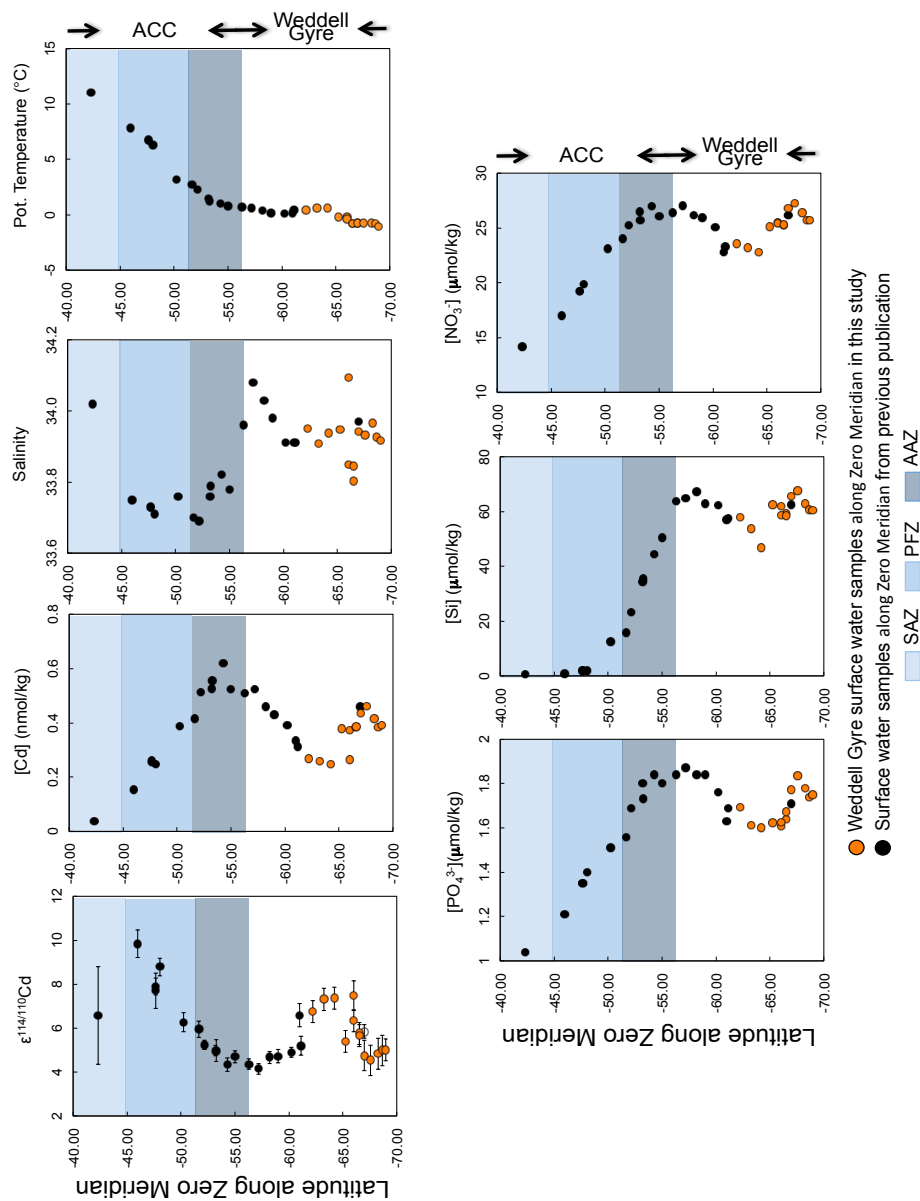


Figure 3.2: The variations of Cd concentration and isotopic composition, hydrologic and nutrient CTD data for the Zero Meridian surface water samples. The samples analyzed in this study are in orange filled dots and the black dots depict the data from a previous study (Abouchami et al., 2011). ACC = Antarctic Circumpolar Current, SAZ = Sub Antarctic Zone, PFZ = Polar Frontal Zone, and AAZ = Antarctic Zone.

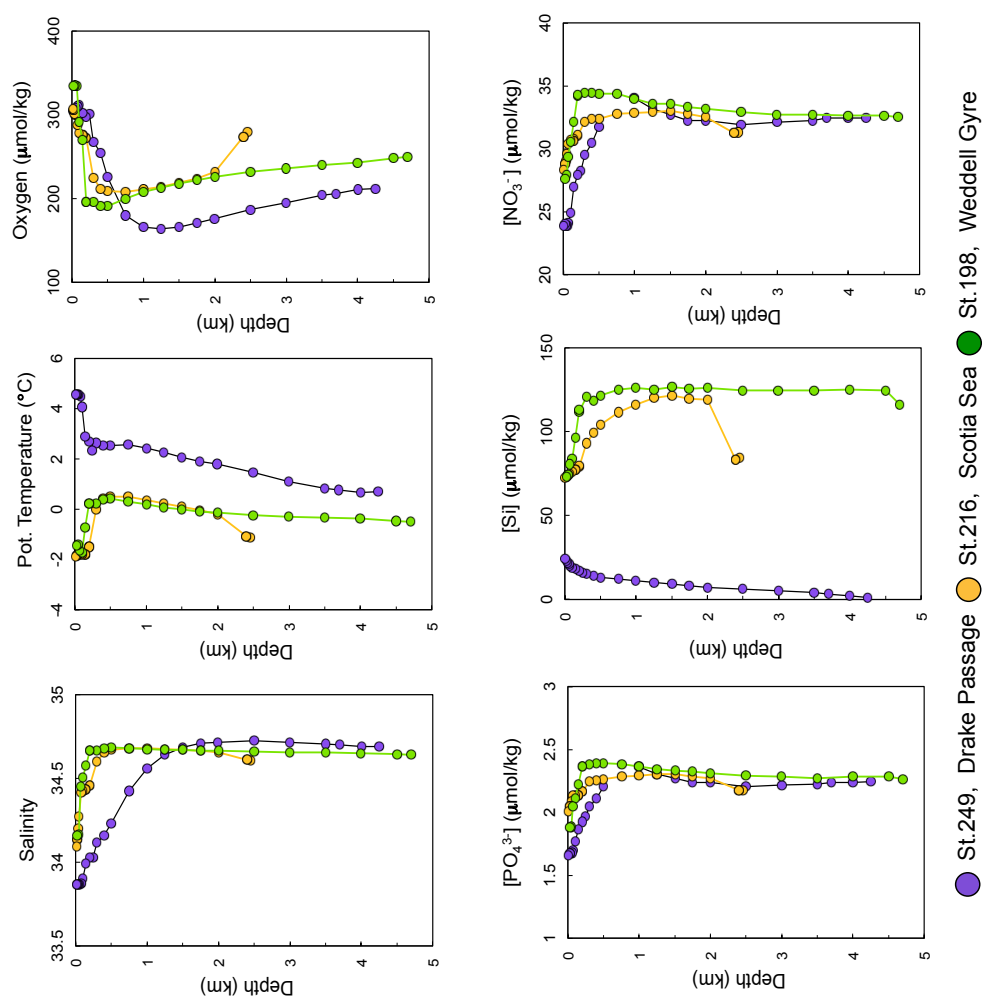


Figure 3.3: Depth distribution of hydrological parameters and nutrient data for Station 249, 216 and 198. Station 249 is in the Drake Passage (in purple), Station 216 is in the Scotia Sea (in yellow) and Station 198 is in the Weddell Gyre (in green).

3.4.4 Hydrology and nutrient concentrations for the depth profiles

The hydrological data and nutrient concentrations for the three depth profiles analyzed in this study are shown in Fig. 3.3 and Table 3.2.. The most obvious feature of this figure is the similarity of the profiles for Stations 198 (Weddell Sea) and Station 216 (Scotia Sea), whilst the results obtained for Station 249 in the Drake Passage are distinctly different. This result is not surprising given that the former Stations both fall within the regime of the Weddell Gyre, whilst the latter is situated to the north of the Polar Front and hence within the ACC system.

In detail, Fig. 3.3 highlights that Stations 198 and 216 display potential temperature and Si concentration profiles that differ fundamentally from Station 249. At Station 249, the potential temperature continuously decreases from 4.6°C at the surface to 2.5°C at 500 m, whilst at Stations 198 and 216, the potential temperature increases from -1.9°C at the surface water to 0.5°C at 500 m depth. Furthermore, the silicate depth profile determined for Station 249 exhibits a distribution with the lower concentration throughout, which is distinguished essentially from that seen at Stations 198 and 216.

Salinity and oxygen present smooth depth profiles for the three stations, however, there are still clear differences between Stations 198, 216 and Station 249 (Fig. 3.3). The salinity increases continuously with depth at all three Stations to a value of about 34.7 at depths > 1500 m, but this increase is much more gradual at Station 249. Similarly, at all three Stations, oxygen decreases from a surface value of about 300 mol/kg to about 200 mol/kg or less at intermediate depths, and then increases modestly. However, this decrease is more gradual at the Station 249 and the oxygen concentration minimum layer occurs significantly deeper, at about 1250 m for Station 249, as compared with at 500 m for Stations 198 and 216 (Fig. 3.3).

In contrast, the depth profiles of phosphate and nitrate concentrations are similar for all three Stations (Fig. 3.3). In particular, all three profiles show that (i) PO_4^{3-} is slightly depleted in the surface waters; (ii) from the surface to 500 m depth the concentrations of PO_4^{3-}

and NO_3^- rise modestly; and (iii) below 500 m, the concentrations of PO_4^{3-} and NO_3^- are nearly constant. It is furthermore noteworthy that such distributions for the macronutrients phosphate and nitrate are typical for a HNLC region.

3.4.5 Cd concentrations and isotope compositions for the depth profiles

At first sight, the depth profiles of Cd concentrations and isotope compositions are relatively similar for all three investigated stations (Fig. 3.4). In particular, Cd is modestly depleted in surface water, with concentrations ranging from ~ 0.4 nmol/kg in the Drake Passage to ~ 0.7 nmol/kg in the Weddell Sea. Such high Cd contents are typical for this HNLC region, where uptake and utilization of Cd from surface waters is incomplete. This is in accord with the less fractionated Cd isotope compositions of the surface seawater samples, which display $\epsilon^{114/110}\text{Cd} \approx +4.0 \pm 0.6$ to $+6.7 \pm 0.6$ (Fig. 3.4). Waters from below 1 km depth have very similar Cd contents of 0.77 ± 0.04 nmol/kg and the Cd isotope compositions are also relatively constant at $\epsilon^{114/110}\text{Cd} \approx +2.5 \pm 0.4$ (1sd, $n = 15$). This latter result is in excellent agreement with the previously published global deep-water average value of $\epsilon^{114/110}\text{Cd} = +2.5 \pm 0.5$ (Ripperger et al., 2007; Xue et al., 2012).

However, above 1 km, Station 249 in the Drake Passage shows significant differences in its Cd concentration and isotope composition compared to the results that were obtained for Stations 198 and 216 (Fig. 3.4). The Drake Passage profile from Station 249 reveals significant Cd isotope fractionations at depth of 250 to 750 m with $\epsilon^{114/110}\text{Cd}$ values of about +4 and this coincides with a kink in the potential temperature profile at 250 m (Fig. 3.3). Whilst Stations 216 and 198 display similar depth profiles of Cd concentrations and isotope compositions, the results obtained for Station 216 are intermediate to the profiles for Stations 198 and 249 in some characteristics (Fig. 3.4). However, both Stations 198 and 216 feature rapidly increasing [Cd] from the surface to maximum concentrations of about 0.89 nmol/kg at depths of 200-400 m. In addition, both profiles show $\epsilon^{114/110}\text{Cd}$ values of about +1 to +2 for depths of about 200-400 m, whereby the lowest yet recorded $\epsilon^{114/110}\text{Cd}$ values for seawater (of $\epsilon^{114/110}\text{Cd} = +1 \pm 0.4$) were recorded in the Weddell Sea at Station 198.

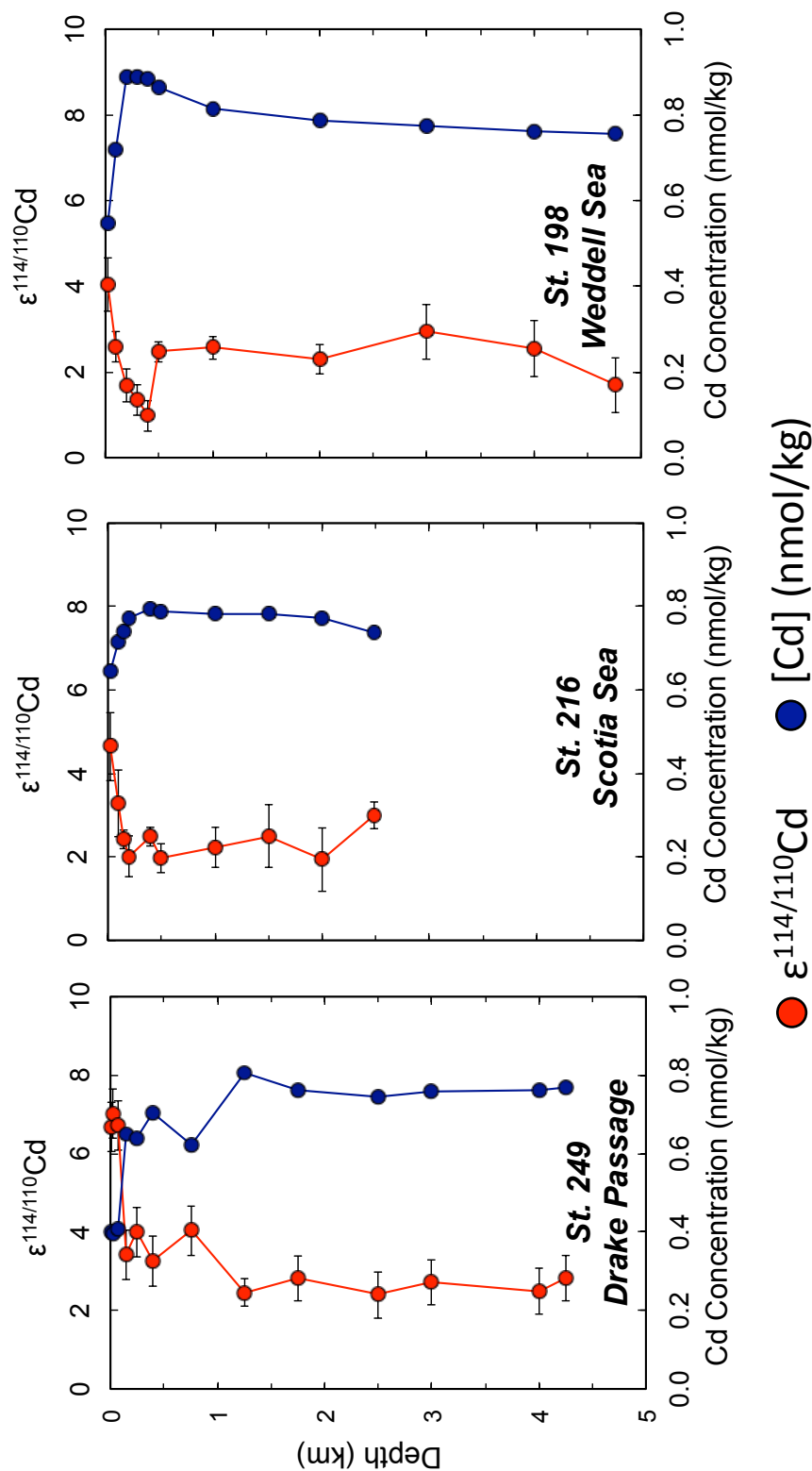


Figure 3.4: Depth profiles of Cd concentrations and isotope compositions for Station 249, 216 and 198. Cd concentration data are shown by dark blue dots and isotope composition data are shown by red dots.

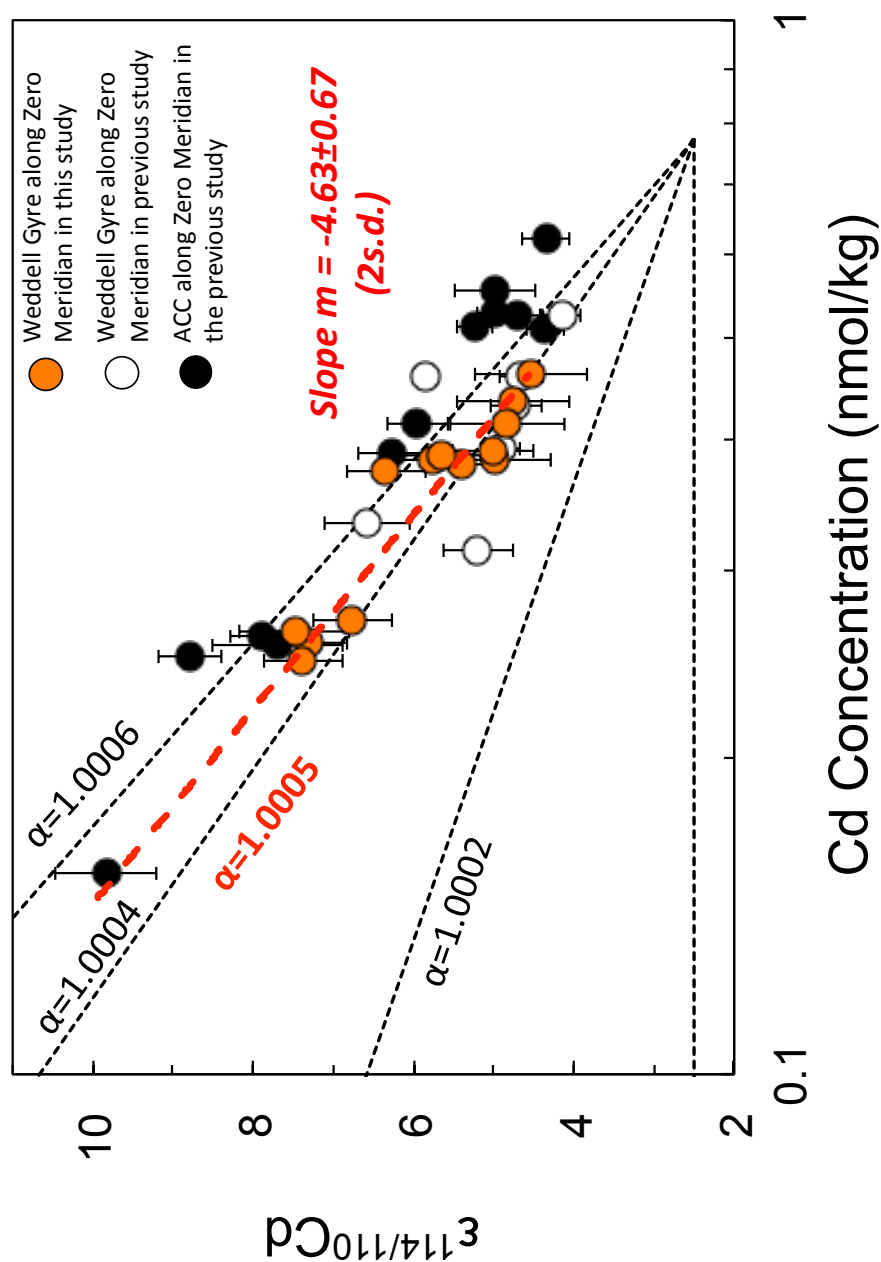


Figure 3.5: Correlation of Cd isotope compositions and concentrations for surface water samples from the ACC and Weddell Gyre along the Zero Meridian. The Cd data from the Weddell Gyre obtained in this study are listed in Table 3.1 and shown in orange dots. The data from the ACC and Weddell Gyre in a previous study (Abouchami et al., 2011) are shown by the black and white dots, respectively. The dashed lines denote calculated Rayleigh fractionation trends for fractionation factors of $\alpha \approx 1.0002$ and 1.0006 .

3.5 Discussion

3.5.1 Biological Cd isotope fractionation of surface water in the Southern Ocean HNLC region

In a diagram of $\epsilon^{114/110}\text{Cd}$ vs. Cd concentration (Fig. 3.5), the surface water data of this study display an excellent logarithmic correlation. Similar correlations have been seen in previous Cd isotope studies of seawater (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011; Xue et al., 2012) and are thought to be due to the closed system Rayleigh isotope fractionation caused by biological uptake and utilization of Cd.

Of particular interest is the combination of the results of the present study with the Cd isotope data of Abouchami et al. (2011) who also analyzed surface seawater that was collected in the Southern Ocean during the Zero & Drake cruise. Abouchami et al. (2011) concluded that samples from different regions display distinct Cd isotope systematics. These differences are particularly apparent in a diagram of Cd isotope compositions versus Cd concentrations, where samples from northern locations (collected between 46.0°S and 56.3°S) define a correlation with a steeper slope compared to most samples from more southern locations (collected between 57.2°S and 61.2°S). Following previous work (Lacan et al., 2006; Ripperger et al., 2007), the observed correlations are most likely produced by closed system Rayleigh fractionation as a result of biological utilization of Cd. The differences in slope are hence indicative of distinct biological fractionation factors that were thought to reflect differences in the phytoplankton biomass, community composition, or their physiological uptake mechanisms.

However, when the data of the present study are combined with the results of Abouchami et al. (2011), we find that there is little evidence for two distinct correlations for different geographical regions. This is particularly evident as three of our samples from the Weddell Gyre with a relatively high $\epsilon^{114/110}\text{Cd}$ of about +7.5 are essentially identical in Cd isotope systematics to two samples from the more northern ACC region that were analyzed by Abouchami et al. (2011). These observations suggest that the identification of two distinct

correlations by Abouchami et al. (2011) was perhaps premature as this is potentially simply an artifact of their more limited dataset. In fact, when the results of this study and the investigation of Abouchami et al. (2011) are combined, the combined dataset exhibits an excellent single logarithmic correlation, with a slope of -4.63 ± 0.67 , which is indicative of a biological fractionation factor of $\alpha = 1.00046 \pm 0.00006$ (Fig. 3.5). This result suggests that the biological fractionation factor is not as readily altered by differences in phytoplankton biomass or species, which was suggested by Abouchami et al. (2011).

3.5.2 Cd isotope fractionation of seawater samples from depth profiles in the Southern Ocean HNLC region

In addition to Fig. 3.4, which summarizes the Cd isotope and concentrations of the seawater obtained at Stations 198 (Drake Passage), 216 (Scotia Sea) and 249 (Drake Passage), Fig. 3.6 shows that the depth profile data agree well with the Closed system Rayleigh fractionation model for Cd in the seawater. The model for Cd isotope fractionation in the seawater has been discussed in section 1.1.5. These figures for Cd concentrations and isotope composition are further discussed below.

The water samples from depths below 1000 m at all these 3 stations have an average Cd isotope composition of $\epsilon^{114/110}\text{Cd} = +2.5 \pm 0.75$ (2 sd.) with mean Cd concentrations of 0.77 ± 0.04 (2 sd) nmol/kg (Table 3.2). These observed Cd concentrations are in accord with literature data for samples from similar locations and depths (Ripperger et al., 2007), whilst the Cd isotope compositions determined from the seawater samples below 1000m depth agree with the finding of a previous study that global deep waters feature a nearly constant $\epsilon^{114/110}\text{Cd}$ value of about $+2.5 \pm 0.50$ (Ripperger et al., 2007).

The Cd isotope compositions of subsurface depth profile samples collected at depths of ≤ 100 m are less fractionated with relatively high Cd concentrations (Figs. 3.4, 3.6). For example, the samples collected at 25 m depth at Stations 198 and 216 (Weddell and Scotia Sea, respectively) display $\epsilon^{114/110}\text{Cd}$ values of about +4.0 to +4.7 at Cd concentrations of about 0.6 nmol/kg. As such, these subsurface samples show Cd systematics, which are

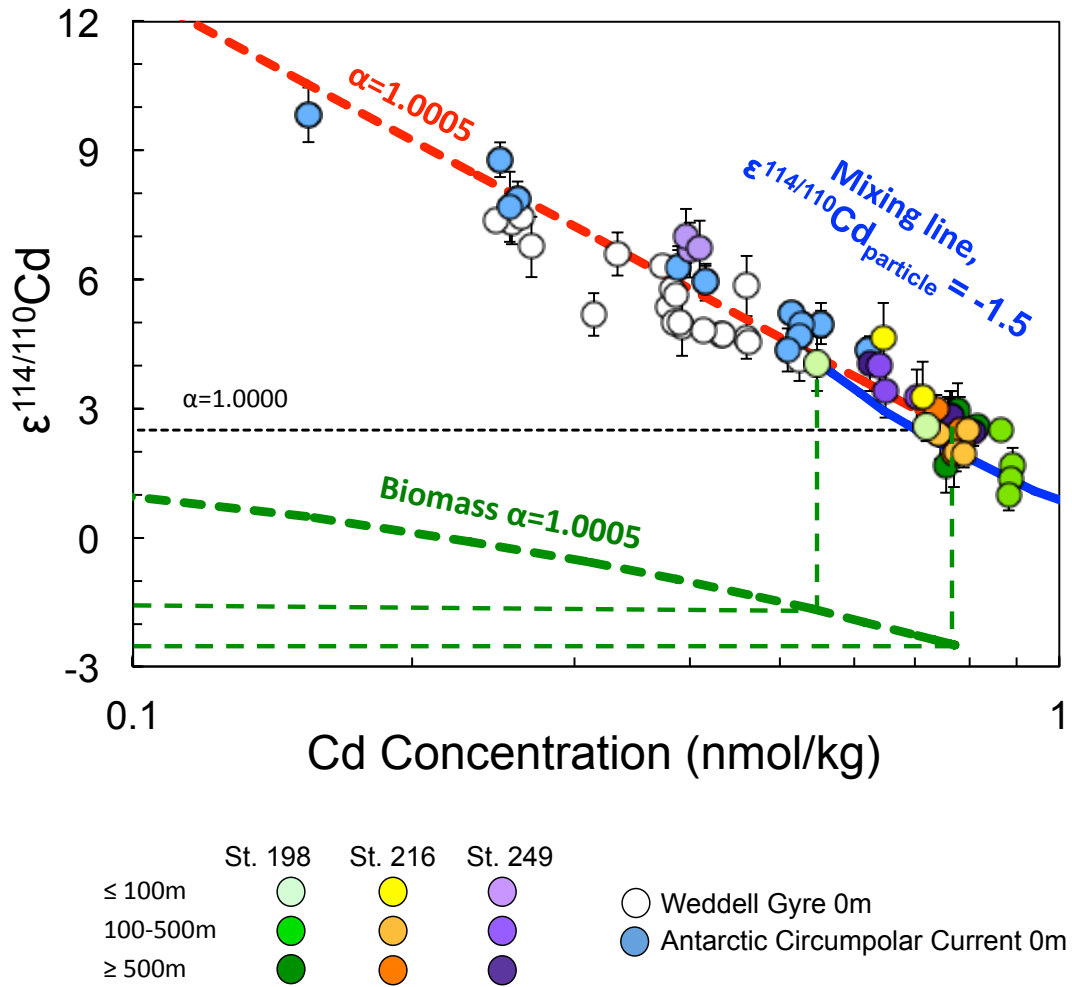


Figure 3.6: Plots of $\epsilon^{114/110}\text{Cd}$ vs. $[\text{Cd}]$ for the seawater samples from depth profiles in the Southern Ocean HNLC region. The Cd data from three depth profiles at Station 249, 216 and 198 are plotted in purple, yellow and green (Table 3.2). The light to dark shading represents water samples from ≤ 100 m, 100-500 m and ≥ 500 m. Surface water samples from the Weddell Gyre along the Zero Meridian (data in this study in Table 3.1 and previous data from Abouchami et al. (2011)) are shown in white dots. The light blue dots present the Zero Meridian Surface water samples from the ACC. The red dashed line denotes calculated Rayleigh fractionation trends for fractionation factors of $\alpha \approx 1.0005$. The blue line demonstrates mixing of surface water from the Weddell Gyre with remineralized biomass with a negative $\epsilon^{114/110}\text{Cd}$ values of about -1.5. The green line illustrates the Rayleigh fractionation trends, which were calculated for the isotope composition of an accumulated biomass preferentially incorporating light Cd with fractionation factor of $\alpha \approx 1.0005$.

akin to the data obtained for the Weddell Sea surface waters of this study. This result is perhaps not surprising, given that the Cd isotope compositions of subsurface samples from depths of less than 100 m are expected to be determined primarily by biological uptake of Cd and show only minor effects of remineralization. Together, these observations support the previous conclusion that modest Cd isotope fractionations coupled with moderate Cd concentrations are a typical HNLC signature.

The most isotope fractionated Cd were measured for the three subsurface samples from depths of 10 m to 75 m from the Drake Passage (Station 249), which display $\epsilon^{114/110}\text{Cd} \approx +6.7$ to $+7.0$ at $[\text{Cd}] \approx 0.4$ nmol/kg. These higher fractionations, which are still moderate compared to results obtained for non-HNLC locations, may reflect that the HNLC conditions are less severe in this more northern location. This interpretation is in accord with the lower concentrations of Cd and the macronutrients phosphate and nitrate that were determined for these samples in comparison to seawater from Stations 198 and 216 (Figs. 3.3, 3.4)

Of additional interest is the observation that the subsurface samples from depths ≤ 100 m are in accord with and fall on the linear fractionation trend that is defined by the Weddell Sea and ACC surface water samples in a diagram of $\epsilon^{114/110}\text{Cd}$ versus $\ln[\text{Cd}]$ (Fig. 3.6). This provides further support to the previous conclusion that biological uptake of Cd in the Southern Ocean HNLC region appears to be characterized by a closed system Rayleigh isotope fractionation factor of $\alpha \approx 1.0005$.

