

Zn and Cd isotopes as proxies for geochemical change in Mesozoic oceans



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Abstract

Mesozoic Oceanic Anoxic Events (OAEs) are characterised by the widespread burial of organic-rich sediments and the spread of low-oxygen marine environments. These intervals represent some of most extreme perturbations to global climate, environment, and ocean chemistry in Earth's history. Understanding the complex interplay of processes that caused and sustained these unusual environmental conditions requires proxies that allow quantification of global changes in ocean chemistry. This study explores the use of Zn- and Cd-isotopes as new palaeo-ocean chemistry proxies by using the Late Cretaceous Cenomanian–Turonian Oceanic Anoxic Event 2 (OAE 2, ~ 94 Ma) as a case study. Previous studies on the cycling of these elements in the modern ocean have suggested Cd and Zn may preserve valuable information on past redox and/or nutrient conditions if such signals are preserved in the sedimentary record. The data presented in this thesis suggest a strong control of local redox conditions on the Cd- and Zn-isotope composition of ancient organic-rich marine sediments. When these local effects are accounted for, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphic profiles offer insight into past change in redox environments at a global scale. Specifically, heavy $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values observed during the main phase of the OAE 2 interval can be associated with an increase in organic-rich sediment burial globally, whereas lower values during the Plenus Cold Event interval can be linked to global oxygenation. The data presented in this study highlight the potential of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ as new proxies for global changes in ocean redox chemistry. With improved understanding of the cycling of these elements in the modern ocean, these proxies may ultimately be used to quantify the global extent of ocean anoxia for past oceans.

Extended Abstract

Widespread deposition of organic-rich black shales during the Cenomanian–Turonian Oceanic Anoxic Event 2 (OAE 2, ~94Ma, Late Cretaceous) occurred during a period of significant global palaeoenvironmental and geochemical change. An increase in nutrient input to the ocean during OAE 2 is a key mechanism proposed to have generated and sustained low-oxygen conditions and high rates of organic-matter burial over timescales of 10^3 – 10^5 years. Proxies used to estimate the extent of anoxia in previous studies are generally mostly applicable to longer timescales due to the long residence times of the elements on which these reconstructions are based. Tracers that are more suitable for the reconstruction of ocean nutrient and/or redox chemistry on timescales of $<10^5$ years are currently not well established.

Zn is a bio-essential micronutrient and its distribution in the modern ocean resembles that of Si. Cd also shows a nutrient-like distribution in the modern ocean similar to that of phosphate. Both Zn and Cd form stable sulphide phases in the presence of free H_2S . Biological uptake of Zn and Cd and/or sulphide formation are associated with isotope fractionation when removal is non-quantitative. If such primary signals are exported and preserved in the sedimentary record the Zn- and Cd-isotope composition of marine sediments might be used to trace past nutrient and/or redox conditions. This study explores this potential application by analysing the Zn- and Cd-isotope composition of a variety of organic-rich and carbonate sediments from the OAE 2 interval.

Organic-rich mudrocks of Cenomanian–Turonian age from the Maverick Basin, a sub-basin of the Western Interior Seaway, are used to address the impact of local redox conditions on the Zn- and Cd-isotope composition of the sedimentary record. Previous studies have revealed highly varying local redox conditions for the studied interval. The $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ analysis of two cores from this basin imply that the proportion of sulphide formation exerts a strong control on the isotope composition of the sediment. Non-quantitative removal of Cd in oxygenated waters results in low $\delta^{114}\text{Cd}$, whereas higher values are observed in euxinic depositional conditions, which are inferred to be due to quantitative removal to sediments. Accounting for such local controls allows reconstruction of seawater isotope compositions, which may then be used to address global changes in past ocean chemistry. As such, similar patterns are found for different sites and different marine sediment archives, which further strengthens the argument for a supra-local control.

$\delta^{66}\text{Zn}$ values for multiple carbonate and black shale successions of Cenomanian–Turonian age generally show comparable values to those observed for modern ocean equivalents. This comparison suggests that similar processes dominated the Zn-isotope cycling during the Late Cretaceous and that established offsets between modern seawater and different ocean sediments may be used to reconstruct past seawater compositions. A multi-site approach to reconstructing past $\delta^{66}\text{Zn}$ of seawater reveals the highest values ($\sim 0.7\text{‰}$) during the main-phase of carbon-burial, significantly higher (by $\sim +0.2\text{‰}$) than the average dissolved $\delta^{66}\text{Zn}$ composition of the modern ocean. This difference in $\delta^{66}\text{Zn}$ can be related to a relatively higher proportion of Zn burial in organic-rich sediments during the studied interval. The lightest $\delta^{66}\text{Zn}_{\text{seawater}}$ values are found for sediments from the Plenus Cold Event interval, a period of cooling and oxygenation recognised in the Northern Hemisphere. This study highlights the Plenus Cold Event interval as a period of considerable change in ocean chemistry and environment. Small sample-to-sample differences between $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ patterns during the Plenus Cold Event may be related to the remobilisation of isotopically light Zn from continental-margin sediments and/or the enhanced input of hydrothermal Zn.

Lower $\delta^{66}\text{Zn}$ values observed for a brief interval just prior to onset of the OAE interval in several sites may be related to enhanced hydrothermal input associated with the onset of Large Igneous Province (LIP) volcanism. This explanation agrees with conceptual and geochemical models that have suggested a role for LIP-driven ocean nutrification as a key driver for the onset of the geochemical change associated with OAEs.

A generally positive relationship is observed in all $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ data from organic-rich sediments, which suggests that similar controls influence the Zn- and Cd-isotope composition of the ancient sedimentary record, at least for the Late Cretaceous. This relationship is remarkable considering highly different patterns for the dissolved isotopic compositions of these two elements in the modern ocean. Mechanisms, sources and sinks for Cd-isotope system are not as well established in the modern ocean, but the data presented in this study imply that several similarities to $\delta^{66}\text{Zn}$ may be expected. It appears that variations in the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions of the sedimentary record are largely driven by ocean redox changes rather than biological uptake.

Ultimately, this study provides compelling evidence for local and global environmental controls on the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ of ancient marine sediments associated with environmental change during the OAE 2 interval. It suggests that, with a growing understanding of Zn and Cd cycling, the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ composition of marine sediments provides a valuable tool for future palaeoenvironmental studies, specifically those addressing global ocean redox change on timescales of 10^3 - 10^5 years.

Contents

List of Figures	ix
1 Introduction	1
1.1 Isotopic tracers for deoxygenation in warming worlds	1
1.1.1 Relevance aims and approach	1
1.2 Background information	4
1.2.1 Oceanic Anoxic Event 2	4
1.2.2 Zn and Cd systematics	9
1.2.3 Analytical methods	22
2 Isotopic evidence for changes in the Zn cycle during OAE 2	26
2.1 Abstract	26
2.2 Introduction	27
2.2.1 Zn-isotope systematics	28
2.3 Material and Methods	30
2.3.1 Analytical Methods	30
2.4 Results	31
2.5 Discussion	32
2.5.1 Contribution of Zn from detrital minerals	32
2.5.2 Carbonates as an archive for $\delta^{66}\text{Zn}$	33
2.5.3 Surface-ocean processes and spatial patterns	33
2.5.4 Zn-cycle perturbation in relation to a magmatic episode –Event A	34
2.5.5 Zinc-cycle perturbation during the Plenus Cold Event –Event B	36
2.6 Conclusion	37
3 Controls on the $\delta^{114}\text{Cd}$ of Late Cretaceous organic-rich mudrocks	38
3.1 Abstract	38
3.2 Introduction	39
3.2.1 Geological context	42
3.3 Methods	44
3.4 Results	45

3.5	Discussion	45
3.5.1	Lithogenic, biological and authigenic fractions	45
3.5.2	Cd-isotope patterns in relation to the carbon cycle	48
3.6	Local redox controls on $\delta^{114}\text{Cd}$	49
3.6.1	Reconstructing the temporal evolution of $\delta^{114}\text{Cd}_{\text{seawater}}$	52
3.6.2	Drivers of $\delta^{114}\text{Cd}_{\text{seawater}}$ change	54
3.7	Conclusion	57
4	Zn- and Cd-isotope evidence for global redox change during OAE 2	59
4.1	Abstract	59
4.2	Introduction	60
4.3	Material and methods	63
4.3.1	Analytical methods	65
4.4	Results	65
4.5	Discussion	67
4.5.1	Chemostratigraphic units	67
4.5.2	Controls on Zn and Cd enrichments	68
4.5.3	$\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ variability during the Plenus Cold Event	71
4.6	Stratigraphic comparison of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$	74
4.6.1	Comparing different archives for $\delta^{66}\text{Zn}$	77
4.7	Conclusion	79
5	A multi-site approach to reconstructing $\delta^{66}\text{Zn}_{\text{ocean}}$ during OAE 2	81
5.1	Abstract	81
5.2	Introduction	82
5.2.1	OAE 2 and the Plenus Cold Event	84
5.2.2	Modern ocean Zn cycling	84
5.3	Material and Methods	87
5.3.1	Sites 1260 and 367	87
5.3.2	Furlo	89
5.4	Discussion	89
5.4.1	Nitrification as a trigger for onset OAE	89
5.4.2	Basin-scale controls on $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$	92
5.4.3	A multi-site approach to reconstructing $\delta^{66}\text{Zn}_{\text{seawater}}$	96
5.5	Conclusion	101

6	Conclusion	103
6.1	Summary and impact	104
6.1.1	Zn and Cd isotopes in organic-rich mud rocks	104
6.1.2	Global change in ocean $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ on geological timescales	105
6.1.3	Impacts on marine Zn- and Cd-isotope systematics	106
6.1.4	Insights into palaeoenvironmental change associated with OAE 2	106
6.2	Future studies	107
6.2.1	Characterising sources, sinks, and internal cycling in the modern ocean	108
6.2.2	Constraining isotope fractionation factors	108
6.2.3	Phase-specific isotope analysis	108
6.2.4	Palaeoenvironmental studies	109
6.3	Outlook	109
	References	110
	Appendices	
A	Supplementary Figures	129
B	Data tables	144

List of Figures

1.1	Mesozoic Oceanic Anoxic Events	6
1.2	Zn-Si and Cd-P relationships in the global ocean	10
1.3	Dissolved $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions of the modern oceans . . .	12
1.4	Dissolved Zn and Cd distributions in the Black Sea and Cariaco Basin	13
1.5	Zn and Cd concentrations in modern organic-rich marine sediments	15
1.6	Schematic diagrams illustrating the global isotopic mass balance of Cd and Zn	17
1.7	Summarised knowledge of Zn- and- Cd-isotope compositions in the marine environment	19
1.8	Anion column chromatography	24
2.1	Paleogeographical reconstruction for the Cenomanian–Turonian bound- ary interval	31
2.2	Zn-isotope stratigraphy of Cenomanian–Turonian carbonates	35
3.1	Palaeogeographical reconstruction of the Cenomanian–Turonian Bound- ary including the Maverick Basin	43
3.2	Cd-isotope stratigraphy for the Innes-1 and Iona-1 cores	46
3.3	Cd abundances relative to Aluminium and Total Organic Carbon .	47
3.4	$\delta^{114}\text{Cd}$ relative to $\delta^{13}\text{C}_{\text{org}}$ for the Innes-1 and Iona-1 cores.	48
3.5	$\delta^{114}\text{Cd}$ compositions relative to Cd/TOC, Mo_{EF} , Cd_{EF} , and Cd . .	50
3.6	Schematic diagram of the proposed conceptual model	51
3.7	Estimated temporal evolution in $\delta^{114}\text{Cd}_{\text{seawater}}$	55
4.1	Palaeogeographical reconstruction of the Cenomanian–Turonian Bound- ary interval with approximate study locations	64
4.2	Cenomanian–Turonian $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ stratigraphy of the S57 core from the Tarfaya Basin	66
4.3	Various cross-plots of geochemical parameters from core S57, Tarfaya	70
4.4	High-resolution geochemical data for the Plenus Cold Event interval	73
4.5	Comparison of Cd, Zn, and Mo isotopes and abundances for the Tarfaya S57 core.	75

4.6	Comparison of $\delta^{66}\text{Zn}$ stratigraphy from this study to time-equivalent data from the Eastbourne chalk section	78
5.1	Simplified summary of the modern ocean Zn cycle	86
5.2	Palaeogeographical reconstruction for the Cenomanian–Turonian Boundary interval (~ 90 Ma) with approximate study locations . .	88
5.3	Multi-site comparison of $\delta^{13}\text{C}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphy for the interval around the onset of the CIE	91
5.4	Cross-plots of $\delta^{66}\text{Zn}$ versus $\delta^{114}\text{Cd}$ values for multiple sites with Cenomanian–Turonian organic-rich mudrocks. All data is plotted stratigraphically in Appendix A	95
5.5	A multi-site approach to reconstructing $\delta^{66}\text{Zn}_{\text{seawater}}$	97
5.6	Simplified mass-balance Zn model for different seawater isotope compositions and average ocean input $\delta^{66}\text{Zn}$ values at steady state conditions	100
A.1	All data plotted stratigraphically	130
A.2	$\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphy for DSDP site 367 (Cape Verde Basin) and ODP site 1260 (Demerara Rise) from the Late Cretaceous Cenomanian–Turonian interval	131
A.3	$\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphy for the disused quarry outcrop near Furlo, Italy	132
A.4	$\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphy for the Innes-1, Iona-1 and Chittim 2H cores from the Maverick Basin (Eagle Ford Fm).	133
A.5	$\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphy for ODP sites 763 (Exmouth Plateau) 1138 (Kerguelen Plateau).	134
A.6	Geographical distribution of $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions for four different time intervals associated with the Cenomanian–Turonian Boundary Event	135
A.7	Multi-site comparison of $\delta^{13}\text{Cd}$, $\delta^{66}\text{Zn}$, and $\delta^{114}\text{Cd}$ stratigraphy for the time interval surrounding the Plenus Cold Event	136
A.8	Multi-site comparison of $\delta^{13}\text{Cd}$, $\delta^{66}\text{Zn}$, and $\delta^{114}\text{Cd}$ stratigraphy for the time interval surrounding the ‘plateau-phase’ of the OAE 2 interval, a period of peak organic-carbon burial	137
A.9	Compilation of $\delta^{13}\text{Cd}$, $\delta^{66}\text{Zn}$, and Cd and Zn abundances for the studied mudrocks.	138
A.10	$\delta^{13}\text{Cd}$ and $\delta^{66}\text{Zn}$ relative to Mo-enrichment factors for the Innes-1 and Iona-1 (Eagle Ford) cores	139
A.11	Enlarged version of Figure 4.3, with data from the Tarfaya S-57 core	140

A.12 Palaeogeographical reconstruction of 90Ma, including approximate study locations and locations of Large Igneous Provinces	141
A.13 Mn/Ca ratios for the Eastbourne section	142
A.14 Cd/Ca ratios for the Eastbourne section	143

1

Introduction

Contents

1.1	Isotopic tracers for deoxygenation in warming worlds	1
1.1.1	Relevance aims and approach	1
1.2	Background information	4
1.2.1	Oceanic Anoxic Event 2	4
1.2.2	Zn and Cd systematics	9
1.2.3	Analytical methods	22

1.1 Isotopic tracers for deoxygenation in warming worlds

1.1.1 Relevance aims and approach

The deoxygenation of marine basins is one of several potential issues associated with greenhouse-gas induced climate change. This phenomenon is due to a mixture of (1) a decrease in the solubility of oxygen in warmer waters (2) a biological response, whereby higher primary productivity ultimately leads to a higher oxygen demand at depths, and (3) decreased ventilation as a result of ocean stratification (e.g. Keeling, Körtzinger & Gruber, Keeling et al.; Shepherd et al., 2017, and references therein). Ocean deoxygenation may have severe and widespread socio-economic consequences

due to its impact on ecosystems and fisheries (Vaquer-Sunyer & Duarte, 2008). The accuracy and precision of efforts to model possible deoxygenation in the future rely on the boundary conditions being used and our understanding of the complex interplay between all processes involved. However, conditions of severe deoxygenation are unprecedented in the recent past, where direct observations can be made and recorded. One approach to improving our understanding of ocean deoxygenation, and ultimately model simulations, is to turn to the geological past, where low-oxygen marine conditions were relatively common (e.g. Meyer & Kump, 2008)

The greenhouse world of the Mesozoic Era (~ 252 –66 Ma) hosts several discrete intervals of widespread enhanced organic-carbon burial (e.g. Jenkyns, 2010). These phenomena are termed Oceanic Anoxic Events (OAEs) due to their association with the expansion of low-oxygen conditions in marine basins (Schlanger & Jenkyns, 1976). OAEs have been linked to a perturbation to the global carbon cycle as an initial forcing function, likely through emplacement of Large Igneous Provinces (LIPs) releasing CO_2 into the ocean-atmosphere system. Through various feedback mechanisms, this is thought to result in ocean nutrification, deoxygenation, and enhanced burial of organic-rich sediments, along with various other perturbations to ocean chemistry (e.g. Jenkyns, 2010). Such events are also associated with the extinction of marine organisms, with deoxygenation being one of several stressors, thereby highlighting potential issues of these changing environmental conditions in the modern oceans (e.g. Bond & Wignall, 2014). Despite their well-studied nature, several fundamental questions surrounding OAEs remain, including:

1. What drives and sustains the unusually high export productivity rates required to explain observed patterns in deoxygenation and organic-carbon burial?
2. What was the spatial extent of marine anoxia/euxinia?
3. How dynamic were (global) ocean redox changes and how quickly did these occur?

Several tools have been developed to reconstruct the redox conditions of past oceans based on the (chemical) composition of marine sediments. Such proxies include tracers based on sedimentology, palaeontology, and organic and inorganic chemistry. However, unless findings from sediment cores and outcrop material can be extrapolated to a larger spatial scale with reasonable confidence, these archives only provide a very limited, locally biased, and often qualitative view on changes in ocean chemistry. The isotopic composition of redox-sensitive and/or chalcophilic trace metals provides one of few possibilities to reconstruct supra-local redox conditions quantitatively.

Recent efforts to map the cycling of such elements and their isotope compositions in the modern ocean and sediments have highlighted the potential of some of these geochemical species as proxies for past environmental conditions, while at the same time emphasizing possible complications (e.g. Mawji et al., 2015, GEOTRACES intermediate data product 2017). As a result, trace metal-based isotope tracers (e.g. Mo) have been used to quantify the global expansion of low-oxygen conditions in the geological past (e.g. Dickson, 2017). However, such studies are often based on elements with long residence times ($>10^5$ years), which limits their applicability to assess more rapidly changing ocean redox conditions. As the ‘rate of change’ is a crucial parameter in understanding complex feedback mechanisms in the ocean–climate system, particularly when drawing analogies with present-day change, proxies based on elements with long residence times do not always suffice. Moreover, ocean deoxygenation is only a part of the complex set of feedback mechanisms associated with Oceanic Anoxic Events. Another, nutrification, generally receives less attention, at least partly due to a lack of applicable proxies.

Observations on the behaviour of zinc- (Zn) and cadmium (Cd) -isotope systematics in the modern ocean have highlighted the potential of these isotope systems in palaeoenvironmental reconstructions (e.g. Conway and John 2014; 2015). The aim of this study, therefore, is to explore the use of the Cd- and Zn-isotope composition of marine sediments as tracers for past environmental conditions related to the cycling of nutrients and/or ocean redox conditions. Studying both elements together,

rather than a single element, allows differences in their response to environmental changes to be compared and contrasted, and may provide more robust information. The Late Cretaceous Oceanic Anoxic Event 2 (OAE 2, Cenomanian–Turonian, ~ 94 Ma, Meyers et al., 2012) is taken as a case study here, as it represents one of the most extreme perturbations to the carbon cycle and ocean chemistry of the Phanerozoic Aeon. Importantly, it is a relatively well-studied event, for which plenty of core and outcrop material is available. This interval therefore allows assessing temporal, as well as spatial patterns, in Zn- and Cd-isotope compositions by analysis of marine sediments from various key localities.

Chapter 2 explores the use of marine carbonates as an archive for $\delta^{66}\text{Zn}$ values in relation to palaeoenvironmental perturbations during the Cenomanian–Turonian. A comparison of $\delta^{114}\text{Cd}$ values from two cores from within the same basin is presented in Chapter 3, which allows an assessment of local palaeoenvironmental effects on isotopic fractionation of Cd into marine mudrocks, as well as the reproducibility of mudrock-derived palaeoenvironmental signals. Chapter 4 is the first chapter to combine $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ analysis to compare and contrast stratigraphic trends for the two elements. The observations made in chapters 2–4 ultimately lead to reconstructions of global $\delta^{66}\text{Zn}_{\text{seawater}}$ variations, associated with ocean chemistry change during the OAE 2 interval in Chapter 5. Finally, Chapter 6 provides some concluding remarks and a perspective on future studies. More detailed background information on the OAE 2 interval, Zn- and Cd-isotope systematics, and analytical methods follows below.

1.2 Background information

1.2.1 Oceanic Anoxic Event 2

Mesozoic OAEs

Oceanic anoxic events (OAEs) in the Mesozoic Era are characterised by the widespread burial of organic-rich sediments and an excursion in the $\delta^{13}\text{C}$ stratigraphy (positive and/or negative) and are associated with a range of environmental and

geochemical change (e.g. Schlanger and Jenkyns, 1976; Jenkyns, 2010). These events vary in their spatial extent and degree of environmental perturbations. Three events with a truly global extent of black-shale deposition are recognised: the Early Jurassic Toarcian OAE (T-OAE, 183 Ma), the Early Cretaceous Early Aptian OAE (OAE 1a, 120 Ma), and the Late Cretaceous Cenomanian–Turonian OAE (OAE 2, ($\sim$ 94 Ma) (e.g. Figure 1.1A; Jenkyns, 2010; Robinson et al., 2017 and references therein).

OAE 2

OAE 2, of Late Cretaceous Cenomanian–Turonian age ($\sim$ 94 Ma), represents one of the most extreme and best-studied examples (Meyers et al., 2012). Large Igneous Province (LIP) volcanism is thought to have been the primary initial driver for the onset of the event, leading to ocean nutrification and global warming that would have stimulated the expansion of low-oxygen marine environments and burial of organic-rich sediments, amongst several other perturbations to ocean chemistry (e.g. Figure 1.1B; Forster et al., 2007; Turgeon and Creaser, 2008; Jenkyns, 2010). The widespread burial of photosynthetically-produced isotopically light planktonic carbon in organic-rich sediments is credited with causing a positive global carbon-isotope excursion in marine sediments associated with this event, which can also be used as correlative tool (e.g. Schlanger & Jenkyns, 1976; Scholle & Arthur, 1980; Tsikos et al., 2004; Jarvis et al., 2006). Depending on the definition of the event, the duration lies between 400,000 and 900,000 years (Sageman et al., 2006; Voigt et al., 2008; Meyers et al., 2012; Ma et al., 2014; Eldrett et al., 2014; Gambacorta et al., 2015).

Large Igneous Provinces and ocean nutrification

Large Igneous Province (LIP) volcanism is thought to be the main initial driver for the onset of processes associated with the OAE 2 interval (Adams et al., 2010; Jenkyns, 2010; Scaife et al., 2017). Os-isotope stratigraphy offers the most substantial evidence for this theory as an unradiogenic shift in Os-isotopes is found in many localities and pre-dates the onset of the positive C-isotope excursion, conventionally taken to define the beginning of the OAE (Turgeon & Creaser,

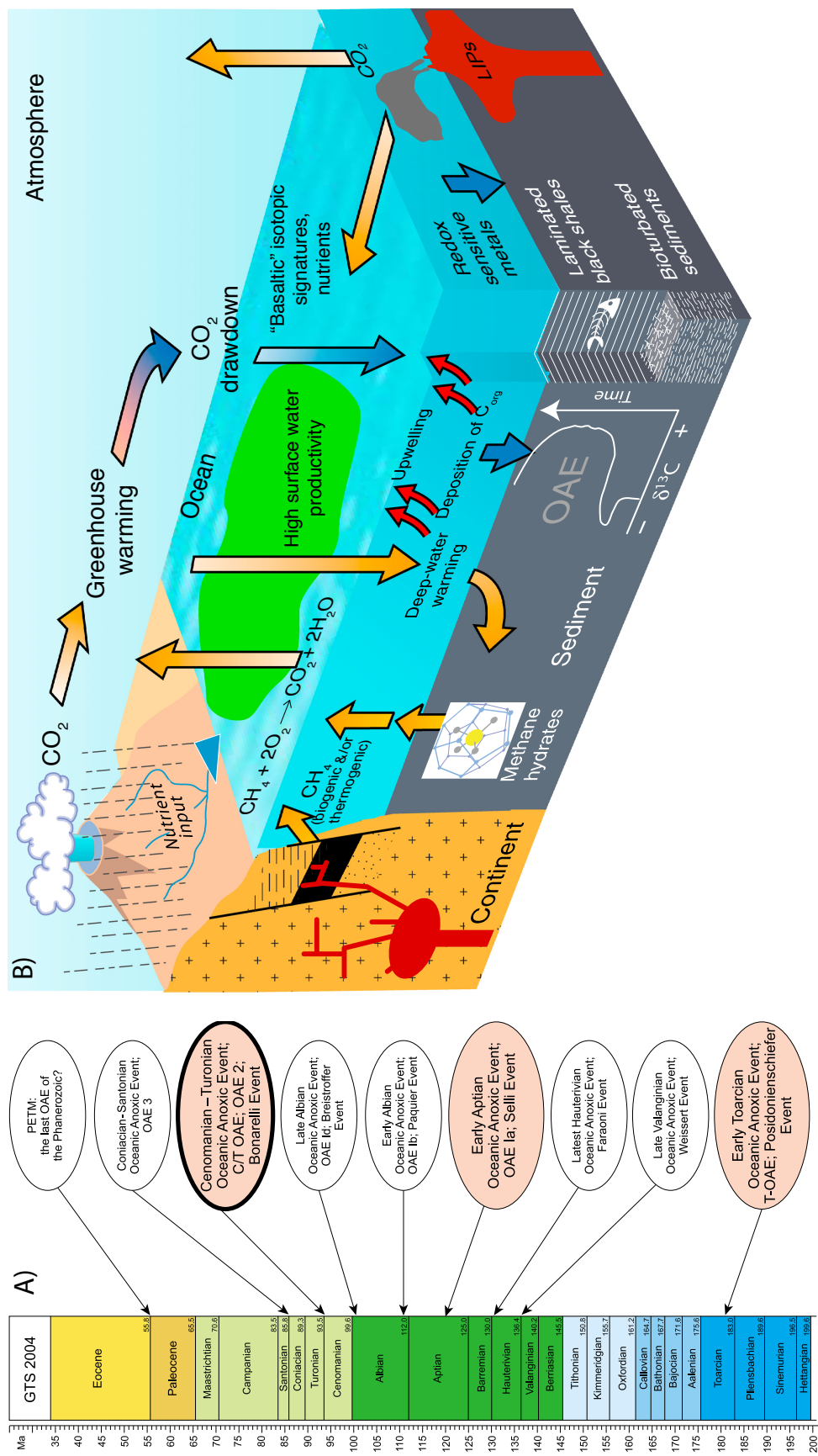


Figure 1.1: A) Stratigraphic occurrence of Mesozoic Oceanic Anoxic Events (figure from Jenkyns, 2010) B) Schematic diagram illustrating feedback mechanisms associated with OAEs. Figure by Robinson et al. (2017), modified from Jenkyns (2010).

2008; Du Vivier et al., 2014, 2015). The enhanced interaction between basalt and seawater as a result of a magmatic episode has likely led to enhanced input of various (trace) elements to the ocean, as evidenced by anomalies in trace metal abundances (Orth et al., 1993; Snow et al., 2005), thereby possibly providing more nutrient-rich conditions. Enhanced input of trace elements may have happened directly, by enhanced basalt–seawater interaction and/or indirectly through enhanced silicate weathering and/or an intensified hydrological cycle caused by the volcanically induced greenhouse warming (Jarvis et al., 2011; Pogge von Strandmann et al., 2013; Blättler et al., 2011; van Helmond et al., 2014; Jenkyns et al., 2017). Volcanically driven ocean nutrification provides an explanation for the nutrient-rich conditions required to drive and sustain the rates of organic-carbon burial and extent of marine anoxia found for the OAE 2 interval.

Geochemical models suggest that temperature alone is not able to reproduce observed patterns of marine deoxygenation, and higher primary productivity rates are needed to explain the degree of ocean redox change (Monteiro et al., 2012). The abundance of major elements phosphorus and nitrogen, which are needed to sustain such high primary productivity rates, may also be explained by changes in the internal ocean cycling of these elements, rather than enhanced input. Phosphorus may have been relatively abundant during the OAE 2 interval due to its regeneration and recycling from anoxic sediments (Van Cappellen & Ingall, 1994; Mort et al., 2007; Kraal et al., 2010). Increased fixation of nitrogen by abundant diazotrophic cyanobacteria utilising atmospheric di-nitrogen in nitrate-depleted seawater may explain the required supply of nitrogen (Kuypers et al., 2004).

However, the enhanced burial of some bio-essential trace elements under anoxic conditions, like Mo and Zn, may be expected to draw down the dissolved pool and decrease overall bio-availability in the world ocean (Hetzl et al., 2009; van Bentum et al., 2009; Owens et al., 2016). Thus, in contrast to the modern ocean, where these elements are normally not bio-limiting (Moore et al., 2013), such elements may have become bio-limiting during extreme deoxygenation in the Mesozoic Era. Enhanced nutrient input directly or indirectly driven by LIP volcanism can explain

abundant supply of trace elements needed for the primary productivity rates, but direct evidence for global ocean nutrification is sparse, mostly due to a lack of relevant proxies. The nutrient-like behaviour of Zn and Cd in the modern ocean suggests these elements may present suitable proxies for past nutrient conditions if such signals are recorded in the sediment.

Ocean anoxia during OAE 2

There is ample evidence for low-oxygen conditions during the OAE 2 interval, from many different sites based on a variety of sedimentological and geochemical evidence (e.g. Damsté & Köster, 1998; Kuypers et al., 2002; Turgeon & Brumsack, 2006; van Bentum et al., 2009; Hetzel et al., 2009; Jenkyns, 2010; Westermann et al., 2014; Poulton et al., 2015; Dickson et al., 2016; Dickson, 2017; Dickson et al., 2017; Owens et al., 2017, 2016). However, these studies generally provide qualitative information mainly focused on a single site. A more quantitative assessment of ocean redox changes on larger scales requires many of such studies to be combined and compared to the output of earth system models. Using Earth System model GENIE, this approach results in estimates for the dysoxic/anoxic ocean volume of >50 % (Monteiro et al., 2012). Alternatively, isotope-based tracers may be used for such estimates. Geochemical modelling using Mo-isotopes and S-isotopes have estimated the extent of seafloor euxinia during OAE 2 at respectively ~ 2 –10 and ~ 2.5 –5%, ~ 13 –67 times more than today (Owens et al., 2013; Dickson, 2017).

The Plenus Cold Event

Significantly, however, environmental conditions were not uniform during OAE 2. In particular, the Plenus Cold Event represents a period of cooling and was associated with major geochemical change (Gale & Christensen, 1996; Jenkyns et al., 2017). TEX₈₆ temperature reconstructions suggest a northern hemisphere cooling of ~ 2.5 –11°C during the Plenus Cold Event, relative to the extremely warm conditions found for the rest of the OAE 2 interval (Forster et al., 2007; Damsté et al., 2010; van Helmond et al., 2014, 2015; Jenkyns et al., 2017). This interval of cooling was associated with more oxygenated conditions, illustrated by

colonisation of formerly anoxic sea floors by benthonic organisms, and coincides with a slight dip in the C-isotope curve, which indicates a temporary drop in global organic-carbon burial rates (Tsikos et al., 2004; Jarvis et al., 2011; van Helmond et al., 2014; Jenkyns et al., 2017).

Trace-element anomalies found in carbonates from Plenus Cold Event interval have been associated with this episode of reoxygenation and related to the temporary loss of anoxic-euxinic sinks for redox-sensitive/chalcophilic elements supplied from mafic igneous sources (Jenkyns et al., 2017). Similar anomalies in trace elements and Cr-isotope stratigraphies from time-equivalent sections from the Western-Interior Seaway have also stressed some sort of mafic/volcanic influence without specific attribution to the changing redox conditions of the Plenus Cold Event (Eldrett et al., 2014; Holmden et al., 2016). Reconstructing the global impact of these more dynamic changes in ocean (redox) chemistry requires isotopic tracers with sufficiently short residence times, which so far are not well established. In summary, Cd and Zn isotopes have potential as proxies for more dynamic redox changes in the geological past due to their affinity for sulphides, and intermediate residence times, and are the focus of this thesis.

1.2.2 Zn and Cd systematics

In oxic waters Zn is mainly present in complexed forms with humic/fulvic acids and partly as soluble Zn^{2+} or ZnCl^+ ions; Zn in compounds or complex ions is only present as Zn(II) (e.g. Tribouvillard et al., 2006; Moynier et al., 2017, and references therein). Zn has five naturally occurring stable isotopes, ^{64}Zn (49.2%), ^{66}Zn (27.8%), ^{67}Zn (4.0%), ^{68}Zn (18.4%) and ^{70}Zn (0.6%). Zn-isotope compositions are reported relative to the ‘JMC-Lyon’ standard in the delta-notation as $\delta^{66}\text{Zn} = [^{66}/^{64}\text{Zn}_{\text{sample}}/^{66}/^{64}\text{Zn}_{\text{JMC-Lyon}}] - 1 \times 1000$. $\delta^{66}\text{Zn}$ values observed for natural Earth surface materials vary between ~ -1.0 and $+1.5$ ‰, with much of this range covered by modern ocean compositions (Moynier et al., 2017 and references therein).

Cd is present only as Cd(II) and present in the ocean as the CdCl^+ ion. The element is comprised of eight stable isotopes, namely ^{106}Cd (1.25%), ^{108}Cd (0.89%),

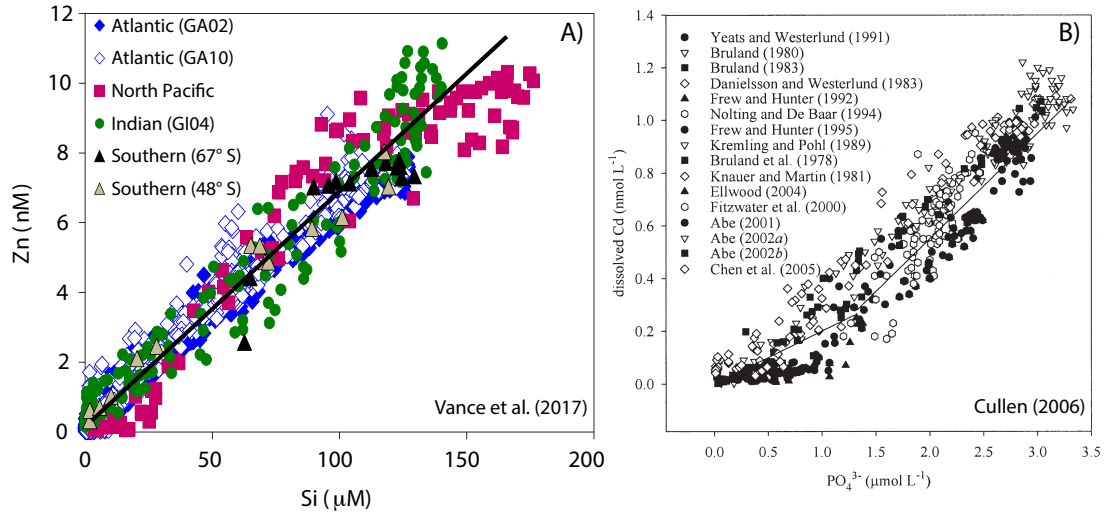


Figure 1.2: A) Zn-Si relationship for the global ocean, by Vance et al. (2017). B) Cd-phosphate relationship for the global ocean, by Cullen (2006)

^{110}Cd (12.49%), ^{111}Cd (12.80%), ^{112}Cd (24.13%), ^{113}Cd (12.22%), ^{114}Cd (28.73%), and ^{116}Cd (7.49%). Cd-isotope compositions are reported in the delta-notation relative to NIST-3108 as $\delta^{114}\text{Cd} = [^{114}/^{110}\text{Cd}_{\text{sample}}/^{114}/^{110}\text{Cd}_{\text{NIST}} - 1] \times 1000$. The Cd-isotope system is not as well characterised, but so far a $\delta^{114}\text{Cd}$ range of natural Earth surface materials of ~ -0.5 to $+5.0\text{‰}$ has been observed, of which most variability is based on (surface) ocean observations (Figures 1.3 and 1.7).

Zn and Cd distribution in the open ocean

Zn and Cd both show a nutrient-like distribution in the modern ocean with near-depleted dissolved concentrations near the surface and higher concentrations at depth, as a result of uptake and subsequent regeneration by primary producers (e.g. Bruland, 1980; de Baar et al., 1994; Baars et al., 2014; Wyatt et al., 2014). The main difference in distribution is a slightly deeper regeneration maximum for zinc, similar to the distribution of dissolved silicon, while Cd closely resembles phosphorus (Figure 1.2). This dissimilarity between Zn and Cd can be largely ascribed to the comparatively high Zn uptake by diatoms (e.g. Twining & Baines, 2013). Relatively high export of Zn and Si (compared to Cd and P) from surface to deeper waters in the diatom-dominated Southern Ocean impacts the ocean chemistry of more

northern waters as these signals are transported (Vance et al., 2017). The function of Zn as a bio-essential, and thereby potentially bio-limiting, micronutrient in several enzymes is well established (e.g. Moore et al., 2013). For Cd, a similar function has been suggested (Lane et al., 2005), though the large majority of Cd uptake by phytoplankton is thought to be non-specific due to the uptake with other divalent metals (Horner et al., 2013).

Zn and Cd isotope distribution in the open ocean

The isotopic composition of the deep ocean (>800m), away from continental margins and hydrothermal plumes, is homogenous for both elements (e.g. Figure 1.3). By contrast, dissolved surface-ocean isotopic compositions are highly variable and show very different patterns for the two elements. For cadmium, there is a strong vertical gradient going into the surface ocean with very heavy (up to $\sim 5\%$) Cd-isotope signatures in the Cd-depleted surface layer, which can be attributed to preferential biological uptake of light Cd (Ripperger et al., 2007; Abouchami et al., 2011; Xue et al., 2013; Conway & John, 2015). However, not all regions display such highly fractionated Cd-isotope compositions for Cd-deficient surface waters (Xie et al., 2017).

Zn-isotope patterns of the modern surface ocean are more complex and spatially diverse although surface-ocean compositions are lighter than the deep ocean (Bermin et al., 2006; Zhao et al., 2014; Conway & John, 2014). Scavenging of isotopically heavy zinc (John & Conway, 2014), the lateral or vertical advection of water masses (Vance et al., 2017), and biological uptake of Zn (John et al., 2007; Kobbereich & Vance, 2017) have been suggested to impact the surface ocean zinc(-isotope) cycling and may impose regional variations on the Zn-isotope composition of surface waters.

Culture studies on the biological uptake of Zn by marine diatoms have shown isotopically lighter cellular Zn (John et al., 2007) as well as values indistinguishable and isotopically heavier $\delta^{66}\text{Zn}$ values relative to growth medium (Köbberich and

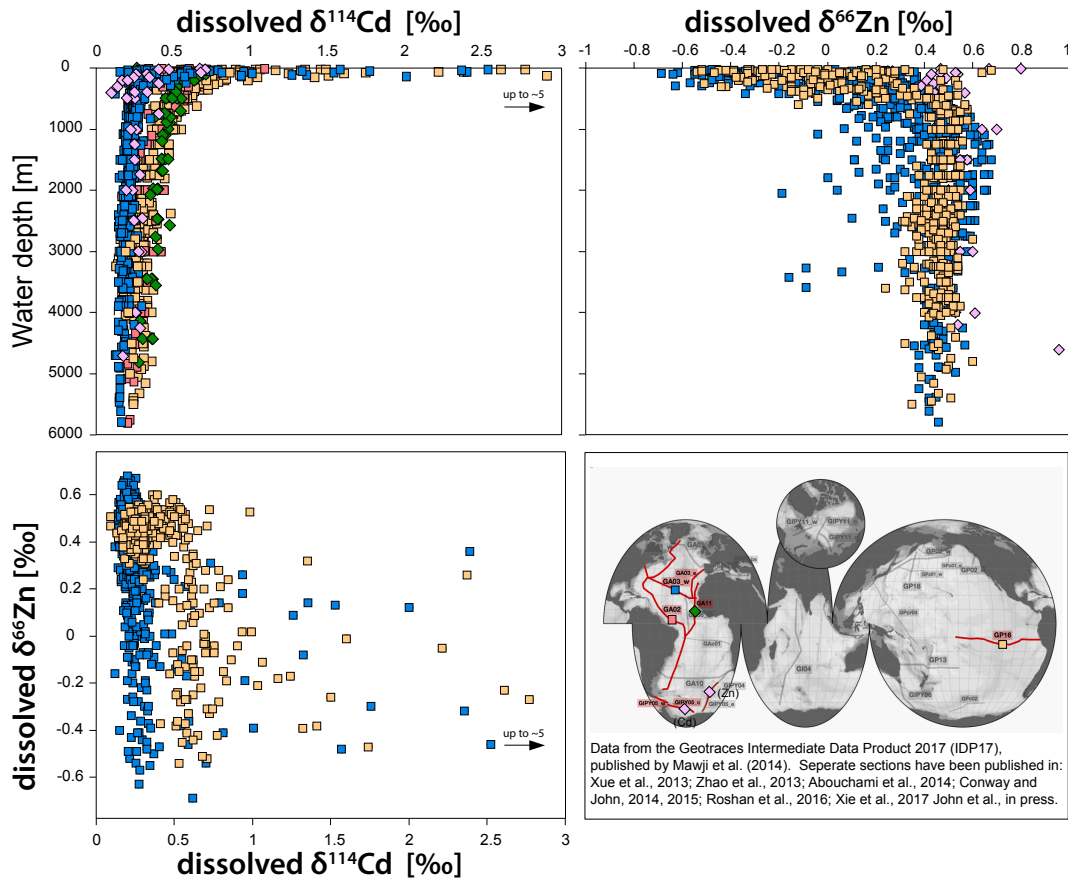


Figure 1.3: Dissolved $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions of the modern oceans. Locations and data sources provided in the bottom right panel.

Vance, 2017). The extent of Zn isotope fractionation by marine primary producers appears to be dependent on type/species of phytoplankton as well as other environmental factors such as the Fe and Zn concentrations.

Regardless of exact mechanisms, the physical, chemical and ecological characteristics of the modern ocean result in isotopically light $\delta^{66}\text{Zn}$ values in the surface relative to the deep ocean. However, patterns in dissolved $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ of past oceans may very well have been different due to different ocean characteristics. Overall, despite its impact on the internal recycling of dissolved Zn in seawater, the impact of biological uptake of Zn only seems to play a minor role on the long-term global isotopic mass balance of Zn, which instead may be more strongly controlled by the formation of sulphides (Vance et al., 2017).

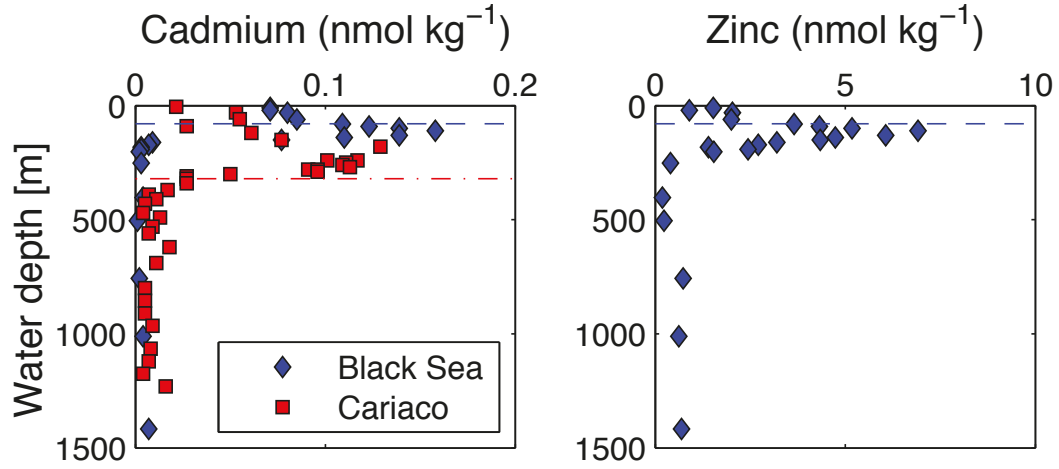


Figure 1.4: Dissolved Zn and Cd distributions in the Black Sea and Cariaco Basin. Figure from Little et al. (2015).