Particularly unusual is the finding that samples from intermediate depths of 200 m to 400 m from Station 198 in the Weddell Sea have $\epsilon^{114/110}\text{Cd}$ values as low as about +1 (Table 3.2). A similar signature may also be present in the depth profile of Station 216 in the Scotia Sea but this is less well resolved as the lowest $\epsilon^{114/110}\text{Cd}$ value is +2 at 400 m depth. Light Cd isotope compositions of $\epsilon^{114/110}\text{Cd} = +1$ have not previously been found for seawater, and hence this might be another typical signature of the Cd distribution in the Southern Ocean HNLC region. It is unlikely that these light Cd isotope compositions are related to the upwelling of deep water, which occurs in the Weddell Sea, because the deep

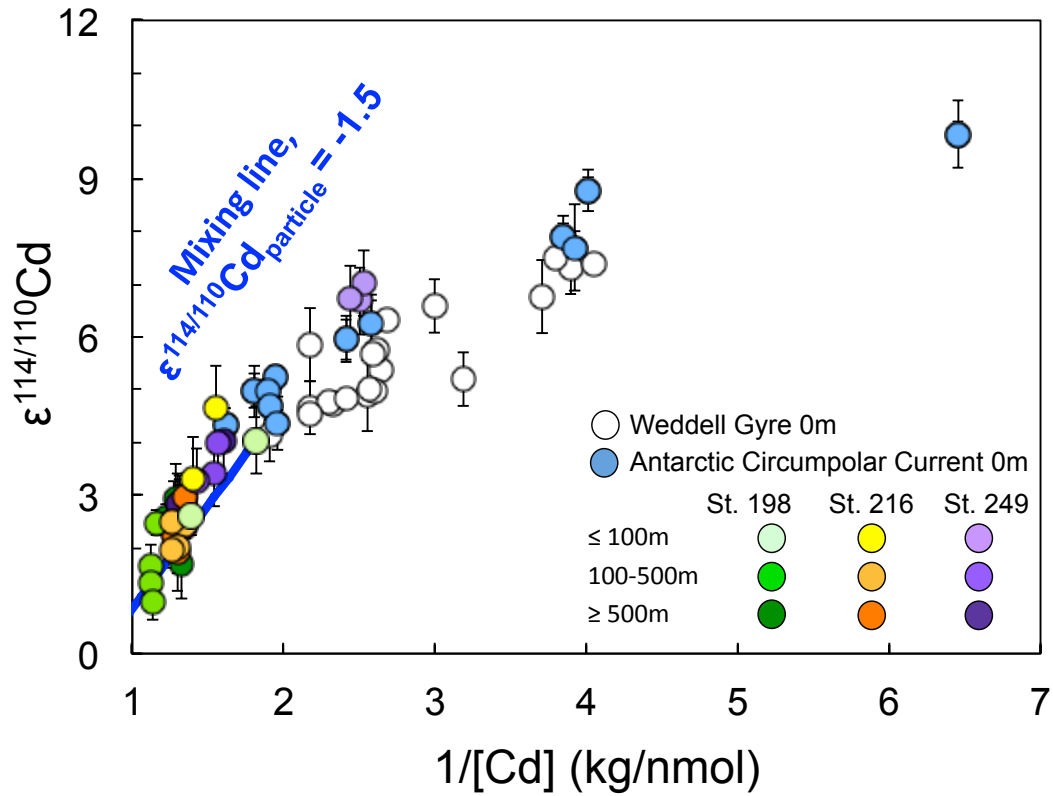


Figure 3.7: Plots of $\epsilon^{114/110}\text{Cd}$ vs. $1/[\text{Cd}]$ for the seawater samples from depth profiles in the Southern Ocean HNLC region. The Cd data from three depth profiles at Station 249, 216 and 198 are plotted in purple, yellow and green (Table 3.2). The shading from light to dark represents water samples from ≤ 100 m, 100-500 m and ≥ 500 m. Surface water samples from the Weddell Gyre along the Zero Meridian (data in this study in Table 3.1 and previous data from Abouchami et al. (2011)) are shown in white dots. The light blue dots show the Zero Meridian Surface water samples from the ACC. The blue line demonstrates mixing of surface water from the Weddell Gyre with remineralized biomass with a negative $\epsilon^{114/110}\text{Cd}$ value of about -1.5. The correlation of Cd isotope compositions and $1/[\text{Cd}]$ clearly illustrates that the mixing of surface waters (from Zero Meridian and depth profiles) with biogenic particles drives the Cd isotope composition with the value of $\epsilon^{114/110}\text{Cd} = +1$ at the intermediate depth (100-500m) in the Weddell Gyre.

waters all record $\epsilon^{114/110}\text{Cd}$ values of higher than about +2 (Fig. 3.4, 3.6).

The lightest Cd isotope compositions for Station 198 and Station 216 are recorded at approximately the same depths, which show the highest Cd concentrations (Fig. 3.4, 3.6). As a result, the samples from intermediate depth extend the linear trend of the Cd data (Fig.

3.6) to lower $\epsilon^{114/110}\text{Cd}$ values and higher [Cd]. Taken together, these findings suggest that the low $\epsilon^{114/110}\text{Cd}$ values are related to the addition or admixture of isotopically light Cd and this is most reasonably derived from remineralization processes in the water column. Support for this conclusion is provided by the observation that essentially all depth profile samples from Stations 198, 216 and 249 fall on a single trend in a diagram of $\epsilon^{114/110}\text{Cd}$ vs. $1/[\text{Cd}]$ (Fig. 3.7) and this trend indicates that binary mixing may play an important role in governing the distribution of Cd.

To account for the light Cd isotope compositions observed in the intermediate depth samples from Station 198 by mixing, the Cd that is derived from the remineralization of biomass must feature $\epsilon^{114/110}\text{Cd}$ values of about 0 or less. Simple modeling shows that such biomass compositions are likely to be common in the HNLC region of the Southern Ocean, where utilization of Cd and other nutrients utilization are only incomplete. The dashed line on Fig. 3.6 indicates the isotopic evolution for the Cd that is accumulated in biomass by biological uptake. These calculations were carried out by assuming closed system Rayleigh fractionation with a fractionation factor of $\alpha = 1.0005$, which was obtained for the Cd isotope fractionation of Weddell Sea surface waters. Hence, it further confirms that biological uptake of Cd in the Southern Ocean HNLC region is characterized by a closed system Rayleigh isotope fractionation factor of $\alpha \approx 1.0005$.

Figs. 3.6 and 3.7 also show mixing curves/lines that are obtained for mixing of biomass associated Cd characterized by $\epsilon^{114/110}\text{Cd} = -1.5$ and residual dissolved seawater Cd from a Cd depleted surface water sample with $\epsilon^{114/110}\text{Cd} = +4.0$ and $[\text{Cd}] = 0.55 \text{ nmol/kg}$. Importantly, similar mixing systematics are also obtained for the addition of biomass Cd to more Cd-rich deep water compositions characterized by $\epsilon^{114/110}\text{Cd} = +2.5$ and $[\text{Cd}] = 0.77 \text{ nmol/kg}$. Taken together, these results demonstrate that the addition of remineralized Cd derived from biomass, which records incomplete nutrient utilization at the surface, can account for the low $\epsilon^{114/110}\text{Cd}$ values and high Cd contents in the intermediate depth seawater from the Weddell Sea. Importantly, the mixing trend produced by this addition of remineralized Cd, is essentially identical to the Rayleigh fractionation line, which is generated by variable Cd uptake and associated isotope fractionation in surface and subsurface samples

(Figs. 3.6, 3.7). Therefore, all the Cd data of the depth profile samples from the Southern Ocean are observed essentially in accord with a single correlation.

At Station 249, samples from intermediate depths of 150-750 m define a plateau in the depth profile at intermediate $\epsilon^{114/110}\text{Cd}$ values of about +4 and Cd concentrations of ~ 0.5 nmol/kg (Fig. 3.4). These Cd systematics are similar to those observed for surface seawater in the Weddell Gyre (Figs. 3.6, 3.7). This interpretation is in accord with previous hydrographic studies, which have shown that Antarctic Intermediate Water (AAIW) can be present at the location of Station 249 at the relevant depths (Sievers and Nowlin Jr, 1984; Naveira Garabato et al., 2009). AAIW is a unique water mass, which forms at depths of above 75 m in the Weddell Gyre and sinks to depths of below 100 m at north of the Polar Front in the Drake Passage. It is delineated by salinity of 34.2-34.4 upon initial formation, a potential temperature of 3 to 7°C and density between 27.13 kg/m³ and 27.55 kg/m³ (Fig 3.8; (Whitworth III et al., 1994)). Therefore, these observations show that Cd isotopes might be applied to distinguish AAIW from other water masses, such as Antarctic Surface Water (AASW) and Upper Circumpolar Deep Water (UCDW) and hence be used to trace the pathway of AAIW.

3.5.3 Comparison of Cd isotope variations for the Southern Ocean HNLC region with global oceans

In Fig. 3.9, the data obtained here and in the study of Abouchami et al. (2011) are compared with previously published results for other seawater samples from non-HNLC locations. This figure clearly highlights the increasing Cd concentrations that are seen along the global deep water convection system from the North Atlantic/Arctic Ocean, to the Southern Ocean and the North Pacific. These differences, which reflect distinct ventilation ages, are also seen in Cd isotope compositions (Fig. 3.9(b)). The deep waters from the Southern Ocean and the North Pacific are both characterized by nearly identical Cd isotope compositions and the current dataset for these samples display a well-defined average $\epsilon^{114/110}\text{Cd}$ value of $+2.5 \pm 0.7$ (2sd, $n = 18$) as well as an average Cd concentrations about 0.80 ± 0.15 nmol/kg (2sd, $n = 18$). In contrast, the deep waters of the North Atlantic and Arctic Oceans

have average Cd isotope compositions relatively fractionated with average $\epsilon^{114/110}\text{Cd}$ values of about $+4.0 \pm 1.7$ (2sd, $n = 5$) and Cd concentrations of about 0.27 ± 0.08 nmol/kg (2sd, $n = 5$) (Fig. 3.9(b)). These marginally more positive values determined for the deep North Atlantic and Arctic Ocean might demonstrate the young ventilation age of these water masses, which implies that Cd isotope data could be used as a proxy to trace water masses. However, this tentative interpretation is necessary to be reexamined as further Cd isotope data for seawater become available.

Furthermore, Fig. 3.9(a) shows that surface seawater from non-HNLC locations in the Atlantic, Arctic and Pacific Ocean generally have much more fractionated $\epsilon^{114/110}\text{Cd}$ values and lower Cd contents in comparison to the HNLC samples from this study and Abouchami et al. (2011). These samples from the HNLC region display only modest Cd isotope fractionations and in most cases $\epsilon^{114/110}\text{Cd}$ does not exceed values of +8. In a number of studies, it has been suggested that the limited biological uptake of Cd and macronutrients in HNLC regions reflects limitation of biological productivity due to the lack of availability of the micronutrient Fe. Moreover, it has been highlighted that the Cd isotope compositions and concentrations of the HNLC samples display a single, well defined logarithmic correlation, which is in accord with a Rayleigh fractionation factor for biological uptake of $\alpha = 1.0005$ (Fig. 3.9). In contrast, the previously published data for surface water from Pacific, Arctic and Atlantic Ocean fall closer to a trend with a slope of $\alpha \approx 1.0002$. Clearly, there is significant scatter about this trend, particularly at low Cd contents. Some of these deviations have been previously discussed; whereby it was suggested that unusually low $\epsilon^{114/110}\text{Cd}$ at low [Cd] may reflect mixing processes. Taking this into account, there appears to be a clear difference in the Cd isotope fractionation factors, which are associated with biological uptake of Cd in the Southern Ocean HNLC region and non-HNLC open ocean areas.

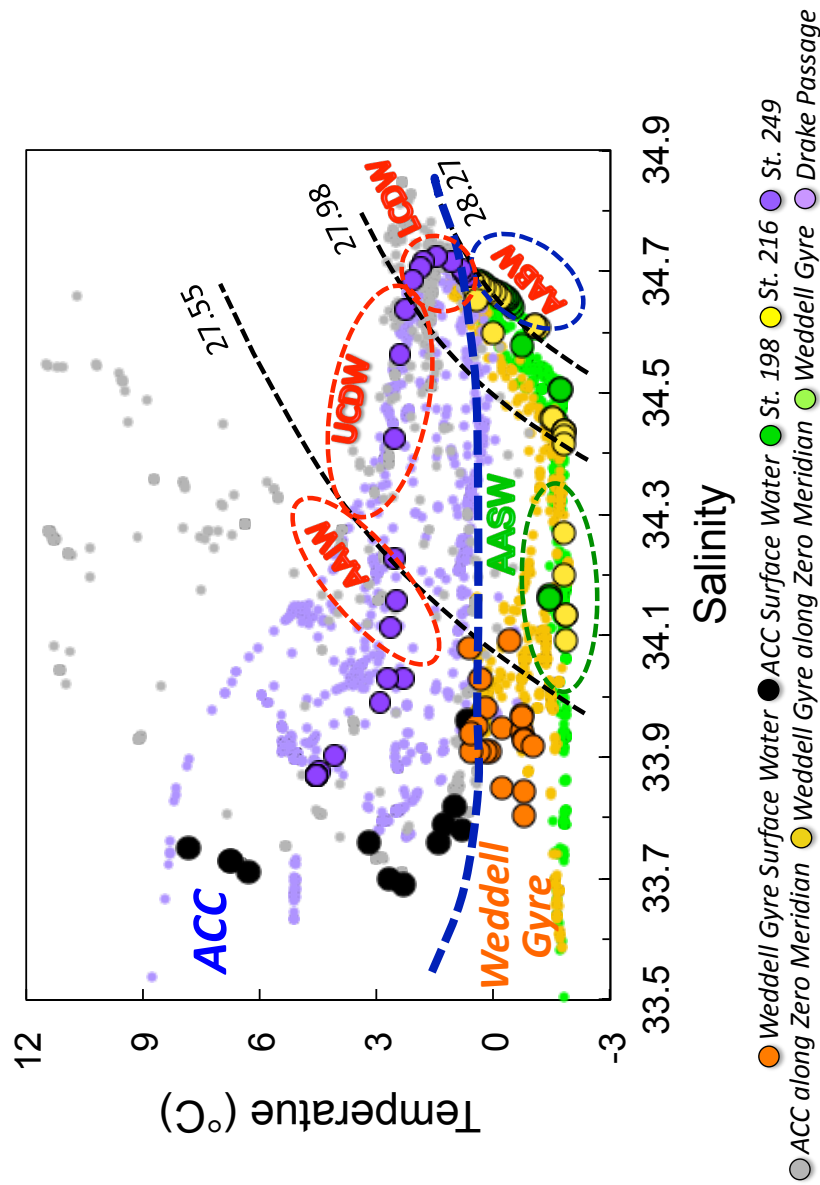
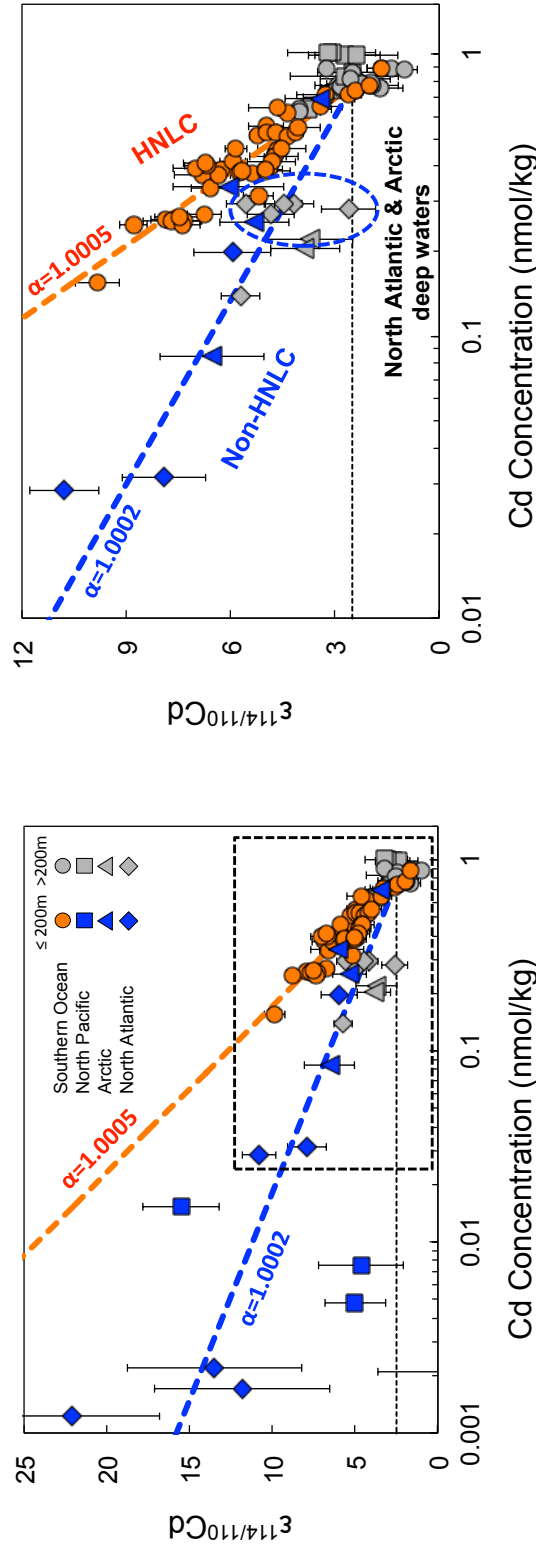


Figure 3.8: The correlation of potential temperature and salinity for the seawater samples from 3 vertical profile stations and the surface water samples along Zero Meridians. The potential temperature and salinity data are from CTD values. The data from Station 198 (in green), 216 (in yellow), 249 (in purple) and the surface water samples from Weddell Gyre (in orange) and ACC (in black) which were discussed in this study and a previous study (Abouchami et al., 2011), are plotted in this figure, along with the CTD data from other stations collected on the same cruise. AAIW = Antarctic Intermediate Water, LCDW = Lower Circumpolar Deep Water, UCDW= Upper Circumpolar Deep Water, AABW = Antarctic Bottom Water, AASW = Antarctic Surface Water.



(a) This figure demonstrates that samples from upper 200m in the Southern Ocean HNLC region display a less fractionated Cd isotope composition, compared to that in the non-HNLC open ocean area - the North Pacific, the North Atlantic and the Arctic Oceans. All the samples from Southern Ocean HNLC area fall on a well-defined linear trend in accord with closed system isotope fractionation with $\alpha \approx 1.0005$, which is distinguished from the non-HNLC open ocean area characterized by a fractionation factor $\alpha \approx 1.0002$.

(b) This figure shows that the Cd isotope composition of deep water below 1000m from 3 depth profiles in this study has a constant value about $\epsilon^{114/110}\text{Cd} = 2.5 \pm 0.7$, which agrees with of the average value of the deep seawater samples from North Pacific Ocean and Southern Ocean reported in a previous study (Ripperger and Rehkämper, 2007). The Cd isotope composition of deep water below 1000m from the Arctic and Atlantic Oceans shows a modest fractionation, which might be due to the younger ventilation.

Figure 3.9: Plots of Cd isotope compositions vs. concentrations for the samples from Southern Ocean HNLC region and non-HNLC open ocean area. The data plotted in this figure are from this study (Table 3.1, 3.2) and previous studies (Ripperger and Rehkämper, 2007; Ripperger et al., 2007; Xue et al., 2012). The samples from upper 200m are shown in orange and blue, respectively, whilst below 200m in grey. The dashed lines are calculated Rayleigh fractionation trends $\alpha \approx 1.0002$ and 1.0005 .

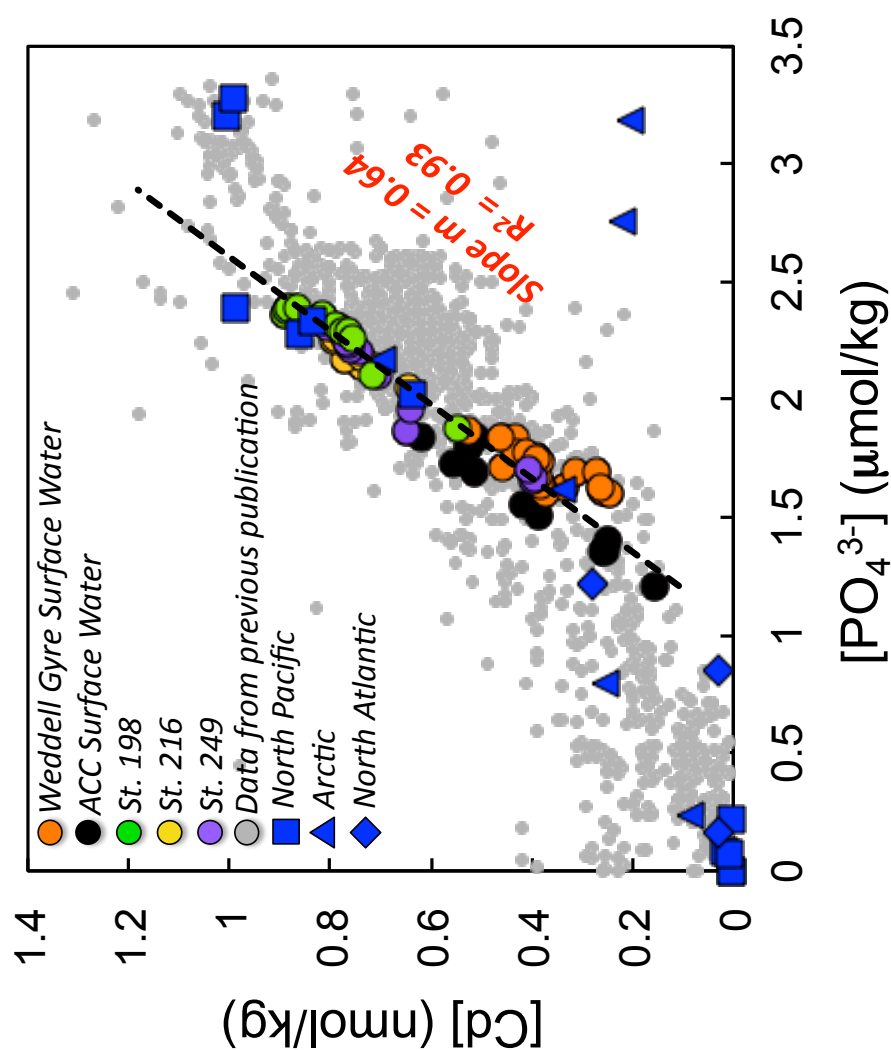


Figure 3.10: The correlation of Cd versus PO_4^{3-} concentrations in the Southern Ocean HNLC region. The grey dots show the Cd and PO_4^{3-} concentrations from a number of previous studies (Bruland et al., 1978; Bruland, 1980; Jones and Murray, 1984; Danielsson et al., 1985; Martin et al., 1989; Martin, 1990; Martin et al., 1990b; Hunter and Ho, 1991; Nolting et al., 1991; Westerlund et al., 1991; Yeats and Westerlund, 1991; Saager et al., 1992; Frew and Hunter, 1992, 1995; de Baar et al., 1994; Löscher et al., 1998; Fitzwater et al., 2000; Lacan et al., 2006). The data (in blue) from the North Pacific (square), the North Atlantic (diamond) and the Arctic Oceans (triangle) plotted in this figure are from Ripperger and Rehkämper (2007). All the data from this study and (Abouchami et al., 2011) show a linear correlation with slope = 0.64 ($R^2 = 0.93$, $n = 66$).

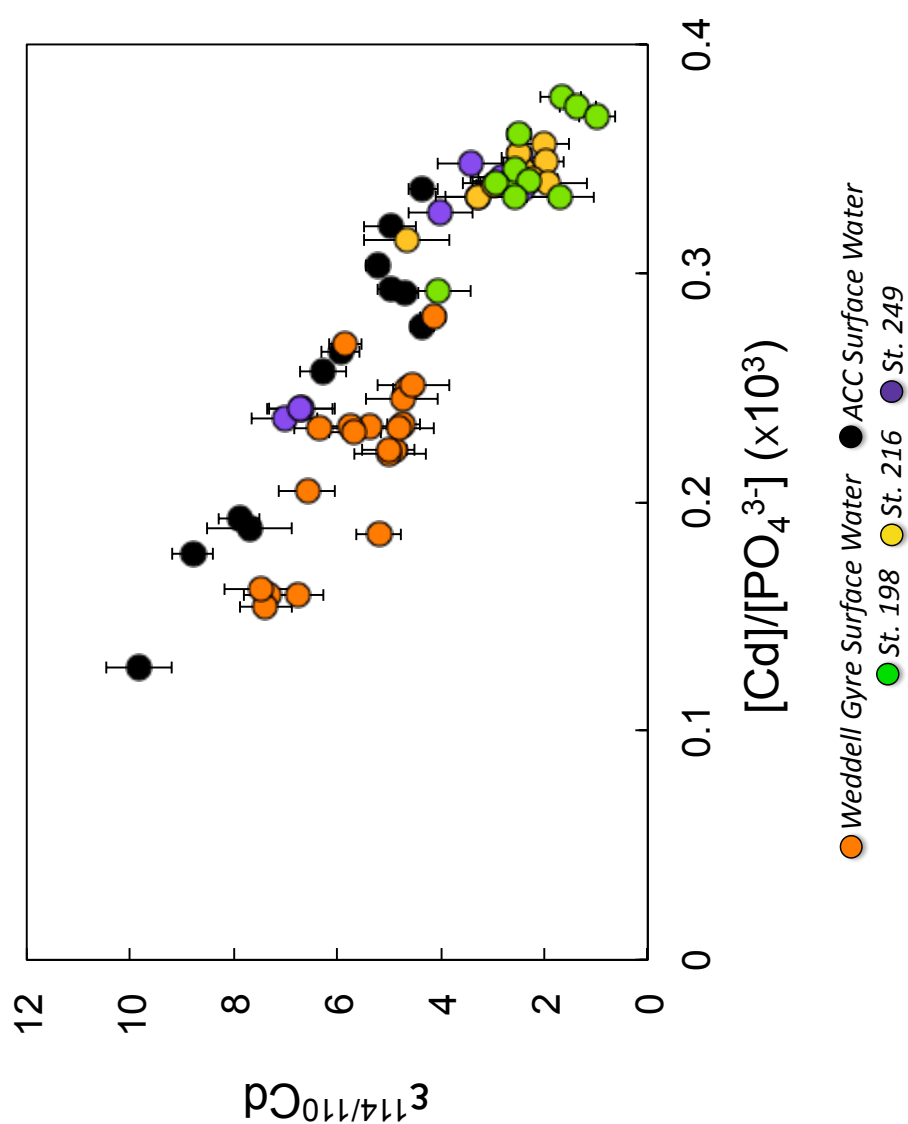


Figure 3.11: Cadmium isotope compositions vs. the ratio of $[\text{Cd}]/[\text{PO}_4^{3-}]$ of the water samples from the Southern Ocean. The three depth profiles at Station 249 (in purple), Station 216 (in yellow) and Station 198 (in green) as well as the surface water samples from Weddell Gyre (in orange) and ACC (in black) along the Zero Meridian from this study together with the data from (Abouchami et al., 2011) are shown.

A number of investigations have previously pointed out that seawater samples from HNLC areas commonly define much steeper correlations in diagrams of Cd versus PO_4^{3-} concentrations in comparison to the great majority of open ocean seawater from other locations (Frew and Hunter, 1992; de Baar et al., 1994; Elderfield and Rickaby, 2000; Cullen, 2006). This distinct Cd - PO_4^{3-} behavior exhibited by HNLC seawater has also been identified as generating the 'kink' or slight curvature that is apparent in compilations of global seawater Cd-phosphate data (Fig. 3.10). The samples from the 'Zero & Drake' cruise that were analyzed here and in the study of Abouchami et al. (2011) are in accord with this general observation as they define a steep trend, which intersects and cuts through the shallower correlation of the global dataset. An important additional observation is that the Cd isotope compositions of the HNLC seawater samples from the 'Zero & Drake' cruise correlate with the observed variations in the Cd/ PO_4^{3-} ratio (Fig. 3.11). This strongly suggests that there is a direct link between the processes, which are responsible for the distinct and steep Cd- PO_4^{3-} correlation and the $\epsilon^{114/110}\text{Cd}$ -Cd trend that are seen for HNLC seawater.

If the above inference is correct, it implies that the processes, which are responsible for the distinct Cd - PO_4^{3-} relationship of HNLC seawater (Fig. 3.10), should also be able to account for the observed $\epsilon^{114/110}\text{Cd}$ -Cd trend. (Fig. 3.11). A number of studies have found evidence for the conclusion that the steeper Cd - PO_4^{3-} trends seen for HNLC regions are related to increased uptake of Cd relative PO_4^{3-} when dissolved seawater Fe concentrations are low (Elderfield and Rickaby, 2000; Cullen et al., 2003; Cullen, 2006). It has furthermore been proposed, that the increased Cd uptake might be caused by upregulation of unspecific divalent metal ion transporters under Fe deficient conditions. Hence, it is not unrealistic to speculate that such a process may also be responsible for the distinct Cd isotope fractionation, characterized by $\alpha = 1.0005$, which was observed for HNLC seawater (Fig. 3.5). This conclusion is further supported by an experimental study, which has shown that marine diatoms present different Zn isotope fractionation patterns at high and low ambient Zn concentrations and these differences were interpreted to reflect biological uptake of Zn by different cellular uptake pathways (John et al., 2007). Hence, it is reasonable to hypothesize that differences in Cd uptake pathways in HNLC regions (characterized by high Cd but low Fe concentrations) versus other open ocean locations

(which typically feature low Cd contents but higher Fe) may generate distinct Cd isotope fractionation patterns.

3.6 Conclusions

This study of the Cd concentration and isotope composition of seawater samples from the Southern Ocean HNLC region has arrived at a number of important observations and interpretations, as summarized below:

- (I) The Cd concentration and isotope composition of surface waters from the Weddell Gyre that were determined in this study and a previous study Abouchami et al. (2011) define a logarithmic correlation, which indicates a biological fractionation factor of $\alpha = 1.00046 \pm 0.00006$. This finding suggests that the biological fractionation factor is not readily altered to a significant extent by differences in phytoplankton biomass or species, as suggested previously Abouchami et al. (2011).
- (II) The data obtained for three depth profiles at Stations 198 (Drake Passage), 216 (Scotia Sea) and 249 (Drake Passage) also show a logarithmic correlation of Cd isotope composition versus Cd concentrations. The water samples from depths of more than 1000 m have an average Cd isotope composition of $\epsilon^{114/110}\text{Cd} = +2.5 \pm 0.75$ (2 s.d.), which agrees very well with the previous conclusion that global deep waters feature a nearly constant $\epsilon^{114/110}\text{Cd}$ value of about $+2.5 \pm 0.50$ (Ripperger et al., 2007). The Cd isotope compositions of samples from depths ≤ 100 m is less fractionated with relatively high Cd concentrations and all these Cd data fall on the linear trend defined by the surface water samples from the Weddell Sea and ACC that were analyzed in the present study and by Abouchami et al. (2011). This demonstrates that less isotopic fractionated Cd coupled with relatively high Cd concentrations is a typical HNLC surface water signature. It also reinforces the conclusion that biological uptake of Cd in the Southern Ocean HNLC region appears to be characterized by a closed system Rayleigh isotope fractionation factor of $\alpha \approx 1.0005$.

- (III) Samples of intermediate depths of 200 m to 400 m from the Weddell Sea have high Cd concentrations and extremely light Cd isotope compositions of $\epsilon^{114/110}\text{Cd} = +1$. Such light isotope compositions were identified for the first time in seawater and they are most likely related to the addition of remineralized Cd derived from biomass, which records incomplete nutrient utilization at the surface. This might be another typical signature of the Cd distribution in the Southern Ocean HNLC region.
- (IV) Samples of intermediate depth water in the Drake Passage show Cd systematics that resembles surface water from the Weddell Gyre. This is in accord with the hydrographic data, which also indicate that AAIW is present in the Drake Passage. Hence, Cd isotopes might be applied to distinguish and trace AAIW from other water masses.
- (V) There is a clear difference in the Cd isotope fractionation factor α that is associated with biological uptake of Cd in the Southern Ocean HNLC region ($\alpha = 1.0005$) and non-HNLC open ocean areas-Pacific, Arctic and Atlantic Oceans ($\alpha \approx 1.0002$). Similarly, it was previously shown that seawater samples from HNLC areas commonly define much steeper correlations in diagrams of Cd versus PO_4^{3-} concentrations than the great majority of open ocean seawater from other locations. It is unlikely that this correspondence is purely fortuitous. Rather, we propose that there exists a direct link between the processes responsible for the distinct and steep Cd- PO_4^{3-} and $\epsilon^{114/110}\text{Cd}$ -Cd trends that are observed in HNLC seawater.

3.7 Acknowledgements

We are grateful to W. Abouchami for providing pre-cleaned seawater sample bottles to us. The authors furthermore thank Barry Coles, Katharina Kreissig, Rasmus Andreasen, Roz Coggon and the other members of the MAGIC team for their help in keeping the mass spec running and the clean lab organized. This research was supported by funding from a NERC research grant to MR, ZX and Andy Ridgwell (Bristol).

References

- Abouchami, W., Galer, S., de Baar, H., Alderkamp, A., Middag, R., Laan, P., Feldmann, H., Andreae, M., 2011. Modulation of the Southern Ocean cadmium isotope signature by ocean circulation and primary productivity. *Earth and Planetary Science Letters* 305, 83 – 91.
- Abouchami, W., Galer, S.J.G., Horner, T.J., Rehkämper, M., Wombacher, F., Xue, Z., Lambellet, M., Gault-Ringold, M., Stirling, C.H., Schönbächler, M., Shiel, A.E., Weis, D., Holdship, P.F., 2012. A Common Reference Material for Cadmium Isotope Studies - NIST SRM 3108. *Geostandards and Geoanalytical Research* .
- de Baar, H.J., Saager, P.M., Nolting, R.F., van der Meer, J., 1994. Cadmium versus phosphate in the world ocean. *Marine Chemistry* 46, 261 – 281.
- de Baar, H.J.W., de Jong, J.T.M., Bakker, D.C.E., Loscher, B.M., Veth, C., Bathmann, U., Smetacek, V., 1995. Importance of iron for plankton blooms and carbon dioxide drawdown in the Southern Ocean. *Nature* 373, 412–415.
- Baars, O., Croot, P.L., 2011. The speciation of dissolved zinc in the Atlantic sector of the Southern Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2720 – 2732.
- Barre, N., Provost, C., Renault, A., Sennechael, N., 2011. Fronts, meanders and eddies in Drake Passage during the ANT-XXIII/3 cruise in January - February 2006: A satellite perspective. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2533 – 2554.

- Behrendt, A., Fahrbach, E., Hoppema, M., Rohardt, G., Boebel, O., Klatt, O., Wisotzki, A., Witte, H., 2011. Variations of Winter Water properties and sea ice along the Greenwich meridian on decadal time scales. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2524 – 2532.
- Bluhm, K., Croot, P., Huhn, O., Rohardt, G., Lochte, K., 2011. Distribution of iodide and iodate in the Atlantic sector of the southern ocean during austral summer. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2733 – 2748.
- Boyle, E., John, S., Abouchami, W., Adkins, J., Echegoyen-Sanz, Y., Flegal, R., Ellwood, M., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkamper, M., Rouxel, O., Sohrin, Y., Stirling, C., Thompson, C., Vance, D., Xue, Z., Zhao, Y., 2012. GEOTRACES IC1 (BATS) Contamination-Prone Trace Element Isotopes Cd, Fe, Pb, Zn, Cu, and Mo Intercalibration. *Limnology and Oceanography: Methods* .
- Boyle, E., Sclater, F., Edmond, J., 1976. On the marine geochemistry of cadmium. *Nature* 263, 42–44.
- Bruland, K.W., 1980. Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth and Planetary Science Letters* 47, 176–198.
- Bruland, K.W., Knauer, G.A., Martin, J.H., 1978. Cadmium in Northeast Pacific Waters. *Limnology and Oceanography* 23, 618–625.
- Croot, P.L., Baars, O., Streu, P., 2011. The distribution of dissolved zinc in the Atlantic sector of the Southern Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2707 – 2719.
- Cullen, J., Chase, Z., Coale, K., Fitzwater, S., Sherrell, R., 2003. Effect of iron limitation on the cadmium to phosphorus ratio of natural phytoplankton assemblages from the Southern Ocean. *Limnology and Oceanography* 48, 1079–1087.
- Cullen, J.T., 2006. On the Nonlinear Relationship between Dissolved Cadmium and Phosphate in the Modern Global Ocean: Could Chronic Iron Limitation of Phytoplankton Growth Cause the Kink? *Limnology and Oceanography* 51, 1369–1380.

- Danielsson, L., Magnusson, B., Westerlund, S., 1985. Cadmium, copper, iron, nickel and zinc in the north-east Atlantic Ocean. *Marine Chemistry* 17, 23–41.
- Elderfield, H., Rickaby, R., 2000. Oceanic Cd/P ratio and nutrient utilization in the glacial Southern Ocean. *Nature* 405, 305–310.
- Fahrbach, E., de Baar, H.J., Garcon, V.C., Provost, C., 2011a. Introduction to physics, carbon dioxide, trace elements and isotopes in the Southern Ocean: The Polarstern expeditions ANT-XXIV/3 (2008) and ANT-XXIII/3 (2006). *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2501 – 2508.
- Fahrbach, E., Hoppema, M., Rohardt, G., Boebel, O., Klatt, O., Wisotzki, A., 2011b. Warming of deep and abyssal water masses along the Greenwich meridian on decadal time scales: The Weddell gyre as a heat buffer. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2509 – 2523.
- Fitzwater, S., Johnson, K., Gordon, R., Coale, K., Smith, W., et al., 2000. Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. *Deep Sea Research Part II: Topical Studies in Oceanography* 47, 3159–3179.
- Foster, T., Carmack, E., 1976. Frontal zone mixing and Antarctic Bottom Water formation in the southern Weddell Sea, in: *Deep Sea Research and Oceanographic Abstracts*, pp. 301–317.
- Frew, R., Hunter, K., 1992. Influence of Southern Ocean waters on the cadmium–phosphate properties of the global ocean. *Nature* 360, 144–146.
- Frew, R., Hunter, K., 1995. Cadmium-phosphorus cycling at the subtropical convergence south of New Zealand. *Marine chemistry* 51, 223–237.
- Gault-Ringold, M., Stirling, C., 2012. Anomalous isotopic shifts associated with organic resin residues during cadmium isotopic analysis by double spike MC-ICPMS. *Journal of Analytical Atomic Spectrometry* 27, 449–459.
- van Heuven, S.M., Hoppema, M., Huhn, O., Slagter, H.A., de Baar, H.J., 2011. Direct observation of increasing CO₂ in the Weddell Gyre along the Prime Meridian during

- 1973-2008. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2613 – 2635.
- Heywood, K., King, B., 2002. Water masses and baroclinic transports in the South Atlantic and Southern oceans. *Journal of Marine Research* 60, 639–676.
- Horner, T., Rickaby, R., Henderson, G., 2011. Isotopic fractionation of cadmium into calcite. *Earth and Planetary Science Letters* 312, 243–253.
- Hunter, K., Ho, F., 1991. Phosphorus-cadmium cycling in the northeast Tasman Sea, 35–40°S. *Marine chemistry* 33, 279–298.
- John, S., Geis, R., Saito, M., Boyle, E., 2007. Zinc Isotope Fractionation during High-Affinity and Low-Affinity Zinc Transport by the Marine Diatom *Thalassiosira oceanica*. *Limnology and Oceanography* 52, 2710–2714.
- Jones, C.J., Murray, J.W., 1984. Nickel, Cadmium, and Copper in the Northeast Pacific Off the Coast of Washington. *Limnology and Oceanography* 29, 711–720.
- Klatt, O., Fahrbach, E., Hoppema, M., Rohardt, G., 2005. The transport of the Weddell Gyre across the Prime Meridian. *Deep Sea Research Part II: Topical Studies in Oceanography* 52, 513–528.
- Klinck, J., Nowlin Jr, W., 2001. Antarctic circumpolar current. *Encyclopedia of Ocean Sciences*. Academic Press, New York , 151–159.
- Klunder, M., Laan, P., Middag, R., Baar, H.D., van Ooijen, J., 2011. Dissolved iron in the Southern Ocean (Atlantic sector). *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2678 – 2694.
- Lacan, F., Francois, R., Ji, Y., Sherrell, R., 2006. Cadmium isotopic composition in the ocean. *Geochimica et Cosmochimica Acta* 70, 5104–5118.
- van der Loeff, M.R., Cai, P.H., Stimac, I., Bracher, A., Middag, R., Klunder, M.B., van Heuven, S.M., 2011. ^{234}Th in surface waters: Distribution of particle export flux across the Antarctic Circumpolar Current and in the Weddell Sea during the GEOTRACES

- expedition ZERO and DRAKE. Deep Sea Research Part II: Topical Studies in Oceanography 58, 2749 – 2766.
- Löscher, B., De Jong, J., De Baar, H., 1998. The distribution and preferential biological uptake of cadmium at 6°W in the Southern Ocean. Marine chemistry 62, 259–286.
- Martin, J., 1990. Glacial-interglacial CO₂ change: The iron hypothesis. Paleoceanography 5, 1–13.
- Martin, J., Fitzwater, S., Gordon, R., 1990a. Iron deficiency limits phytoplankton growth in Antarctic waters. Global Biogeochemical Cycles 4, 5–12.
- Martin, J., Gordon, R., Fitzwater, S., 1990b. Iron in Antarctic waters. Nature 345, 156–158.
- Martin, J., Gordon, R., Fitzwater, S., Broenkow, W., 1989. VERTEX: phytoplankton/iron studies in the Gulf of Alaska. Deep Sea Research Part A. Oceanographic Research Papers 36, 649–680.
- Meredith, M., Garabato, A., Gordon, A., Johnson, G., 2008. Evolution of the Deep and Bottom Waters of the Scotia Sea, Southern Ocean, during 1995-2005*. Journal of Climate 21, 3327–3343.
- Middag, R., de Baar, H., Laan, P., Cai, P., van Ooijen, J., 2011a. Dissolved manganese in the Atlantic sector of the Southern Ocean. Deep Sea Research Part II: Topical Studies in Oceanography 58, 2661 – 2677.
- Middag, R., van Slooten, C., de Baar, H., Laan, P., 2011b. Dissolved aluminium in the Southern Ocean. Deep Sea Research Part II: Topical Studies in Oceanography 58, 2647 – 2660.
- Naveira Garabato, A., Jullion, L., Stevens, D., Heywood, K., King, B., 2009. Variability of Subantarctic Mode Water and Antarctic Intermediate Water in the Drake Passage during the late-twentieth and early-twenty-first centuries. Journal of Climate 22, 3661–3688.
- Nelson, D.M., Smith, Walker O., J., 1991. Sverdrup Revisited: Critical Depths, Maximum Chlorophyll Levels, and the Control of Southern Ocean Productivity by the Irradiance-Mixing Regime. Limnology and Oceanography 36, 1650–1661.

- Neven, I.A., Stefels, J., van Heuven, S.M., de Baar, H.J., Elzenga, J.T.M., 2011. High plasticity in inorganic carbon uptake by Southern Ocean phytoplankton in response to ambient CO₂. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2636 – 2646.
- Nolting, R., De Baar, H., Van Bennekom, A., Masson, A., 1991. Cadmium, copper and iron in the Scotia Sea, Weddell Sea and Weddell/Scotia Confluence (Antarctica). *Marine chemistry* 35, 219–243.
- Orsi, A., Johnson, G., Bullister, J., 1999. Circulation, mixing, and production of Antarctic Bottom Water. *Progress in Oceanography* 43, 55–109.
- Orsi, A., Smethie Jr, W., Bullister, J., 2002. On the total input of Antarctic waters to the deep ocean: A preliminary estimate from chlorofluorocarbon measurements. *Journal of Geophysical Research* 107, 3122.
- Orsi, A.H., III, T.W., Jr., W.D.N., 1995. On the meridional extent and fronts of the Antarctic Circumpolar Current. *Deep Sea Research Part I: Oceanographic Research Papers* 42, 641 – 673.
- Provost, C., Renault, A., Barre, N., Sennechael, N., Garçon, V., Sudre, J., Huhn, O., 2011. Two repeat crossings of Drake Passage in austral summer 2006: Short-term variations and evidence for considerable ventilation of intermediate and deep waters. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2555 – 2571.
- Rehkämper, M., Wombacher, F., Horner, T., Xue, Z., 2011. Natural and anthropogenic Cd isotope variations. *Handbook of Environmental Isotope Geochemistry*, 125–154.
- Renault, A., Provost, C., Sennechael, N., Barre, N., Kartavtseff, A., 2011. Two full-depth velocity sections in the Drake Passage in 2006 - Transport estimates. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2572 – 2591.
- Ripperger, S., Rehkämper, M., 2007. Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS. *Geochimica et cosmochimica acta* 71, 631–642.

- Ripperger, S., Rehkämper, M., Porcelli, D., Halliday, A., 2007. Cadmium isotope fractionation in seawater—A signature of biological activity. *Earth and Planetary Science Letters* 261, 670–684.
- Saager, P., De Baar, H., Howland, R., 1992. Cd, Zn, Ni and Cu in the Indian Ocean. *Deep Sea Research Part A. Oceanographic Research Papers* 39, 9–35.
- Sievers, H., Nowlin Jr, W., 1984. The stratification and water masses at Drake Passage. *Journal of Geophysical Research* 89, 10489–10.
- Stichel, T., Frank, M., Rickli, J., Haley, B., 2012. The hafnium and neodymium isotope composition of seawater in the Atlantic sector of the Southern Ocean. *Earth and Planetary Science Letters* 317, 282–294.
- Stramma, L., England, M., 1999. On the water masses and mean circulation of the South Atlantic Ocean. *Journal of Geophysical Research* 104, 20863–20883.
- Sudre, J., Garcon, V., Provost, C., Sennechaël, N., Huhn, O., Lacombe, M., 2011. Short-term variations of deep water masses in Drake Passage revealed by a multiparametric analysis of the ANT-XXIII/3 bottle data. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2592 – 2612.
- Thuroczy, C.E., Gerringa, L., Klunder, M., Laan, P., de Baar, H., 2011. Observation of consistent trends in the organic complexation of dissolved iron in the Atlantic sector of the Southern Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2695 – 2706.
- Venchiarutti, C., van der Loeff, M.R., Stimac, I., 2011. Scavenging of ^{231}Pa and thorium isotopes based on dissolved and size-fractionated particulate distributions at Drake Passage (ANTXXIV-3). *Deep Sea Research Part II: Topical Studies in Oceanography* 58, 2767 – 2784.
- Westerlund, S., et al., 1991. Cadmium, copper, cobalt, nickel, lead, and zinc in the water column of the Weddell Sea, Antarctica. *Geochimica et Cosmochimica Acta* 55, 2127–2146.

- Whitworth III, T., Nowlin Jr, W., Orsi, A., Locarnini, R., Smith, S., 1994. Weddell Sea shelf water in the Bransfield Strait and Weddell-Scotia confluence. *Deep Sea Research Part I: Oceanographic Research Papers* 41, 629–641.
- Xue, Z., Rehkämper, M., Schönbächler, M., Statham, P., Coles, B., 2012. A new methodology for precise cadmium isotope analyses of seawater. *Analytical and Bioanalytical Chemistry* 402, 883–893.
- Yeats, P., Westerlund, S., 1991. Trace metal distributions at an Arctic Ocean ice island. *Marine chemistry* 33, 261–277.

Chapter 4

Cd Cycling in the Eastern Equatorial Pacific Ocean (3°S-14°S)

The study discussed in this chapter has been prepared for submission to EPSL.

Abstract:

Recent studies have recognized that micronutrient elements, such as cadmium (Cd), play an important role in marine biological productivity. The distribution of dissolved Cd in seawater is correlated with that of phosphate, with low concentrations in surface waters due to biological utilization and higher abundances at depth from remineralization of organic material. The biological uptake of Cd in surface seawater can generate significant Cd isotope variability. Whilst the deep ocean appears to be characterized by a relatively constant Cd isotope composition of $\epsilon^{114/110}\text{Cd} \approx +2.5$, which is roughly similar to results obtained for the silicate Earth ($\epsilon^{114/110}\text{Cd}$ is the deviation of the $^{114}\text{Cd}/^{110}\text{Cd}$ ratio of a sample from the NIST 3108 Cd isotope standard in parts per 10,000). The most fractionated Cd isotope compositions have been determined for highly nutrient depleted open ocean surface waters from the Atlantic Ocean and the Pacific Ocean, which exhibit $\epsilon^{114/110}\text{Cd}$ values of up to +20 to +40. In contrast, the comparatively nutrient rich surface waters of the Southern Ocean High Nutrient Low chlorophyll (HNLC) region display relatively high Cd contents of up to 0.2 nmol/kg and only limited Cd isotope fractionation with $\epsilon^{114/110}\text{Cd}$ values of between +5 and +8. These results provide new constraints on the cycling of the micronutrient Cd in the oceans. In addition, they suggest that Cd isotopes may be a useful proxy for the study of past changes in marine nutrient utilization.

These conclusions are supported by further results obtained in the present investigation for seawater samples from the oxygen minimum zone (OMZ) in the South Pacific Ocean off Peru. Cadmium concentration and isotope data were obtained for 9 depth profiles in this region between 3°S and 14°S. The surface water samples from these locations display $\epsilon^{114/110}\text{Cd}$ -[Cd] signatures that are distinct from those found in the Southern Ocean HNLC region and nutrient depleted open ocean areas. In the Peruvian OMZ, seawater from depths of 0 -50 m displays highly variable Cd contents (of between 0.01 and 0.3 nmol/kg) combined with surprisingly constant Cd isotope compositions with the value of $\epsilon^{114/110}\text{Cd} \approx +5$ to +8. This signature most likely reflects a quasi steady-state situation, whereby the removal of Cd by biological utilization (and associated isotope fractionation) is balanced by Cd input from upwelling of Cd-rich water masses that feature intermediate isotope compositions. The deep water samples from the OMZ exhibit a mean $\epsilon^{114/110}\text{Cd}$ value of $+3 \pm 1$,

which is essentially identical to the global deep water average value.

4.1 Introduction

The geochemistry of Cd in the oceans and marine sediments has attracted significant scientific interest for more than 30 years (Rehkämper et al., 2011). This interest is primarily based on the observation that the dissolved Cd concentrations of seawater show a nutrient-like distribution, which very closely resembles the distribution of the marine macronutrient phosphate (Boyle et al., 1976; Bruland, 1980), as it displays low concentrations in surface waters due to biological utilization and higher concentrations in deep water from remineralization of organic material.

Recent studies have recognized that biological uptake of Cd in the surface ocean generates significant Cd isotope variability, whilst the deep ocean appears to be characterized by a relatively constant Cd isotope composition of $\epsilon^{114/110}\text{Cd} \approx +2.5$ (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011), which is roughly similar to the results obtained for the silicate Earth with $\epsilon^{114/110}\text{Cd} \approx -0.3$ (Schmitt et al., 2009). The most fractionated Cd isotope compositions have been determined for highly nutrient-depleted surface waters from open ocean areas, such as the Atlantic Ocean and the Pacific Ocean, which exhibit $\epsilon^{114/110}\text{Cd}$ values of between +20 and +40 (Ripperger et al., 2007; Xue et al., 2012). In contrast, the nutrient and Cd relatively-rich surface waters from the Southern Ocean HNLC region displays only limited Cd isotope fractionation with $\epsilon^{114/110}\text{Cd}$ values of up to +8 at Cd concentrations of no less than 0.2 nmol/kg (Chapter 3). All together, these results indicate that Cd isotopes provide new insights into marine micronutrient cycling and may be used for studies of past changes in marine nutrient utilization.

However, at present, the published Cd isotope database for seawater samples is still limited (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011; Xue et al., 2012). In particular, no study of Cd marine cycling based on isotopes for a major marine oxygen minimum zone (OMZ) has been published so far. However, such research may shed new light on macro- and micro-nutrient cycling in OMZ. To address this shortcoming, this

study presents new coupled Cd concentration and isotope data for a suite of 74 seawater samples from the OMZ in the Eastern Equatorial Pacific Ocean (EEP), one of the world's strongest and most extensive upwelling regions.

4.2 Samples and hydrographic background

4.2.1 Samples

In this study, Cd concentrations and isotope compositions were determined for 74 seawater samples from the OMZ in the EEP off the coast of Peru (Fig. 4.1). The samples are from 9 depth profiles located between 3°S - 14°S and 77°W - 86°W. These profiles cover two meridional (north-south) sections and one zonal (west-east) section. The two meridional sections are at 85.83°W (offshore Stations 109, 134, 97, 93) and between 77.06°W and 82.02°W (near-shore Stations 117, 124, 11, 78). The zonal section at 14°S includes Stations 93, 86, and 78.

All samples were collected with an ultraclean CTD system between December 27th, 2008 and February 18th, 2009 during legs M77/3 and M77/4 of a German expedition with the R/V Meteor to the tropical eastern Pacific Ocean (Oschlies et al., 2012; Stramma, 2009; Pfannkuche et al., 2011). After collection, the samples were immediately passed through 0.2 μm nominal size cutoff filter cartridges, transferred into appropriate pre-cleaned containers and then acidified to pH 2 using distilled 6 M HCl.

4.2.2 Current System of the Eastern Equatorial Pacific Ocean

The Peru Chile Current System (PCCS) of the EEP is also known as the Humboldt Current System (HCS) and it extends from central Chile ($\sim 40^\circ\text{S}$) to northern Peru ($\sim 4^\circ\text{S}$) (Fig. 4.2). The PCCS is complex and subject to significant inter-annual variability as a consequence of the El Niño Southern Oscillation cycle (ENSO) (Strub et al., 1998). The PCCS includes several currents:

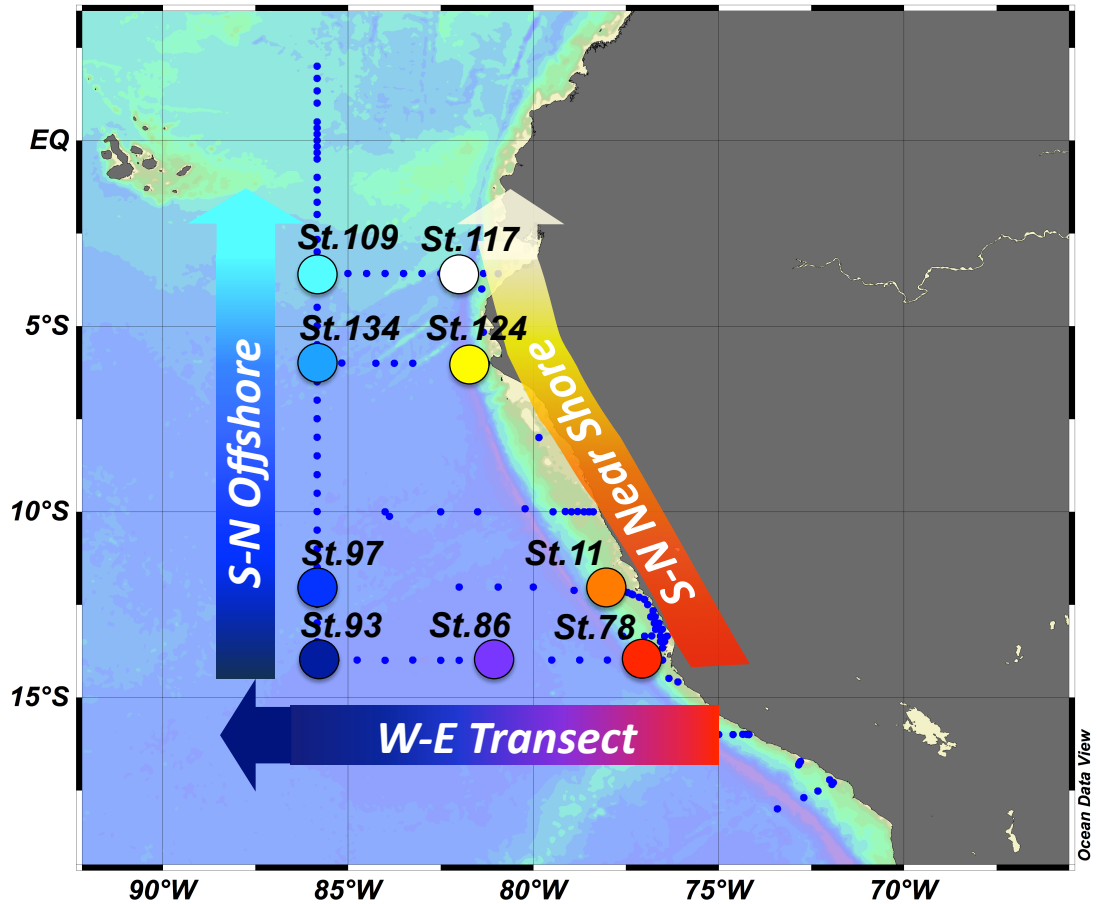


Figure 4.1: Locations of seawater samples analyzed in this study. Cd concentrations and isotope compositions were determined for 74 seawater samples from the oxygen minimum zone (OMZ) in the Eastern Equatorial Pacific Ocean (EEP) off the coast of Peru during the research cruise METEOR M77/3 and M77/4. The samples are from 9 depth profiles located at about 3°S-14°S and 77°W - 86°W. These profiles cover: (A) two meridional (north-south) sections - (1) at 85.83°W (offshore Stations 109, 134, 97, 93; in blue colors) and (2) between 77.06°W and 82.02°W (nearshore Stations 117, 124, 11, 78; in red colors); (B) one zonal (west-east) section at 14°S (Stations 93, 86, and 78; in blue, purple and red, respectively).

- (i) The coastal currents, Chile Coastal Current (CCoastalC) and Peru Coastal Current (PCoastalC), flow northward in the near surface layer (0-100 m) with a width of about 100 km (Strub et al., 1998). They are located at the level of the thermal front generated by the upwelling of cooler water at the coast (Smith, 1978, 1983).
- (ii) The Peru-Chile Counter Current (PCCC), a southward flowing surface current, is observed 100-300 km offshore from the coast (Strub et al., 1995, 1998).
- (iii) The West Drift Current (WDC), is located further offshore and constitutes the return current of the South Eastern Pacific subtropical gyre. It flows towards the South American coast between 35°S and 48°S, then separates into two branches and one of these flows northward as the Humboldt Current (Strub et al., 1998).
- (iv) The Peru-Chile Undercurrent (PCUC) is a poleward flowing subsurface current, which extends over the continental shelf and slope off the west coast of South America with a core located between 100 and 300 m depth. The PCUC transports warm, salty Equatorial Subsurface Water (ESSW) from the eastern tropical Pacific to as far south as 48°S (Silva and Neshyba, 1979). PCUC is the main source for coastal upwelling off Peru and northern Chile (Huyer et al., 1987) and is associated with the oxygen minimum layer (Wyrтки et al., 1966).