Zn and Cd abundances in organic-rich sediments and low oxygen environments

Equilibrium thermodynamics predicts both Zn and Cd form stable sulphides in the presence of free HS^- and appear to form their own sulphide phase, rather than being incorporated into pyrite (Al-Farawati & van den Berg, 1999; Morford & Emerson, 1999). Cd and Zn diffusing into pore waters, or released upon degradation of organic matter, therefore may be bound in the sediment after formation of insoluble sulphides. Low concentrations of Zn and Cd below the redoxcline in modern anoxic basins (Black Sea and Cariaco Basin) suggests sulphides may also be forming in the water column, acting as another major export mechanism to the sediment in addition to sinking organic matter (Jacobs et al., 1987; Tankere et al., 2001, Figure 1.4).

Organic-rich sediments from modern restricted marine basins and highly productive continental margin settings are often enriched in Zn and Cd (Figure 5). These enrichments may be due to high transport to the sediment as a result of high export productivity rates and/or high preservation (and possibly transport) due to sulphide formation in sulphidic (pore) waters. Cadmium is especially enriched as a result of higher $[\text{TM}]_{\text{seawater}}/[\text{TM}]_{\text{average shale}}$ ratios, increasing the potential for authigenic enrichment (e.g. Little et al., 2015). Cd abundances for the very highly productive Peruvian and Namibian Margins are unusually high, which is likely

related to high availability, export and preservation of Cd at these sites (Sweere et al., 2016). This in contrast to restricted basins like the Black Sea, where export productivity and trace metal supply are lower. The lack of sulphide availability in highly productive but more oxygenated settings like the Arabian Sea likely limits extreme Cd enrichment for these open ocean sites.

Zn and Cd isotopes in organic-rich sediments and low oxygen environments

Evidence from ab initio calculations (for Zn, Fujii, 2011) and experimental data (for Cd, Bryan et al., in prep a) suggest that the precipitation of sulphides is associated with the preferential uptake of the lighter isotopes for both Zn and Cd. Isotopically light CdS may form in the water column in open ocean oxygen-deficient zones, although evidence for such findings is not consistent with respect to the degree of oxygen depletion of the different study sites (Janssen et al., 2014; Conway & John, 2015, John et al., in press).

High $\delta^{66}\text{Zn}$ values of waters from below the chemocline in the highly restricted and euxinic Black Sea provide observational evidence that supports the preferential removal of isotopically light Zn in ZnS. Sediments from the deep Black Sea show $\delta^{66}\text{Zn}$ values ($\sim 0.50 \pm 0.08$ ‰, 2SD) indistinguishable from average dissolved ocean compositions due to near-quantitative removal in this basin. Cd concentration profiles for the Black Sea are highly similar to those of Zn (Tankere et al., 2001), which together with some first unpublished results on Black Sea sediments (Bryan et al., in prep. b) suggests Cd is also near-quantitatively removed in restricted euxinic basins. Furthermore, the $\delta^{114}\text{Cd}$ compositions of modern marine sediments from different redox regimes from the open ocean also approach that of overlying seawater if H_2S is present in pore waters, which suggests near-quantitative removal of Cd under such conditions (Bryan et al., in prep. b).

From the discussion above it follows that $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions of marine sediments may be isotopically lighter than overlying waters if Zn or Cd associated with sulphides or organic matter (for Cd) comprises a considerable proportion of the total sediment inventory, but only if removal in these phases

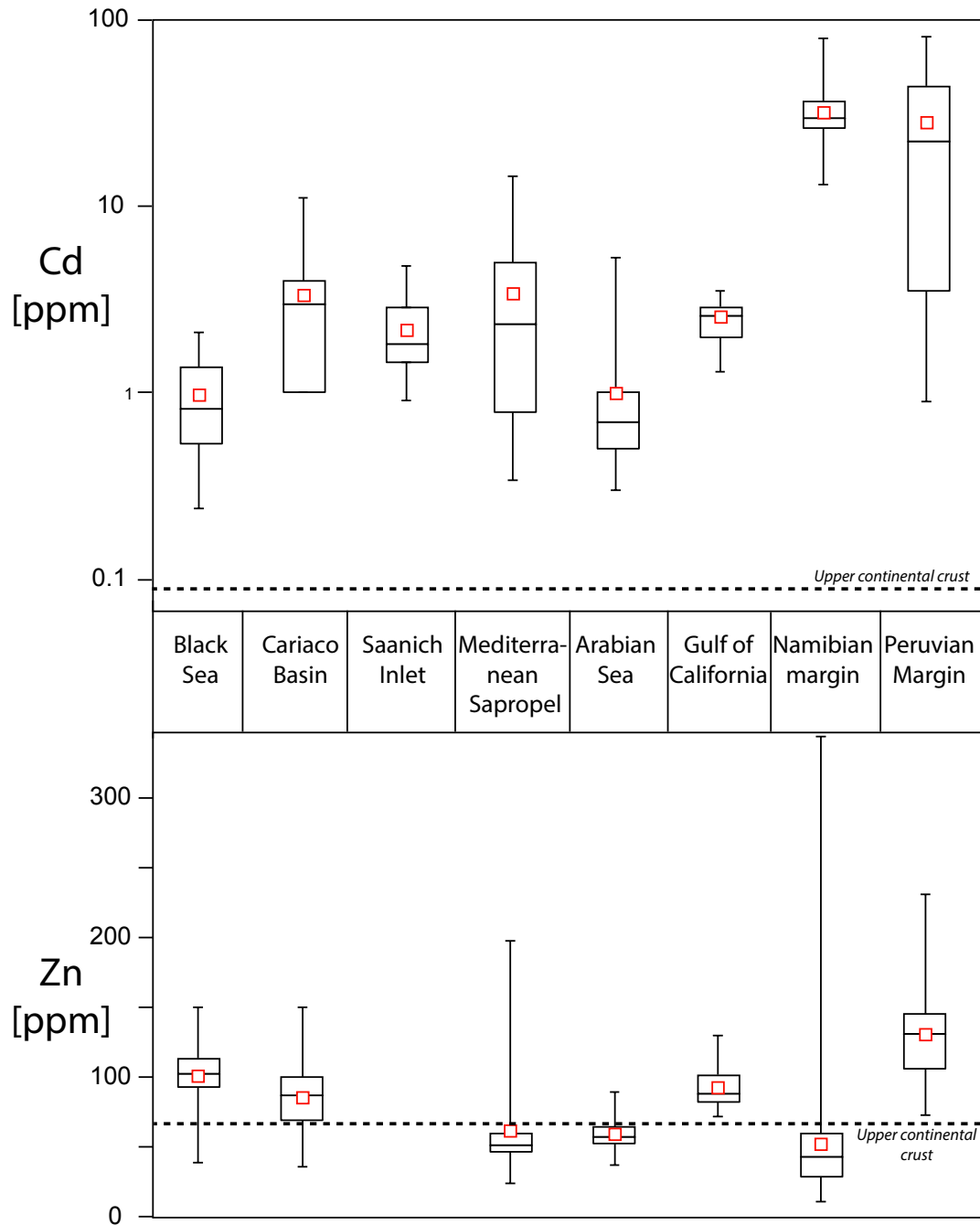


Figure 1.5: Zn and Cd concentrations in modern organic-rich ($\text{TOC} > 1\%$) marine sediments relative to average upper continental crust compositions (Rudnick & Gao, 2003). This data compilation was made as part MSc-thesis project at Utrecht University by the author and partly published in Sweere et al. (2016). Data from: Hirst (1974); Brongersma-Sanders et al. (1980); Brumsack (1989); Russell & Morford (2001); Piper & Dean (2002); Böning et al. (2004); Arnaboldi & Meyers (2006); van der Weijden et al. (2006) Hirst (1974); Brongersma-Sanders et al. (1980); Brumsack (1989); Russell and Morford (2001); Piper and Dean (2002); Hubner et al. (2003); Boning et al., (2004); Arnaboldi and Meyers (2006); Van der Weijden et al. (2006.)

from seawater is non-quantitative. For Zn, such sediments have been identified. Organic-rich margin sediments represent the main sink for isotopically light Zn and are -0.4 – -0.6‰ lighter than the average ocean value, likely due to non-quantitative removal in sulphides (Little et al., 2016).

Sediments from the Peruvian margin are an exception and, with average values of $\sim 0.3\text{‰}$, are only $\sim -0.2\text{‰}$ lighter than average ocean compositions. The Peru margin upwelling region is micronutrient-limited and represents more reducing conditions (ferruginous to anoxic) than most of the other organic-rich sediments that have a broader range in bottom-water oxygen contents (typically manganiferous to ferruginous). Zn has therefore likely undergone near-quantitative removal to the sediment in the Peru margin, which explains the heavier isotopic composition compared to other continental-margin sediments (Little et al., 2016).

The isotopic mass balance of Zn and Cd

An updated schematic diagram illustrating the global ocean isotopic mass balances for Zn and Cd are presented in Figure 1.6 (modified from Little et al., 2014). Figure 1.7, as updated and modified from Vance et al. (2016) summarises current knowledge on the isotopic composition Zn and Cd cycles, thereby providing some indication of errors associated with the numbers presented in Figure 1.6.

The average isotopic composition of dissolved Zn ($\sim 0.49 \pm 0.07\text{‰}$, 1 SD) and Cd ($\sim 0.38 \pm 0.07\text{‰}$, 1 SD) is isotopically heavier than known sources to the ocean (rivers, dust and hydrothermal) (data based on a compilation by John et al., 2017). Organic-rich margin sediments are so far the only documented sink for isotopically light Zn with an average isotope composition of $\sim 0.0\text{‰}$. All known open ocean sinks for Zn are isotopically heavier than input and average ocean compositions. Carbonate-rich sediments, Fe-Mn oxides, and siliceous sediments, remove isotopically heavy Zn and are on average $\sim +0.4\text{‰}$ relative to average ocean composition, though it should be noted this figure is based on glacial–interglacial carbonate sediments, which could imply possible temporal differences relative to the modern ocean (Pichat et al., 2003; Andersen et al., 2011; Little et al., 2014). Of these heavy sinks, Fe-Mn

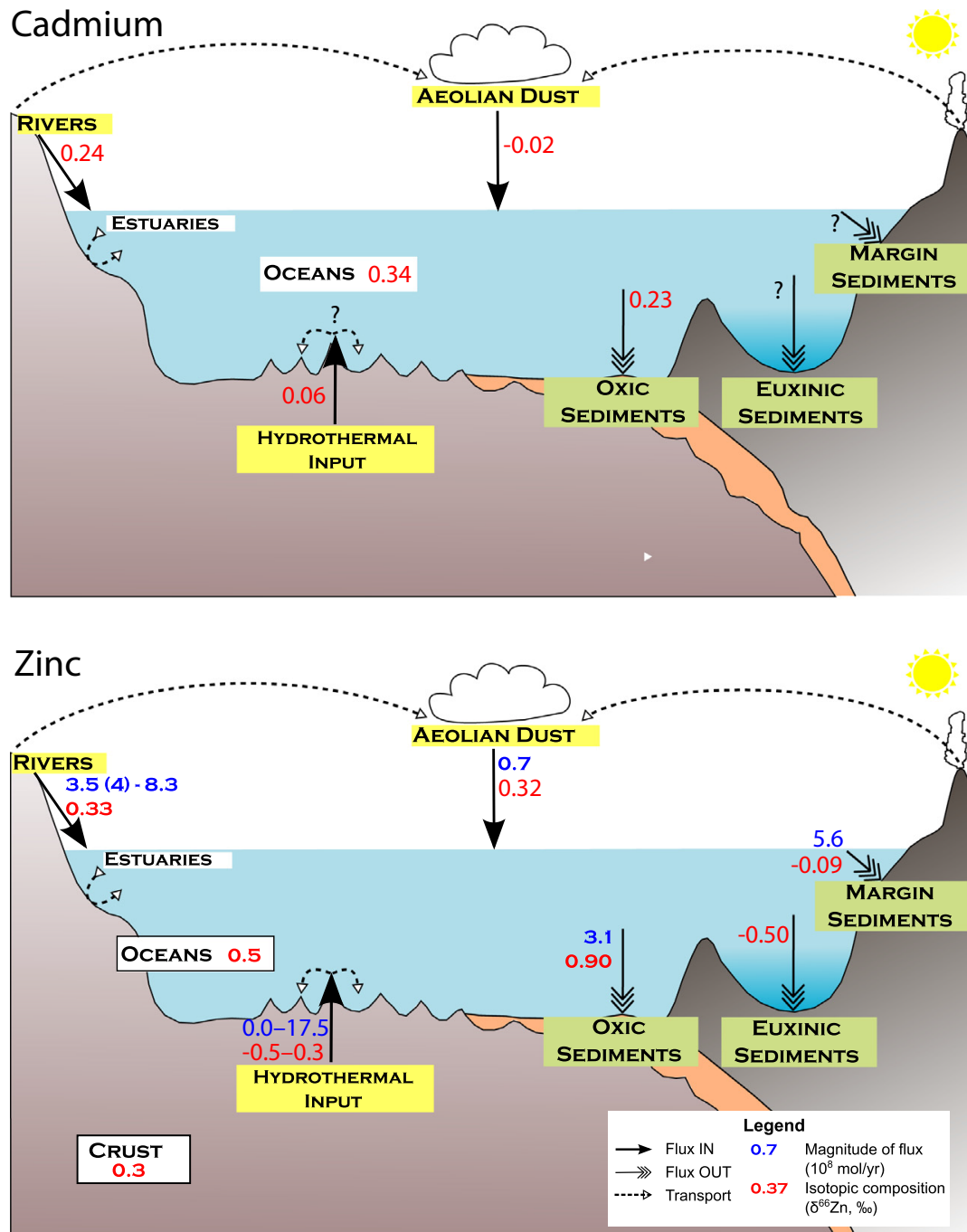


Figure 1.6: Schematic diagrams illustrating the global isotopic mass balance of Cd and Zn, updated from Little et al. (2014). Data sources for Zn in can be found in the original version (Little et al., 2014) and are updated with data from Little et al. (2016); Roshan et al. (2016); Vance et al. (2016). Data sources for Cd are Schmitt et al. (2009); Horner et al. (2010); Lambelet et al. (2013), as compiled by John et al. (2017). The Cd-isotope composition for the ocean is taken from the GEOTRACES intermediate data product 2017 (Mawji et al., 2015) as presented in Figure 1.3, and represents the average value of waters >800m water depth.

oxides are likely quantitatively most relevant, and are isotopically heavy as the result of sorption to (Fe-)Mn oxides (Little et al., 2015; Bryan et al., 2015).

Rivers constitute the primary source of Zn to the ocean with a weighted mean isotopic composition of 0.33‰ (Little et al., 2014). This figure is within error identical to average lithogenic Zn (0.27‰), and aeolian dust compositions (0.32‰); the latter is considered to be the second largest source of Zn to the ocean (Little et al., 2014). The flux of hydrothermal input of Zn is often considered to be small relative to these other ocean inputs, although recent evidence from the South Pacific Ocean has suggested such inputs are a substantial source of Zn to the modern ocean (Roshan et al., 2016). If correct, this would have a significant impact on previous estimates for the other fluxes and the residence time of Zn, which Roshan et al. (2016) estimate to be 3000 ± 600 years, considerably shorter than previous estimates (11,000 years, Little et al., 2014).

The isotopic composition of hydrothermal Zn input to the oceans is not very well constrained. Dissolved $\delta^{66}\text{Zn}$ analyses of waters from around the Mid-Atlantic Ridge suggests hydrothermal venting is a source of isotopically light Zn to the modern ocean, for which the hydrothermal end-member is estimated at -0.5‰ (Conway and John, 2014). Direct analysis of hydrothermal fluids reveals a range of values, which are largely isotopically lighter than the $\sim 0.3\text{‰}$ of input by rivers and dust (white smoker: 0.13 to 0.31‰, black smoker, 0.0 to 0.25‰, weighted mean: 0.24‰ John et al., 2008). Zn-sulphide formation may be responsible for the wide variety of values observed as it can cause heterogeneities in fluids analysed (John et al., 2008; Conway and John, 2014). Finally, there is localised evidence for (isotopically light) Zn input by remobilisation of Zn from margin sediments (Conway & John, 2014; Roshan & Wu, 2015), which are currently only considered to be a possibly minor source of Zn but are not very well constrained. The relative proportion of the different inputs and removal between the different marine sediments sets the average modern ocean composition to $\sim 0.5\text{‰}$ (e.g. Conway and John, 2014 or compilations by Vance et al., 2016; John et al., 2017).

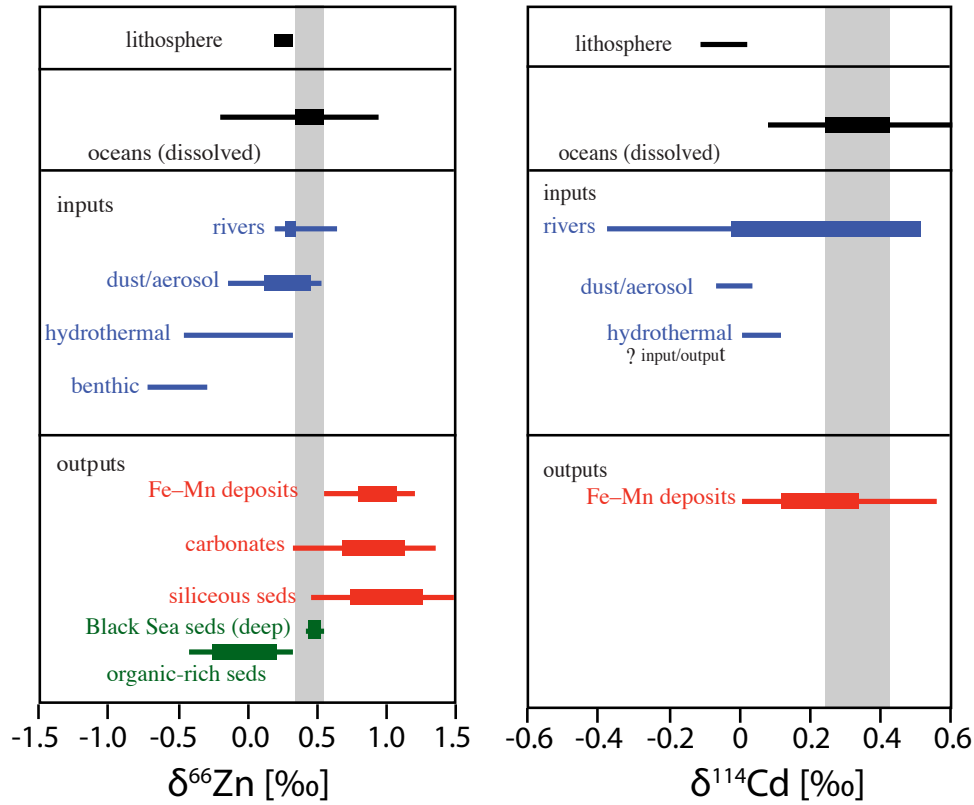


Figure 1.7: Summarised knowledge of Zn- and- Cd-isotope compositions in the marine environment, modified from Vance et al. (2016). Seawater data are presented as average data and 1 SD for all samples below 800 m by the thicker portions and the total range in the thinner line. For all other data, the full ranges are shown as thin lines while the thicker portions represent the average and 1 SD, except for the Zn river data where the thicker portions of the lines show the discharge- and concentration-weighted average isotope composition, thus representing the global dissolved riverine flux to the oceans. Zn data sources as presented by Vance et al. (2016), now including lithosphere from Little et al. (2014) and the ocean data is based on the GEOTRACES intermediate data product 2017 as presented in Figure 1.3 (Mawji et al., 2015). Cd data as compiled by John et al. (2017) and based on data from Schmitt et al. (2009), Horner et al., (2010), Lambelet et al. (2013) apart from the seawater data, which is from the GEOTRACES intermediate data product 2017.

With only a few studies available, the Cd-isotope composition of ocean inputs and outputs are not very well constrained. The average lithosphere ($\sim -0.04\text{‰}$), and riverine ($\sim 0.24\text{‰}$), aeolian ($\sim -0.02\text{‰}$) and hydrothermal ($\sim 0.06\text{‰}$) inputs to the ocean (Schmitt et al., 2009; Lambelet et al., 2013) are all isotopically lighter than the average dissolved modern ocean composition of 0.38‰ (compilation by John et al., 2017). However, in contrast to Zn, hydrothermal vents appear to be a (minor) sink for isotopically light Cd as observed by analysis of dissolved [Cd] and $\delta^{114}\text{Cd}$ of waters around hydrothermal vents (Conway and John, 2015). Fe-Mn crusts are not associated with significant isotope fractionation and record (deep) seawater isotope compositions, and therefore do not likely represent a significant sink for isotopically light Cd, although average $\delta^{114}\text{Cd}$ compositions for Fe-Mn sediments are slightly lighter ($\sim 0.23\text{‰}$) than the average ocean composition (Schmitt et al., 2009; Horner et al., 2010; John et al., 2017). Organic-rich sediments may represent an isotopically light sink for Cd, as is the case for Zn, although this sink has not yet been geochemically characterised in the modern ocean.

With residence times of $\sim 3,000\text{--}11,000$ years (Little et al., 2014; Roshan et al., 2016) and $\sim 50,000$ years (Bruland, 1980) for Zn and Cd, respectively, these elements have the potential to trace rapid global perturbations to micronutrient cycles and redox conditions.

Hypothetical controls on the Zn- and Cd-isotope compositions of the sedimentary record

To summarise, based on current knowledge the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ composition of the sedimentary record may be impacted by 1) changes in the global isotopic mass balance, which would impact average seawater compositions globally; 2) local and regional heterogeneities in global ocean chemistry related to biological cycling and water mass advection that control the isotope composition of waters locally; 3) isotopic fractionation between dissolved and solid-phase Zn and Cd that is exported to the sediment; 4) (early) diagenetic processes that may alter the primary isotope composition of material that reaches the sediment-water interface.