4.2.3 Water masses of the Eastern Equatorial Pacific Ocean

Off Peru, the warm and salty Subtropical Surface Water (STSW; $20^{\circ}\text{C} < \text{Temperature} < 28^{\circ}\text{C}$; $\text{Salinity} > 35.0$) features high oxygen contents and it overlies Equatorial Subsurface Water (ESSW; $8.5^{\circ}\text{C} < \text{Temperature} < 10.5^{\circ}\text{C}$; $34.4 < \text{Salinity} < 34.8$), which has much lower oxygen contents at depths below 100-150 m in the offshore regions (Wyrki et al., 1966; Enfield, 1976). Equatorial Surface Water (ESW) is characterized by temperatures of 20°C to 24°C and salinities of 33.5 to 35.0, and is formed by mixing of Peru Coastal Current (PCoastalC; $\text{Temperature} < 19^{\circ}\text{C}$; $33.5 < \text{Salinity} < 35.0$), Subtropical Surface Water (STSW) and Tropical Surface Water (TSW; $\text{Temperature} 25^{\circ}\text{C}$; $\text{Salinity} < 33.5$) in a narrow band along the equator between 3°N and 4°S (Wyrki et al., 1966; Enfield, 1976).

There are two important intermediate water masses in the South East Pacific, which are Antarctic Intermediate Water (AAIW) and the shallower Eastern South Pacific Intermediate Water (ESPIW). AAIW is formed by the subduction of Antarctic Surface Water at the Antarctic Convergence (at about 50°S to 60°S) and it flows northward to a latitude of approximately 20°S (Talley, 1999; Kawabe and Fujio, 2010). With a temperature of about 3 to 5°C and a salinity of 34.3 to 34.5, AAIW occurs below 500-600 m depth but sometimes approaches the surface during periods of strong upwelling (Strub et al., 1998). ESPIW deepens from its source region at about 32°S in a westward and northward direction and reaches depths of 150 m. ESPIW is characterized by a salinity of about 34.0 to 34.4 (Emery, 2001), which is clearly distinguished from AAIW.

The densest water mass in the Pacific basin is the Lower Circumpolar Deep Water (LCDW) (Wijffels et al., 1996).

4.2.4 Hydrography of the Peruvian Oxygen Minimum Zone

Regions of the interior ocean that are relatively poor in oxygen are commonly called oxygen minimum zones (OMZ), however, a clear and generally accepted definition in terms of environmental parameters is not available. In previous studies, OMZs have been defined by oxygen concentrations of less than $50\text{ }\mu\text{mol/kg}$, $20\text{ }\mu\text{mol/kg}$ or $5\text{ }\mu\text{mol/kg}$. Hence, in this

study, the OMZ in the EEP off Peruvian coast is defined by oxygen concentrations of less than $5 \mu\text{mol/kg}$. The formation of OMZs is a consequence of a combination of sluggish ocean ventilation, which leads to a limited replenishment of oxygen, and enhanced respiration, whereby oxygen is rapidly consumed particularly by remineralization (Karstensen et al., 2008). The upwelling area in the EEP off the coast of Peru is one of the world's largest OMZs, as this extends from 3°S to 15°S , at depths of about 100 to 900 m. The formation of this large OMZ is discussed below, based on published literature (Strub et al., 1998; Montecino et al., 2006).

In the South Eastern Pacific Ocean, the Peru Chile current system (PCCS) is one of the most productive systems in the world ocean and it features permanent and seasonal upwelling cells along the coasts of Peru and Chile. The upwelling off Peru can be observed as far as 400 km away from shore (Strub et al., 1998). The most intense coastal upwelling occurs in the upper 50 m and within 50 km of the coast. Associated with the PCCS, a shallow oxygen minimum zone is present, which extends far offshore. On average, the OMZ is located at depths between about 30-70 m (upper boundary) and 300-400 m (lower boundary), and hence, it approximately coincides with the base of the euphotic zone. The strong primary productivity in the euphotic layer is an important source of particulate organic matter, which is exported to subsurface layers. When the flux of exported carbon is high, remineralisation and thus oxygen consumption at depth increases, which leads to the generation of an OMZ. Once the OMZ is established, the oxygen deficit severely limits remineralisation and hence, stimulates downward export of particulate organic matter. Therefore, OMZ regions are associated with a significant export of carbon and particulate organic matter. In summary, high productivity and intense remineralisation are the main biogeochemical processes in the OMZ off Peru, which are needed to generate and maintain OMZs.

The combination of low latitude upwelling, which generates high primary productivity, with the equatorward flowing surface flow and poleward undercurrent of the PCCS, plays an important role in the formation of the OMZ in the EEP. In particular, biological productivity in the upper ocean off Peru features a downward flux of organic matter

which is decomposed at depth, thereby further depleting the low oxygen levels present in the poleward undercurrent (PCUC). Upwelling brings nutrients back into the equatorward surface layer, fueling productivity and creating a semi-closed 'nutrient trap' that maintains enhanced productivity (Montecino et al., 2006). Therefore, the net result is that the PCUC off Peru has very low oxygen contents (Montecino et al., 2006).

4.3 Analytical methods

A recent publication provides a detailed description of the analytical techniques that were used in this study (Xue et al., 2012; Chapter 2). Hence, only a brief summary of the methods is provided here, focusing on modifications to the published techniques.

Based on preliminary Cd concentration analyses ((Xue et al., 2012); Chapter 2), the separation of Cd from the sample matrix prior to isotopic analysis was carried out using two different techniques. For samples with $[Cd] \geq 0.1$ nmol/kg, about 0.3 to 3 L of seawater were weighed to obtain 30 ng of natural Cd and then mixed with a suitable amount of a ^{111}Cd - ^{113}Cd double spike to achieve a spike-sample ratio of $S/N=1$. The Cd separation for these samples was then carried out using a three-stage column chemistry procedure only, as described in Xue et al. (2012) and Chapter 2. For seawater with Cd concentrations of less than 0.1 nmol/kg, samples volumes of about 3 to 20 L were used for the Cd isotope analyses. For all samples with $[Cd] \leq 0.015$ nmol/kg, the maximum available sample volume of about 20 L was employed for the analyses. After weighing and addition of the Cd double spike, the Cd was first isolated from these samples by co-precipitation with $Al(OH)_3$. Following this, further purification was achieved using the standard column chemistry procedure ((Xue et al., 2012); Chapter 2).

The purified Cd fractions were subsequently analyzed by mass spectrometry for the determination of the Cd stable isotope composition. The analyses were carried out with a Nu Plasma HR MC-ICP-MS at the MAGIC Laboratories, Imperial College London. Mass spectrometry and data reduction techniques are described in (Ripperger et al., 2007; Xue et al., 2012) and chapter 2. The Cd isotope data collected during the mass spectromet-

ric analyses were processed to calculate the 'true' isotope compositions of the unspiked samples, which were corrected for both instrumental mass bias and isobaric interferences. These data were then used to determine the reported $\epsilon^{114/110}\text{Cd}$ values of the samples relative to an isotopic standard (std):

$$\epsilon^{114/110}\text{Cd} = \left[\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{sample}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{std}}} - 1 \right] \times 10,000$$

In this study, the $\epsilon^{114/110}\text{Cd}$ data are reported relative to NIST SRM 3108 Cd, which is a new proposed Cd isotope reference material. The secondary Cd isotope reference materials BAM-I012 Cd, JMC Cd Münster, and Alfa Cd Zurich were routinely analyzed alongside with seawater samples and these measurements yielded results that were identical, within error, to previously published data (Rehkämper et al., 2011).

The chemical separation procedures routinely achieved Cd yields of better than 90% during the course of this study. All Cd concentration data were corrected for the procedural blank of about 20 pg. This implies that the blank contributes only about 0.03% to the indigenous Cd present in the samples. As the blank contamination had only a negligible effect on the measured isotope compositions, no corrections were applied to these results.

4.4 Results and discussion

4.4.1 Hydrological data

Profiles of salinity, temperature and oxygen for the 9 stations are shown in Fig. 4.3a. Given that below 400 m depth, the profiles of salinity, temperature and oxygen are very similar for all the stations, detailed hydrology data for the upper 400 m are presented in Fig. 4.3(b).

Based on the salinity profiles for the upper 150 m (Fig. 4.3(b)), the 9 stations can be divided into three distinct groups: (I) At the near-shore stations 124, 11 and 78, located at 6°S-14°S, salinity increases modestly from 35.0 at the surface to approximately 35.2 at about 30 m depth, and then decreases gently to about 35.0 at 50 m depth. The salinity is

roughly constant at 35.0 between depths of 50 to 150 m. (II) At stations 109, 117 and 134 at 4°S - 6°S, the salinity of the surface water has an extremely low value of about 34.4. At depth, salinity increases rapidly from the surface value to 35.0 at 30 m depth, and then decreases slightly to about 34.95 at 150 m depth. (III) The salinity trends of the offshore stations 86, 93, 97 at 12°S - 14°S are distinct in the upper 150 m of the water column. The highest values of 35.2 to 35.6 are observed in surface water. Salinity continuously decreases to about 34.7-34.8 at depths of 100-120 m and then increases modestly to 34.9 at 150 m.

In general, the temperature profiles for the 9 stations show very similar trends, whereby temperature continuously decreases from the surface to a depth of about 3000 m. Below 3000 m, the temperature is constant at about 1.8°C. However, there are minor differences in the temperature profiles for the upper 150 m. The near shore stations 11, 78, 117, 124 are distinct in that they exhibit surface water temperatures of only about 20°C - 22°C. In contrast, the offshore stations 86, 93, 97, 109, 134 have higher surface water temperatures of about 25°C to 27°C. Moreover, the temperatures at the offshore stations 109 and 134, located at 4 - 6°S, decrease rapidly from 25°C at the surface to 15°C at 50 m depth, and then show the same value at 50-150 m depth as the near shore stations 11, 78, 117 and 124.

The salinity and temperature profiles demonstrate that (Fig. 4.4): (1) The 9 sampling stations feature two different dominant surface water masses. Stations 86, 93, 97, in the core of the STSW, are characterized by $20^{\circ}\text{C} < \text{Temperature} < 28^{\circ}\text{C}$ and $\text{Salinity} > 35.0$, whereas Stations 109, 117, 134 are affected by ESW, which is characterized by $20^{\circ}\text{C} < \text{Temperature} < 24^{\circ}\text{C}$ and $33.5 < \text{Salinity} < 35.0$ (Fig. 4.4); (2) The surface water of the near shore stations 11, 78, 124 has a distinct character, with salinities that are similar to those measured at 50 m depth and relatively low temperatures (Fig. 4.4). These characteristics may be a consequence of strong coastal upwelling, which brings subsurface water to the surface.

The oxygen profiles for the 9 stations are shown in Fig. 4.3(b). The oxygen content of the surface waters is as high as 200-250 $\mu\text{mol/kg}$ due to exchange with the atmosphere.

From the surface to subsurface/intermediate depths (50-300 m), oxygen concentrations decrease continuously and rapidly to values as low as 2-3 $\mu\text{mol/kg}$ which are maintained to depths of up to 500 m. Below 500 m, the oxygen concentrations increase with increasing depth.

In this study, the boundary of the OMZ is defined by an oxygen concentration of 5 $\mu\text{mol/kg}$. Based on this definition, the upper boundary of the OMZ at the 9 stations occurs at depths ranging from 50 m to 300m. At the near shore station 11, 78, 124, the upper boundary of the OMZ is particularly shallow at depths of about 50 m. In contrast, at the offshore stations 86, 93, 97, and 134 the upper boundary is situated at a depth of about 100-150 m. The upper boundary of the OMZ appears even deeper, at 200-300 m depth, for the stations 109 and 117, which are at located at 4°S.

Considering that the OMZ of the EEP is related to the upwelling of water masses, the vertical oxygen profiles (Fig. 4.3) illustrate that, in general, the OMZ is expressed at depths of between 50 m and 500 m. Furthermore, the variation in the depth of the OMZs indicates that upwelling is generally stronger at the coast than offshore and stronger at 6°S, 12°S, and 14°S than at 4°S. The latter is clearly apparent in the W-E sections of salinity, temperature and oxygen, which are shown in Fig. 4.5. It is important to note that the data shown in Fig. 4.5 are based not only on data collected at the 9 sampling stations in this study. Rather, they were constructed using all of the CTD data collected during cruise M77/3 and M77/4.

At 4°S, there are no conspicuous variations in salinity, temperature and oxygen along the W-E transect and the upper boundary of the OMZ is constant at about 200 m depth. This suggests that the upwelling at 4°S has a similar intensity at both coastal and offshore locations. At 6°S, the upper boundary of the OMZ along the W-E transect is shallower than at 4°S. Here, the upper boundary of the OMZ is located at a depth of about 100 m in the offshore region; however, the boundary moves to depths as shallow as 50 m, close to the coast. This upwelling is more intense at the coast, which is also apparent in transects at 10°S, 12°S and 14°S (Fig. 4.5). At these locations, the coastal and near-shore surface water features lower salinity and lower temperatures. Moreover, oxygen concentrations at

10°S, 12°S and 14°S reveal that the upper boundary of the OMZ is located at depths of 30 to 50 m, which is even shallower than that at 6°S.

Furthermore, figure 4.5 shows variations of salinity, temperature and oxygen along two N-S transects, which are at near shore and at 85.83°W offshore. They further confirm that (1) in general, upwelling is stronger in coastal regions than in offshore areas; (2) in agreement with earlier studies (Strub et al., 1998; Montecino et al., 2006), the most intense coastal upwelling occurs at between 10°S and 14°S; (3) the OMZ in the study area is located at depths of between 30 m and 500 m in the water column; (4) the upper boundary of the OMZ varies in depth between about 30 and 200 m.

4.4.2 Cd concentration and isotope composition profiles and their relationship with oxygen contents

Profiles of Cd concentrations and isotope compositions (Fig. 4.6) display broadly similar trends for all 9 stations. In particular, Cd is depleted in the surface water, with concentrations of about 0.1 to 0.3 nmol/kg at the near-shore Stations 11, 78, 117, and 124 where upwelling is particularly strong. In contrast, the offshore Stations 86, 93, 97, 109, and 134 have lower Cd contents of about 0.01 to 0.04 nmol/kg. Furthermore, at all stations the surface seawater features Cd isotope compositions of $\epsilon^{114/110}\text{Cd} \approx +5$ to $+8$. Such relatively constant surface water Cd isotope compositions that are coupled with variable Cd contents appear to be a typical characteristic for the Peruvian upwelling region.

From surface to subsurface depths above the upper boundary of the OMZ, the samples display generally increasing Cd contents and lower Cd isotope fractionation. These observations are in accord with water mass upwelling and remineralization of biological material. At 200 m depth, all 9 stations have nearly identical Cd contents of about ~ 0.7 nmol/kg and Cd isotope compositions of about $\epsilon^{114/110}\text{Cd} \approx +5.5$ (Fig. 4.6). In this context, upwelling water masses generally come from depths of about 100-300 m, both in coastal and offshore locations (Huyer et al., 1987; Strub et al., 1998).

At intermediate water depths, remineralization of biological material can only occur at high oxygen levels, which appears below the lower boundary of the OMZ (Fig. 4.7). As a result, Cd concentrations increase to about 1 nmol/kg at 1 km depth. At this depth, the Cd isotope compositions observed for all stations are also relatively constant at $\epsilon^{114/110}\text{Cd} \approx +4$ (Fig. 4.7). Below 1 km, both Cd concentrations and $\epsilon^{114/110}\text{Cd}$ values decrease slightly, possibly as a result of mixing between intermediate water (AAIW and/or ESPIW) and deep water masses (LCDW) (Fig. 4.4). At depths of 3 to 4 km, the water sampled at all stations has a similar Cd content of about 0.9 nM. Furthermore, the Cd isotope compositions of these samples are essentially identical at $\epsilon^{114/110}\text{Cd} \approx +2.5$ (Fig. 4.7), which is in excellent agreement with average values published for the Pacific and Southern Ocean deep-water (>1km) with $\epsilon^{114/110}\text{Cd} = +2.5 \pm 0.7$, ((Ripperger et al., 2007; Rehkämper et al., 2011); chapter 3).

A significant observation is that the Cd concentration profiles reveal clear differences between the near-shore stations 11, 78, 117, 124 and the offshore stations 86, 93 97, 109, 134 (Fig. 4.7). At station 11 and 78, the strong coastal upwelling brings water masses with high Cd but low oxygen contents from about 100 - 300 m depth to or close to the surface. As a consequence, the surface and subsurface waters display relatively high Cd contents, which increase rapidly from 0.1-0.3 nmol/kg at the surface to 0.8 nmol/kg at depths of 50-200 m. This strong coastal upwelling extends through the upper boundary of the OMZ to depths as shallow as 50 m. Hence, the Cd concentrations in the water column above the upper boundary of the OMZ are determined by the interplay of biological utilization of Cd, release of particulate Cd by remineralization of biological materials and Cd replenishment by water mass upwelling.

The oxygen contents display a minimum value of $< 5\mu\text{mol/kg}$ between depths of 50 m and 450 m and at such low oxygen concentrations the remineralization of particulate organic matter is severely limited. Therefore, in the OMZ between 50 m and 450 m depth, the Cd content of the seawater is primarily a function of biological utilization and replenishment of Cd by upwelling.

At Station 124 (situated at 6°S), coastal upwelling is weaker than it is in the central upwelling region between 10 - 14°S. Hence, the upper boundary of the OMZ is observed at a depth of about 170 m, which is much deeper than that observed at 10-14°S. From the surface to a depth of 50 m, Cd concentrations at Station 124 only increase to 0.7 nmol/kg, which indicates that upwelling is weaker at this locality to replenish the low Cd contents in the surface water.

At station 117, the upwelling is even weaker and consequently only a relatively thin oxygen minimum layer is developed between depths of 300 m and 350m. Hence, the OMZ is located below the depth from which water mass upwelling is sourced. Furthermore, a Cd concentration of only about 0.4 nmol/kg is observed at 50m depth, as the weaker upwelling only leads to modest replenishment of the Cd contents.

In comparison to the Cd profiles for the near-shore stations in the coastal upwelling region, the Cd contents in the surface water at the offshore stations at 85.83°W are distinguished by much low Cd concentrations of about 0.01-0.04 nM (Fig. 4.7). In general, the upwelling at offshore locations is much weaker than the coastal upwelling at the same latitude (Strub et al., 1998; Montecino et al., 2006). This inference is supported by the observation that the upper boundaries of the OMZ at offshore stations are generally observed at greater depths (of about 150 to 300 m) than at the near-shore stations. This reflects that the offshore upwelling is not strong enough to bring water masses with high Cd and low oxygen contents close to the surface. Hence, the surface waters at the offshore stations have low Cd contents as a result of the less Cd-replenishment from upwelling.

The oxygen and temperature sections along 85.5°W (Fig. 4.5) demonstrate that (1) offshore upwelling is strongest at about 6.5°S; (2) the intensity of upwelling decreases from 6.5°S to 14°S. This conclusion is supported by the Cd contents of surface and subsurface water. At Station 93 and 97, the Cd concentrations are extremely low in the upper 50 m. This is because the offshore upwelling is too weak to replenish depleted Cd in the surface and subsurface waters. In contrast, at Station 134 extreme depletion of Cd to about 0.04 nmol/kg, is only observed in surface water (Fig. 4.7). At a depth of 25 m, the Cd concen-

tration rises to about 0.1 nmol/kg, which is much higher than the Cd concentrations that are observed at Stations 93 and 97 at the similar depths.

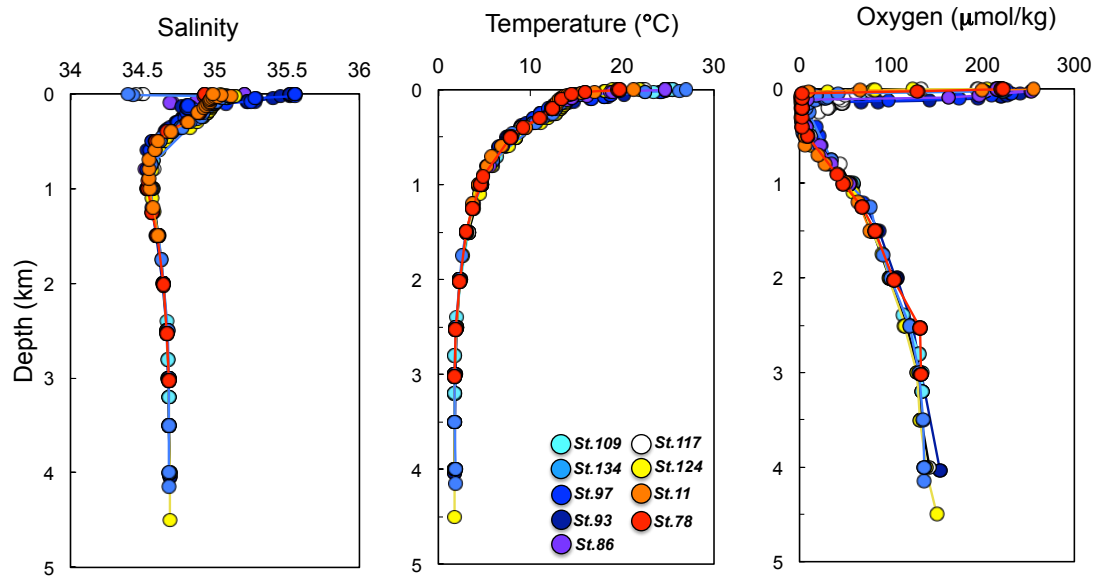
At 4°S, the Cd profile at the offshore Station 109 is very similar to that of the near-shore Station 117, even for the upper 200 m. The oxygen profiles (Fig. 4.7) are also very similar. Together, these observations suggest that the intensity of the water mass upwelling at 4°S is similar at offshore and near-shore localities and weak compared to the near-shore upwelling observed at 10 - 14°S (Fig. 4.7).

The key differences in the Cd profiles between offshore and near-shore localities in the center of the Peruvian upwelling region at about 14°S are highlighted in Fig. 4.8. In all cases, the water mass at 100-300 m depths is characterized by an average value of [Cd] $\approx$ 0.7 nmol/kg and $\epsilon^{114/110}\text{Cd} \approx +6$. This is important, because the upwelling water at both offshore and near-shore areas is sourced approximately from these depths (Strub et al., 1998; Montecino et al., 2006; Hormazabal et al., 2006). Upwelling brings oxygen depleted but Cd-rich water masses close to the surface. As a consequence, the upper boundary of the OMZ extends to shallower depths and the Cd content of surface and subsurface water is replenished, where upwelling takes place. Hence, the intensity of upwelling has a major influence on the depth of the upper boundary of the OMZ and the Cd contents, which are observed in the upper water column to depths of about 200 m.

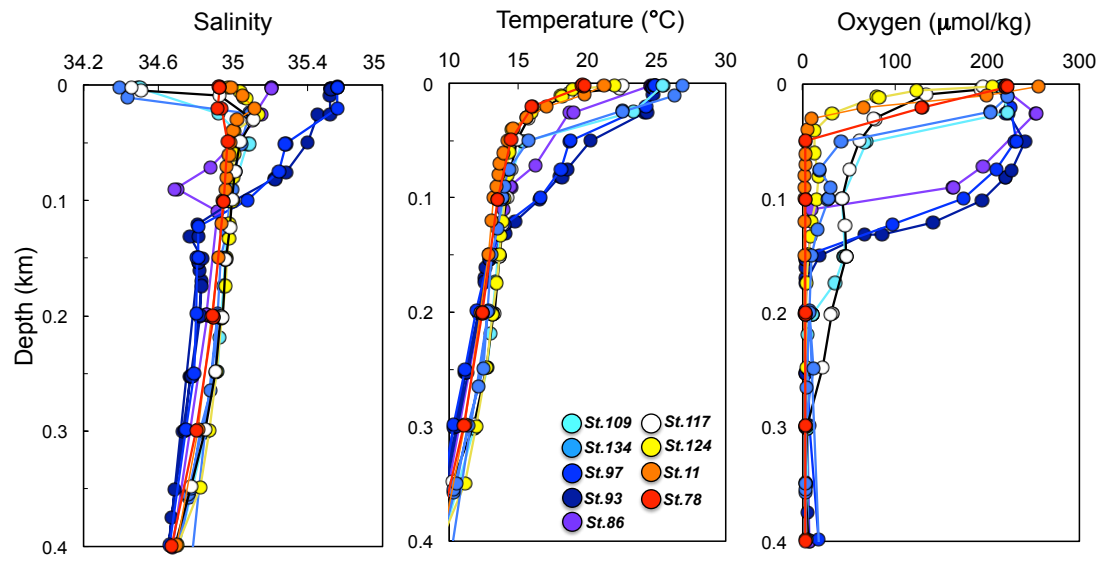
These effects can be clearly seen in the 3 depth profiles from the W-E transect at 14°S (Fig. 4.8). Here, upwelling is thought to be weakest at the offshore location of Station 93. Clearly, the depth of upper boundary of the OMZ increases from 170 m at Station 93 to about 50 m at Station 78. Cadmium is furthermore extremely depleted in the upper 50 m at Station 93, whereas at Station 78, the Cd content of the surface water is about as 10 times higher than that observed at Station 93. In addition, a much more rapid rise in Cd content is observed in subsurface water at depths of < 100 m at the near-shore Station 78 than at offshore Station 93.

In the upper water column, to the depth of the upper boundary of the OMZ, Cd contents

are determined primarily by the intensity of upwelling, biological utilization and remineralization of organic matter. From the upper boundary of the OMZ to about 200 m depth, the Cd concentrations are dominantly affected by the intensity of upwelling, as both biological utilization and remineralization are limited by the low oxygen content of the water column. The Cd concentrations show a general increase between 200 m and 1 km, as the higher oxygen concentrations at intermediate depths again support remineralization. Below 1 km, the Cd concentrations decrease slightly, presumably as a consequence of mixing between intermediate water with higher Cd contents (from remineralization) and deep water, which is characterized by a relatively lower Cd concentration.



(a) Profiles of salinity, temperature and oxygen.



(b) Profiles of salinity, temperature and oxygen for the upper 400m of the water column.

Figure 4.3: The depth variations of salinity, temperature and oxygen CTD data for the 9 stations in this study.

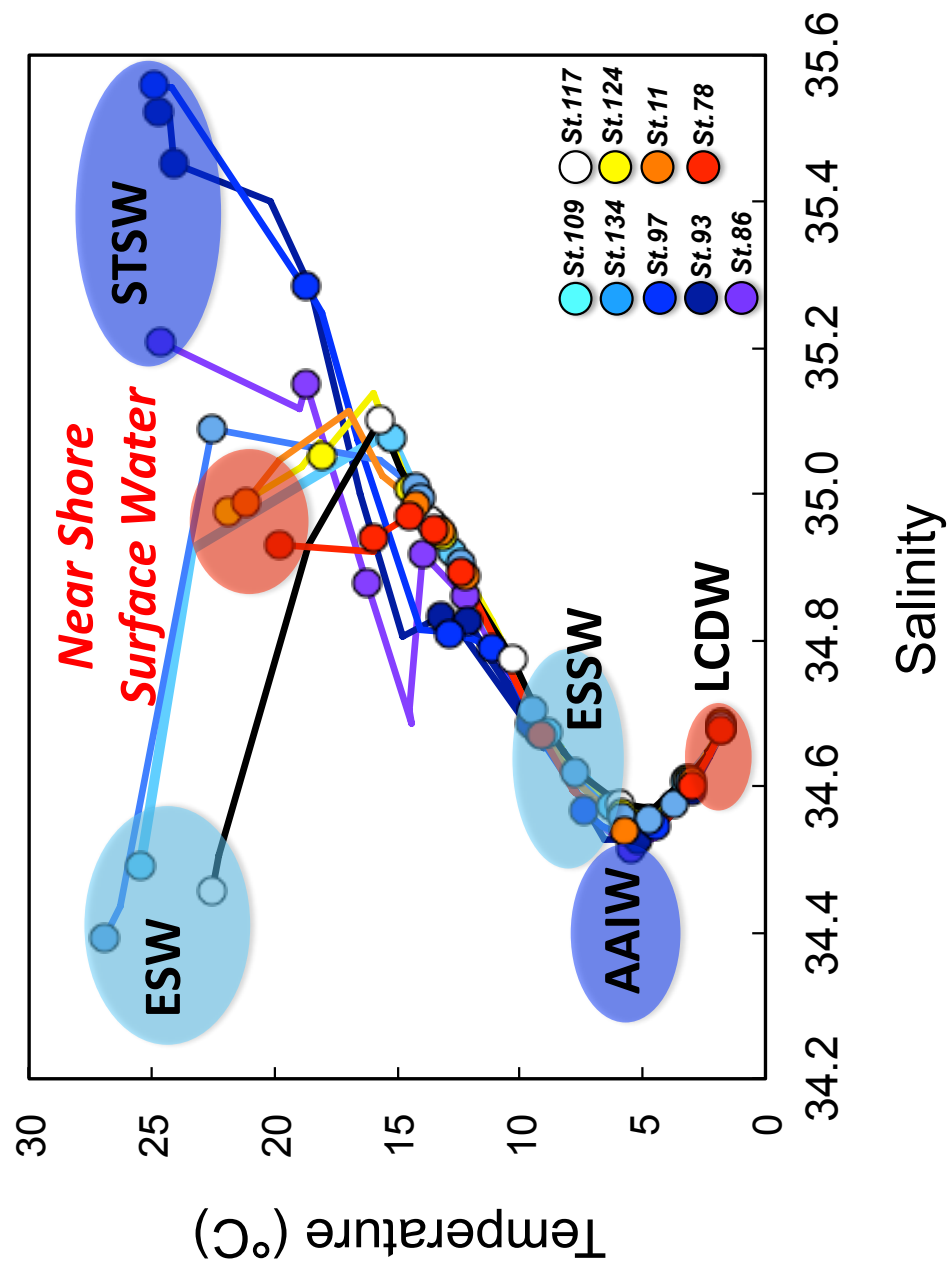
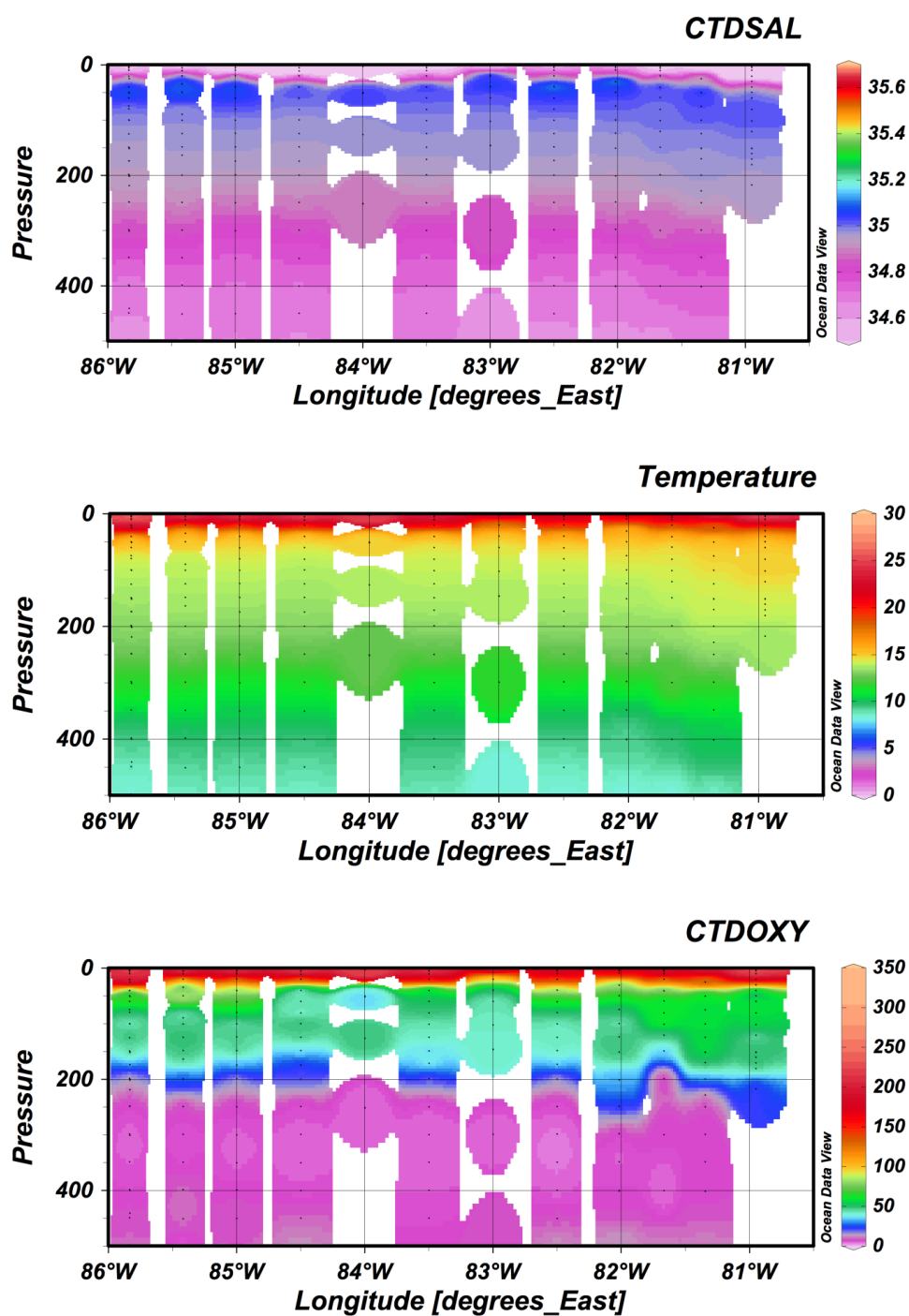
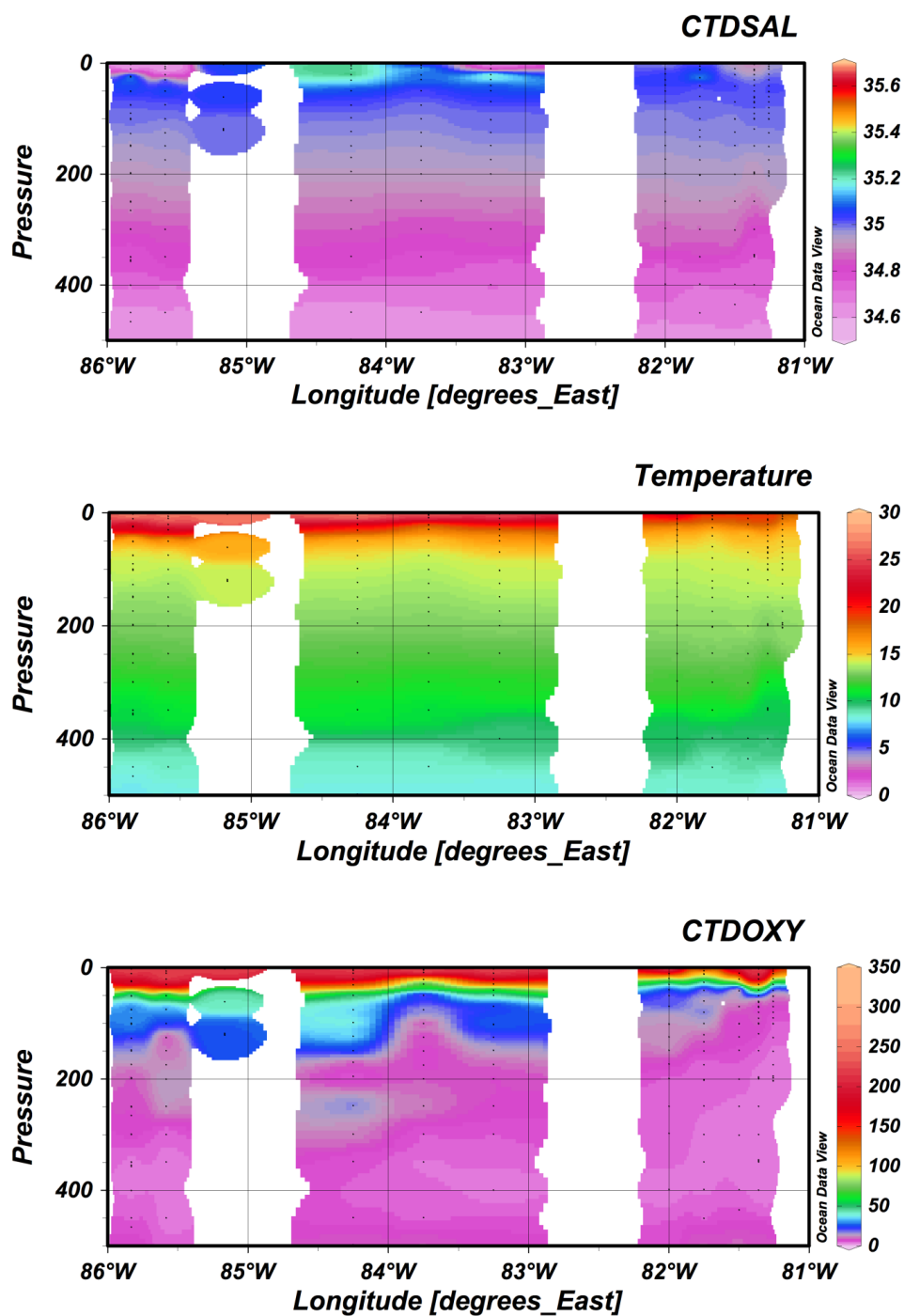


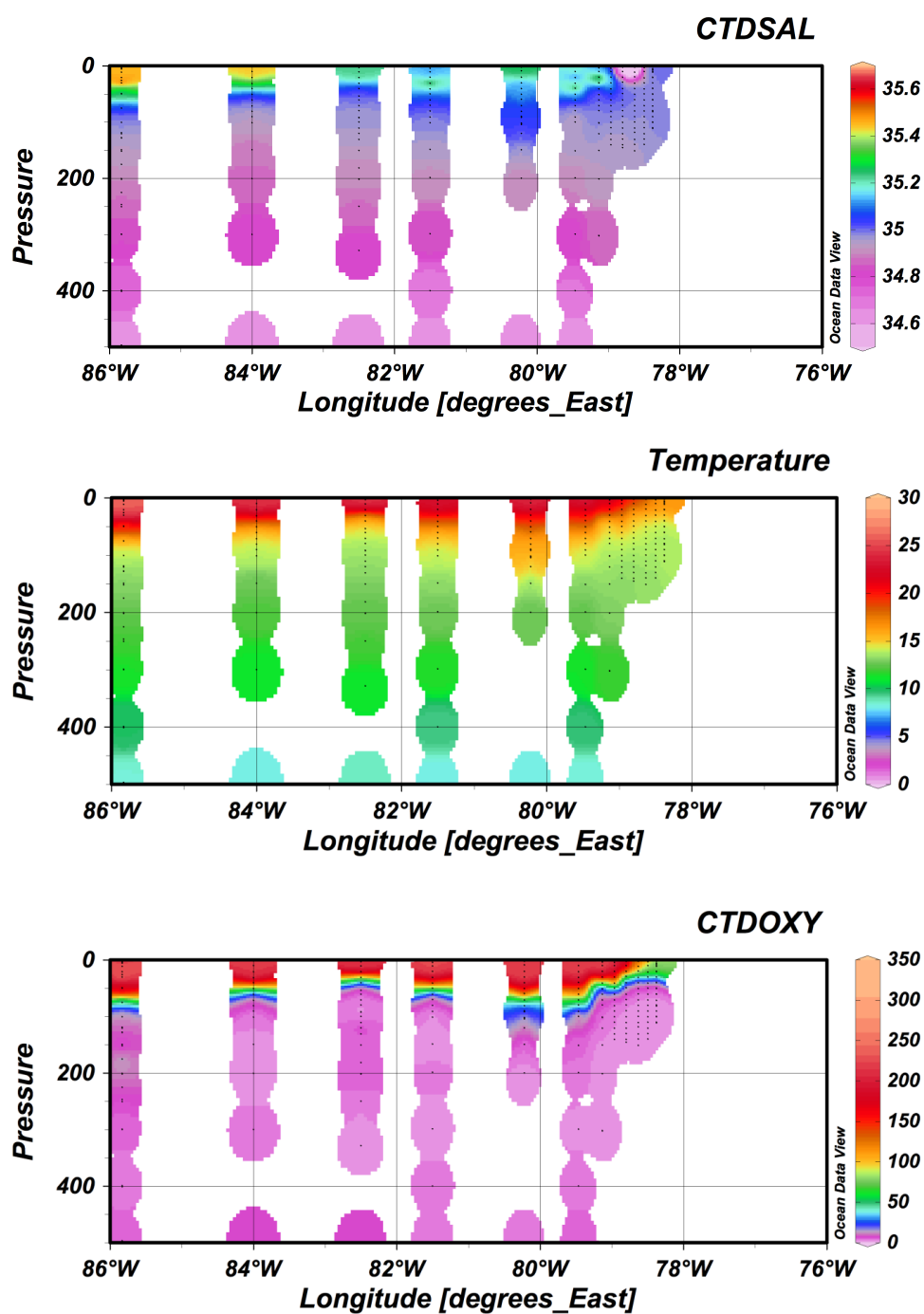
Figure 4.4: Temperature versus salinity for seawater samples from the 9 vertical profiles. ESW = Equatorial Surface Water, STSW = Subtropical Surface Water, SAAW = Subantarctic Intermediate Water, ESPW = Eastern South Pacific Intermediate Water, AAIW = Antarctic Intermediate Water, LCDW = Lower Circumpolar Deep Water.



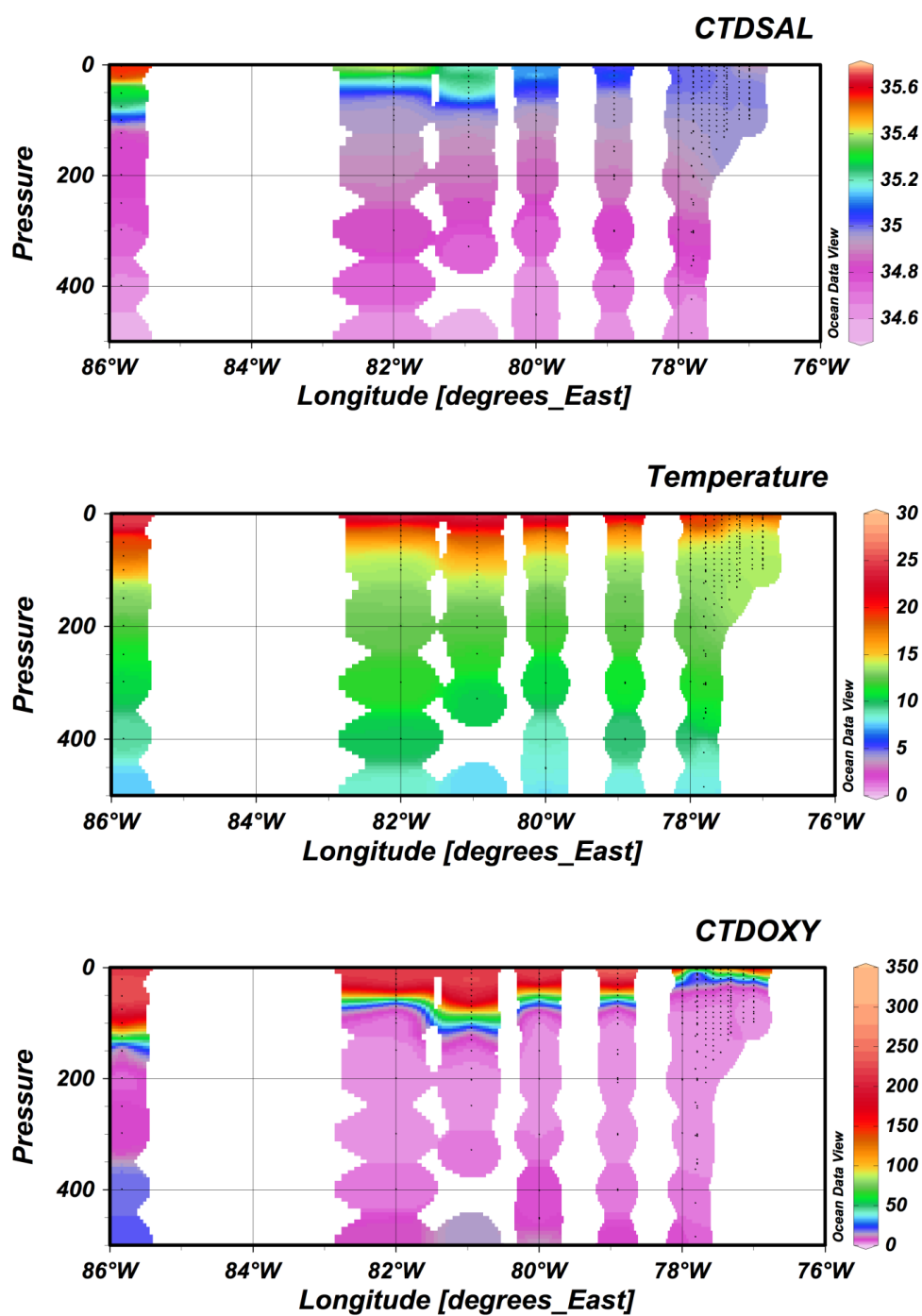
(a) The hydrology section profile of the W-E transect at 4°S.



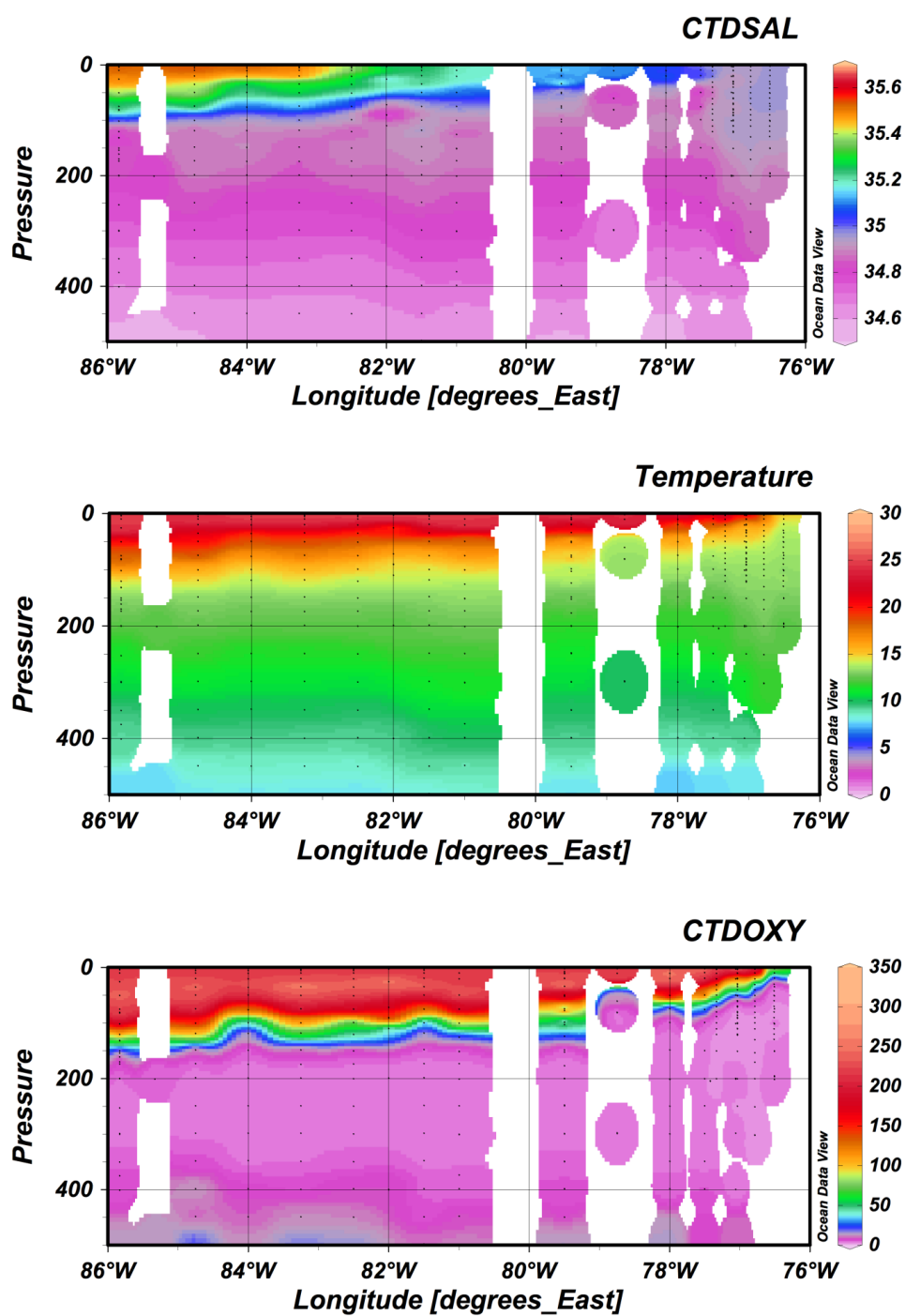
(b) The hydrology section profile of the W-E transect at 6°S.



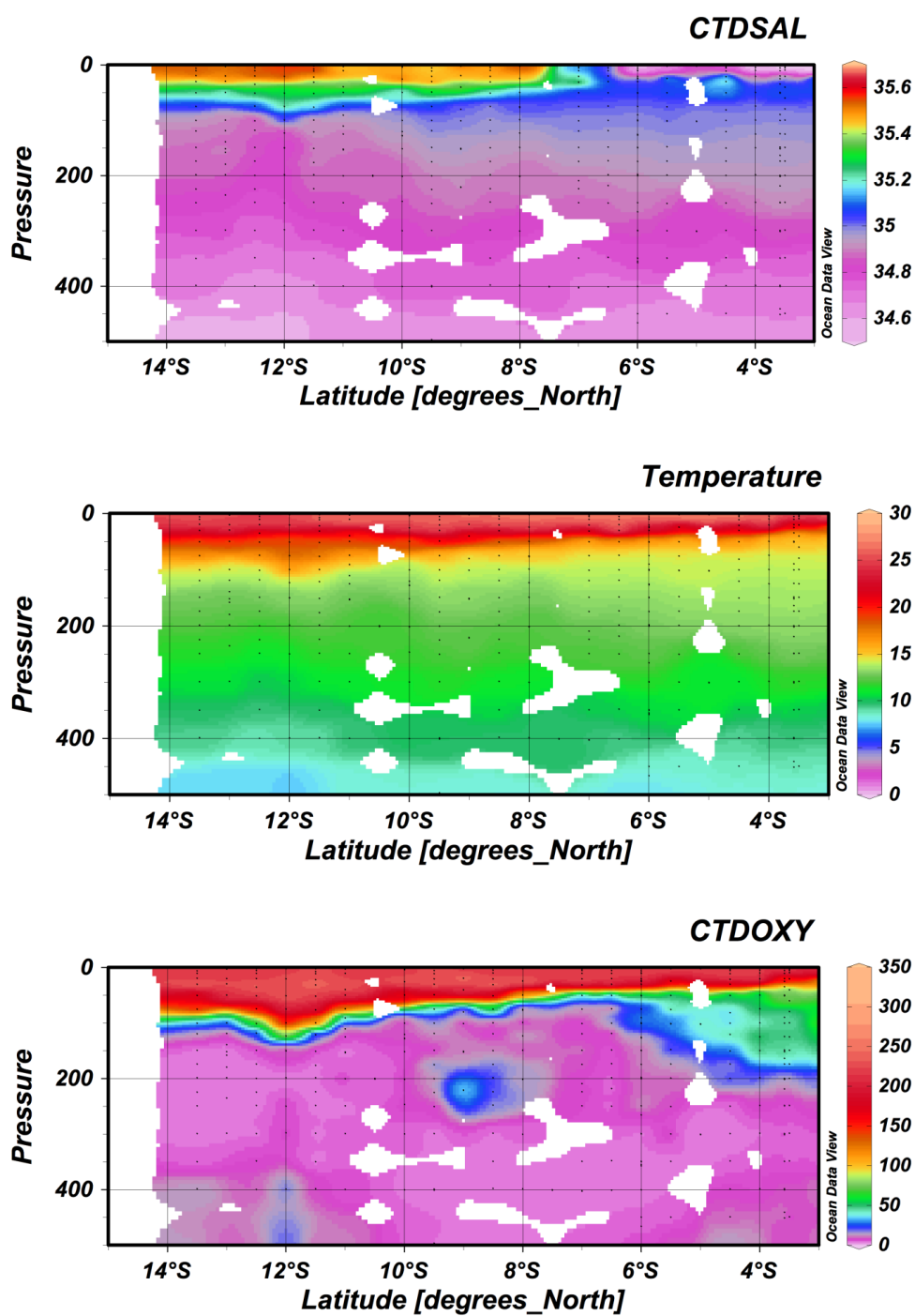
(c) The hydrology section profile of the W-E transect at 10°S.



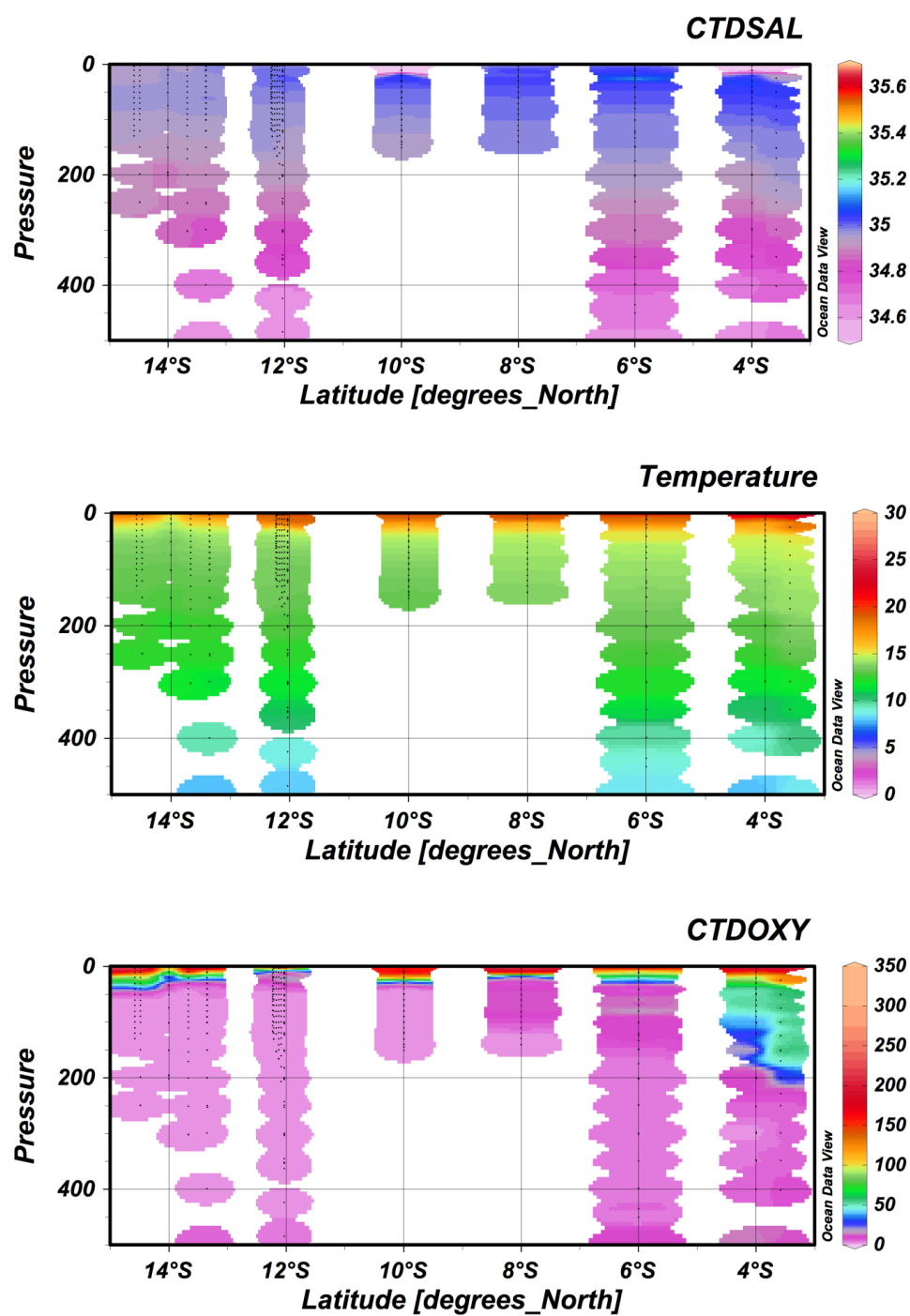
(d) The hydrology section profile of the W-E transect at 12°S.



(e) The hydrology section profile of the W-E transect at 14°S.

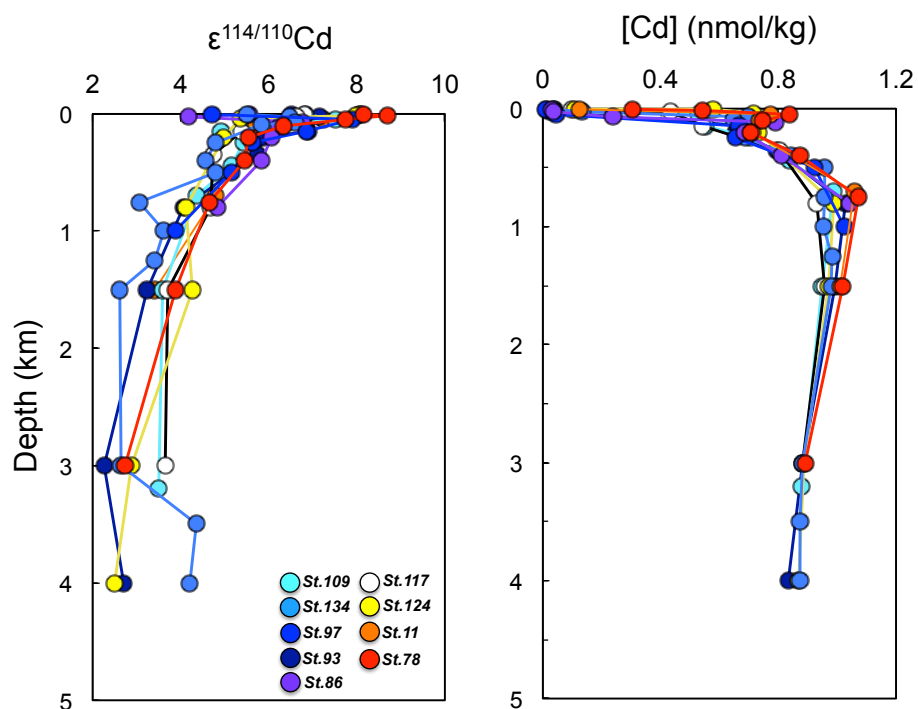


(f) The hydrology section profile of the N-S offshore transect at 85.5°W

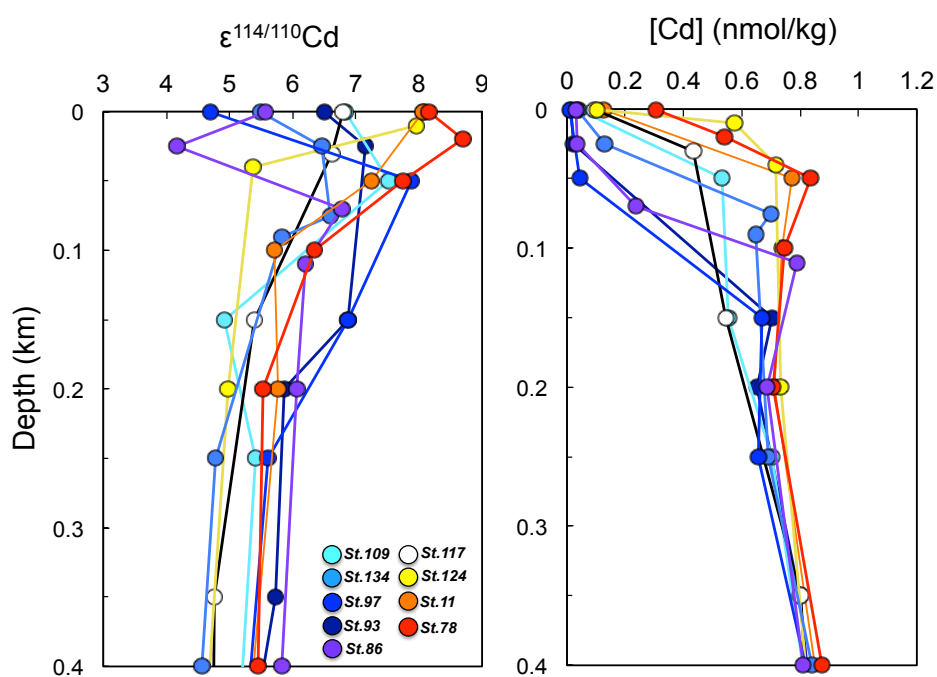


(g) The hydrology section profile of the N-S transect nearshore.