Global changes in the $\delta^{66}\text{Zn}$ of seawater may be caused by changes in the relative proportion of ocean outputs or inputs. Regarding ocean inputs, likely only dramatic changes in the balance between hydrothermal and riverine inputs may significantly alter steady state average ocean compositions, but only if $\delta^{66}\text{Zn}$ values for hydrothermal input are significantly lower than the riverine input. A change in the relative proportion of ocean outputs is more likely, particularly for the Cenomanian–Turonian where dramatic changes in ocean chemistry have been recognised. Ocean (de-)oxygenation would impact global ocean isotope compositions by altering the relative proportion of oxic and organic-rich sediment sinks for Zn. The different sources and sinks for Cd are not established well enough to provide similar projections.

Varying circulation patterns, the hydrographic configuration, local inputs of Cd and Zn, biological activity, scavenging and adsorption processes, and the precipitation of sulphides in the water column may all impact the isotope composition of waters on local to regional scales. For organic-rich mudrocks transport of Zn and Cd to the sediment likely predominantly occurs as part of sinking organic material and in some cases as sulphide precipitates. Isotope fractionation of the exported material relative to overlying seawater will only be observed if removal is non-quantitative. It is unclear how scavenging/adsorption to sinking organic material would impact the isotope composition of the sedimentary records. The impact of scavenging on sedimentary isotope compositions will likely depend at least partly on whether isotopically heavy Zn, adsorbed to sinking organic material (John and Conway, 2014), reaches the sediment-water interface, which is presumably more likely in more deoxygenated conditions. If scavenged Zn does not reach the sediment-water interface, the main impact of scavenging would be that it leaves the surface ocean, and thus the source for biologically exported Zn, isotopically light (John et al., 2017).

The isotopic composition of material that reaches the sediment-water interface may be altered after deposition, particularly if porewater redox gradients below the sediment-water interface are steep. Oxidation of organic material may release Zn and Cd to porewaters, while sulphidic pore waters might encourage the formation

isotopically light Zn and Cd-sulfides. If this process is non-quantitative, the isotopic composition of the sediment ends up being lighter than that of initially deposited material. This process has been used to explain isotopically light Zn compositions of organic-rich margin sediments (Little et al., 2016).

Thermal maturation of organic-rich mudrocks and associated hydrocarbon generation may be hypothesized to impact primary isotope signatures if it is accompanied by the expulsion of Cd and Zn-rich organic fluids. First results on mudrocks with varying thermal maturities suggests primary $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ signals are unaffected by hydrocarbon generation (Dickson et al., in prep; Dickson, Sweere et al., in prep.). The impact of thermal maturation will therefore not be further discussed in this study.

1.2.3 Analytical methods

Sample preparation

Carbonate rocks Samples were selected based on visual inspection and available data (e.g. %TOC, % insoluble, elemental abundances) to minimise contribution from any non-carbonate sources of Zn, and crushed using an agate pestle and mortar. A leaching procedure similar to previously established methods was used to preferentially dissolve the carbonate fraction for these samples (Pichat et al., 2003; Kunzmann et al., 2013; Liu et al., 2017). 0.5–1 g of crushed material was treated with 1M KCl and then rinsed and sonicated in Milli-Q ultrapure water to remove the exchangeable fraction (Tessier et al., 1979). The carbonate phase was selectively dissolved using 0.5M cold acetic acid, which was added slowly in 0.5 ml aliquots to allow the dissolving carbonate to act as a pH buffer. After centrifugation to remove undissolved phases, an aliquot of the supernatant was taken to be analysed for Zn abundances on a ThermoFisher ELEMENT 2 ICP-MS or, using isotope dilution, on a MC-ICP-MS at the University of Oxford. Another aliquot was then spiked with a ^{67}Zn - ^{64}Zn double spike to obtain a spike:sample ratio of ~ 1.4 (Rudge et al., 2009).

Organic-rich sediments Samples were crushed using an agate pestle and mortar and subsequently treated with inverse aqua regia (iAR, 3 parts HNO₃, 1 part HCl) for partial shale digestion. This method has been shown to preferentially dissolve authigenic shale components but leaves some detrital minerals intact (Xu et al., 2012), and has been successfully used in a previous Cd-isotope study on shales (Georgiev et al., 2015). Where concentration data was available, crushed samples were spiked prior to digestion. For Cd, a ¹¹¹Cd-¹¹³Cd double spike was added appropriately to obtain a spike:sample ratio of 1. For Zn, a ⁶⁷Zn-⁶⁴Zn double spike was added to obtain a spike:sample ratio of ~1.4. When no concentration data was available prior to digestion un-spiked samples were digested, after which an aliquot of the digested sample was taken to be analysed by ICP-MS for elemental abundances. Different aliquots were then spiked appropriately with ⁶⁷Zn-⁶⁴Zn or ¹¹¹Cd-¹¹³Cd double spikes and subsequently prepared for separation from major element cations and interferences by anion column chromatography.

Anion column chromatography

Zn and Cd were separated from matrix and isobaric interferences in a two-stage column chromatography procedure using AG1X-8 anion exchange resin (200–400 mesh) loaded onto Biorad and shrink-fit Teflon columns with resin beds of 2 mL and 200 μ L respectively. A summary of the procedure can be found in Figure 1.8. All chemistry was done in Teflon using distilled acids.

Stable-isotope analysis

Zinc Stable-isotope measurements were performed using a Nu Plasma MC-ICP-MS in medium-resolution mode, on 120 ppb (spike plus sample) Zn solutions. Zn-isotope compositions were measured relative to the IRMM 3702 standard (Moeller et al., 2012) and then expressed relative to AA-ETH Zürich Zn +0.28 ‰, as suggested by Archer et al. (2017), as AA-ETH Zürich Zn and IRMM 3702 are isotopically indistinguishable. $\delta^{66}\text{Zn} = ([^{66/64}\text{Zn}_{\text{sample}}/^{66/64}\text{Zn}_{\text{IRMM}}]-1)*1000 + 0.28$. Data reduction was done offline using isotopes ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, and ⁶⁸Zn, whereas

1 st stage for Cd: 2mL AG1X-8 anion exchange resin (200–400 mesh)			
Eluent	Quantity (mL)	Purpose	
7.5 M HNO ₃	10	resin cleaning	
MQ Ultrapure water	2	rinse	
6 M HCl	10	resin cleaning	
1 M HCl	30	resin cleaning	
1 M HF / 0.5 M HCl	6	resin conditioning	
1 M HF / 0.5 M HCl	6	elute matrix (In)	
(sample solution)			
1 M HF / 0.5 M HCl	8	elute matrix (majors, In)	
4 M HCl	8	elute matrix (Zr)	
0.5 M HF / 0.1 M HBr	12	elute matrix (Zn)	
3 M HNO ₃ / 0.1 M HBr	12	elute matrix (Mo, Sn)	
3 M HNO ₃	7	elute Cd	
2 nd stage for Cd and 1 st and 2 nd stage for Zn: 0.2mL AG1X-8 anion exchange resin (200–400 mesh)			
Eluent	Quantity (mL)	Purpose	
7.5 M HNO ₃	1	resin cleaning	
MQ Ultrapure water	0.2	rinse	
6 M HCl	1	resin cleaning	
1 M HCl	3	resin cleaning	
1 M HF / 0.5 M HCl	0.6	resin conditioning	
1 M HF / 0.5 M HCl	0.6	elute matrix (In)	
(sample solution)			
1 M HF / 0.5 M HCl	1.2	elute matrix (majors, In)	
4 M HCl	1	elute matrix (Zr)	
0.5 M HF / 0.1 M HBr	2.2	elute Zn	
3 M HNO ₃ / 0.1 M HBr	1	elute matrix (Mo, Sn)	
3 M HNO ₃	1	elute Cd	

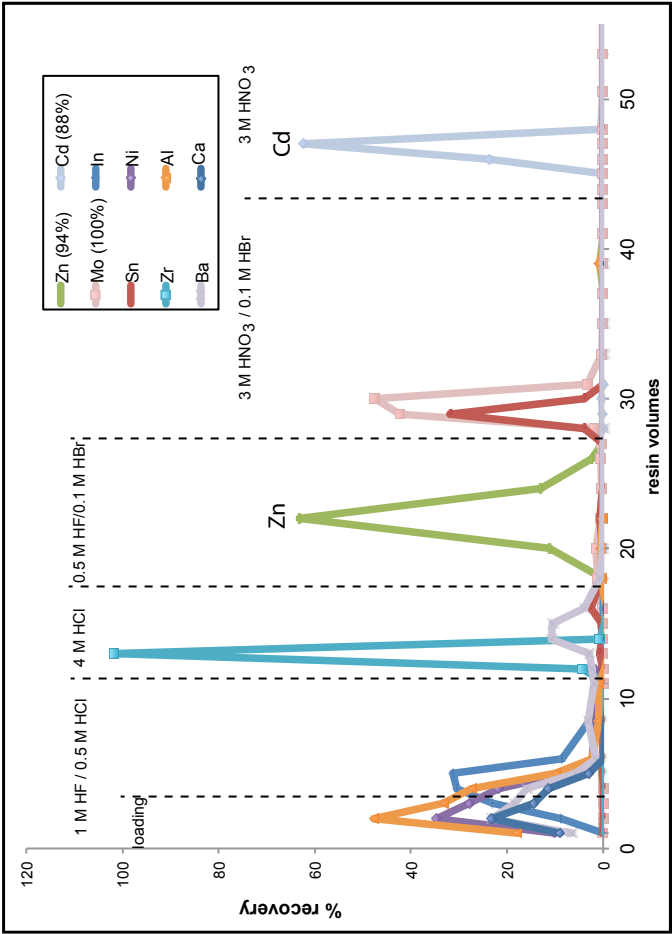


Figure 1.8: Anion column chromatography

masses 62 and 69 were monitored for possible interferences by Ni and Ba. Error bars represent the propagated uncertainties based on 2 standard errors of the counting statistics and reproducibility of bracketing standards. External reproducibility was estimated by analysis of carbonate reference material BCS-CRM 393 (ECRM 752-1) with a $\delta^{66}\text{Zn}$ composition of $0.75 \pm 0.09 \text{ ‰}$ (2 SD, $n = 4$), shale reference material SDO-1 with a composition of $\delta^{66}\text{Zn}_{\text{SDO-1}} = 0.43 \pm 0.07 \text{ ‰}$ (2 SD, $n=9$), and secondary isotope standard ‘London Zn’ with a $\delta^{66}\text{Zn}$ of $0.09 \pm 0.08 \text{ ‰}$ (2 SD, $n = 19$), which is in agreement with published values (Moeller et al., 2012). Procedural blanks were determined per batch using isotope dilution and were always $<2 \text{ ng}$ ($n = 22$), which is $<1 \text{ ‰}$ of all Zn processed.

Cadmium Stable-isotope analyses were performed on a Nu Instruments Nu Plasma multi-collector ICP-MS at the University of Oxford. Samples were measured at 50ppb (spike plus sample) concentrations and were bracketed by a spiked NIST-3108 solution to correct for instrumental drift. Data were processed offline using an exponential mass-bias correction and including a correction for Sn interference. Isotopes ^{111}Cd , ^{112}Cd , ^{113}Cd , and ^{114}Cd are used to calculate the isotope compositions, which are expressed in the delta-notation relative to NIST-3108 as $\delta^{114}\text{Cd} = [^{114}/^{110}\text{Cd}_{\text{sample}}/^{114}/^{110}\text{Cd}_{\text{NIST}} - 1] \times 1000$. Internal errors are propagated from the reproducibility of the bracketing standards and the counting statistics of each sample analysis. External reproducibility and accuracy of Cd-isotope analysis were estimated by analysis of pure Cd-isotope standards ‘OxCad’ ($-0.86 \pm 0.05 \text{ ‰}$, 2 SD, $n=15$); ‘Alpha Cd Zurich’ ($-0.01 \pm 0.06 \text{ ‰}$, 2 SD, $n=8$); ‘BAM I012’ ($-1.31 \pm 0.07 \text{ ‰}$, 2 SD, $n=7$), which are in agreement with previously published values Abouchami et al. (2013). The analysis of rock standard SDO-1 ($0.13 \pm 0.06 \text{ ‰}$, 2 SD, $n=5$), for which different aliquots were processed in different batches provides the quoted external reproducibility.

2

Isotopic evidence for changes in the Zn cycle during OAE 2

Contents

2.1	Abstract	26
2.2	Introduction	27
2.2.1	Zn-isotope systematics	28
2.3	Material and Methods	30
2.3.1	Analytical Methods	30
2.4	Results	31
2.5	Discussion	32
2.5.1	Contribution of Zn from detrital minerals	32
2.5.2	Carbonates as an archive for $\delta^{66}\text{Zn}$	33
2.5.3	Surface-ocean processes and spatial patterns	33
2.5.4	Zn-cycle perturbation in relation to a magmatic episode	
–Event A		34
2.5.5	Zinc-cycle perturbation during the Plenus Cold Event	
–Event B		36
2.6	Conclusion	37

2.1 Abstract

Widespread deposition of organic-rich shales during the Late Cretaceous Oceanic Anoxic Event 2 (OAE 2, ~ 94 Ma) occurred during a period of significant global palaeoenvironmental and geochemical change. An increase in nutrient input to the

ocean during OAE 2 is a key mechanism proposed to have generated and sustained high rates of organic-matter burial over timescales of 10^3 – 10^5 years. Zinc is a bio-essential micronutrient and its isotopic composition in seawater can be traced using marine carbonates. The first zinc-isotope records dating from the Cretaceous are presented here from three coeval carbonate successions: two from Europe (southern England and southern Italy) and one from Central America (southern Mexico). The new data demonstrate two significant changes in the oceanic zinc cycle coincident with shifts in environmental conditions during OAE 2. These Zn-isotope excursions can be linked to the input of magmatic zinc, changes in its burial rate into organic-rich sediments, and/or the liberation of previously buried zinc during an episode of widespread seafloor re-oxygenation during OAE 2 (the Plenus Cold Event). The observed changes in the zinc cycle during the Plenus Cold Event may be related to the nutrification of the surface ocean and the extinction of large benthic foraminifera in shallow-marine carbonate settings.

2.2 Introduction

Several distinct intervals of widespread deposition of organic-rich black shales occurred during some of the most extreme perturbations to global climate and oceanography of the Phanerozoic Eon. Mesozoic Oceanic Anoxic Events (OAEs) have been associated with rapid warming, the spread of low-oxygen marine environments and perturbations to floral and faunal diversity and biogeochemical cycles (e.g. Leckie et al., 2002; Jenkyns, 2003; Erba, 2004; Owens et al., 2016; Dickson, 2017).

For the Late Cretaceous OAE 2 (Cenomanian–Turonian, ~ 94 Ma), initiation and maintenance of high rates of organic-matter production would have required an increase in oceanic nutrient inventories, as implied by geochemical models (Monteiro et al., 2012). Indeed, proxy evidence suggests that widespread volcanism may have caused an increased supply of nutrients to the ocean, either through basalt–seawater interaction, and/or indirectly by warming-induced intensification of (silicate) weathering of mafic and felsic rocks and an intensified hydrological cycle (e.g. Pogge von Strandmann et al., 2013; Du Vivier et al., 2015; Jenkyns et al.,

2017). Although these observations constitute evidence for potential changes in nutrient inventories, direct evidence for the availability of bio-limiting nutrients in the oceans is currently limited, largely due to a lack of applicable proxies.

Bio-availability of trace metals may be particularly important during OAEs, because the major nutrients phosphorus and nitrogen are thought to have been relatively abundant due to regeneration of the former from anoxic sediments (Mort et al. 2007 and references therein) and increased fixation of the latter by abundant diazotrophic cyanobacteria utilizing atmospheric di-nitrogen in nitrate-depleted seawater (Kuypers et al., 2004). Extensive burial of organic matter during OAEs may therefore have triggered a biotic response as redox-sensitive bio-limiting metals were removed from global seawater (e.g. Owens et al., 2016). Assessing the importance of feedback mechanisms between trace-metal availability, biotic response, and the carbon cycle requires proxies for trace-metal availability in seawater. During times of major global change, such as the OAEs, proxies that enable reconstruction of nutrient supply at a regional or global scale are particularly valuable. Zinc isotopes in marine carbonates have the potential to track Zn inventory changes in the ocean and the balance between different sources and sinks of the element to and from the global ocean.

2.2.1 Zn-isotope systematics

Although not limiting to overall productivity in the modern ocean, Zn is fundamental for many life processes and its concentration is reduced to near zero values by biological activity in the surface ocean (e.g Wyatt et al 2014). Zn has a present-day oceanic residence time of $\sim 11,000$ years (Little et al., 2014). The Zn-isotope composition of today’s deep ocean is homogeneous ($\delta^{66}\text{Zn} = \sim 0.5 \text{ ‰} \pm 0.14$; 2 SD, Conway and John, 2014) and is isotopically heavier than the bulk silicate Earth ($0.28 \text{ ‰} \pm 0.05$) and than sources of Zn to the ocean such as rivers, dust, hydrothermal springs, and benthic inputs ($\sim 0.2\text{--}0.4\text{‰}$) (Little et al., 2014; Vance et al., 2016 and references therein). Reported oxic sinks of Zn (e.g. Fe-Mn oxyhydroxides) are isotopically heavier than input and deep-ocean values ($\delta^{66}\text{Zn} > \sim 0.5$) (e.g. Little

et al., 2014). Organic-rich continental-margin sediments and sediments in euxinic basins are so far the only documented sinks of isotopically light Zn, probably due to a relatively high proportion of the lighter isotope residing in organic matter and sulfides (Little et al., 2016; Vance et al., 2016).

Alteration of the input and output fluxes of Zn to and from the ocean in concert with global environmental changes might thus be expected to have impacted on the oceanic cycling of Zn. An increased removal flux of Zn from seawater into organic-rich sediments would lower Zn concentrations in global seawater and cause a shift towards an isotopically heavier Zn-isotope composition in the global ocean, as observed locally within the modern water column of the Black Sea (Vance et al., 2016). There are several processes that might lead to the opposite – a lighter zinc isotope composition of seawater. These processes include: a decrease in output fluxes into organic-rich sediments; an increase in removal fluxes of isotopically heavy Zn into oxic sediments; a relative increase in input of hydrothermally or volcanically derived isotopically light Zn; and the remobilization of Zn buried in organic-rich sediments back into seawater.

Modern surface-ocean $\delta^{66}\text{Zn}$ values are generally lower than the deep ocean by $\sim 0.5\text{‰}$, but show a high degree of spatial variability ($\delta^{66}\text{Zn} = -1.1$ to $+0.9\text{‰}$, Conway and John, 2014). These variations are likely caused by biological uptake of isotopically light Zn, scavenging of isotopically heavy Zn, and/or the lateral or vertical advection of water masses (Conway and John, 2014; Vance et al., 2017).

Pelagic and shallow-water carbonates have previously been used to reconstruct upper-ocean Zn-isotope compositions for intervals of Quaternary, Neoproterozoic, and Late Permian–Early Triassic time (Pichat et al., 2003; Kunzmann et al., 2013; Liu et al., 2017). The use of such deposits as archives for past seawater chemistry requires consideration of Zn-isotope effects caused by the balance of inputs and outputs to the local upper-ocean, superimposed on slower changes in the global mass balance of Zn that might lead to changes in homogenous deep water composition.

2.3 Material and Methods

Zn-isotope data are presented for three marine carbonate successions that span the Cenomanian–Turonian boundary interval: the nannofossil-rich pelagic English chalk exposed near Eastbourne, southern England, and shallow-water platform carbonates exposed near Raia del Pedale, Southern Apennines, Italy, and the Barranca el Canon section in the state of Guerrero, southern Mexico (Figure 2.1). The Eastbourne chalk, primarily comprising coccoliths and planktonic foraminifera formed in the photic zone, was largely deposited in waters that locally may have been as deep as 600m (Hancock, 1975). The platform carbonates found at the other two locations are primarily formed from skeletal carbonates in shallower waters (i.e., a few tens of meters or less). The well-studied Eastbourne locality is used as the primary dataset here because it has a stratigraphically expanded and well-documented OAE 2 succession, containing sediments with little diagenetic alteration and relatively low amounts of detrital and/or organic matter (Tsikos et al., 2004). The other two outcrops have well-established carbon-isotope and/or bio-stratigraphic profiles that allow direct comparison with the Eastbourne succession (Parente et al., 2008; Elrick et al., 2009; Jenkyns et al., 2017), but are less ideal geochemical archives due to their more variable original carbonate mineralogy (aragonite and calcite) and greater degree of lithification.

2.3.1 Analytical Methods

Full details of analytical methods are provided in Chapter 1. Zn-isotope data were measured on carbonates that were selectively leached from bulk rocks. Leachates were mixed with a ^{67}Zn - ^{64}Zn double-spike followed by purification of Zn by anion-exchange chromatography and then measured using a Nu Plasma MC-ICP-MS at the University of Oxford. Values are reported in the δ -notation (parts per thousand deviation from the value of a standard, see SI). Zn-isotope compositions were measured relative to the IRMM 3702 standard and reported after adding +0.28‰ to make values directly comparable to the 'JMC-Lyon' Zn standard, which allows direct

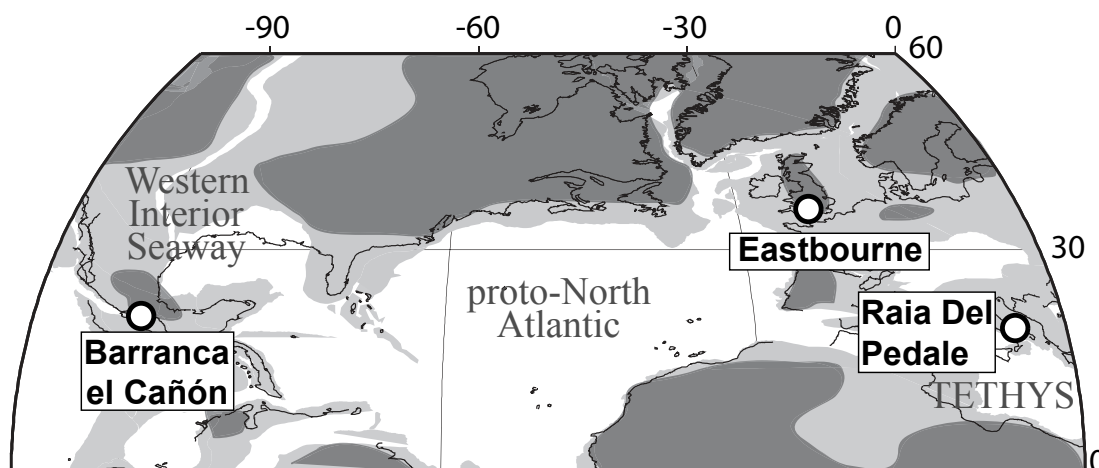


Figure 2.1: Paleogeographical reconstruction for the Cenomanian–Turonian boundary interval, modified from Owens et al. (2013) with approximate sample locations. Dark grey indicates landmasses; light grey represents shallow-marine settings; and white corresponds to deep-marine settings.

comparison with previously published Zn-isotope values. External reproducibility was estimated by analysis of carbonate reference material BCS-CRM 393 (ECRM 752-1) and a pure zinc solution ‘London Zn.’ For ECRM 752-1, four aliquots were processed through the complete leaching and purification procedure. These standards gave a $\delta^{66}\text{Zn}$ composition of $0.75 \pm 0.09 \text{ ‰}$ (2 SD, $n = 4$). ‘London Zn’ gave a $\delta^{66}\text{Zn}$ of $0.09 \pm 0.08 \text{ ‰}$ (2 SD, $n = 19$), which is in agreement with published values (Moeller et al., 2012). Zn/Ca ratios are based on ICP-MS analysis of a different set of leaches on a larger sample-set (Eastbourne and Barranca el Cañón) or a combination of ICP-MS and isotope dilution (MC-ICP-MS) data (Raia del Pedale).

2.4 Results

$\delta^{66}\text{Zn}$ values average $1.06 \pm 0.38 \text{ ‰}$ (2 s.d., $n=28$), $1.14 \pm 0.51 \text{ ‰}$ (2 s.d., $n=22$), and $0.89 \pm 0.49 \text{ ‰}$ (2 s.d., $n=14$) for the Eastbourne, Raia del Pedale and Barranca el Cañón datasets respectively (Fig. 3), and are comparable to data from other palaeoenvironmental studies on biogenic carbonates ($\sim 0.91\text{‰}$, Pichat et al., 2003; $\sim 0.75\text{‰}$, Liu et al., 2017). The most striking features of the primary Eastbourne data are two $\sim 0.5\text{‰}$ shifts towards lighter $\delta^{66}\text{Zn}$ values, marked ‘A’ and ‘B’ in Figure 2.2, separated by an increase towards heavier values. A similar shift to light

$\delta^{66}\text{Zn}$ is also seen in the Raia del Pedale data at Event B. Isotope data from Barranca el Cañón are too sparse and scattered to resolve clear trends, despite their rather similar average value to that at other sites. Events A and B in $\delta^{66}\text{Zn}$ correspond with recognised features of the $\delta^{13}\text{C}$ stratigraphy of OAE 2 (Tsikos et al., 2004), namely the first increase in $\delta^{13}\text{C}$ at the onset of OAE 2 (which occurs after the start of Event A) and the decrease in $\delta^{13}\text{C}$ that corresponds with the Plenus Cold Event (Event B).

Zn/Ca values average 15 ± 21 (2 s.d., $n=48$), 3.6 ± 7.1 (2 s.d., $n=21$), and 14 ± 38 (2 s.d., $n=46$) $\mu\text{mol/mol}$ for the Eastbourne, Raia del Pedale and Barranca el Cañón datasets respectively (Fig. 3), and are comparable to the range in Zn/Ca observed in marine calcifiers (e.g. Zn/Ca in benthic foraminifera: $\sim 3.3 \mu\text{mol/mol}$, Marchitto et al., 2000; planktonic foraminifera: $\sim 35 \mu\text{mol/mol}$, Boyle, 1981). Marked stratigraphic features in Zn/Ca include an increase in Zn/Ca in Eastbourne during Event B and increases in Barranca el Cañón during Event B and the Early Turonian.

2.5 Discussion

2.5.1 Contribution of Zn from detrital minerals

The high abundance of Zn in detrital minerals means that liberation of Zn from non-carbonate phases during chemical preparation may obscure these primary trends. Zn/Al ratios can be used to estimate the proportion of Zn leached from detrital minerals relative to total leached Zn, where Al is taken to represent the amount of leaching from detrital minerals. Stratigraphic Zn/Al patterns do not show signs of increased leaching from detrital minerals (i.e. drops to lower Zn/Al values) during intervals of lithological or $\delta^{66}\text{Zn}$ change, which suggests the leaching of Zn from detrital minerals does not impact stratigraphic $\delta^{66}\text{Zn}$ patterns. If leaching of Zn and Al from detrital minerals is assumed to be proportional, these abundances can be used to estimate the amount of zinc liberated from the lithogenic component as a fraction of total leached zinc using: $X_{\text{lith}} = [(\text{Zn/Al})_{\text{lith}}/(\text{Zn/Al})_{\text{carb}}]*100\%$ with X_{lith} being the lithogenic (detrital) fraction of Zn in the leachate, $(\text{Zn/Al})_{\text{lith}}$ based on the average composition of upper continental crust (Rudnick and Gao,

2003), and $(\text{Zn}/\text{Al})_{\text{carb}}$ the measured concentrations in the leachate. Following this approach, the maximum X_{lith} found are 0.13 and 0.51% for Eastbourne and Barranca el Cañón sections respectively. Given this low detrital component, no attempt to correct carbonate $\delta^{66}\text{Zn}$ values for detrital input was made.

2.5.2 Carbonates as an archive for $\delta^{66}\text{Zn}$

Differences between $\delta^{66}\text{Zn}$ observed in this study, other carbonate studies, and the modern ocean might reflect changes in the $\delta^{66}\text{Zn}$ value of the global oceans through time. However, interpretation is challenging because carbonate sediments are likely to record shallow-water seawater composition, which can vary significantly relative to bulk ocean composition. Carbonate $\delta^{66}\text{Zn}$ values considerably higher than that of modern deep-waters (0.5‰) are challenging to explain, because surface seawater (0–1000m) generally has lower $\delta^{66}\text{Zn}$ than deep-water. This difference may suggest a significant systematic isotope fractionation ($>+0.4\text{‰}$) during incorporation of Zn into marine carbonates or adsorbed to calcite surfaces, as has been recently suggested by Dong and Wasylenki (2016). Rather than seeking to more precisely quantify this offset, in this study we avoid this complexity by focus on relative changes in the $\delta^{66}\text{Zn}$ values within a single time-period.

2.5.3 Surface-ocean processes and spatial patterns

For large parts of the Cenomanian–Turonian, $\delta^{66}\text{Zn}$ values between the three sites are similar, which is surprising considering the heterogeneity of dissolved $\delta^{66}\text{Zn}$ in the modern surface ocean. During such intervals, the fraction of Zn utilized in the surface ocean must be similar at the three sites. Common stratigraphic variations in $\delta^{66}\text{Zn}$ (i.e. Event B), which approach amplitudes of $\sim 0.5\text{‰}$, may be caused by near-synchronous changes in the expression of local processes on upper-ocean Zn cycling at each location (e.g. a change in the removal rate of light or heavy Zn to the subsurface by biological fixation or adsorption). However, such a process seems unlikely considering the different Zn/Ca patterns during this time interval. Where (the upper part of) the Event B record is associated with higher

Zn abundances, values at Raia del Pedale are relatively constant, excluding the notion of a proportion of Zn being removed by biological fixation or adsorption as a likely explanation for the observed $\delta^{66}\text{Zn}$ at both sites. Hence, the common Zn-isotope stratigraphic fluctuations at Eastbourne and Raia del Pedale more plausibly record changes in the ‘deep’ ocean Zn, and thus represent changes in the global cycling of Zn during OAE-2.

2.5.4 Zn-cycle perturbation in relation to a magmatic episode –Event A

Osmium-isotope data suggest that increased basalt-seawater interaction persisted throughout much of OAE 2 (Turgeon and Creaser, 2008; Du Vivier et al., 2015), a phenomenon that likely favoured the elevated input of dissolved trace metals into the ocean (e.g. Elrick et al., 2009). The initial unradiogenic Os-isotope shift, like that of $\delta^{66}\text{Zn}$, pre-dates the onset of the positive carbon-isotope excursion, conventionally taken to record the beginning of OAE 2. This shift in Os isotopes has been related to the input of unradiogenic Os from volcanism or some other form of basalt-seawater interaction involving one or more Large Igneous Provinces (Turgeon and Creaser, 2008; Du Vivier et al., 2015; Jenkyns et al., 2017). The first drop in $\delta^{66}\text{Zn}$ (Event A, Figure 2.2) might thus be explained by a particularly strong pulse of isotopically light Zn to the ocean from hydrothermal fluids and/or other low temperature reactions between seawater and mafic rocks (cf, Liu et al., 2017). A rapid input may have created heterogeneities in the isotopic composition of surface waters, which could explain the variable magnitude of the negative Zn-isotope excursions at Raia del Pedale and Eastbourne. This observation would directly link volcanic activity with ocean nutrification as a trigger for increased carbon burial during the initial phase of OAE 2. Increased Zn burial into globally expanding organic-rich sediments shortly after Event A (and the initial unradiogenic Os-isotope shift), can explain the pattern of gradually increasing Zn-isotope compositions, despite consistently unradiogenic osmium-isotope values during this time interval.

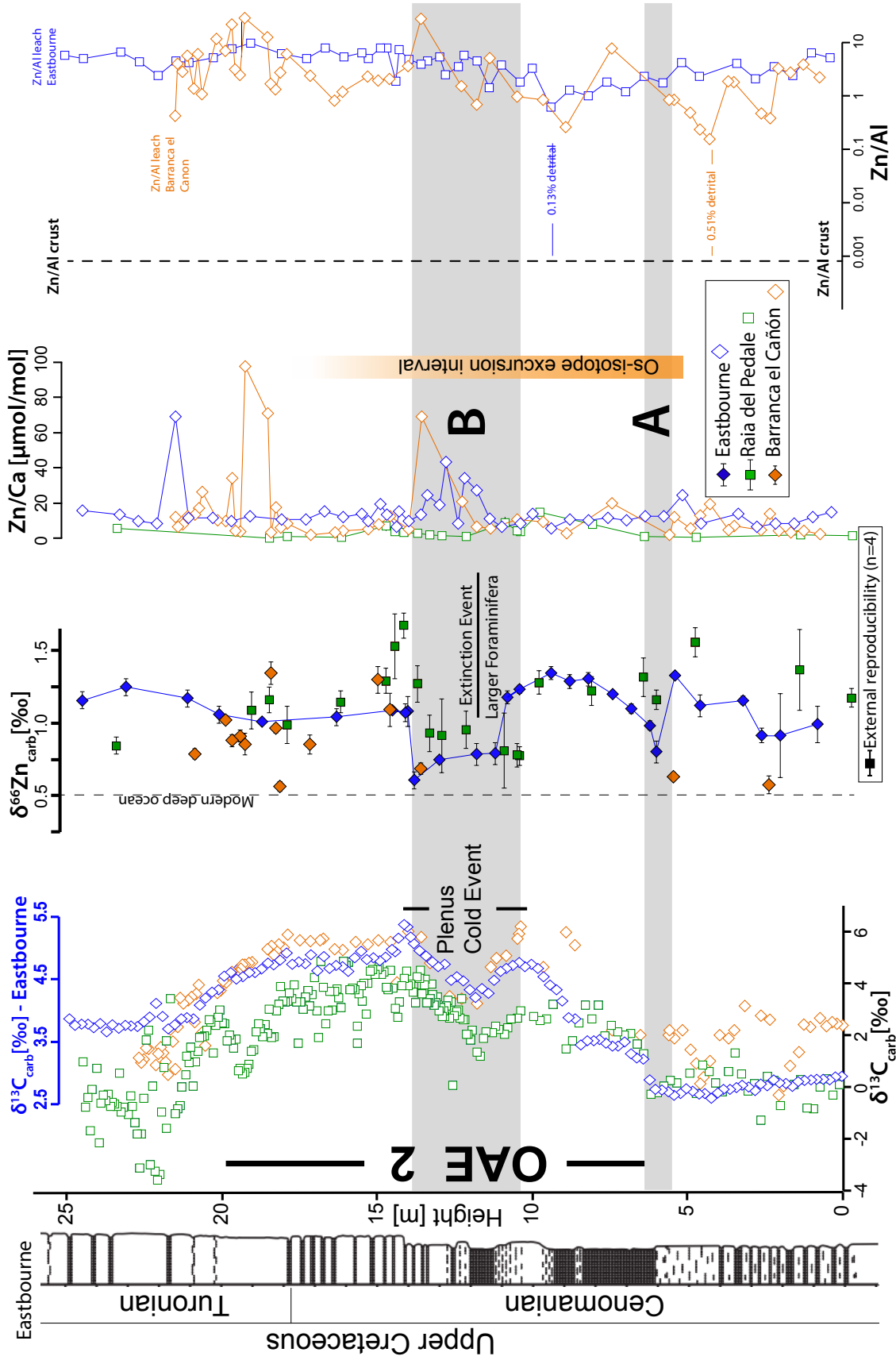


Figure 2.2: Zn-isotope ($\delta^{66}\text{Zn}$) stratigraphy of Cenomanian–Turonian carbonates. Samples from Raia del Pedale and Barranca el Cañón were correlated to the Eastbourne depth scale by tying key inflection points from the published high-resolution carbon-isotope stratigraphies available for each location (Tsikos et al., 2004; Parente et al., 2008; Elrick et al., 2009). Grey shading (A and B) highlights decreases towards lighter Zn-isotope ($\delta^{66}\text{Zn}$) compositions. The horizontal black line marks the extinction level of larger foraminifera as recorded in the Raia del Pedale section (Parente et al., 2008). The vertical orange band represents the time interval associated with unradiogenic Os-isotope seawater compositions in the global ocean (Jenkyns et al., 2017).

2.5.5 Zinc-cycle perturbation during the Plenus Cold Event –Event B

The second drop towards lighter $\delta^{66}\text{Zn}$ values (Event B, Figure 2.2) occurred during the Plenus Cold Event, which had a major effect on ocean chemistry, being associated with re-oxygenation in many locations due to global cooling of marine waters (Jenkyns et al., 2017). A relative decrease in the size of organic-rich sinks for isotopically light Zn as a result of improved bottom-water oxygenation satisfactorily explains lighter values observed at both Eastbourne and Raia del Pedale. An additional factor driving the observed Zn-isotope variations during the Plenus Cold Event and explanation for elevated Zn/Ca ratios in Eastbourne during this time interval may have been the release of isotopically light Zn from organic-rich continental-margin sediments as a result of an increase in (aerobic) biodegradation of organic matter and sulphides. Elevated concentrations of conservative redox-sensitive trace metals (e.g. Mo/Ca, U/Ca) observed previously at both Eastbourne and Raia del Pedale have been linked to the re-oxidation of previously buried organic-rich sediments (Jenkyns et al., 2017). By contrast, the absence of elevated Zn/Ca ratios at Raia del Pedale (Figure 2.2) is probably due to the very shallow (less than a few tens of metres) setting of this site and the high efficiency of Zn removal that is likely to have occurred from surface waters in extremely oligotrophic conditions.

The Plenus Cold Event has been associated with biotic turnover and changes in the distribution of phytoplankton (Parente et al., 2008; van Helmond et al., 2016 and references therein). The new Zn-isotope data suggest that, in addition to oxygenation and cooling, perturbations to micronutrient cycles might have played a role in driving these palaeoecological changes. A perturbation to the Zn cycle and nitrification of the surface ocean during the Plenus Cold Event, as inferred from relatively light Zn-isotope compositions and elevated Zn/Ca ratios in Eastbourne and Barranca el Cañón, can be directly correlated with the extinction of larger benthic foraminifera, as recorded in the Southern Apennines of Italy. These K-strategists, characterized by long life-cycles and low reproductive potential, were adapted to nutrient-poor conditions and therefore suffered from the switch to more

nutrient-rich conditions (Parente et al., 2008). During the Plenus Cold Event, only those species that could tolerate mesotrophic conditions survived, while strictly oligotrophic species became extinct. Surface-ocean nutrification during the Plenus Cold Event was inferred previously from the distribution of foraminifera alone (Parente et al., 2008). The data presented here support this model of a perturbation to the (micro)nutrient cycle, and point to nutrification of the surface ocean as a cause for this biotic extinction event.

2.6 Conclusion

Zn-isotope trends in marine carbonates from England, Italy and Mexico demonstrate perturbations to the zinc cycle during the Cenomanian–Turonian interval, with isotopically light Zn-isotope compositions observed just prior to the onset of OAE 2 and during the Plenus Cold Event. This work constitutes the first isotopic evidence for changes in the Zn cycle during the Cretaceous and supports the hypothesis that ocean nutrification was of paramount importance in driving widespread and intense organic-carbon burial during OAE 2. Specifically, the correlation between Zn-isotope variations and the extinction of benthic foraminifera recorded in platform carbonates of the Southern Apennines is consistent with a link between the abundance of micronutrients and the extinction of marine fauna adapted to oligo- and mesotrophic conditions. In addition to the reproducibility of stratigraphic Zn-isotope patterns in spatially and lithologically diverse carbonate successions, this observation suggests that Zn isotopes may be an important tool to reconstruct the significance of organic-matter burial and nutrient dynamics in ancient oceans.

3

Controls on the $\delta^{114}\text{Cd}$ of Late Cretaceous organic-rich mudrocks

Contents

3.1	Abstract	38
3.2	Introduction	39
3.2.1	Geological context	42
3.3	Methods	44
3.4	Results	45
3.5	Discussion	45
3.5.1	Lithogenic, biological and authigenic fractions	45
3.5.2	Cd-isotope patterns in relation to the carbon cycle	48
3.6	Local redox controls on $\delta^{114}\text{Cd}$	49
3.6.1	Reconstructing the temporal evolution of $\delta^{114}\text{Cd}_{\text{seawater}}$	52
3.6.2	Drivers of $\delta^{114}\text{Cd}_{\text{seawater}}$ change	54
3.7	Conclusion	57

3.1 Abstract

Cadmium concentrations have a nutrient-like distribution in the modern ocean. This distribution is mirrored by Cd isotopes, which are fractionated during uptake by marine primary producers in the near-surface ocean. This behaviour has led to the suggestion that, if such signals are exported and preserved in the sedimentary record, the cadmium-isotope composition of marine sediments may provide insight into the

nutrient dynamics of past oceans. However, the formation of stable Cd-sulphides complicates such use. This study explores the potential of the cadmium isotope composition of organic-rich mudrocks to trace marine paleo-nutrient conditions in the past. Cd-isotope analyses of samples from two cores from the southern Western Interior Seaway, spanning the Cenomanian–Turonian stages, provide insight into the preservation of Cd-isotope signals in the sedimentary record in relation to global and local changes in depositional environments.

Stratigraphic $\delta^{114}\text{Cd}$ patterns show reproducible trends for the two cores. Positive relationships between $\delta^{114}\text{Cd}$ and Mo_{EF} and Cd/TOC imply that the proportion of Cd removal as Cd sulphides exerts a strong control on the $\delta^{114}\text{Cd}$ composition of the sedimentary record. Non-quantitative removal of Cd in oxygenated waters results in low $\delta^{114}\text{Cd}$, whereas higher values are observed due to near-quantitative removal in euxinic waters. Accounting for the variable effect of non-quantitative removal of Cd into sediments allows a first reconstruction of the $\delta^{114}\text{Cd}_{\text{seawater}}$ of the Maverick Basin during the Early Cenomanian. This reconstruction suggests a relatively constant local seawater Cd-isotope composition, which varied between ~ 0.2 and 0.3‰ . These values are similar to those observed in the modern deep ocean. $\delta^{114}\text{Cd}_{\text{seawater}}$ values started dropping from ~ 0.3 to 0.0‰ around Late Cenomanian time and continued into the OAE 2 interval. This geochemical evolution can be related either to a perturbation in the global mass balance of Cd and/or regional changes in the circulation of water masses in the Western-Interior Seaway. Ultimately, observations presented in this study imply that Cd-isotope records from organic-rich sediments may preserve valuable palaeoenvironmental information on past redox conditions, rather than on biological utilisation.

3.2 Introduction

The distribution of cadmium (Cd) in the modern ocean largely mimics that of the macronutrient phosphorus (e.g. Bruland, 1980; De Baar et al., 1994). A pattern of depleted surface waters and a gradual increase to higher concentrations at depth is associated with the uptake of Cd by marine primary producers in the surface ocean,

and remobilisation of Cd at depth upon organic-matter degradation. This typical nutrient-like distribution is observed in most parts of the modern ocean (e.g. Baars et al., 2014; Conway and John, 2015). It has been suggested that cadmium substitutes for zinc in carbonic anhydrase (e.g. Lane et al., 2005), though more recently it has been shown that the majority of cadmium uptake is likely non-specific and followed by internal storage in the cell (Horner et al., 2013). Regardless, the similarities of cadmium and phosphorus distributions in the modern ocean are striking and therefore have led to the suggestion that cadmium concentrations in foraminiferal tests (e.g. Boyle, 1988; Elderfield & Rickaby, 2000) and shales (e.g. Brumsack, 1986, 2006) may preserve valuable information on past nutrient conditions.

More recently, efforts to map and understand the isotopic distribution of dissolved cadmium in the modern ocean have revealed a vertical gradient (Ripperger et al., 2007; Abouchami et al., 2011; Xue et al., 2013; Conway and John, 2015). Preferential uptake of the lighter isotopes by primary producers in the surface ocean creates heterogeneities but generally leaves the surface ocean strongly enriched in the heavier isotopes (up to $\sim 5\text{‰}$). Remobilisation of isotopically light Cd upon degradation of sinking organic material explains the lighter ($\sim 0.2\text{--}0.3\text{‰}$) isotope composition of the homogeneous modern deep ocean. The strong biological control on the dissolved Cd-isotope composition of the modern ocean has recently led to several studies that explore the use of Cd-isotopes as a proxy for past nutrient conditions in carbonate (Hohl et al., 2017; John et al., 2017) and shale (Georgiev et al., 2015) successions.