Figure 4.5: The hydrology section profiles of the W-E transects and N-S transects in the upper 500m.

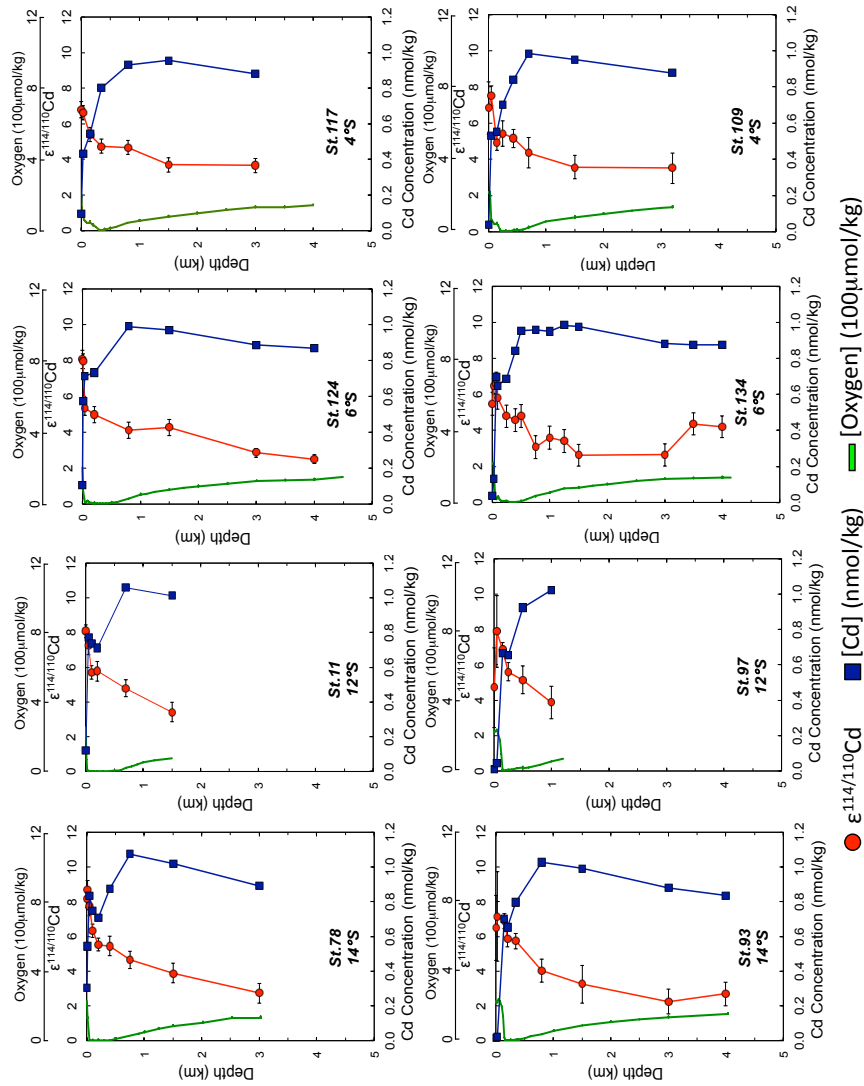


(a) The full depth distribution of Cd concentrations and isotope compositions.

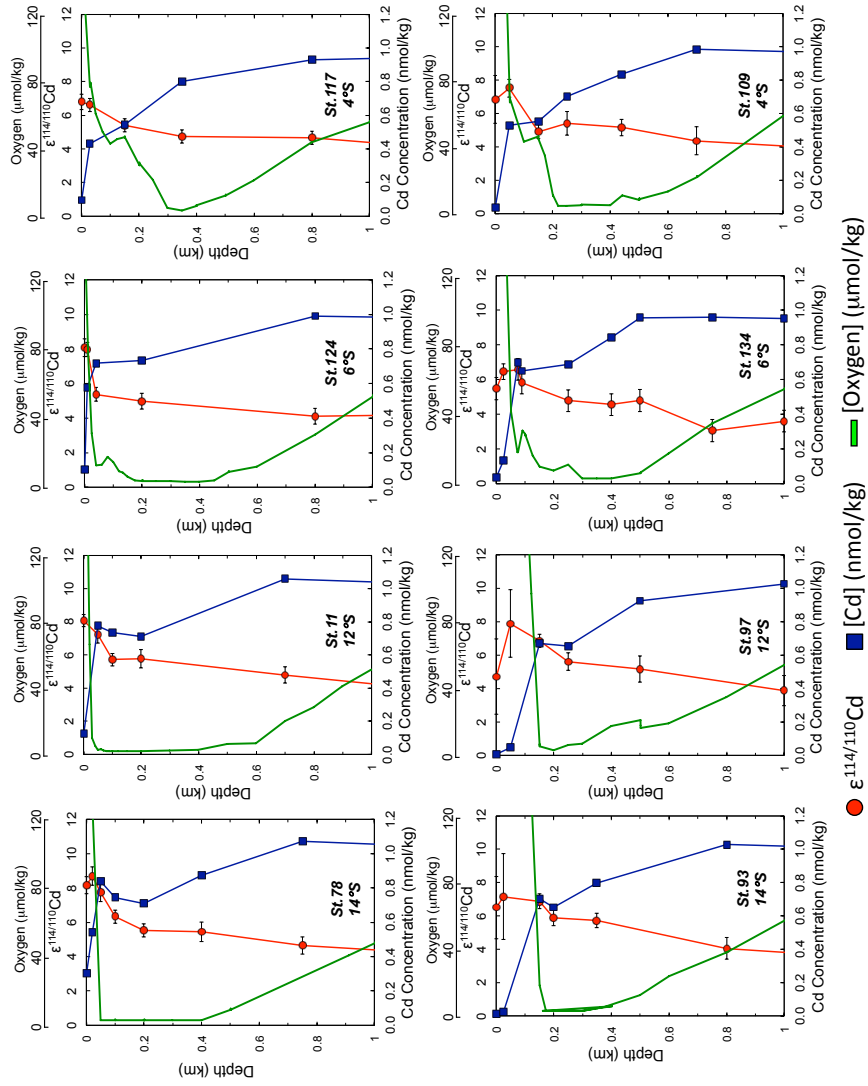


(b) Depth variation of Cd concentrations and isotope compositions for the upper 400m.

Figure 4.6: Cd concentrations and isotope compositions for 9 stations.



(a) Profiles of [Cd], $\epsilon^{114/110}\text{Cd}$ and [Oxygen] in the nearshore and offshore N-S sections



(b) Profiles of [Cd], $\epsilon^{114/110}\text{Cd}$ and [Oxygen] in the nearshore and offshore N-S sections in the upper 1 km.

Figure 4.7: Vertical profiles of Cd concentration, Cd isotope compositions and oxygen contents in the nearshore and offshore N-S sections. Cd concentration data are shown in dark blue squares; Cd isotope composition data are shown in red dots; oxygen concentrations are shown in the green solid line.

4.4.3 Comparison of Cd concentration and isotope composition depth profiles for the OMZ in the EEP with data for other locations

In the following, typical [Cd] and $\epsilon^{114/110}\text{Cd}$ depth profiles for the OMZ in the EEP are compared with data for the Southern Ocean HNLC region and non-HNLC open ocean areas. For this comparison, the following locations were selected (Fig. 4.9): (1) the BATS station in the North Atlantic (Chapter 2), which is representative of an oligotrophic ocean region; (2) Station 198 from the Weddell Sea (Chapter 3), which represents an HNLC environment; (3) the depth profile of Station 78 at 14°S which characterizes the Peruvian OMZ, as it was previously shown that the Cd distribution at this location is clearly affected by the strong coastal upwelling and the presence of an OMZ at shallow depth.

The data that were acquired for the GEOTRACES intercomparison samples from the BATS station provide the first comprehensive depth profile of Cd and Cd isotope composition in the oligotrophic North Atlantic Ocean (Fig. 4.9). For this station, water samples from depths of less than 250 m have extremely low Cd contents (of 0.0012 to 0.035 nmol/kg) and they feature large isotope fractionations with $\epsilon^{114/110}\text{Cd}$ values of greater than +10. In contrast, below 1 km, the water exhibits almost identical Cd concentrations of about 0.29 nmol/kg and $\epsilon^{114/110}\text{Cd} \approx +4.4 \pm 0.4$ (relative to NIST 3108 Cd standard). This $\epsilon^{114/110}\text{Cd}$ value is slightly more positive than deep water results obtained for localities in the Southern and Pacific Ocean, which define a deep water average value of $\epsilon^{114/110}\text{Cd} = 2.5 \pm 0.7$. It was previously inferred that the more fractionated Cd isotope composition of the North Atlantic Ocean deep water may reflect the relatively young ventilation age of this water mass (Chapter 2).

In the Southern Ocean HNLC region, biological uptake of Cd and macronutrients is limited, most likely due to the restriction of biological productivity by the lack of the micronutrient Fe. The Cd concentration and isotope composition depth profiles obtained for samples from Station 198 in the Weddell Sea clearly exhibit this HNLC signature (Fig. 4.9). At the surface and shallow depths, Cd is only modestly depleted and the Cd isotope compositions $\epsilon^{114/110}\text{Cd}$ is only up to + 4. At depths of 200-400 m, the water column

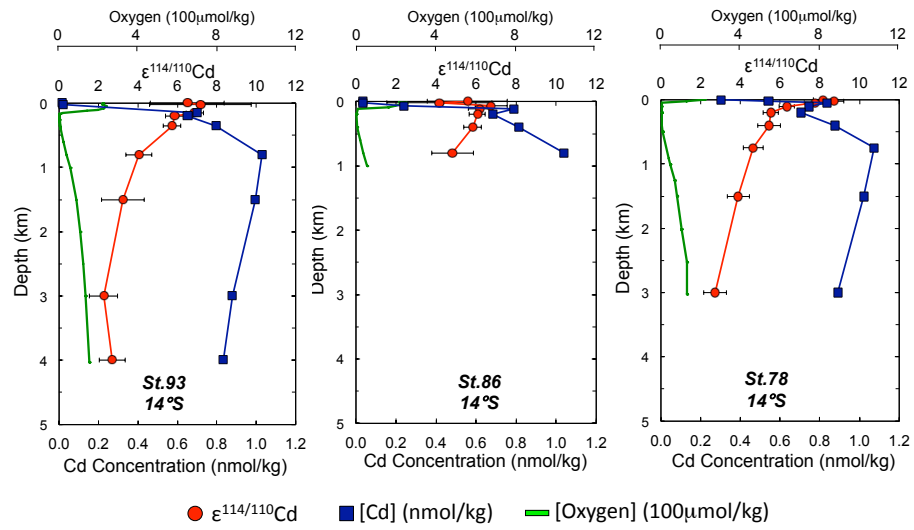
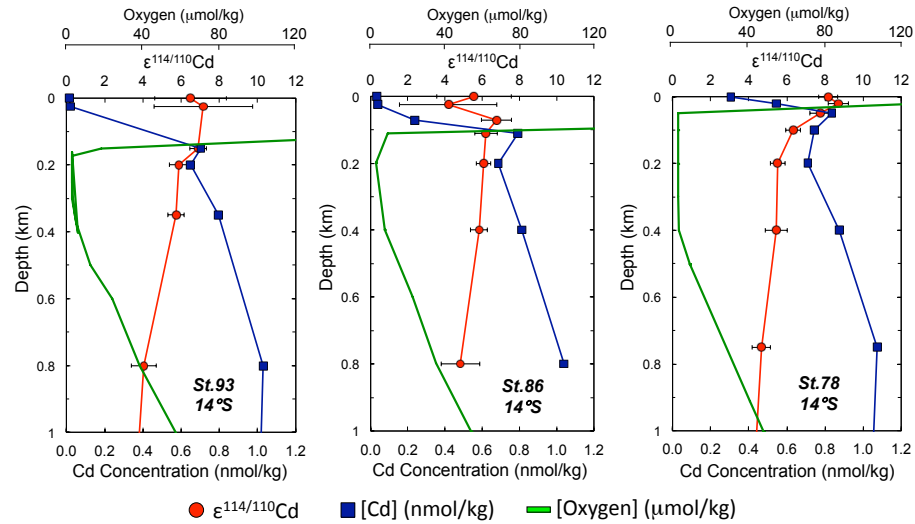
(a) Full profiles of $[\text{Cd}]$, $\epsilon^{114/110}\text{Cd}$ and $[\text{Oxygen}]$ in the W-E section at 14°S.(b) Profiles of $[\text{Cd}]$, $\epsilon^{114/110}\text{Cd}$ and $[\text{Oxygen}]$ in the W-E section at 14°S in the upper 1 km of the water column.

Figure 4.8: Profiles of Cd concentration, Cd isotope compositions and oxygen contents in the W-E section at 14°S. Cd concentration data are shown in dark blue squares; Cd isotope composition data are shown in red dots; oxygen concentrations are shown in the green solid line.

features the lightest yet measured Cd isotope compositions for open-ocean seawater, with $\epsilon^{114/110}\text{Cd} \approx +1$. These light isotope compositions are likely caused by the release of Cd from remineralized organic matter, which is characterized by a negative $\epsilon^{114/110}\text{Cd}$, as a

consequence of incomplete Cd utilization in the HNLC environment of the Weddell Sea. Such light Cd isotope compositions in the upper part of the water column may therefore be typical for the Southern Ocean HNLC region (Chapter 3). Waters from below 1 km depth have Cd contents of about 0.8 nmol/kg and the Cd isotope compositions are relatively constant at $\epsilon^{114/110}\text{Cd} \approx +2.5 \pm 0.4$ (1s, $n = 15$), which is in excellent agreement with the published Pacific and Southern Ocean deep-water average value of $\epsilon^{114/110}\text{Cd} = +2.5 \pm 0.5$.

In the EEP off the Peruvian coast, the combination of intense upwelling, high primary productivity, remineralisation and presence of a shallow OMZ have a distinct impact on the distribution of Cd in the water column. This can be clearly seen in the Cd concentration and isotope composition profiles for Station 78 at 14°S, close to the Peru coast (Fig. 4.9). At this location, surface water is only modestly depleted in Cd and the Cd concentrations rise rapidly within the upper 50 m. Furthermore, Cd isotope fractionations with $\epsilon^{114/110}\text{Cd} \approx +5$ to $+8$ are seen in this upper part of the water column. Particularly noteworthy is that the Cd concentrations do not increase further but are relatively constant (with a 'kink') at depths of about 50 m to 400 m, where the oxygen depletion is most prevalent. The Cd isotope compositions are also nearly constant in this depth interval. The coastal upwelling in this region is thought to be sourced primarily from the depths of about 100-300 m. At Station 78, this depth is within the oxygen minimum zone and characterized by $[\text{Cd}] \approx 0.7$ nmol/kg and $\epsilon^{114/110}\text{Cd} \approx +6$. Therefore, upwelling delivers oxygen-depleted but Cd-rich water to the surface. This replenishment of Cd, acting in combination with remineralization, can explain the rapid rise of $[\text{Cd}]$ in the upper 50m of the water column and the only moderate depletion of Cd in surface waters, despite high productivity. The rapid rise of the Cd with depth ends at the upper boundary of the OMZ, as the low oxygen concentrations that are encountered within the OMZ severely limit the remineralization of organic matter and hence, the release of Cd. Below the OMZ, down to about 1 km, the Cd concentrations increase moderately with a small concomitant change in Cd isotope composition, presumably due to either water mass mixing and/or remineralization reactions that occur in the more oxygen-rich waters found at greater depth.

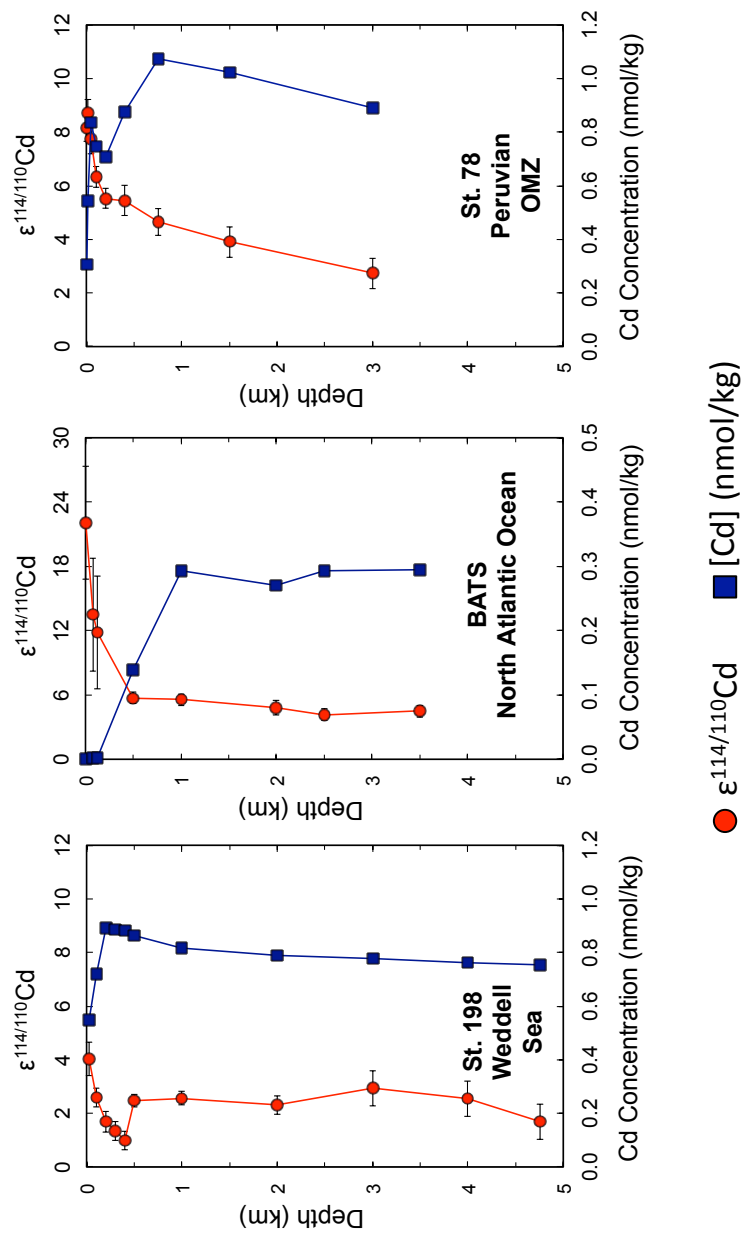


Figure 4.9: Comparison of vertical profiles of Cd concentrations and isotope compositions from the Weddell Sea, the North Atlantic Ocean and the Eastern Equatorial Pacific Ocean. Cd concentration data are shown in dark blue squares and isotope composition data are shown in red dots.

Table 4.1: Cd concentrations and isotope compositions of seawater depth profiles in the Peruvian OMZ

Sample Station	Date	Latitude	Longitude	Water Depth (m)	Salinity	Temperature (°C)	[Oxygen] (μmol/kg)	[PO ₄ ³⁻] (μmol/kg)	[NO ₃ ⁻] (μmol/kg)	[NO ₂ ⁻] (μmol/kg)	[Si] (μmol/kg)	[Si*] (μmol/kg)	[Cd] (nmol/kg)	ε ^{114/110} Cd	2 s.d.	Sample Volume (L)
11	08/01/2009	12.03°S	78.00°W	0	34.99	21.18	255.09	1.10	0.63	0.19	1.74	1.11	0.12	8.07	0.37	2.41
11	08/01/2009	12.03°S	78.00°W	50	34.98	14.21	2.78	2.65	30.00	0.29	17.72	-12.28	0.77	7.25	0.53	0.39
11	08/01/2009	12.03°S	78.00°W	100	34.95	13.19	1.91	2.88	20.90	4.91	27.10	6.20	0.74	5.71	0.38	0.41
11	08/01/2009	12.03°S	78.00°W	200	34.89	12.26	2.11	2.78	28.24	2.84	24.67	-3.57	0.71	5.77	0.57	0.42
11	08/01/2009	12.03°S	78.00°W	700	34.54	5.79	20.20	3.50	51.30	0.10	56.65	5.35	1.06	4.79	0.49	0.28
11	08/01/2009	12.03°S	78.00°W	1500	34.61	3.01	76.50	3.23	44.87	0.13	100.79	55.92	1.01	3.42	0.57	0.30
78	28/01/2009	14.00°S	77.06°W	0	34.93	19.77	222.17	-	-	-	-	-	0.31	8.17	0.50	0.98
78	28/01/2009	14.00°S	77.06°W	20	34.94	16.00	129.69	-	-	-	-	-	0.54	8.70	0.53	0.55
78	28/01/2009	14.00°S	77.06°W	50	34.97	14.49	2.83	-	-	-	-	-	0.84	7.74	0.53	0.36
78	28/01/2009	14.00°S	77.06°W	100	34.95	13.48	2.84	-	-	-	-	-	0.75	6.34	0.38	0.40
78	28/01/2009	14.00°S	77.06°W	200	34.89	12.38	2.99	-	-	-	-	-	0.71	5.53	0.38	0.42
78	28/01/2009	14.00°S	77.06°W	400	34.67	9.15	3.15	-	-	-	-	-	0.87	5.45	0.57	0.34
78	28/01/2009	14.00°S	77.06°W	750	-	-	-	-	-	-	-	-	1.07	4.66	0.49	0.28
78	28/01/2009	14.00°S	77.06°W	1500	34.60	2.99	82.69	-	-	-	-	-	1.02	3.90	0.57	0.29
78	28/01/2009	14.00°S	77.06°W	3000	34.68	1.78	132.12	-	-	-	-	-	0.89	2.73	0.57	0.34
86	30/01/2009	14.00°S	82.00°W	0	35.21	24.63	215.53	-	-	-	-	-	0.03	5.56	2.00	9.60
86	30/01/2009	14.00°S	82.00°W	25	35.15	18.67	252.52	-	-	-	-	-	0.04	4.17	2.62	8.38
86	30/01/2009	14.00°S	82.00°W	70	34.88	16.22	195.51	-	-	-	-	-	0.24	6.77	0.80	1.27
86	30/01/2009	14.00°S	82.00°W	110	34.92	13.98	9.05	-	-	-	-	-	0.79	6.20	0.61	0.38
86	30/01/2009	14.00°S	82.00°W	200	34.86	12.25	2.97	-	-	-	-	-	0.68	6.06	0.40	0.44
86	30/01/2009	14.00°S	82.00°W	400	34.67	9.22	7.69	-	-	-	-	-	0.81	5.83	0.45	0.37
86	30/01/2009	14.00°S	82.00°W	800	34.51	5.51	35.11	-	-	-	-	-	1.04	4.83	1.04	0.29
93	31/01/2009	14.00°S	85.83°W	0	35.52	24.72	221.17	0.53	3.72	0.08	0.22	-3.50	0.02	6.50	1.87	19.26
93	31/01/2009	14.00°S	85.83°W	25	35.45	24.13	223.15	0.62	4.79	0.14	0.62	-4.17	0.02	7.16	2.59	14.40
93	31/01/2009	14.00°S	85.83°W	150	34.83	13.26	18.27	2.68	21.15	0.18	18.89	-2.26	0.70	6.88	0.44	0.43
93	31/01/2009	14.00°S	85.83°W	200	34.83	12.14	2.97	2.73	20.86	1.72	24.79	3.93	0.65	5.87	0.48	0.46
93	31/01/2009	14.00°S	85.83°W	350	34.69	9.60	4.41	2.87	35.42	0.00	30.20	-5.22	0.80	5.74	0.44	0.38
93	31/01/2009	14.00°S	85.83°W	800	34.53	5.19	37.99	3.26	45.76	0.01	65.13	19.37	1.03	4.05	0.66	0.29
93	31/01/2009	14.00°S	85.83°W	1500	34.59	3.02	86.60	3.02	41.03	0.00	110.19	69.16	0.99	3.25	1.08	0.30
93	31/01/2009	14.00°S	85.83°W	3000	34.68	1.82	132.76	2.66	37.58	0.01	138.71	101.13	0.88	2.25	0.72	0.34
93	31/01/2009	14.00°S	85.83°W	4000	34.69	1.77	153.06	2.52	35.50	0.01	127.87	92.37	0.83	2.69	0.67	0.36
97	01/02/2009	12.00°S	85.83°W	0	35.56	24.90	218.90	0.54	4.05	0.09	0.68	-3.37	0.01	4.71	2.25	20.00
97	01/02/2009	12.00°S	85.83°W	50	35.28	18.69	229.82	0.73	2.81	0.21	1.30	-1.51	0.04	7.88	2.03	6.76
97	01/02/2009	12.00°S	85.83°W	150	34.81	12.91	5.25	2.66	21.35	0.02	19.08	-2.27	0.67	6.87	0.39	0.45
97	01/02/2009	12.00°S	85.83°W	250	34.79	11.13	6.34	2.67	31.09	0.00	26.36	-4.73	0.65	5.61	0.52	0.46
97	01/02/2009	12.00°S	85.83°W	500	34.57	7.41	16.43	3.06	40.83	0.00	39.16	-1.67	0.92	5.15	0.79	0.32
97	01/02/2009	12.00°S	85.83°W	1000	34.55	4.49	54.06	3.19	43.29	0.01	81.17	37.88	1.02	3.88	0.91	0.29

^a The uncertainties quoted for the samples are based on the 2sd uncertainties determined for multiple analyses of matching standard solutions that were analyzed before and after each sample measurement. ^b Cd concentration and isotope composition data were analyzed at MAGIC group, Imperial College London. ^c The rest of the data in this table were obtained by CTD, which are from German expedition cruises M77/3 and M77/4 of a with the R/V Meteor. ^d [Si*] value is calculated by $[\text{Si}^*] = [\text{Si}(\text{OH})_4] - [\text{NO}_3^-]$.

Sample Station	Date	Latitude	Longitude	Water Depth (m)	Salinity	Temperature (°C)	[Oxygen] (μmol/kg)	[PO ₄ ³⁻] (μmol/kg)	[NO ₃ ⁻] (μmol/kg)	[NO ₂ ⁻] (μmol/kg)	[Si] (μmol/kg)	[Si*] (μmol/kg)	[Cd] (nmol/kg)	$\epsilon^{147/110}\text{Cd}$	2 s.d.	Sample Volume (L)
109	04/02/2009	3.58°S	85.83°W	0	34.49	25.49	214.99	0.59	6.33	0.19	1.03	-5.30	0.04	6.84	1.44	7.49
109	04/02/2009	3.58°S	85.83°W	50	35.08	15.26	69.21	1.74	24.00	0.85	13.57	-10.43	0.53	7.52	0.54	0.56
109	04/02/2009	3.58°S	85.83°W	150	34.96	13.52	44.93	2.00	27.64	0.01	19.57	-8.07	0.55	4.92	0.42	0.54
109	04/02/2009	3.58°S	85.83°W	250	34.92	12.78	4.63	2.44	31.91	0.00	23.90	-8.01	0.70	5.42	0.71	0.43
109	04/02/2009	3.58°S	85.83°W	439	34.67	8.84	10.98	2.87	38.47	0.01	41.02	2.55	0.84	5.16	0.49	0.36
109	04/02/2009	3.58°S	85.83°W	700	34.57	6.28	22.08	3.20	44.72	0.00	61.00	16.28	0.99	4.37	0.84	0.30
109	04/02/2009	3.58°S	85.83°W	1500	34.61	3.24	80.04	3.02	40.83	0.00	118.06	77.23	0.95	3.58	0.64	0.32
109	04/02/2009	3.58°S	85.83°W	3200	34.68	1.78	134.31	2.67	37.09	0.01	143.63	106.54	0.88	3.52	0.85	0.34
117	06/02/2009	3.58°S	82.02°W	0	34.46	22.53	195.24	0.74	7.67	0.21	2.69	-4.98	0.10	6.80	0.46	3.12
117	06/02/2009	3.58°S	82.02°W	30	35.10	15.72	79.37	1.63	21.90	0.67	12.80	-9.10	0.43	6.62	0.40	0.69
117	06/02/2009	3.58°S	82.02°W	150	34.96	13.64	47.08	1.97	26.95	0.01	19.18	-7.77	0.54	5.40	0.40	0.55
117	06/02/2009	3.58°S	82.02°W	350	34.77	10.28	3.28	2.81	33.94	0.24	37.18	3.24	0.80	4.75	0.40	0.37
117	06/02/2009	3.58°S	82.02°W	800	34.58	5.91	43.88	3.00	41.23	0.01	68.18	26.95	0.93	4.67	0.40	0.32
117	06/02/2009	3.58°S	82.02°W	1500	34.61	3.18	79.61	2.99	40.64	0.00	121.07	80.43	0.96	3.70	0.40	0.31
117	06/02/2009	3.58°S	82.02°W	3000	34.68	1.78	129.94	2.66	36.70	0.01	144.61	107.91	0.88	3.66	0.40	0.34
124	08/02/2009	6.00°S	81.75°W	0	34.97	21.90	205.36	1.00	10.13	0.36	5.68	-4.45	0.11	8.08	0.51	2.84
124	08/02/2009	6.00°S	81.75°W	10	35.05	18.05	80.23	2.07	26.56	0.74	14.16	-12.40	0.58	7.97	0.41	0.52
124	08/02/2009	6.00°S	81.75°W	40	35.01	14.53	12.60	2.19	30.05	0.08	17.96	-12.09	0.72	5.37	0.41	0.42
124	08/02/2009	6.00°S	81.75°W	200	34.94	13.15	3.73	2.42	31.28	0.01	23.31	-7.97	0.73	4.98	0.46	0.41
124	08/02/2009	6.00°S	81.75°W	800	34.56	5.82	30.28	3.17	44.28	0.00	65.92	21.64	0.99	4.11	0.46	0.30
124	08/02/2009	6.00°S	81.75°W	1500	34.61	3.14	79.20	3.04	41.54	0.01	120.68	79.14	0.97	4.26	0.46	0.31
124	08/02/2009	6.00°S	81.75°W	3000	34.68	1.79	127.82	2.70	37.58	0.01	145.60	108.02	0.89	2.87	0.25	0.34
124	08/02/2009	6.00°S	81.75°W	4000	34.68	1.80	137.83	2.62	36.40	0.02	138.71	102.31	0.87	2.50	0.25	0.35
134	09/02/2009	6.00°S	85.83°W	0	34.39	26.90	218.81	0.39	4.18	0.11	1.52	-2.66	0.04	5.49	0.64	8.18
134	09/02/2009	6.00°S	85.83°W	25	35.09	22.50	202.92	0.96	10.52	0.36	3.37	-7.15	0.13	6.47	0.44	2.29
134	09/02/2009	6.00°S	85.83°W	75	35.01	14.26	18.21	2.12	29.31	0.06	16.92	-12.39	0.70	6.60	0.64	0.43
134	09/02/2009	6.00°S	85.83°W	90	34.99	14.02	30.73	2.16	29.41	0.06	16.82	-12.59	0.65	5.82	0.64	0.46
134	09/02/2009	6.00°S	85.83°W	250	34.91	12.44	11.19	2.39	32.36	0.00	22.72	-9.64	0.69	4.79	0.64	0.44
134	09/02/2009	6.00°S	85.83°W	400	34.71	9.47	3.21	2.77	32.66	0.81	32.46	-0.20	0.84	4.56	0.64	0.36
134	09/02/2009	6.00°S	85.83°W	500	34.62	7.72	6.37	3.13	42.51	0.01	45.26	2.75	0.96	4.80	0.64	0.31
134	09/02/2009	6.00°S	85.83°W	750	34.56	5.85	34.78	3.21	44.43	0.01	63.34	18.91	0.96	3.07	0.64	0.31
134	09/02/2009	6.00°S	85.83°W	1000	34.56	4.70	54.71	3.20	43.63	0.00	81.78	38.15	0.95	3.61	0.64	0.32
134	09/02/2009	6.00°S	85.83°W	1250	34.57	3.75	77.62	3.07	41.82	0.00	99.37	57.55	0.98	3.41	0.64	0.31
134	09/02/2009	6.00°S	85.83°W	1500	34.61	3.08	82.96	3.04	41.82	0.00	119.04	77.22	0.98	2.63	0.61	0.31
134	09/02/2009	6.00°S	85.83°W	3000	34.68	1.78	130.75	2.69	37.57	0.01	142.95	105.38	0.88	2.65	0.61	0.34
134	09/02/2009	6.00°S	85.83°W	3500	34.68	1.80	135.27	2.65	37.58	0.01	141.66	104.08	0.88	4.36	0.61	0.34
134	09/02/2009	6.00°S	85.83°W	4000	34.68	1.83	136.49	2.66	37.39	0.01	141.66	104.27	0.87	4.20	0.61	0.34

^a The uncertainties quoted for the samples are based on the 2sd uncertainties determined for multiple analyses of matching standard solutions that were analyzed before and after each sample measurement. ^b Cd concentration and isotope composition data were analyzed at MAGIC group, Imperial College London. ^c The rest of the data in this table were obtained by CTD, which are from German expedition cruises M77/3 and M77/4 of a with the R/V Meteor. ^d [Si*] value is calculated by [Si*] = [Si(OH)₄] - [NO₃⁻].

4.4.4 Cd isotope fractionation in the Peruvian OMZ

Comparison of Cd isotope variations in the Peruvian OMZ with data for other locations

The distinct $\epsilon^{114/110}\text{Cd}$ vs. $[\text{Cd}]$ trends that are exhibited by samples from primarily oligotrophic open ocean areas, the Southern Ocean HNLC region and the OMZ of the EEP, are shown in Fig. 4.10 and further discussed in this section.

The clear difference between the trends, which are exhibited by seawater from oligotrophic oceans and the Southern Ocean HNLC region, were previously discussed in Chapter 3. The main conclusions of this discussion are summarized below. The Cd isotope compositions and concentrations of the HNLC samples display a single, well defined logarithmic correlation, which is in accord with a closed system Rayleigh fractionation factor of $\alpha = 1.0005$ for biological uptake of Cd. In contrast, water samples from non-HNLC open ocean areas, such as the Pacific, Arctic and Atlantic Ocean, are in good accord with closed system Rayleigh fractionation trend that has a much lower slope, which is equivalent to $\alpha \approx 1.0002$.

In comparison to the samples from HNLC and non-HNLC regions, the water samples from the OMZ in the EEP display distinct systematics (Fig. 4.10). In particular, the seawater samples from surface and subsurface depths of ≤ 50 m show broadly constant $\epsilon^{114/110}\text{Cd}$ values of about +5 to +8, despite highly variable Cd contents of between 0.01 nM and 0.3 nM. Between depths of 50 m to about 1.5 km, seawater samples from this region cluster $\epsilon^{114/110}\text{Cd}$ values of about +4 to +6, whilst Cd contents range between 0.7 nmol/kg and 1.1 nmol/kg. Furthermore, the majority of these samples define a positive correlation between $\epsilon^{114/110}\text{Cd}$ and Cd concentration.

Water samples from depths below 3 km are characterized by an average $\epsilon^{114/110}\text{Cd}$ value of +2.5, which is in excellent agreement with the mean value ($\epsilon^{114/110}\text{Cd} = +2.5 \pm 0.7$) of the Pacific and Southern Ocean deep-water (discussed in Chapter 3). In addition, the Cd concentrations of these deep waters are in accord with the trend of increasing Cd con-

tents that are encountered along the global deep-water convection system from the North Atlantic/Arctic Ocean, to the Southern Ocean and the North Pacific.

Interpretation of the Cd isotope fractionation trends observed for the Peruvian OMZ

In the following, a detailed interpretation of the Cd isotope fractionation trends that are observed for the EEP is attempted. This interpretation assumes that the presence of the OMZ in association with intense water mass upwelling, high primary productivity and remineralisation of organic matter have a key impact on the cycling of Cd in this environment.

The surface and near-surface seawater from depths of ≤ 50 m in the Peruvian OMZ shows only modest Cd isotope fractionation and broadly constant $\epsilon^{114/110}\text{Cd}$ values of about +5 to +8. Furthermore, these samples exhibit highly variable Cd contents of between 0.01 nmol/kg and 0.3 nmol/kg. As a result, the data for the surface seawater from the OMZ in the EEP are not in accord with Cd isotope fractionation trends identified for samples from other localities (Fig. 4.10). Rather, the unusual Cd isotope and concentration systematics of these samples require a different explanation.

In the EEP off the coast of Peru, strong upwelling continuously supplies Cd and other nutrients to the surface and shallow subsurface depths to replenish the Cd that is utilized by biological productivity. Hence, it appears that a steady state open system fractionation model may be most appropriate to describe the Cd cycling in the Peruvian OMZ in the EEP. The Cd isotope compositions and concentrations of such a steady-state system are linked by the equation:

$$\epsilon^{114/110}\text{Cd}_{\text{seawater}} = \epsilon^{114/110}\text{Cd}_{\text{seawater},0} - 10,000 \cdot \frac{1}{\alpha} \cdot (1 - f)$$

where $[\text{Cd}_{\text{seawater},0}]$ and $\epsilon^{114/110}\text{Cd}_{\text{seawater},0}$ denote the initial Cd concentration and isotope composition of the surface water, $[\text{Cd}_{\text{seawater}}]$ and $\epsilon^{114/110}\text{Cd}_{\text{seawater}}$ are the Cd concentration and isotope composition of surface seawater that has been affected by biological uptake of

Cd, f is the depletion factor given by $f = [\text{Cd}_{\text{seawater},0}] / [\text{Cd}_{\text{seawater}}]$, and α is the Cd isotope fractionation factor.

Hydrological data support the conclusion that upwelling supplies water from depths of about 100-300 m to the surface ocean. Hence, based on the available data, the calculations assume that the initial composition of seawater is characterized by values of about $\epsilon^{114/110}\text{Cd}_{\text{seawater},0} = +4.5$ to $+6.5$ and $[\text{Cd}_{\text{seawater},0}] \approx 0.7$ to 0.9 nmol/kg. Based on these values, the calculated open system Cd isotope fractionation trends are shown in Figs. 4.11 for fractionation factors α of between 1.0001 and 1.0003.

A comparison of the calculated trends with the results obtained for seawater from depths of ≤ 50 m shows that, with only very few exceptions, the samples are in accord with systematics predicted by the open system isotope fractionation model. In particular, the model can explain why the surface and near-surface seawater of the OMZ in the EEP shows a large range in Cd concentrations with only relatively constant $\epsilon^{114/110}\text{Cd}$ values. In general, upwelling at offshore locations is less intense compared to that observed in coastal regions (particularly at 10 to 14°S). This is in accord with the observation that that surface and near-surface water samples from offshore stations have the lowest Cd contents, as the weaker upwelling at these locations is unable to effectively replenish biologically utilized Cd.

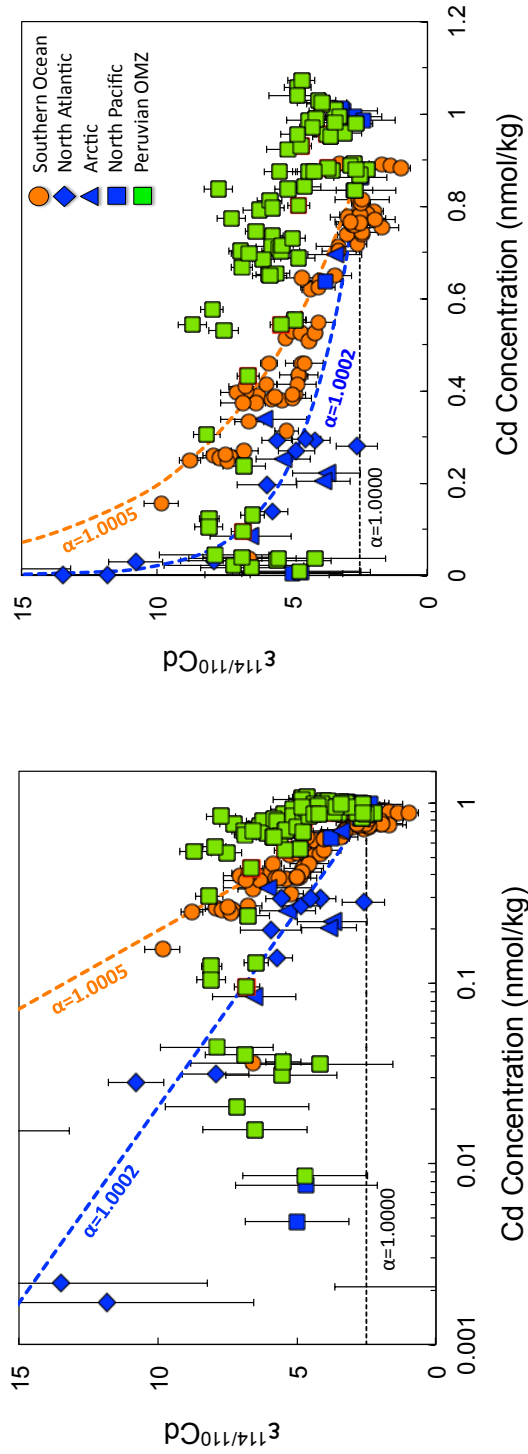
There are, however, a few samples that are not in accord with the calculated open-system fractionation trends. In particular, these are samples that were collected at 0 to 50 m depth either above or from within the oxygen minimum zone at near-shore locations (Figs. 4.11 ; Table 4.1). The origin of the distinct $\epsilon^{114/110}\text{Cd}$ -[Cd] systematics of these samples is presently unclear, but there are a number of possible explanations for the Cd isotope fractionations that are coupled with comparatively high Cd concentrations. Firstly, it is possible that Cd isotope fractionation at these particular locations was governed by a higher fractionation factor α or by closed system Rayleigh fractionation, potentially due to distinct local conditions before and at the time of sampling. Alternatively, these samples may reflect Cd uptake from an unusually Cd-rich and fractionated initial isotope compo-

sition. In fact, such a composition may be exhibited by two of the unusual samples from Stations 11 and 78 at 50 m with $[Cd] \approx 0.8$ nmol/kg and $\epsilon^{114/110}Cd \approx 7.5$. The origin of these unusual Cd systematics is also unclear. However, it is noteworthy that both samples featured very low oxygen contents and were collected in close proximity to the upper boundary of the OMZ at near-shore stations, where upwelling is particularly strong. Hence, it can be speculated, for example, that the high Cd contents of these samples may be due to desorption of Cd from organic particulate matter that is available in situ. Alternatively, additional fluxes of Cd may be derived from anoxic sediments, which have been previously inferred to release Cd into the water column (Böning et al., 2004, 2009).

The Cd isotope compositions of the seawater from the intermediate depths between 200 m and 1.5 km display a positive correlation with Cd concentrations. This correlation is, furthermore, in accord with trends expected for either closed- or open-system stable isotope fractionation at $\alpha \approx 1.0005 - 1.0006$ (Fig. 4.12), which is appropriate for biological utilization. For example, an appropriate Rayleigh fractionation trend can be calculated with a fractionation factor of $\alpha \approx 1.0005$ and an initial composition akin to seawater from 1500 m depth, with $[Cd] = 1.0$ nmol/kg and $\epsilon^{114/110}Cd = +4$. Alternatively, open system Cd fractionation is also in accord with the observed trend, assuming the same initial composition and a fractionation factor of $\alpha = 1.0006$.

Given that this trend is defined by samples that were collected either from within the OMZ or from depths below the photic zone, it is doubtful that the correlation is a consequence of in situ biological uptake of Cd. Rather, it is more likely to be product of binary mixing between two endmembers that have distinct Cd concentrations and isotope compositions. This interpretation is supported by the observation that changes in both parameters are also roughly correlated with depth. In detail, the correlation may be generated by mixing of a deeper water mass (from about 1500 m) with $[Cd] \approx 1.0$ nmol/kg and $\epsilon^{114/110}Cd \approx +4$ and a shallower water mass (that is present at about 200 m depth), which features $[Cd] \approx 0.7$ nmol/kg and $\epsilon^{114/110}Cd \approx +6$ (Fig. 4.13). In addition, the higher Cd contents may also be a consequence of Cd additions, which are provided by the remineralization of organic matter at depth (Fig. 4.14).

Regardless of the origin of the higher Cd contents, the observation of Cd isotope compositions with $\epsilon^{114/110}\text{Cd}$ values of greater than +5 at depths of about 200 m is also unusual. It is likely that such compositions constitute an inherited water mass signature, which was formed in the surface ocean by biological uptake of Cd and associated isotope fractionation. For example, a previous study (Huyer, 1990; Strub et al., 1998) suggested that Peru Chile Undercurrent (PCUC) often reaches to the surface water, which may lead to this uncommon Cd isotope composition at about 200 m depths.. However, it is also conceivable that these unusual Cd isotope features are produced by distinct processes, which are linked to the OMZ environment. For instance, they may be associated with denitrification reactions, which occur at the boundary of an OMZ or with the release of Cd from particulate organic matter or carbon-rich shelf sediments. Clearly, further work is needed to better understand some aspects of the Cd distribution in this and probably most other OMZs.



(a) Plot of $\epsilon^{114/110}\text{Cd}$ vs. $\ln[\text{Cd}]$ for water samples from the OMZ in the Eastern Equatorial Pacific Ocean, the Southern Ocean HNLC region, and non-HNLC open ocean areas.

(b) Plot of $\epsilon^{114/110}\text{Cd}$ vs. $[\text{Cd}]$ for water samples from the OMZ in the Eastern Equatorial Pacific Ocean, the Southern Ocean HNLC region, and non-HNLC open ocean areas.

Figure 4.10: Correlation of Cd isotope compositions and Cd concentrations for water samples from the OMZ in the Eastern Equatorial Pacific Ocean, the Southern Ocean HNLC region, and non-HNLC open ocean areas. The data plotted in this figure are from this study (Table 4.1) and previous studies ((Ripperger and Rehkämper, 2007; Abouchami et al., 2011; Xue et al., 2012); Chapter 3 - Table 3.1, 3.2). The samples from the OMZ in the Eastern Equatorial Pacific Ocean and the Southern Ocean HNLC region are shown in the green squares and orange dots. The Cd data presented for non-HNLC open ocean areas are from the Arctic, the North Atlantic and the North Pacific Ocean, which are shown in blue triangles, diamonds and squares, respectively. The dashed lines denote the calculated Rayleigh fractionation trends for closed system fractionation factors of $\alpha \approx 1.0002$ and 1.0005 with deep water $[\text{Cd}] = 0.77\text{nM}$ and $\epsilon^{114/110}\text{Cd} = 2.5$.

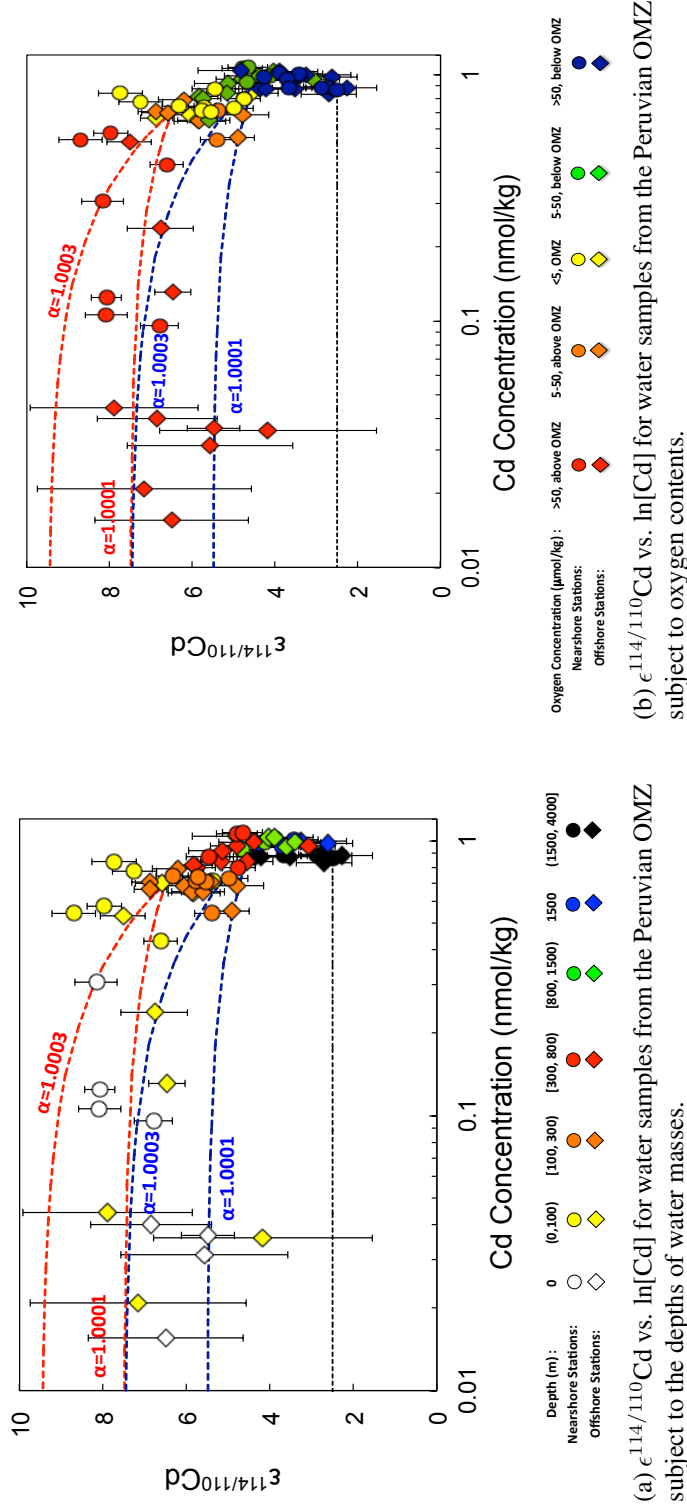


Figure 4.11: Steady state model for Cd isotope fractionation of seawater from the upper 50 m in the Peruvian OMZ. Cd data (Table 4.1) from the offshore and nearshore stations are shown in diamonds and dots, respectively. In this steady state model, the initial Cd concentration and isotope compositions of the upwelled water masses are applied with $[\text{Cd}] = 0.7 - 0.9 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +4.5 - 6.5$, which are the values from seawater at 100-300m in the Peruvian OMZ. The Cd concentrations and isotope compositions of the seawater from upper 50m in the Peruvian OMZ analyzed in this study, fall along the calculated Cd isotope fractionation trends with steady state model and fractionation factor α between 1.0001 and 1.0003.

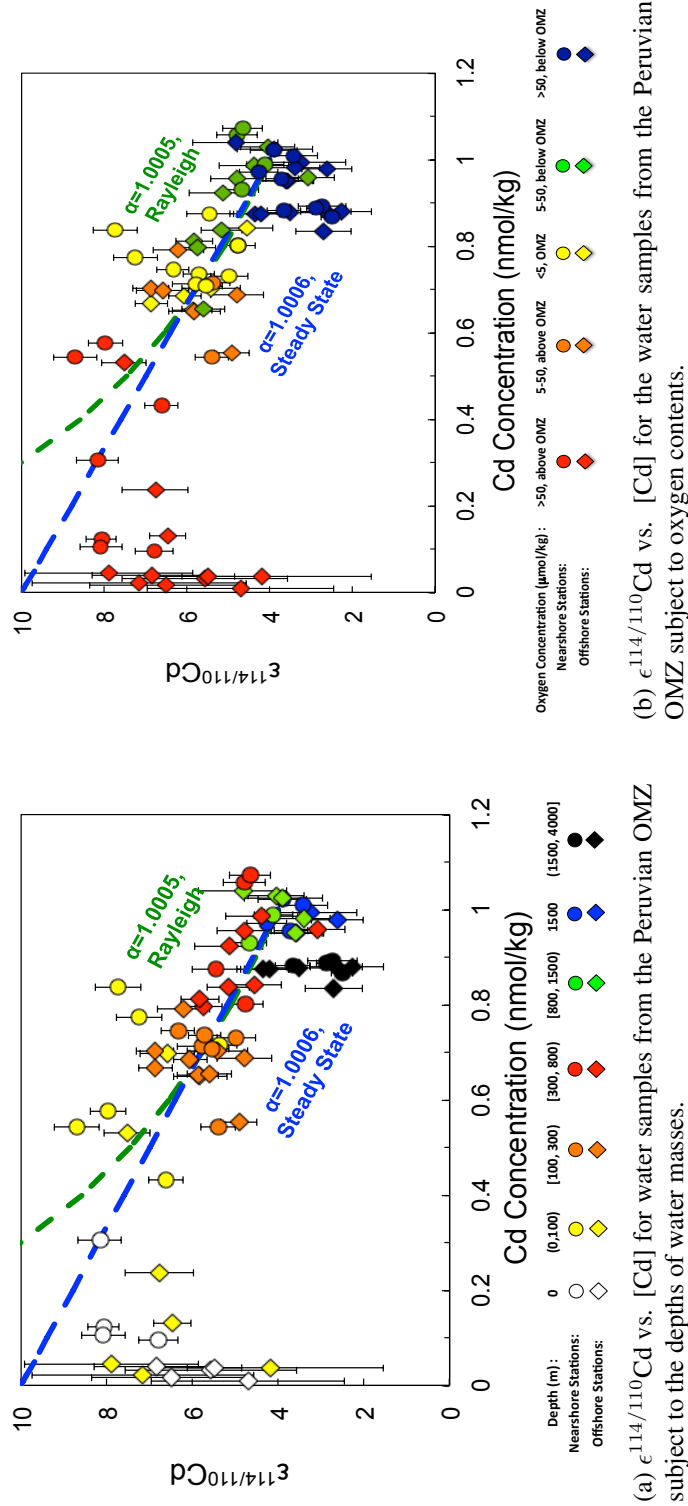
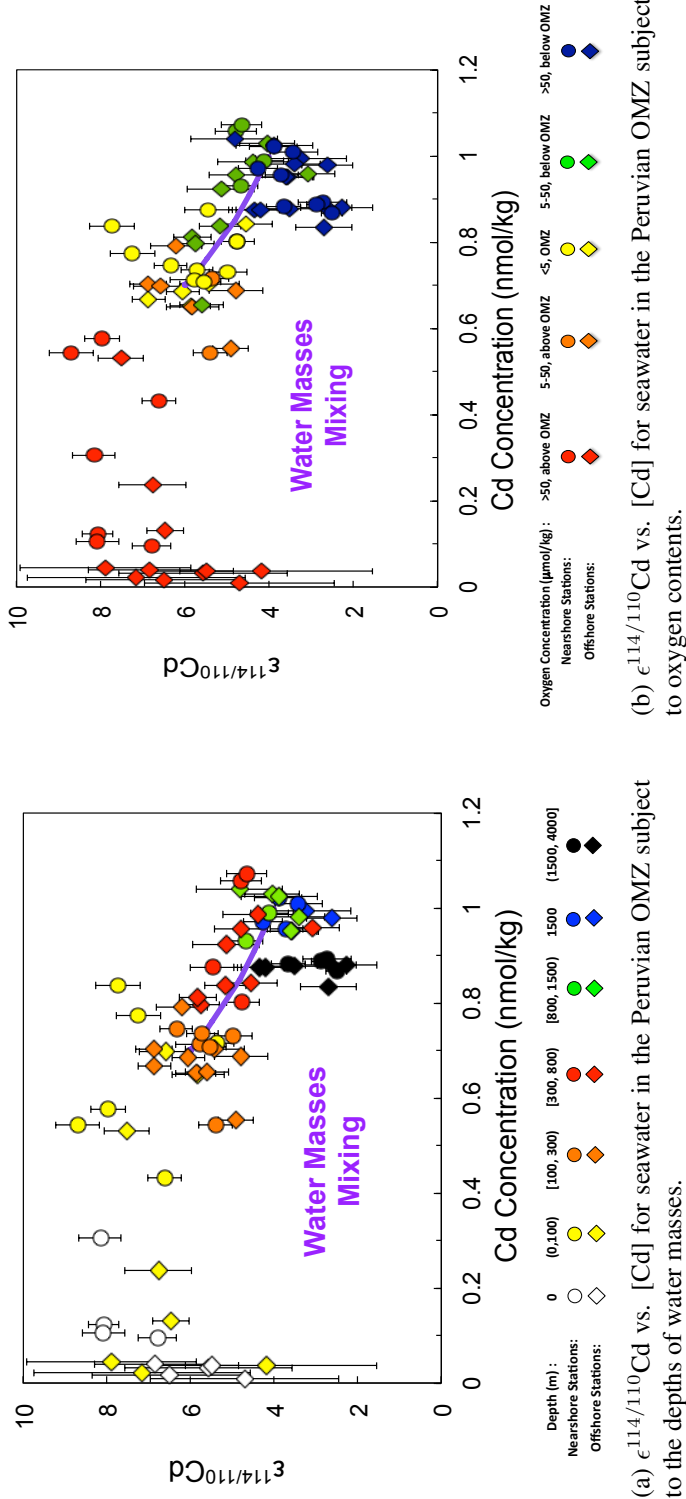


Figure 4.12: Cd isotope fractionations of seawater at the intermediate depth (200–1500m) in the Peruvian OMZ. Cd data (Table 4.1) from the offshore and nearshore stations are shown in diamonds and dots, respectively. Assuming that water mass upwell from 1500m, the blue dashed lines represent the open system Cd isotope fractionation trend, which is calculated using steady state model with fractionation factor $\alpha \approx 1.0006$. If Cd isotope variations in the seawater at the intermediate depth happen in the closed system, the green dashed line indicates the Cd isotope fractionation trend calculated using Rayleigh fractionation model with fractionation factor of $\alpha \approx 1.0005$. The water mass from 1500m has the average value of $[\text{Cd}] = 1.0 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +4$. The steady state model and Rayleigh fractionation model have been discussed in section 1.1.5.