However, the formation of Cd-sulphides provides complexities for the use of cadmium isotopes as a tracer for past nutrient dynamics and/or primary productivity patterns. Equilibrium thermodynamics predicts that cadmium forms a stable sulphide phase in the presence of free H_2S , rather than being incorporated into pyrite (Al-Farawati & van den Berg, 1999; Morford & Emerson, 1999). Any cadmium released to pore waters by degradation of organic material therefore may be bound in the sediment by the formation of insoluble sulphides below the sulphate reduction front. Cadmium may also form sulphides in the water column, either in euxinic micro-environments around degrading organic material in oxygen-deficient zones

in the open ocean (Janssen et al., 2014) or below the chemocline in stratified restricted basins. Strongly depleted cadmium concentrations below the chemocline in euxinic waters of the Black Sea and Cariaco Basin suggest near-complete removal of cadmium in such highly reducing marine basins (Jacobs and et al., 1987; Tankere et al., 2001). Recent experimental evidence (Bryan et al., in prep.) supports indirect observational evidence (Janssen et al., 2014) that the $\delta^{114}\text{Cd}$ composition of CdS formed is isotopically lighter than ambient seawater. Consequently, although the formation of CdS does not appear to control the dissolved $\delta^{114}\text{Cd}$ composition of most parts of the modern ocean, it may impact the Cd-isotope composition of the sedimentary record, particularly for intervals of time that experienced a greater burial of sulphides worldwide.

Together, uptake of Cd by primary producers and the formation of Cd sulphides control most of the internal cycling of the element in the world ocean. Both processes are associated with the preferential uptake of the lighter isotopes. The $\delta^{114}\text{Cd}$ composition of the material exported to the sediment therefore is expected to be isotopically lighter than ambient seawater, if this removal is non-quantitative. $\delta^{114}\text{Cd}$ compositions of the sedimentary record are expected to reflect this internal cycling of Cd, in both the water column and during early diagenesis, superimposed on spatial and/or temporal variability of the $\delta^{114}\text{Cd}$ of the overlying seawater. The average lithosphere ($\sim -0.04\text{‰}$), and riverine ($\sim 0.24\text{‰}$), aeolian ($\sim -0.02\text{‰}$) and hydrothermal ($\sim 0.06\text{‰}$) inputs of cadmium to the ocean (Schmitt et al., 2009; Lambelet et al., 2013) are all isotopically lighter than the average dissolved modern ocean composition of 0.38‰ (compilation by John et al., 2017). Fe-Mn crusts are not associated with significant isotope fractionation and record (deep) seawater isotope compositions, and therefore do not likely represent a significant sink for isotopically light Cd, although average $\delta^{114}\text{Cd}$ compositions for Fe-Mn sediments are slightly lighter ($\sim 0.23\text{‰}$) than the average ocean composition (Schmitt et al., 2009; Horner et al., 2010; John et al., 2017). Following the discussion above, organic-rich sediments likely represent an isotopically light sink for Cd although this sink has not yet been geochemically characterised in the modern ocean.

This study aims to explore how the processes that affect $\delta^{114}\text{Cd}$ compositions of the modern ocean relate to the Cd-isotope composition preserved in the sedimentary record, specifically for organic-rich shales. Additionally, it aims to determine if the Cd-isotope composition of such successions may preserve valuable palaeoenvironmental information. The Boquillas (Eagle Ford) Formation (Fm) hosts Cenomanian–Turonian marls and limestones and provides an interesting case study as it covers a time interval of changing redox and environmental conditions on both local and global scales (e.g. Eldrett et al., 2014, 2015). Several industry cores have been recovered within close geographical proximity, which additionally allows assessment of the reproducibility of stratigraphic $\delta^{114}\text{Cd}$ patterns within a basin (Figure 3.1).

3.2.1 Geological context

The Upper Cretaceous Boquillas (Eagle Ford) Formation (Fm), found at the southern gateway of the Cretaceous Western Interior Seaway, is an organic-rich formation of astronomically forced alternating marls and limestones (Eldrett et al., 2015) deposited on a shallow carbonate platform. This study is based on two research cores drilled in close proximity to each other in this setting; the Innes-1 core comes from the Comanche carbonate shelf whereas the Iona-1 core represents the more distal edge of the Maverick intra-shelf basin (Eldrett et al., 2017, Figure 3.1). Both cores roughly cover the same time interval but contain significant unconformities in the upper Cenomanian and lower Turonian. Most notably, a considerable hiatus (~ 2 Myr) in the Turonian is recognised in the Innes-1 core, which is of much shorter duration (~ 0.2 Myr) in the Iona-1 core (Eldrett et al., 2017). Both cores include the positive carbon-isotope excursion associated with Oceanic Anoxic Event 2, an interval of globally widespread enhanced organic-carbon burial and the spread of low-oxygen marine environments (e.g. Schlanger and Jenkyns, 1976; Scholle and Arthur, 1980; Tsikos et al., 2004; Jenkyns, 2010; Eldrett et al., 2014, 2017; Scaife et al., 2017). However, this interval is locally characterised by organic-lean deposits reflecting more oxygenated conditions (Eldrett et al., 2014). This interval of more

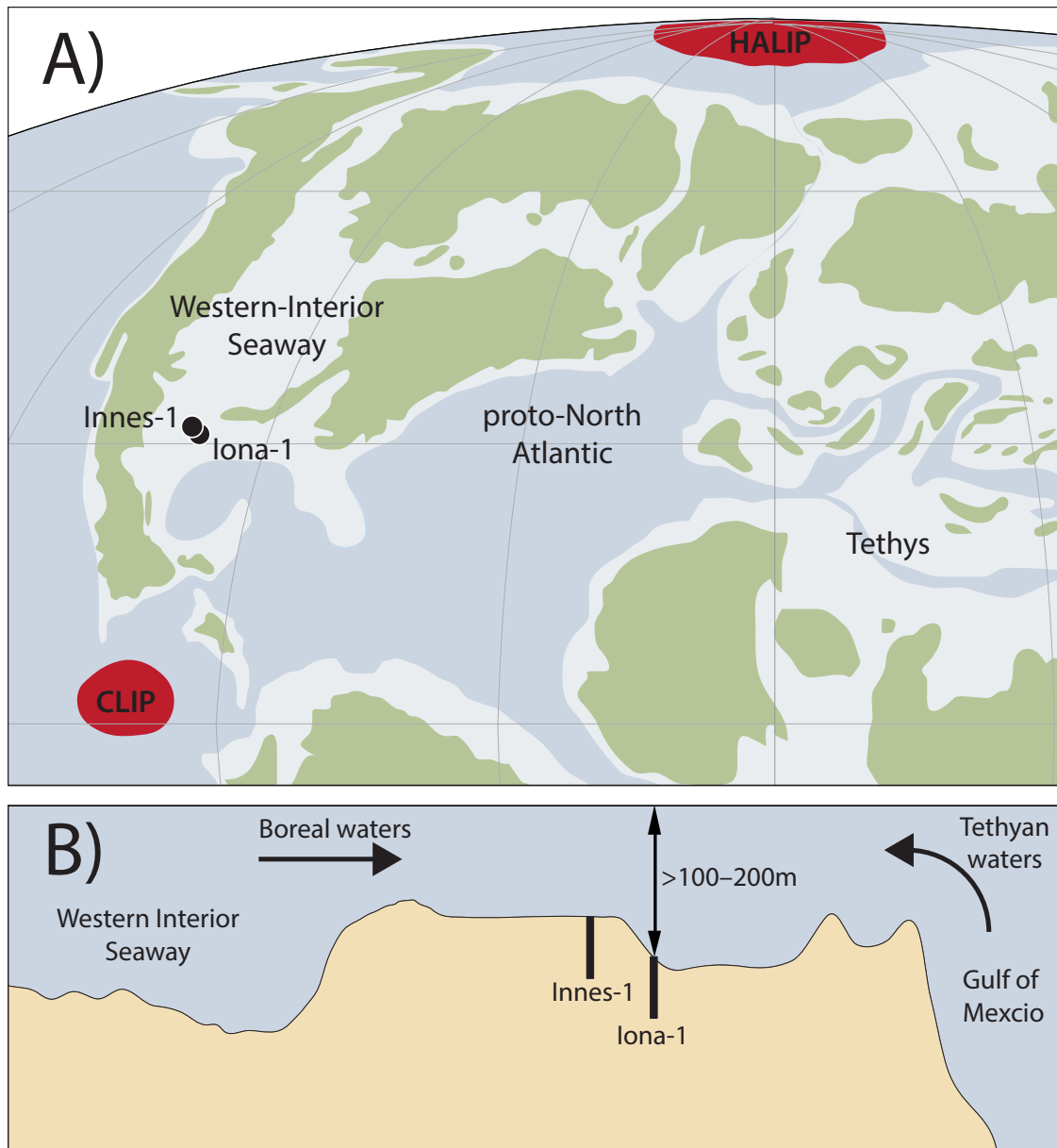


Figure 3.1: A) Palaeogeographical reconstruction of the Cenomanian–Turonian Boundary interval with approximate study locations. Courtesy of Lauren O’Connor, modified from Jarvis et al. (2011). (B) Reconstruction of basin characteristics for the Maverick Basin, modified from Eldrett et al. (2017)

oxygenated bottom-water conditions separates the highly organically enriched Lower Eagle Ford from the more organic-lean Upper Eagle Ford (see Figure 3.2). Evidence from trace metal abundances, sedimentology, and organic biomarker data suggest that the basin was mostly euxinic during the Lower Eagle Ford, and suboxic–anoxic during the Upper Eagle Ford (Eldrett et al., 2014; Sun et al., 2016).

3.3 Methods

Methods were discussed in more detail in Chapter 1. In short, core samples were crushed using an agate pestle and mortar and subsequently treated with inverse aqua regia (iAR, 3 parts HNO_3 , 1 part HCl) for partial shale digestion. This method has been shown to dissolve preferentially authigenic shale components but leaves some detrital minerals intact (Xu et al., 2012), and has been successfully used in a previous Cd-isotope study on shales (Georgiev et al., 2014). The elemental abundances for the Iona-1 core come from bulk-rock digestion undertaken by Eldrett et al. (2014). For the Innes-1 core, an aliquot of the digested sample was taken to be analysed by ICP-MS to determine elemental abundances. Samples from both cores were then spiked appropriately with a ^{111}Cd - ^{113}Cd double spike to obtain a spike:sample ratio of 1, and subsequently separated from major element cations and interferences by anion column chromatography. A summary of the column method is provided in Table 1.

Cd stable-isotope analyses were performed on a Nu Instruments Nu Plasma multi-collector ICP-MS at the University of Oxford. Samples were measured at 50ppb (spike plus sample) concentrations and were bracketed by a spiked NIST-3108 solution to correct for instrumental drift. Data were processed offline using an exponential mass-bias correction and including a correction for Sn interference on mass 114. Cd-isotope values are reported as $\delta^{114}\text{Cd}$ relative to NIST-3108, which is defined as $\delta^{114}\text{Cd} = [^{114}/^{110}\text{Cd}_{\text{sample}}/^{114}/^{110}\text{Cd}_{\text{NIST}} - 1] \times 1000$. Internal errors are propagated from the reproducibility of the bracketing standards and the counting statistics of each sample analysis. External reproducibility and accuracy of Cd-isotope analysis were estimated by analysis of pure Cd-isotope standards ‘OxCad’ ($-0.86 \pm 0.05 \text{ ‰}$, 2 SD, $n=15$); ‘Alpha Cd Zurich’ ($-0.01 \pm 0.06 \text{ ‰}$, 2 SD, $n=8$); ‘BAM I012’ ($-1.31 \pm 0.07 \text{ ‰}$, 2 SD, $n=7$), which are in agreement with previously published values (Abouchami et al., 2013). The analysis of rock standard SDO-1 ($0.13 \pm 0.06 \text{ ‰}$, 2 SD, $n=5$), for which different aliquots were processed in different batches, provides the quoted external reproducibility in figures in the discussion.

3.4 Results

All samples are enriched in cadmium relative to average upper continental crust (Rudnick and Gao, 2003). The enrichment factor (EF) is defined as $\text{Cd}_{\text{EF}} = (\text{Cd}/\text{Al})_{\text{sample}} / (\text{Cd}/\text{Al})_{\text{crust}}$ and ranges from 2.4 to 314 with an average of 66 ± 156 (2 SD, $n = 27$) for the Iona-1 core and from 3.8 to 131 with an average of 54 ± 77 (2 SD, $n = 18$) for the Innes-1 core. $\delta^{114}\text{Cd}$ values vary between -0.17 and 0.39 ‰ with an average of 0.15 ± 0.26 ‰ (2 SD, $n = 39$) for the Iona-1 core and between -0.18 and 0.41 ‰ with an average of 0.17 ± 0.27 (2 SD, $n = 25$) for the Innes-1 core. $\delta^{114}\text{Cd}$ values are thus similar for the two cores and vary stratigraphically. A comparison between the two cores highlights the similarities in stratigraphic $\delta^{114}\text{Cd}$ patterns, which vary during key intervals of palaeoenvironmental change (Figure 3.2). The heaviest values are generally found in the bottom part of the Lower Eagle Ford, the most organic-rich interval, whereas the lightest values are found during OAE 2, locally characterised by the most organic-lean sediments. Cd-isotope compositions for the Upper Eagle Ford are mostly lighter than those of the Lower Eagle Ford.

3.5 Discussion

3.5.1 Lithogenic, biological and authigenic fractions

Cadmium concentrations in the upper continental crust are very low relative to abundances in seawater and organic-matter compared to other nutrient-like transition metals such as Ni, Cu and Zn (e.g. data compiled by Little et al., 2015). This observation allows authigenic Cd enrichments to be easily discerned from detrital Cd. For a mechanistic understanding of the stratigraphic changes in $\delta^{114}\text{Cd}$ compositions it is essential to address where the Cd of these samples resides. Cd versus aluminium (Al) concentrations in these sediments illustrate the high enrichments of Cd relative to the crustal composition for these cores (Figure 3.3). The maximum proportion of detrital Cd in these rocks is 41% of total Cd, with an average of 5.5%, based on the average upper continental crust composition by Rudnick and Gao (2003) and Al abundances from Eldrett et al. (2014). As a

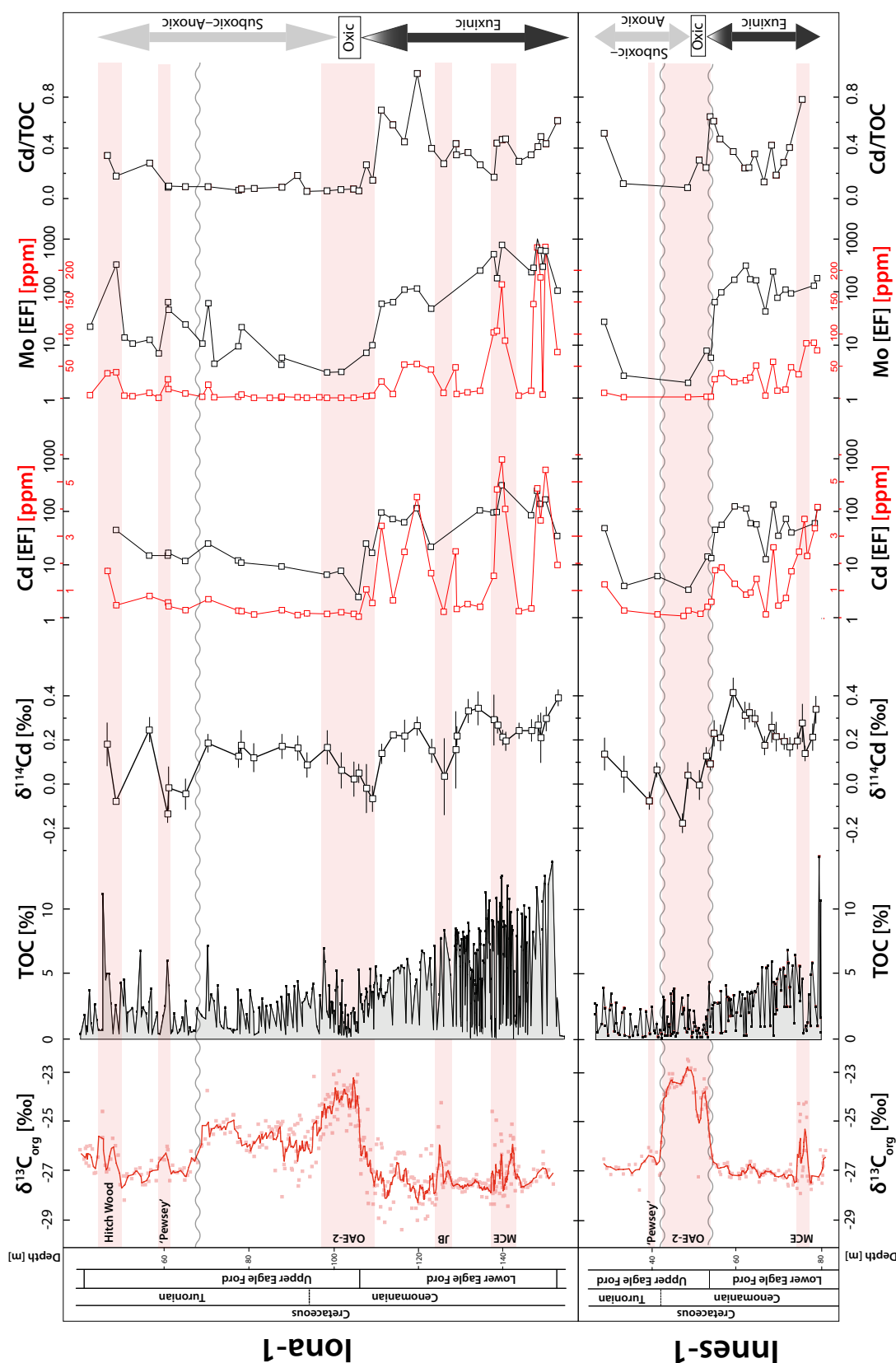


Figure 3.2: Cd-isotope stratigraphy for the Innes-1 and Iona-1 cores. Horizontal red bands mark recognised intervals of positive carbon-isotope excursions. The right column represents general redox conditions as inferred from previous studies on trace metal and organic geochemistry (Eldrett et al., 2014; Sun et al., 2016). The $\delta^{13}\text{C}_{\text{org}}$ and TOC data come from Eldrett et al. (2014), Scaife et al. (2017) and Ruhl (in prep.). The Mo (EF) data come from Eldrett et al. (2014) and Dickson (in prep.).

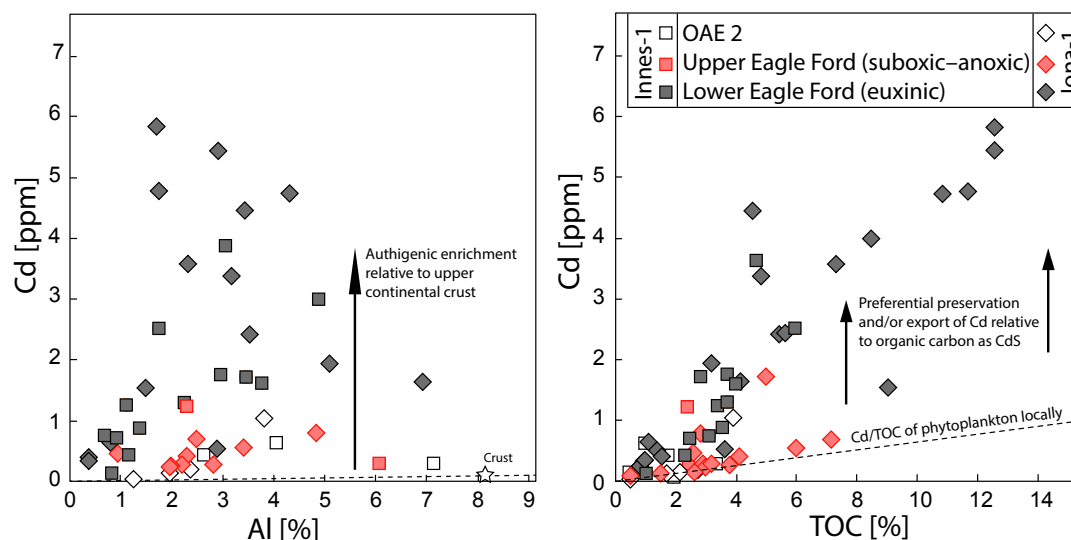


Figure 3.3: Cd abundances relative to Aluminium and Total Organic Carbon

result, no correction for the lithogenic component of Cd in these sediments was performed on $\delta^{114}\text{Cd}$, as it is negligible for most samples.

The concentration of Cd relative to total organic carbon (TOC, wt%) can provide insight as to whether authigenic Cd resides within inorganic or organic fractions (Figure 3.3). The lowest Cd/TOC ratios are mainly found for samples from the Upper Eagle Ford and the OAE interval, where dominantly suboxic–anoxic conditions are observed (Eldrett et al., 2014; Sun et al., 2016). Samples from the Lower Eagle Ford, primarily deposited under euxinic conditions, show Cd/TOC values considerably enriched in Cd, for both cores. Cd/TOC values found for all data from these two cores are within Cd/C ratios of cultured phytoplankton, which vary considerably between species (Ho et al., 2003).

The difference between the Upper and Lower Eagle Ford sediments therefore may principally be explained by varying Cd/TOC of phytoplankton species. However, this would require a considerable change in local ecologies, and although differences between the Lower and Upper Eagle Ford marine palynology are observed, these are not that dramatic (Eldrett et al., 2017). More likely, the differences in Cd/TOC ratios between the Upper and Lower Eagle Ford sediments may be explained by the precipitation of CdS under euxinic conditions in the Lower Eagle Ford (Figure 3.2).

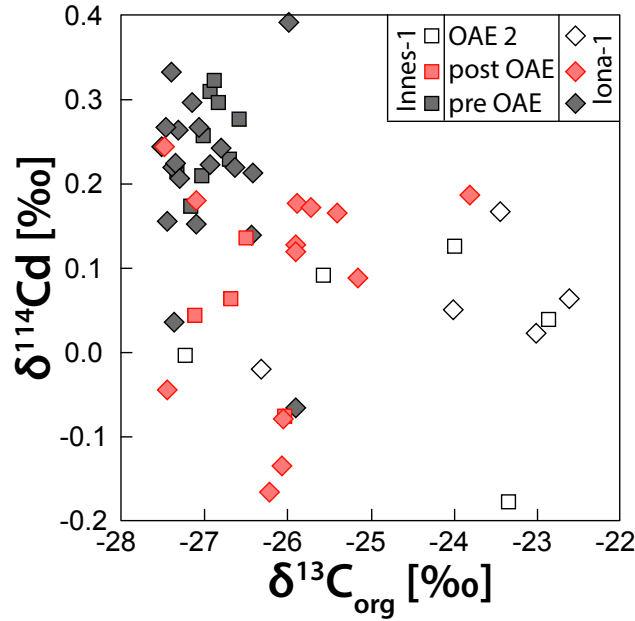


Figure 3.4: $\delta^{114}\text{Cd}$ relative to $\delta^{13}\text{C}_{\text{org}}$ for the Innes-1 and Iona-1 cores.

Strong enrichments of Cd relative to TOC are thus explained by the preferential export and/or preservation of Cd as CdS (Figure 3.3).

3.5.2 Cd-isotope patterns in relation to the carbon cycle

Clear and reproducible stratigraphic patterns can be observed in $\delta^{114}\text{Cd}$ for both cores. These patterns often appear to be associated with $\delta^{13}\text{C}_{\text{org}}$ excursions, where lighter $\delta^{114}\text{Cd}$ values occur during intervals with positive C-isotope excursions. This apparent correlation is particularly obvious for OAE 2, the largest and best-studied positive carbon-isotope excursion during the Cenomanian–Turonian, but also appears to be a feature of the more minor carbon-isotope excursions observed in the two cores. The Mid-Cenomanian Event, Jukes-Browne Event, ‘Pewsey’ and Hitch Wood events (Jarvis et al., 2006; Eldrett et al., 2017) are all associated with a relatively light $\delta^{114}\text{Cd}$ composition relative to background conditions. The consistency with which even such minor carbon-isotope excursions appear to be associated with lighter Cd-isotope compositions implies an underlying mechanism coupling the cadmium-isotope compositions of the Western Interior Seaway mudrocks with the global carbon cycle. A cross-plot of $\delta^{114}\text{Cd}$ and $\delta^{13}\text{C}_{\text{org}}$ values does

not reveal a significant negative relationship (Figure 3.4). However, this may not necessarily be expected if $\delta^{114}\text{Cd}$ and $\delta^{13}\text{C}_{\text{org}}$ respond to different forcing mechanisms and/or on different timescales. Also, many of these events are relatively short considering the data resolution of this study, thereby not providing enough basis for a statistically significant relationship. Higher $\delta^{114}\text{Cd}$ data resolution is needed to test the apparent stratigraphic relationship between $\delta^{114}\text{Cd}$ and $\delta^{13}\text{C}_{\text{org}}$, and provide more detailed information.

3.6 Local redox controls on $\delta^{114}\text{Cd}$

The apparent coupling of the Cd and carbon cycles is an interesting observation and might provide information on the driving mechanisms of the positive carbon-isotope excursions. However, these observations cannot directly be extrapolated to the global ocean and Cd- and C-cycles because local controls on $\delta^{114}\text{Cd}$ may dominate stratigraphic patterns. Also, as discussed before, the Maverick Basin shows patterns in carbon burial that are anomalous to those observed on a global scale. These patterns seem to have been dominated by local redox conditions (e.g. Eldrett et al., 2014), which likely also impacted the local cycling of Cd, considering its affinity for sulphides. Temporal variations in the redox conditions of the Maverick Basin and its effects on the $\delta^{114}\text{Cd}$ composition of the sediment therefore have to be evaluated.

Molybdenum (Mo) concentrations of marine sediments are a well-established proxy for local redox conditions as a result of its relatively high concentrations in marine waters and behaviour during low-oxygen conditions; Mo is highly reactive in sulphidic (pore) waters and therefore enriched in the sediments from low-oxygen marine basins, particularly when sulphidic conditions reach into the water column (e.g. Erickson & Helz, 2000; Scott & Lyons, 2012). Cd sulphides may form in sulphidic waters resulting in the relative enrichment of cadmium compared to its abundance in phytoplankton. Cd/TOC ratios can thus provide information on the relative proportion of cadmium residing in the biological and non-biological fractions, with high Cd/TOC ratios indicative of a relatively high portion of Cd as a result of CdS formation. Cross-plots of Mo_{EF} , Cd/TOC ratios, and Cd abundances

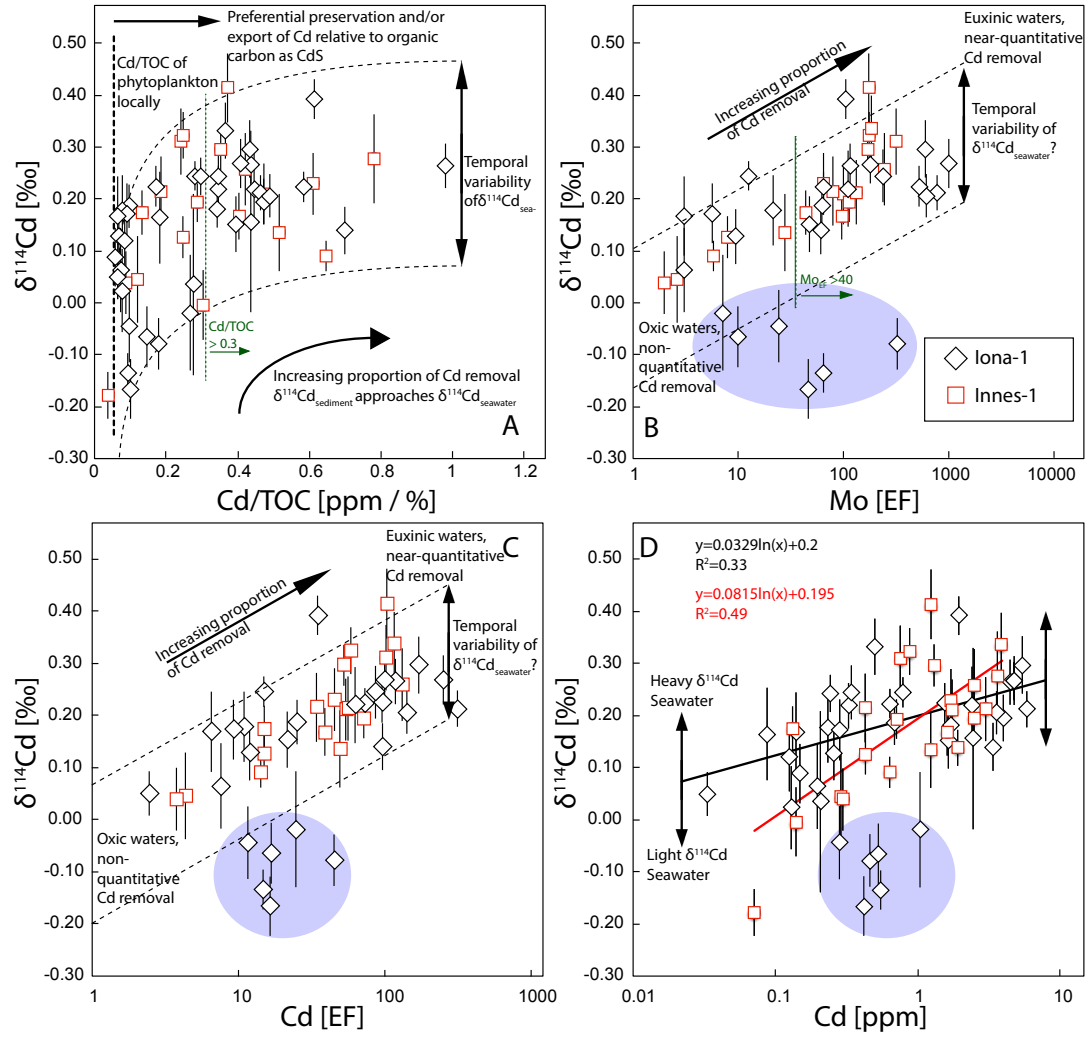


Figure 3.5: $\delta^{114}\text{Cd}$ compositions relative to Cd/TOC, Mo_{EF} , Cd_{EF} , and [Cd]. The positive relationships observed are suggested to be caused by the proportion of Cd-sulphide formation. The variability in $\delta^{114}\text{Cd}$ on top of these positive relationships is proposed to be the result of temporal changes in $\delta^{114}\text{Cd}_{\text{seawater}}$. The blue shading in plots B, C, and D marks a group of outliers, which are highlighted stratigraphically later in Figure 7. The regression line calculated in plot D excludes this group of outliers.

with $\delta^{114}\text{Cd}$ can be used to address the effect of varying redox-conditions and the proportion of Cd residing in the authigenic fraction on the observed stratigraphic patterns in $\delta^{114}\text{Cd}$ (Figure 3.5).

The positive relationships observed between $\delta^{114}\text{Cd}$ with Mo_{EF} , Cd/TOC, and Cd abundances, suggest a control of local redox conditions on $\delta^{114}\text{Cd}$ compositions. High Mo enrichments, indicative of sulphidic conditions and a high supply of Mo (e.g. Scott and Lyons, 2012; Dickson et al., in prep.), correspond with the heaviest $\delta^{114}\text{Cd}$

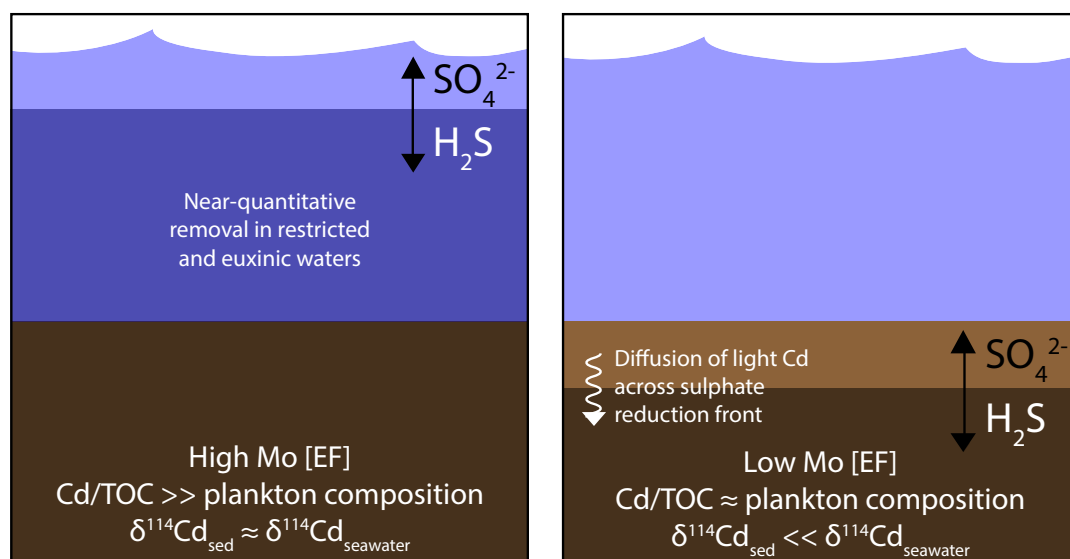


Figure 3.6: Schematic diagram of the proposed conceptual model for the positive relationships observed in Figure 5. Darker portions of the sediment/water column represent sulphidic (pore) water conditions.

compositions. In modern euxinic basins, like the Black Sea and Cariaco Basin, dissolved cadmium concentrations below the chemocline are very low, suggesting near-complete removal of cadmium to the sediment in such conditions (Jacobs and et al., 1987; Tankere et al., 2001). The $\delta^{114}\text{Cd}$ composition of samples highly enriched in Mo and Cd may therefore be expected to represent near-quantitative removal of Cd to the sediment and the $\delta^{114}\text{Cd}$ compositions of the sediment to approach that of initial seawater composition.

By contrast, more oxygenated conditions are likely to result in low Mo_{EF} and Cd abundances and only partial removal of Cd from the water column, allowing the preferential uptake of the isotopically lighter Cd isotopes and transfer of this geochemical signature into the sediment. This effect may be due to the non-quantitative formation of CdS and/or by non-quantitative removal of Cd by primary producers in the surface ocean. A sulphate reduction front in the sediment or near the sediment-water interface in non-euxinic conditions can allow non-quantitative removal of Cd. Diffusive transport of isotopically light Cd from (pore) waters above the sulphate reduction front into sulphidic pore waters would leave the sediments

enriched in the lighter isotopes. This conceptual model (Figure 3.6) would imply that relatively heavy $\delta^{114}\text{Cd}$ isotope compositions should be observed in modern-day pore- and/or bottom-waters just above the sulphidic zone. Additionally, variations in the relative proportion of Cd exported from the water column to the sediment in the biological rather than sulphidic fraction may explain lower $\delta^{114}\text{Cd}$ values in more oxygenated conditions. Under such circumstances, a higher proportion of Cd associated with the biological fraction would allow lighter $\delta^{114}\text{Cd}$ signatures to be exported to the sediment, assuming that removal by primary producers in the surface ocean was non-quantitative.

3.6.1 Reconstructing the temporal evolution of $\delta^{114}\text{Cd}_{\text{seawater}}$

The fraction of Cd delivered to the seafloor buried as Cd-sulphides explains the positive relationship between $\delta^{114}\text{Cd}$ with Mo_{EF} and Cd abundances and with that much of the stratigraphic variation in $\delta^{114}\text{Cd}$. However, there is considerable variation in $\delta^{114}\text{Cd}$ compositions, even for samples high in Mo and Cd ratios. For example, there is a group of samples with relatively high Mo and Cd abundances but a comparably light $\delta^{114}\text{Cd}$ composition (shaded blue in Figure 3.5), which plot distinctly from the main data population. It is postulated here that this variability may derive from temporal changes in $\delta^{114}\text{Cd}_{\text{seawater}}$ coming into the basin. Any internal cycling of Cd and its effects on the $\delta^{114}\text{Cd}$ composition of the sediment, as discussed above, would then have been superimposed on temporal changes in $\delta^{114}\text{Cd}_{\text{seawater}}$.

Following this discussion, past $\delta^{114}\text{Cd}_{\text{seawater}}$ may be reconstructed by excluding any data that are thought to result from non-quantitative Cd removal. The remaining samples can then be used to constrain the minimum value of the $\delta^{114}\text{Cd}_{\text{seawater}}$ in the basin. In order to isolate appropriate samples, the data were filtered to include only samples with $\text{Cd}/\text{TOC} > 0.3$, which is five times higher than the inferred local Cd/TOC of phytoplankton (Figure 3.5). The high enrichment of Cd relative to organic carbon implies the presence of a relatively high proportion of Cd-sulphides and thus near-complete removal of Cd. Alternatively, the criteria

for euxinic conditions, and therefore near-quantitative removal, may be based on the Mo contents of these samples. In this case, samples with $\text{Mo}_{\text{EF}} > 40$ were used (Figure 3.5). These Cd/TOC and Mo_{EF} cut-off values are taken to represent the flattening of the relationship to $\delta^{114}\text{Cd}$. The samples that were isolated using these approaches are plotted stratigraphically in Figure 3.7. In order to assess the possible evolution of $\delta^{114}\text{Cd}_{\text{seawater}}$ in the basin, data from the Innes-1 core were converted to the Iona-1 depth scale (Eldrett et al., 2017).

The two approaches result in similar absolute values and stratigraphic patterns (Figure 3.7). However, these procedures effectively filter data from outside of euxinic depositional conditions, thereby limiting the temporal coverage of the inferred $\delta^{114}\text{Cd}_{\text{seawater}}$ record. The evolution of $\delta^{114}\text{Cd}_{\text{seawater}}$ for the non-euxinic intervals may be reconstructed by correcting for the effects of local redox, which are probably superimposed on trends in $\delta^{114}\text{Cd}_{\text{seawater}}$. In an attempt to correct for such local effects the regression lines for the $\delta^{114}\text{Cd}$ versus [Cd] cross-plots were calculated, excluding the outliers marked in blue. Subsequently, the deviation in $\delta^{114}\text{Cd}$ from this regression line may provide some information on the relative variability in $\delta^{114}\text{Cd}_{\text{seawater}}$. These relative variations were then anchored to the absolute $\delta^{114}\text{Cd}_{\text{seawater}}$ compositions as reconstructed before, to offer absolute $\delta^{114}\text{Cd}_{\text{seawater}}$ estimates throughout all of the studied intervals (Figure 3.7). However, it should be noted there are other processes that may impact the deviation from this regression line, and reconstructed values should be taken as a best estimate only, particularly for samples with low Cd abundances. For example, biological uptake and or sedimentation rates (by affecting sulphide formation) may impact the Cd concentration and/or $\delta^{114}\text{Cd}$ of the sediment. A more detailed understanding of Cd-isotope systematics, particularly with regards to early diagenesis, may allow more robust reconstructions in future studies.

Based on these reconstructions, the $\delta^{114}\text{Cd}_{\text{seawater}}$ of the Maverick Basin during much of the Cenomanian (Lower Eagle Ford) varies between ~ 0.2 and 0.3‰ , similar to compositions of the modern deep ocean (e.g. Conway and John, 2015). The isotopically lightest values of $\sim 0.2\text{‰}$ during Early Cenomanian are found

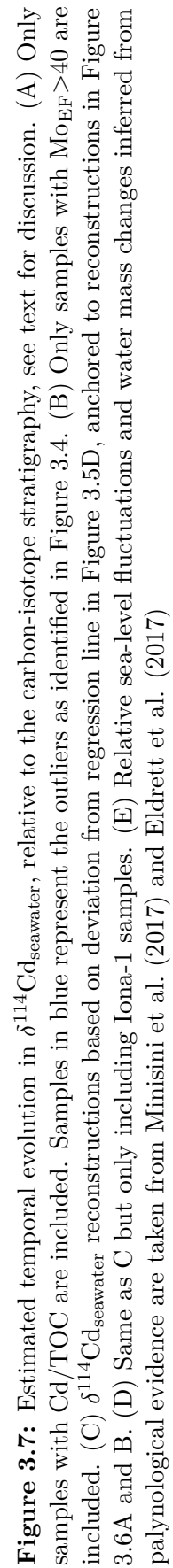
during the positive $\delta^{13}\text{C}_{\text{org}}$ excursion associated with the Jukes-Browne and Mid-Cenomanian Events, though these shifts are insignificant relative to the uncertainties associated with this reconstruction. Passing stratigraphically upwards from the Late Cenomanian and into the level of Oceanic Anoxic Event 2, values gradually drop from ~ 0.3 to 0.0‰ in both cores. $\delta^{114}\text{Cd}_{\text{seawater}}$ values recover to $\sim 0.2\text{--}0.3\text{‰}$ after the OAE 2 interval in the Early Turonian to then drop again by $\sim 0.2\text{‰}$ after the hiatus in the mid-Turonian.

$\delta^{114}\text{Cd}_{\text{seawater}}$ for the two cores show similar stratigraphic patterns and absolute values. However, there are intervals where data for the two cores diverge considerably, particularly during the interval around the Jukes-Browne Event, at $\sim 120\text{--}130\text{m}$ depth. This divergence may be due to a difference in local effects on the $\delta^{114}\text{Cd}$ cycling, but this seems unlikely considering that the regression lines were drawn separately for the two cores. Alternatively, this may represent an error associated with the conversion from the Innes-1 to Iona-1 depth scale. Focused on the Iona-1 $\delta^{114}\text{Cd}_{\text{seawater}}$ reconstructions alone, which excludes such errors, more detailed stratigraphic patterns emerge. The Iona-1 seawater reconstructions suggest lighter $\delta^{114}\text{Cd}_{\text{seawater}}$ composition during positive C-isotope excursions, as was apparent from the raw data.

To summarise, reconstructed $\delta^{114}\text{Cd}_{\text{seawater}}$ for the Maverick basin average around $\sim 0.2\text{--}0.3\text{‰}$ during most of the Cenomanian–Turonian interval, which is comparable to the modern deep ocean (Ripperger et al., 2007; Xue et al., 2013; Conway and John, 2015, John et al., in press.). Lower $\delta^{114}\text{Cd}_{\text{seawater}}$ of values $\sim 0.0\text{‰}$ are found for the OAE 2 interval and the interval stratigraphically upward from the mid–Turonian hiatus. Other positive C-isotope excursions (Mid-Cenomanian Event, Jukes Browne Event) also appear to be associated with brief intervals of lower $\delta^{114}\text{Cd}_{\text{seawater}}$ of $\sim 0.1\text{--}0.2\text{‰}$, at least for the Iona-1 core.

3.6.2 Drivers of $\delta^{114}\text{Cd}_{\text{seawater}}$ change

Positive carbon-isotope excursions are thought to be associated with the enhanced burial of ^{12}C in organic-rich sediments at a global scale (Scholle and Arthur, 1980;



Schlanger et al., 1987; Arthur et al., 1987). One of the critical factors in conceptual models for intervals of enhanced carbon deposition is the nutrification of (surface) oceans, which would drive and sustain high primary productivity rates, directly or indirectly triggered by enhanced volcanism (e.g. Jenkyns, 2010).

The interval just before OAE 2 has been associated with the onset of a large-scale magmatic episode, as evidenced by an unradiogenic osmium-isotope excursion found in several marine basins around the world (e.g. Turgeon and Creaser, 2008; Du Vivier et al., 2014, 2015). This process is thought to have resulted in the nutrification of surface waters, either directly by enhanced basalt-seawater interaction (e.g. Jenkyns et al., 2017) and/or indirectly by warming-induced enhanced silicate weathering of oceanic and continental crust (Pogge von Strandmann et al., 2013) and/or intensification of the hydrological cycle promoting increased fluvial input (Van Helmond et al., 2014).

Regionally, evidence for enhanced (submarine) volcanism during OAE 2 and the Mid-Cenomanian Event intervals has recently been observed based on increased Hg abundances during these intervals (Scaife et al., 2017). Furthermore, peaks in mafic elements and decreases in chromium-isotope compositions of seawater during OAE 2 in the Western-Interior Seaway have previously been linked to Large Igneous Province (LIP) volcanism in the Caribbean and High Arctic (Orth et al., 1993; Snow et al., 2005; Eldrett et al., 2014; Holmden et al., 2016). If such magmatic episodes were associated with the enhanced input of isotopically light Cd, globally and/or locally bringing down the average $\delta^{114}\text{Cd}$ of input into the Maverick Basin, these processes would have had the potential to explain the lighter $\delta^{114}\text{Cd}$ composition of the seawater and sediments. Alternatively, an enhanced input flux may have caused a temporary increase in the proportion of non-quantitative removal of Cd to sediments.

Burial of isotopically light Cd in globally expanding organic-rich sediment deposits (as evidenced from a positive C-isotope excursion) may subsequently lead to the gradual increase in $\delta^{114}\text{Cd}$ of the ocean, and ultimately sediment, back to background values. For the intervals where the resolution in $\delta^{114}\text{Cd}$ stratigraphy allows assessment of the temporal evolution of $\delta^{114}\text{Cd}$ during these events (i.e. OAE

2 in the Iona-1 core), values indeed appear to be lightest near the onset of the C-isotope excursion and increase gradually during the event interval. However, for most of the isotope excursions in each core, the data resolution is too low to identify trends at this level of stratigraphic detail.