(a) $\epsilon^{114/110}\text{Cd}$ vs. $[\text{Cd}]$ for seawater in the Peruvian OMZ subject to the depths of water masses.

(b) $\epsilon^{114/110}\text{Cd}$ vs. $[\text{Cd}]$ for seawater in the Peruvian OMZ subject to oxygen contents.

Figure 4.13: Water masses mixing trend for Cd isotope fractionation at the intermediate depths. Cd data (Table 4.1) from the offshore and nearshore stations are shown in diamonds and dots, respectively. The purple line shows the water masses mixing at the intermediate depth, which is calculated using the water masses mixing model with water mass from 1500m having average value of $[\text{Cd}] = 1.0 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +4$ and water mass from 100-300m having $[\text{Cd}] = 0.7 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +6$. The water masses mixing model has been discussed in section 1.1.5.

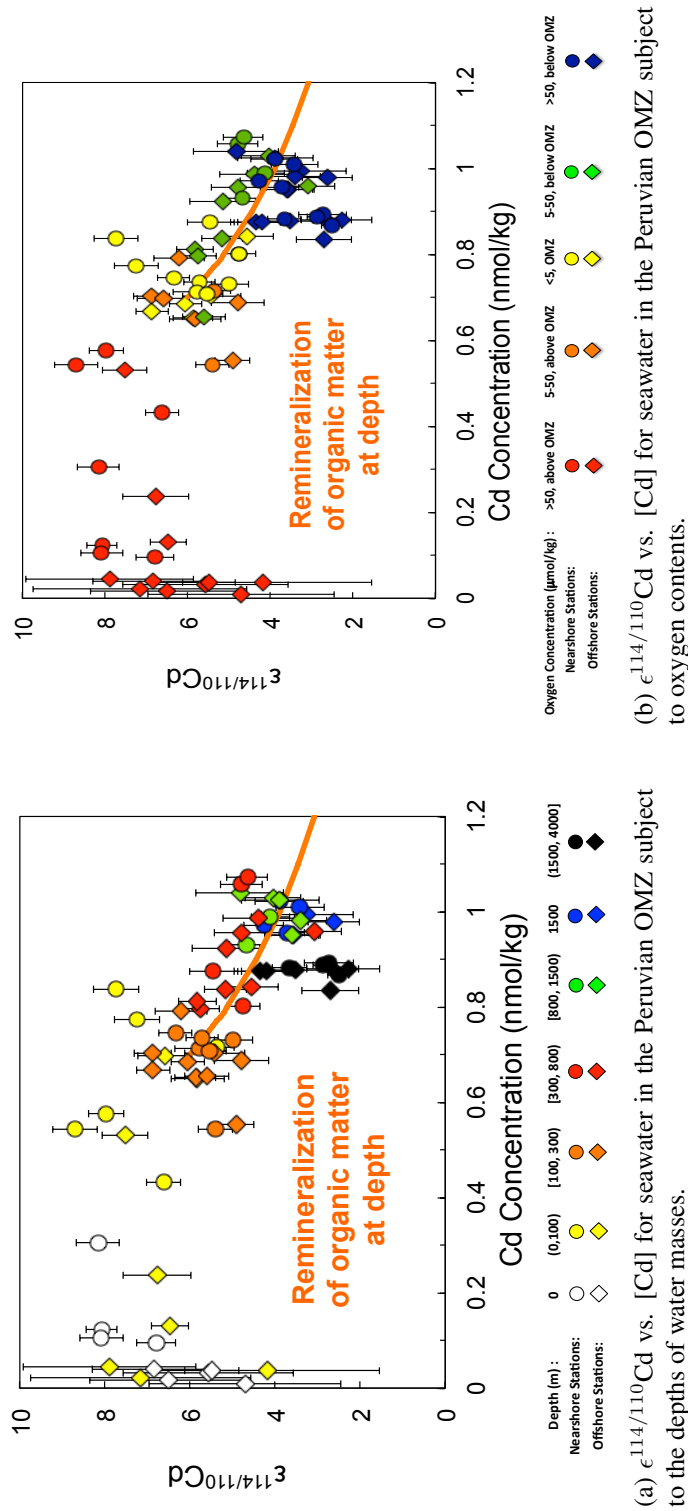


Figure 4.14: Cd isotope fractionation trend at intermediate depth associated with organic material remineralization. Cd data (Table 4.1) from the offshore and nearshore stations are shown in diamonds and dots, respectively. The water mass from 100-300m with $[\text{Cd}] = 0.7 \text{ nmol/kg}$ and $\epsilon^{114/110}\text{Cd} = +6$ is applied as the initial Cd value to the organic material remineralization model. The calculated trend demonstrates Cd isotope variations at the intermediate depth in association with a continued release of Cd from organic material remineralization.

4.5 Conclusion

This investigation has revealed key characteristics of the Cd distribution and isotope fractionation in a major OMZ.

- (1) The Peruvian OMZ is expressed at depths of between 30 m and 500 m and its formation is directly related to the intense upwelling, which occurs in this region. In general, coastal upwelling is stronger than upwelling observed further offshore. The most intense upwelling is centered on coastal localities at between 10°S and 14 °S.
- (2) This study and previous work (Huyer, 1990; Strub et al., 1998) shows that the water masses upwelling to the surface at both offshore and near-shore locations are derived from depths of about 100-300 m. The present investigation reveals that the upwelling water is characterized by $[Cd] \approx 0.7 \text{ nmol/kg}$ and $\epsilon^{114/110}Cd \approx +5$ to $+6$. Hence, upwelling brings oxygen-poor but Cd-rich water masses to shallow depths. This replenishes the Cd content of surface and subsurface seawater, which would otherwise feature low Cd concentrations due to biological utilization. Both upwelling and enhanced biological productivity, act to extend the upper boundary of the OMZ to shallow depths.
- (3) Cd distribution in the Peruvian OMZ is determined by the interplay of various processes and conditions, such as the location of OMZ, biological utilization, remineralization of biological material as well as the intensity of upwelling. In particular, surface waters above 50m in the Peruvian OMZ are distinguished by variable Cd contents, which are coupled with relatively constant Cd isotope composition with $\epsilon^{114/110}Cd$ approximate values between $+5$ and $+8$. This may be caused by the replenishment of Cd from upwelled water masses from 100-300m.
- (4) A positive correlation between Cd concentrations and isotope compositions is observed for water samples from depths of about 200 m to 1.5 km. This correlation is most reasonably explained by either water mass mixing and/or the continued release of Cd from remineralization of organic matter at greater depth. In addition, the trend

indicates that water masses are present in the OMZ region at depths of at least 200 m, which likely have inherited a biological fractionation signature at significantly shallower depths.

- (5) The marine environment of an OMZ generates distinct Cd concentration and isotope signatures in the water column. The correlation between Cd concentrations and isotope compositions of water samples from the OMZ in the EEP is distinguished from oligotrophic open ocean areas and the Southern Ocean HNLC region.

4.6 Acknowledgements

Many thanks Martin Frank and Lothar Stramma for offering the chance to go to the cruise METEOR M77/3 and M77/4 to collect the seawater samples in this study. We are grateful to all the people who funded and organized this cruise in the context of the Sonderforschungsbereich (SFB-754, 'Climate - Biogeochemistry Interactions in the Tropical Ocean'). Many thanks Patricia Grasse for providing extra pre-cleaned seawater sample bottles to us, sharing the lab with me during the cruise and helpful discussion. Much appreciated for the help of the researchers and crew on the M77/4. The authors furthermore thank Barry J Coles, Katharina Kreissig, Rasmus Andreasen, Roz Coggon and the other members of the MAGIC team for their help in keeping the mass spec running and the clean lab organized. This research was made possible by funding from a NERC research grant to MR, ZX and Andy Ridgwell (Bristol).

References

- Abouchami, W., Galer, S., de Baar, H., Alderkamp, A., Middag, R., Laan, P., Feldmann, H., Andreae, M., 2011. Modulation of the Southern Ocean cadmium isotope signature by ocean circulation and primary productivity. *Earth and Planetary Science Letters* 305, 83 – 91.
- Böning, P., Brumsack, H., Böttcher, M., Schnetger, B., Kriete, C., Kallmeyer, J., Borchers, S., 2004. Geochemistry of Peruvian near-surface sediments. *Geochimica et Cosmochimica Acta* 68, 4429–4451.
- Böning, P., Brumsack, H., Schnetger, B., Grunwald, M., 2009. Trace element signatures of Chilean upwelling sediments at 36°S. *Marine Geology* 259, 112–121.
- Boyle, E., Sclater, F., Edmond, J., 1976. On the marine geochemistry of cadmium. *Nature* 263, 42–44.
- Bruland, K.W., 1980. Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth and Planetary Science Letters* 47, 176–198.
- Emery, W., 2001. Water Types and Water Masses, in: Steele, J., Turekian, K., Thorpe, S. (Eds.), *Encyclopedia of Ocean Sciences (Second Edition)*. Academic Press, Oxford, Second edition edition. pp. 291 – 299.
- Enfield, D., 1976. Oceanography of the region north of the equatorial front, physical aspects, in: *Proceedings of the Workshop on the El Nino Phenomenon*, pp. 4–12.
- Hormazabal, S., Shaffer, G., Silva, N., Navarro, E., 2006. The Peru-Chile undercurrent and the oxygen minimum zone variability off central Chile. *Gayana (Concepc.)* 70, 37–45.

- Huyer, A., 1990. *Ocean Engineering Science*. Wiley-Interscience. chapter 12. Shelf Circulation. p. 423.
- Huyer, A., Smith, R., Paluszkiewicz, T., et al., 1987. Coastal upwelling off Peru during normal and El Niño times, 1981-1984. *Journal of Geophysical Research* .
- Karstensen, J., Stramma, L., Visbeck, M., 2008. Oxygen minimum zones in the eastern tropical Atlantic and Pacific oceans. *Progress in Oceanography* 77, 331–350.
- Kawabe, M., Fujio, S., 2010. Pacific Ocean circulation based on observation. *Journal of oceanography* 66, 389–403.
- Lacan, F., Francois, R., Ji, Y., Sherrell, R., 2006. Cadmium isotopic composition in the ocean. *Geochimica et Cosmochimica Acta* 70, 5104–5118.
- Montecino, V., Strub, T., Chavez, F., Thomas, A., Tarazona, J., Baumgartner, T., 2006. Bio-physical interactions off western South-America. Robinson AR & KH Brink. *The global coastal ocean: interdisciplinary regional studies and syntheses* (eds.). *The Sea* 14A , 329–390.
- Oschlies, A., Brandt, P., Schelten, C., Stramma, L., 2012. SFB754: Climate-Biogeochemistry Interactions in the Tropical Ocean. *Exchanges* 58, 11–14.
- Pfannkuche, O., Frank, M., Schneider, R., Stramma, L., 2011. Climate- biogeochemistry interactions in the tropical ocean of the SE-American oxygen minimum zone, Cruise No. 77, Leg 1 - 4. *METEOR-Berichte* 11-2 11.
- Rehkämper, M., Wombacher, F., Horner, T., Xue, Z., 2011. Natural and anthropogenic Cd isotope variations. *Handbook of Environmental Isotope Geochemistry* , 125–154.
- Ripperger, S., Rehkämper, M., 2007. Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS. *Geochimica et cosmochimica acta* 71, 631–642.
- Ripperger, S., Rehkämper, M., Porcelli, D., Halliday, A., 2007. Cadmium isotope fractionation in seawater—A signature of biological activity. *Earth and Planetary Science Letters* 261, 670–684.

- Schmitt, A., Galer, S., Abouchami, W., 2009. Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. *Earth and Planetary Science Letters* 277, 262–272.
- Silva, S., Neshyba, S., 1979. On the southernmost extension of the Peru-Chile Undercurrent. *Deep Sea Research Part A. Oceanographic Research Papers* 26, 1387–1393.
- Smith, R., 1978. Poleward propagating perturbations in currents and sea levels along the Peru coast. *Journal of Geophysical Research* 83, 6083–6092.
- Smith, R., 1983. Peru coastal currents during El Nino: 1976 and 1982. *Science* 221, 1397–1399.
- Stramma, L., 2009. Short cruise report METEOR cruise leg M77/4: Climate-biogeochemistry interactions in the tropical ocean of the SE-American oxygen minimum zone From Callao, Peru to Colon, Panama January 27 to February 19, 2009. Technical Report. IFM-GEOMAR, Kiel.
- Strub, P., Mesias, J., James, C., 1995. Altimeter observations of the Peru-Chile countercurrent. *Geophysical Research Letters* 22, 211–214.
- Strub, P., Mesías, J., Montecino, V., Rutllant, J., Salinas, S., 1998. Coastal ocean circulation off western South America. *The sea* 11, 273–313.
- Talley, L., 1999. Some aspects of ocean heat transport by the shallow, intermediate and deep overturning circulations. *Geophysical Monograph - American Geophysical Union* 112, 1–22.
- Wijffels, S., Toole, J., Bryden, H., Fine, R., Jenkins, W., Bullister, J., 1996. The water masses and circulation at 10°N in the Pacific. *Deep Sea Research Part I: Oceanographic Research Papers* 43, 501–544.
- Wyrtki, K., et al., 1966. Oceanography of the eastern equatorial Pacific Ocean. *Oceanography and Marine Biology: an annual review* 4.

- Xue, Z., Rehkämper, M., Schönbächler, M., Statham, P., Coles, B., 2012. A new methodology for precise cadmium isotope analyses of seawater. *Analytical and Bioanalytical Chemistry* 402, 883–893.

Chapter 5

Conclusions and Outlook

5.1 Summary and conclusions

This PhD research project has generated a number of important achievements and findings, as summarized below.

To improve the understanding of the marine cycling of Cd and its isotopic variations, a new methodology has been developed for precise and accurate Cd isotope analyses by MC-ICP-MS. This enables the analysis of large-volume seawater samples with low Cd concentrations. In detail, the procedure is suitable for processing seawater samples with volumes as large as 10 to 20 L and Cd concentrations as low as 1 pmol/L. The procedure involves the application of new ^{111}Cd - ^{113}Cd double spike and Cd purification by $\text{Al}(\text{OH})_3$ co-precipitation and ion chromatography. The overall Cd yield of the new method is consistently better than 85% and an external precision (2sd) of about 0.1 to 0.2 ‰/amu is routinely achieved, when samples with 30 ng of natural Cd are analysed.

With the help of this method, Cd stable isotope variations were investigated in different marine environments and this work has led to a number of important findings. In particular, the study obtained the first Cd isotope profile for the North Atlantic Ocean. In addition, the first comprehensive coupled [Cd]-Cd isotope surface water and depth profile data for the Southern Ocean HNLC region and the oxygen minimum zone (OMZ) of the eastern

tropical Pacific Ocean were generated. Importantly, we find that each marine environment shows a different Cd distribution that is reflected in distinct trends of the datasets in diagrams of $\epsilon^{114/110}\text{Cd}$ versus [Cd].

These findings underline that Cd isotope compositions can indeed provide valuable new insights into biogeochemical processes and that Cd isotope have the potential to be developed as a paleoceanographic proxy of nutrient cycling and utilization.

5.2 Outlook for future work

5.2.1 Further investigation of Cd isotope fractionation mechanisms in the ocean

Whilst there is good evidence that biological utilization primarily governs Cd isotope fractionations in the oceans, there is a great need to further investigate the fractionation mechanisms. Although new Cd isotopic datasets are currently being generated in a number of laboratories, the overall number of marine, and in particular, seawater Cd isotope data available is still limited. Hence, larger Cd isotopic datasets should be obtained for ocean regions not yet investigated, such as the Indian Ocean and the South Atlantic Ocean. These results can be applied to re-examine the currently suggested mechanisms for the marine behavior and isotope fractionation of Cd.

Furthermore, studies are required to reexamine the uptake mechanisms of Cd by marine microorganisms and its biological function in phytoplankton and bacteria in different ocean regions. For instance, there are 3 major OMZs in the oceans, located in the eastern tropical Pacific Ocean, the northern reaches of the tropical Indian Ocean and the tropical Atlantic Ocean (Stramma et al., 2008). Hence, whether the present mechanisms for Cd distribution and isotope fractionation in the tropical Pacific OMZ are also suitable for the other two OMZs, should be explored.

In addition, Cd isotope analyses of phytoplankton biomass collected from the water

column can be used to test the mechanism for Cd isotope fractionations in seawater by biological utilization. If the current mechanisms that were inferred from and modeled for Cd isotope fractionation in seawater are correct, the Cd contents and isotope fractionations of the biomass should provide compatible results.

5.2.2 Investigation of the sources and sinks of Cd in the oceans

Previous studies demonstrate that Cd is provided to the ocean by rivers through estuarine systems, atmospheric dust particles and hydrothermal fluids. In the oceans, Cd participates in many internal cycles of assimilation into biogenic matter and remineralisation, and is finally incorporated into marine sediments, which are the primary Cd sink (Collier and Edmond, 1984; Rosenthal et al., 1995). The isotopic compositions of these different sources and sinks of Cd in the oceans are essentially unstudied at present; however, they are likely to exhibit differences in $\epsilon^{114/110}\text{Cd}$. Therefore, the Cd isotope compositions of the main sources and sinks of marine Cd should be investigated. The $\epsilon^{114/110}\text{Cd}$ value of the oceans is also affected by any isotopic fractionation that occurs during incorporation of Cd into marine sediments. In this case, the isotopic fractionation that occurs when Cd substitutes into calcite and ferromanganese oxyhydroxides has been characterized (Horner et al., 2010, 2011). However, Cd fractionations associated with the incorporation of Cd contents into other sediments, such as C-rich anoxic/suboxic shelf sediments, which are known to have high Cd contents (Böning et al., 2004), are unstudied so far. Such key gaps in understanding need to be closed.

Furthermore, such information when combined with Cd concentration data can be used to re-evaluate the marine residence time of Cd, which is presently only poorly characterized at about 10 to 100 kyr (Bewers and Yeats, 1977; Martin and Whitfield, 1983; Ruttenger, 2003).

5.2.3 Understanding the $\epsilon^{114/110}\text{Cd}[\text{Cd}]$ correlations of the modern ocean as a basis for developing the Cd isotope proxy for past oceans

The $\epsilon^{114/110}\text{Cd}[\text{Cd}]$ seawater data features distinct trends for different marine environments, such as the Southern Ocean HNLC area, oligotrophic regions and the OMZ in the eastern Pacific Ocean. Although further seawater analyses are needed to confirm these distinct trends and to better understand their origin, the correlation of coupled seawater Cd isotope and concentration obtained from currently available Cd dataset implies a potential important application of the Cd isotope as a proxy for the study of past oceans. This $\epsilon^{114/110}\text{Cd}[\text{Cd}]$ correlation would be valuable for paleoceanographic research to study past changes in ocean circulation and to distinguish between different modes and mechanisms of nutrient cycling and utilization. Hence, the investigation of $\epsilon^{114/110}\text{Cd}[\text{Cd}]$ correlation in foraminifera will help to examine this hypothesis.

References

- Bewers, J.M., Yeats, P.A., 1977. Oceanic residence times of trace metals. *Nature* 268, 595–598.
- Böning, P., Brumsack, H., Böttcher, M., Schnetger, B., Kriete, C., Kallmeyer, J., Borchers, S., 2004. Geochemistry of Peruvian near-surface sediments. *Geochimica et Cosmochimica Acta* 68, 4429–4451.
- Collier, R., Edmond, J., 1984. The trace element geochemistry of marine biogenic particulate matter. *Progress In Oceanography* 13, 113 – 199.
- Horner, T., Rickaby, R., Henderson, G., 2011. Isotopic fractionation of cadmium into calcite. *Earth and Planetary Science Letters* 312, 243–253.
- Horner, T., Schönbächler, M., Rehkämper, M., Nielsen, S., Williams, H., Halliday, A., Xue, Z., Hein, J., 2010. Ferromanganese crusts as archives of deep water Cd isotope compositions. *Geochemistry Geophysics Geosystems* 11, Q04001.
- Martin, J., Whitfield, M., 1983. The significance of the river input of chemical elements to the ocean. *Trace metals in sea water*, 265–296.
- Rosenthal, Y., Lam, P., Boyle, E., Thomson, J., 1995. Authigenic cadmium enrichments in suboxic sediments: Precipitation and postdepositional mobility. *Earth and Planetary Science Letters* 132, 99–111.
- Ruttenberg, K., 2003. The global phosphorus cycle. *Treatise on geochemistry* 8, 585–643.
- Stramma, L., Johnson, G., Sprintall, J., Mohrholz, V., 2008. Expanding oxygen-minimum zones in the tropical oceans. *Science* 320, 655–658.

Appendix A

List of publications

Some of the research presented in this thesis can also be found in other sources.

A.1 Published journal papers:

1. Boyle, E., John, S., Abouchami, W., Adkins, J., Echegoyen-Sanz, Y., Flegal, R., Ellwood, M., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkämper, M., Rouxel, O., Sohrin, Y., Stirling, C., Thompson, C., Vance, D., Xue, Z., Zhao, Y., 2012. GEOTRACES IC1 (BATS) Contamination-Prone Trace Element Isotopes Cd, Fe, Pb, Zn, Cu, and Mo Intercalibration. *Limnology and Oceanography: Methods* . (Boyle et al., 2012)
2. Abouchami, W., Galer, S.J.G., Horner, T.J., Rehkämper, M., Wombacher, F., Xue, Z., Lambelet, M., Gault-Ringold, M., Stirling, C.H., Schönbächler, M., Shiel, A.E., Weis, D., Holdship, P.F., 2012. A Common Reference Material for Cadmium Isotope Studies - NIST SRM 3108. *Geostandards and Geoanalytical Research* . (Abouchami et al., 2012)
3. Xue, Z., Rehkämper, M., Schönbächler, M., Statham, P., Coles, B., 2012. A new methodology for precise cadmium isotope analyses of seawater. *Analytical and Bioanalytical Chemistry* 402, 883-893. (Xue et al., 2012)

4. Rehkämper, M., Wombacher, F., Horner, T., Xue, Z., 2011. Natural and anthropogenic Cd isotope variations. *Handbook of Environmental Isotope Geochemistry*, 125-154. (Rehkämper et al., 2011)

A.2 Published conference abstracts:

1. Lambelet, M., Rehkämper, M., van de Flierdt, T., Xue, Z., Kreissig, K., Coles, B., Andersson, P., Porcelli, D., 2011. Cd Behaviour in Arctic Estuarine Systems Using Cd Isotopes and Concentrations Analysis, in: *Goldschmidt Conference*, p. 1267. (Lambelet et al., 2011)
2. Xue Z, Rehkämper M, van de Flierdt T, Grasse P, Frank M (2011). Cadmium Isotope Constraints on Nutrient Cycling in the Peruvian Oxygen Minimum Zone, *European Geosciences Union General Assembly 2011* (Xue et al., 2011)
3. Xue, Z., Rehkämper, M., van de Flierdt, T., Grasse, P., Frank, M., 2010b. Cadmium Isotope Constraints on Nutrient Cycling in the Peruvian Oxygen Minimum Zone, in: *Goldschmidt Conference*, p. 1166. (Xue et al., 2010b)
4. Rehkämper, M., Xue, Z., van de Flierdt, T., Middag, R., de Baar, H., 2010. Cd Isotope Constraints on Nutrient Cycling in the Southern Ocean, in: *Goldschmidt Conference*, p. 857. (Rehkämper et al., 2010)
5. Abouchami, W., Rehkämper, M., Galer, S., Horner, T., Xue, Z., Henderson, G., Wombacher, F., Schönbächler, M., Gault-Ringold, M., Stirling, C., 2010. In Search of a Common Reference Material for Cadmium Isotope Studies, in: *Goldschmidt Conference*, p. 2. (Abouchami et al., 2010)
6. Horner, T., Schönbächler, M., Rehkämper, M., Nielsen, S., Williams, H., Halliday, A., Xue, Z., Hein, J., 2010. Ferromanganese crusts as archives of deep water Cd isotope compositions. *Geochemistry Geophysics Geosystems* 11, Q04001. (Horner et al., 2010)

7. Xue, Z., Rehkämper, M., van de Flierdt, T., Middag, R., de Baar, H., 2010a. Cadmium Isotope Fractionation in the Southern Ocean, in: Eos Trans. AGU 2010 Ocean Sciences Meeting, 91(26), Ocean Sci. Meet. Suppl., Abstract CO15C-12, American Geophysical Union, 2000 Florida Ave., N. W. Washington DC 20009 USA, Portland, OR. (Xue et al., 2010a)
8. Xue, Z., Rehkämper, M., Statham, P., 2009. A New Methodology for Precise Cadmium Isotope Analyses of Seawater, in: Goldschmidt Conference, p. 1467. (Xue et al., 2009)

A.3 The following journal paper has been submitted:

1. Lambelet, M., Rehkämper, M., van de Flierdt, T., Xue, Z., Kreissig, K., Coles, B., Porcelli, D., Andersson, P., (TBA) Isotopic analysis of Cd in the mixing zone of Siberian rivers with the Arctic Ocean - new constraints on marine Cd cycling and the isotope composition of riverine Cd. Submitted to Earth and Planetary Science Letters.

A.4 The following journal papers are in preparation:

1. Xue, Z., Rehkämper, M., van de Flierdt, T., Grasse, P., Frank, M., (TBA). Cadmium Cycling in the South Eastern Equatorial Pacific Ocean (3°S - 14°S). In preparation for submission to Earth and Planetary Science Letters.
2. Xue, Z., Rehkämper, M., van de Flierdt, T., Middag, R., de Baar, H.J., (TBA). Cadmium Isotope Fractionation in the Southern Ocean. In preparation for submission to Earth and Planetary Science Letters.

References

- Abouchami, W., Galer, S.J.G., Horner, T.J., Rehkämper, M., Wombacher, F., Xue, Z., Lambelet, M., Gault-Ringold, M., Stirling, C.H., Schönbächler, M., Shiel, A.E., Weis, D., Holdship, P.F., 2012. A Common Reference Material for Cadmium Isotope Studies - NIST SRM 3108. *Geostandards and Geoanalytical Research* .
- Abouchami, W., Rehkämper, M., Galer, S., Horner, T., Xue, Z., Henderson, G., Wombacher, F., Schönbächler, M., Gault-Ringold, M., Stirling, C., 2010. In Search of a Common Reference Material for Cadmium Isotope Studies, in: *Goldschmidt Conference*, p. 2.
- Boyle, E., John, S., Abouchami, W., Adkins, J., Echegoyen-Sanz, Y., Flegal, R., Ellwood, M., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkämper, M., Rouxel, O., Sohrin, Y., Stirling, C., Thompson, C., Vance, D., Xue, Z., Zhao, Y., 2012. GEOTRACES IC1 (BATS) Contamination-Prone Trace Element Isotopes Cd, Fe, Pb, Zn, Cu, and Mo Intercalibration. *Limnology and Oceanography: Methods* .
- Horner, T., Schönbächler, M., Rehkämper, M., Nielsen, S., Williams, H., Halliday, A., Xue, Z., Hein, J., 2010. Ferromanganese crusts as archives of deep water Cd isotope compositions. *Geochemistry Geophysics Geosystems* 11, Q04001.
- Lambelet, M., Rehkämper, M., van de Flierdt, T., Xue, Z., Kreissig, K., Coles, B., Anderson, P., Porcelli, D., 2011. Cd Behaviour in Arctic Estuarine Systems Using Cd Isotopes and Concentrations Analysis, in: *Goldschmidt Conference*, p. 1267.
- Rehkämper, M., Wombacher, F., Horner, T., Xue, Z., 2011. Natural and anthropogenic Cd isotope variations. *Handbook of Environmental Isotope Geochemistry* , 125–154.

- Rehkämper, M., Xue, Z., van de Flierdt, T., Middag, R., de Baar, H., 2010. Cd Isotope Constraints on Nutrient Cycling in the Southern Ocean, in: Goldschmidt Conference, p. 857.
- Xue, Z., Rehkämper, M., van de Flierdt, T., Middag, R., de Baar, H., 2010a. Cadmium Isotope Fractionation in the Southern Ocean, in: Eos Trans. AGU 2010 Ocean Sciences Meeting, 91(26), Ocean Sci. Meet. Suppl., Abstract CO15C-12, American Geophysical Union, 2000 Florida Ave., N. W. Washington DC 20009 USA, Portland, OR.
- Xue, Z., Rehkämper, M., Schönbächler, M., Statham, P., Coles, B., 2012. A new methodology for precise cadmium isotope analyses of seawater. *Analytical and Bioanalytical Chemistry* 402, 883–893.
- Xue, Z., Rehkämper, M., van de Flierdt, T., Grasse, P., Frank, M., 2010b. Cadmium Isotope Constraints on Nutrient Cycling in the Peruvian Oxygen Minimum Zone, in: Goldschmidt Conference, p. 1166.
- Xue, Z., Rehkämper, M., van de Flierdt, T., Grasse, P., Frank, M., 2011. Cadmium Isotope Variations in the Peruvian Oxygen Minimum Zone - New Constraints on Micronutrient Cycling, in: European Geosciences Union General Assembly.
- Xue, Z., Rehkämper, M., Statham, P., 2009. A New Methodology for Precise Cadmium Isotope Analyses of Seawater, in: Goldschmidt Conference, p. 1467.