Alternatively, local changes in circulation and/or relative sea level may explain shifts towards lighter $\delta^{114}\text{Cd}$ compositions. The lightest $\delta^{114}\text{Cd}$ values during the Cenomanian occurred during a time interpreted as maximum flooding surface (Minisini et al., 2017, Figure 3.7). Relative sea-level rise might have allowed deeper, and thus isotopically lighter, waters to flow into the Maverick Basin, thereby causing a shift towards lower $\delta^{114}\text{Cd}$ values in the sediments. Palynological evidence suggests incursions of boreal water masses, instead of Tethyan, during the OAE 2 interval and the hiatus in the Turonian (Eldrett et al., 2017). This change in circulation patterns may explain relatively lighter $\delta^{114}\text{Cd}$ compositions if this boreal water mass consisted of isotopically light cadmium. Increased basalt-seawater interaction due to emplacement of the High-Arctic Large Igneous Province (HALIP), lying to the north of the Western-Interior Seaway, may explain an isotopically light $\delta^{114}\text{Cd}$ composition for boreal waters. A better understanding of modern ocean Cd-isotope systematics may in the future be used to assess the feasibility of these different scenarios.

3.7 Conclusion

- Stratigraphic patterns in $\delta^{114}\text{Cd}$ are reproducible between different cores in the same basin and vary with key changes in other palaeoenvironmental parameters.
- A positive relationship is found between $\delta^{114}\text{Cd}$ with Mo_{EF} and Cd/TOC . These relationships imply that the proportional removal of Cd to sediments as Cd-sulphides exerts a primary control on the $\delta^{114}\text{Cd}$ composition of these sediments, which is thus indirectly controlled by locally varying redox conditions. Near-complete removal of Cd in sulphidic environments might be

taken to record the coeval $\delta^{114}\text{Cd}_{\text{seawater}}$ values, whereas isotopically lighter values are observed in more oxygenated conditions.

- The effects of local redox conditions are superimposed on the temporal evolution of $\delta^{114}\text{Cd}_{\text{seawater}}$ of the basin. The evolution of $\delta^{114}\text{Cd}_{\text{seawater}}$ may be reconstructed by isolating samples that were deposited in euxinic conditions, where the authigenic enrichment of CdS is far in excess of biological enrichment recorded by Cd/TOC co-variation. Alternatively, the evolution of $\delta^{114}\text{Cd}_{\text{seawater}}$ may be estimated by correcting for local redox effects.
- Minimum estimates of $\delta^{114}\text{Cd}_{\text{seawater}}$ compositions for the Maverick basin vary between ~ 0.0 and 0.3 for the Cenomanian–Turonian interval, which are comparable to values observed in the modern deep ocean. The lower values typically occur during positive isotope excursions, particularly during the OAE 2 interval.
- Intervals of lighter $\delta^{114}\text{Cd}_{\text{seawater}}$ may have been caused by enhanced Cd input associated with magmatic episodes, the influx of boreal waters, and/or relative sea level changes.
- There is no clear evidence for a dominant control of surface ocean nutrient dynamics on the $\delta^{114}\text{Cd}$ composition of these sediments.

4

Zn- and Cd-isotope evidence for global redox change during OAE 2

Contents

4.1	Abstract	59
4.2	Introduction	60
4.3	Material and methods	63
4.3.1	Analytical methods	65
4.4	Results	65
4.5	Discussion	67
4.5.1	Chemostratigraphic units	67
4.5.2	Controls on Zn and Cd enrichments	68
4.5.3	$\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ variability during the Plenus Cold Event	71
4.6	Stratigraphic comparison of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$	74
4.6.1	Comparing different archives for $\delta^{66}\text{Zn}$	77
4.7	Conclusion	79

4.1 Abstract

The Cd- and Zn-isotope analysis of marine sediments holds promise as a tool to reconstruct the nutrient and/or redox dynamics of past oceans. This study explores the use of organic-rich sediment as an archive for the Cd- and Zn-isotope composition of past seawater. Organic-rich sediments from the Tarfaya Basin are used as a case study of the Cenomanian–Turonian interval (Late Cretaceous). These

deposits include an expression of Oceanic Anoxic Event 2 (OAE 2, ~ 94 Ma), an interval associated with the widespread burial of organic-rich sediments and the spread of low-oxygen marine environments in a global context.

The Tarfaya Basin was placed in a region of upwelling of nutrient-rich deep waters and experienced relatively stable redox conditions locally. This allows stratigraphic variations in the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ to be largely be interpreted as changes in the seawater isotopic composition of the deep proto-North Atlantic, thereby providing information on regional to global scale processes.

As such, positive shifts of ~ 0.1 and 0.4 ‰ in both $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ respectively are observed relative to background conditions during the main phase of the positive carbon isotope excursion associated with OAE 2, an interval considered to represent peak organic-carbon burial globally. This change in isotope composition is associated with a drop in Cd/TOC (and to a lesser extent Zn/TOC) and can thus be taken to represent the drawdown of Cd and Zn seawater inventories as a result of extensive burial in organic-rich marine sediments.

In general, stratigraphic patterns in $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ are similar. However, there are marked differences in the records of two isotope systems during the interval of the Plenus Cold Event, a period of cooling and oxygenation recognised in the Northern Hemisphere. Low $\delta^{66}\text{Zn}$ values compared to near stable $\delta^{114}\text{Cd}$ patterns during this interval may be related to the remobilisation of isotopically light Zn from continental-margin sediments and/or the enhanced input of hydrothermal Zn.

Similar stratigraphic patterns in $\delta^{66}\text{Zn}$ have been observed previously in the organic-lean English chalk near Eastbourne (UK), supporting a supra-local control. This study thereby illustrates the potential of the combined analysis of Zn and Cd isotopes on organic-rich sediments to trace global scale ocean chemistry changes.

4.2 Introduction

The widespread deposition of organic-rich sediments during a number of intervals in the Mesozoic Era has been associated with global warming, the spread of low-oxygen marine environments, and other perturbations to ocean chemistry and

marine flora and fauna (e.g. Leckie et al., 2002; Jenkyns, 2003, 2010; Erba, 2004; Forster et al., 2007; Naafs and Pancost, 2016; Dickson, 2017). One of the most severe and best-studied examples of these events is the Cenomanian–Turonian (Late Cretaceous, ~ 94 Ma) Oceanic Anoxic Event 2 (OAE 2) (Schlanger and Jenkyns, 1976; Meyers et al., 2012). To drive and sustain the high export productivity rates required to reproduce the oceanic redox change associated with this event in geochemical models requires high availability of nutrients in the surface ocean for timescales in the order of 105 years (Monteiro et al., 2012). The availability of major nutrients phosphate and nitrogen can be explained by their particular behaviour in anoxic conditions. Phosphorus regeneration from anoxic sediments and the increased fixation of nitrogen by cyanobacteria can explain why both elements remain available despite the widespread burial of organic carbon (e.g. van Cappellen and Ingall, 1994; Kuypers et al., 2004; Mort et al., 2007; Kraal et al., 2010; Monteiro et al., 2012). However, the availability of bio-essential trace elements may be more problematic considering their affinity for sulphides and/or sensitivity to changes in ocean redox conditions. Removal of redox-sensitive trace elements has been shown to draw down the dissolved pool during OAE 2 (Algeo, 2004; Hetzel et al., 2009; van Bentum et al., 2009; Owens et al., 2016). Redox-sensitive, bio-essential trace elements may therefore become bio-limiting during intervals of widespread low-oxygen conditions.

The geographical extent of low-oxygen marine environments is one of the key parameters that are needed to understand the complex interplay of processes involved during OAE intervals. Most tools used to reconstruct past redox conditions provide primarily local information. Isotope analyses of redox-sensitive trace elements have potential to reconstruct redox conditions on a regional to global scale if past seawater isotope compositions can be estimated. Several studies have successfully used this rationale (e.g. Westermann et al., 2014; Goldberg et al., 2016; Dickson, 2017), but so far these studies are largely limited to conservative elements (i.e. Mo) with long residence times ($\sim 400,000$ years, Miller et al., 2011) and therefore have limited applicability to address geologically more rapid changes. Recent studies have suggested that redox conditions during OAE intervals can be more

dynamic than generally considered (e.g. the Plenus Cold Event interval, a period of colder ocean temperatures and enhanced oxygenation during OAE 2, Jenkyns et al., 2017). Reconstructing more rapid changes in marine redox conditions of past oceans, beyond sample localities, requires redox-sensitive isotopic tracers with shorter residence times.

This study aims to explore the use of relatively novel isotopic tracers (Cd and Zn) to ultimately address the following two questions: 1) How and why did the availability of bio-essential micronutrients change during OAE intervals, and how did that impact carbon-burial; and 2) What was the geographical extent of low-oxygen conditions, and how (temporally) variable were these conditions? Answering these questions requires reliable estimates of past seawater compositions for these isotopic tracers. This approach requires the impact of local environmental conditions on the isotopic composition of the chosen archive should be of second-order importance, or that they can be corrected for.

The combined Cd- and Zn-isotope analysis of the sedimentary record has the potential to address both these questions because these elements show an affinity for sulphides and a nutrient-like distribution in the modern ocean (Chapter 1 and references therein). Sulphide formation in sulphidic (pore) waters is associated with the preferential uptake of the lighter isotopes for both elements, which may lead to isotope fractionation if removal is non-quantitative (Little et al., 2016; Vance et al., 2016; Bryan et al., in prep; Chapter 3). Biological uptake of isotopically light Cd results in high $\delta^{114}\text{Cd}$ in the modern surface ocean whereas the $\delta^{66}\text{Zn}$ of surface waters is generally lower than deep waters (e.g. Conway and John, 2014; 2015). The relative proportion of isotopically heavy oxic sinks for Zn to isotopically light sinks in organic-rich sediments and the isotopic composition of ocean inputs set the average $\delta^{66}\text{Zn}$ composition of the modern ocean to $\sim 0.5\text{‰}$ (e.g. compilations in Little et al., 2016; Vance et al., 2016; John et al., 2017). For Cd, the different ocean inputs and outputs are not as well established (see Chapter 1 for details).

Recent efforts to reconstruct changes in the Zn cycle during OAE 2 based on the study of organic-lean carbonate rocks have indeed suggested considerable variability

in the global mass balance of zinc associated with global scale redox changes (Chapter 2). However, complexities in the cycling of Zn in the surface ocean, insufficient understanding of the magnitude of Zn-isotope partitioning between seawater and carbonate archives, and the need for clean sedimentary carbonate archives currently limit this approach. Organic-rich sediments are more prevalent during OAEs and therefore may allow a more thorough assessment of spatial patterns. Cd-isotope analysis of organic-rich sediments of Cenomanian–Turonian age has shown interesting stratigraphic trends in relation to the carbon-isotope stratigraphy and have highlighted the impact of local redox environments (Chapter 3).

Here, the combined use of organic-rich sediments as a suitable archive for the Zn- and Cd-isotope composition of seawater is evaluated. Comparing and contrasting the two isotope systems allows a more detailed assessment of past environmental changes than would be possible from one of the systems in isolation. With residence times of $\sim 11,000$ years (Little et al., 2014) and $\sim 50,000$ years (Bruland, 1980) for Zn and Cd respectively, these elements have the potential to trace global perturbations to micronutrient cycles and/or redox conditions, if past deep-water compositions can be reconstructed.

4.3 Material and methods

Sediments from the Tarfaya Basin, Morocco contain a well-studied Cenomanian–Turonian boundary interval (e.g. Tsikos et al., 2004). The focus in this study is on core S57, which contains ~ 37 m of cyclically bedded organic-rich calcareous sediments of Cenomanian–Turonian age with a very low abundance of detrital minerals (Kolonic et al., 2005). During deposition, the basin was located in an open shelf setting at $\sim 15^\circ\text{N}$ and the area is thought to have been fed by the upwelling of nutrient-rich waters from the deep ocean (Lüning et al., 2004; Kolonic et al., 2005; Kuhnt et al., 2005; Wagner et al., 2013, Figure 1)(Luning et al., 2004; Kolonic et al., 2005; Wagner et al., 2013, Figure 4.1). The $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ of waters feeding the Tarfaya Basin are thus considered here to represent compositions of the deep proto-North Atlantic despite estimated palaeo-water depths of only a few hundred

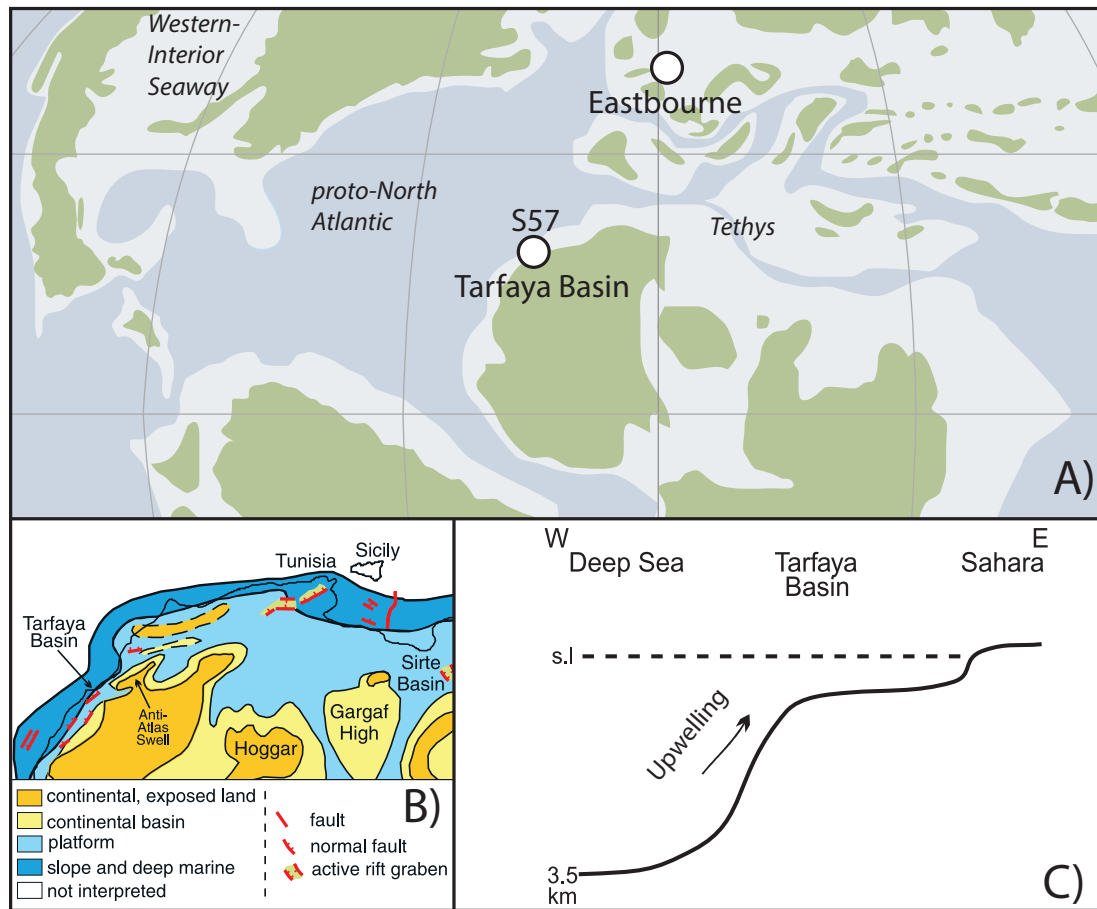


Figure 4.1: A) Palaeogeographical reconstruction of the Cenomanian–Turonian Boundary interval with approximate study locations. Courtesy of Lauren O'Connor, modified from Jarvis et al. (2011). B) Late Cenomanian palaeogeography of North-West Gondwana, adjusted from Luning et al., 2004, after Stampfli et al., 2001. C) Simplified representation of inferred hydrographical conditions of the Tarfaya Basin, after Luning et al., 2004.

meters (Kolonic et al., 2005; Kuhnt et al., 2005). Organic biomarker, Fe-speciation, and trace metal data from high-resolution studies on part of this core have revealed dominantly euxinic conditions with short perturbations towards anoxic ferruginous conditions (Poulton et al., 2015; Goldberg et al., 2016). These conditions may be extrapolated to the rest of this core as a minimum estimate for the degree of anoxia with reasonable confidence, considering higher Mo-enrichments throughout the rest of the core (Kolonic et al., 2005; Goldberg et al., 2016; Dickson et al., 2016).

4.3.1 Analytical methods

Chemical preparation and analytical methods were described in more detail elsewhere (Chapter 1). In short, an inverse aqua regia digestion was employed which leaves most detrital minerals intact but dissolves the authigenic metal phase and organic matter (Xu et al., 2012). Samples were spiked with a ^{67}Zn - ^{64}Zn or ^{113}Cd - ^{111}Cd double spike before purification by anion column chromatography. Stable-isotope analyses were performed on a Nu Instruments Nu Plasma I multi-collector ICP-MS at the University of Oxford. Data were processed offline using an exponential mass-bias correction, measured relative to NIST-3108 Cd and IRMM-3702 Zn solutions, and reported as $\delta^{114}\text{Cd} = ([^{114}/^{110}\text{Cd}_{\text{sample}}/^{114}/^{110}\text{Cd}_{\text{NIST}}]-1)*1000$ and $\delta^{66}\text{Zn} = ([^{66}/^{64}\text{Zn}_{\text{sample}}/^{66}/^{64}\text{Zn}_{\text{IRMM}}]-1)*1000 + 0.28$.

External reproducibility is estimated based on analyses of SDO-1 shale reference material: $\delta^{66}\text{Zn}_{\text{SDO-1}} = 0.43 \pm 0.07 \text{ ‰}$ (2 SD, n=9) and $\delta^{114}\text{Cd}_{\text{SDO-1}} = 0.13 \pm 0.06 \text{ ‰}$ (2 SD, n = 5). Reported errors are the 2 standard error propagated uncertainties based on the reproducibility of the bracketing standards and the internal error of sample analysis. Enrichment factors (EF) are calculated relative to average upper continental crust concentrations (Rudnick and Gao, 2003) as $\text{EF} = (\text{TM}/\text{Al})_{\text{sample}}/(\text{TM}/\text{Al})_{\text{crust}}$.

4.4 Results

Both zinc and cadmium are heavily enriched with a Zn_{EF} range of ~ 3.2 –207 and average of 40 (n = 35), and a Cd_{EF} range of ~ 20 –850 and an average of 238 (n = 36). Enrichments of Zn and Cd follow similar stratigraphic patterns, as highlighted by a strong linear correlation between Zn_{EF} and Cd_{EF} . Chemostratigraphic unit 1 (white, background conditions) generally contains the highest Cd and Zn enrichments relative to TOC, though for Zn the differences between the units are smaller; lowest enrichments are found for unit 2 (dark grey, Plenus Cold Event).

Zn- and Cd-isotope compositions for the S57 core show stratigraphic patterns coincident with changes in other geochemical parameters. $\delta^{66}\text{Zn}$ values range from

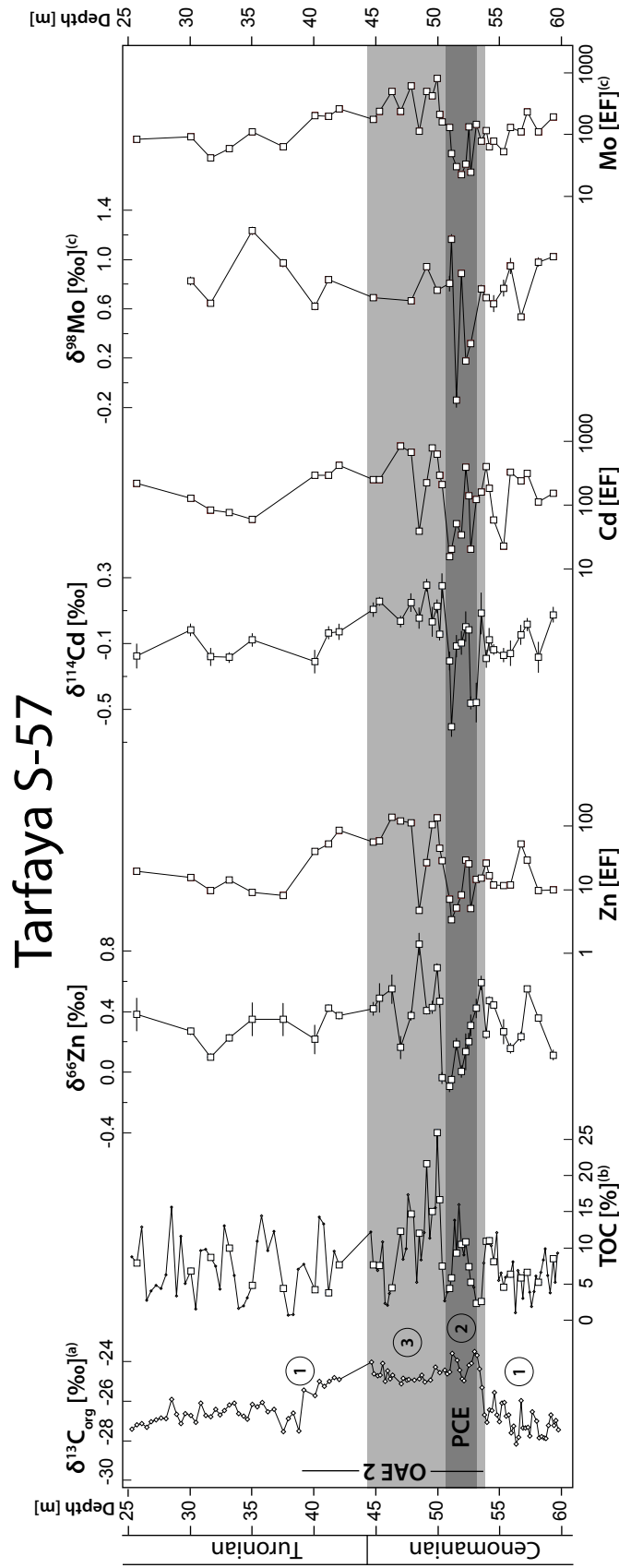


Figure 4.2: Cenomanian–Turonian $\delta^{114}Cd$ and $\delta^{66}Zn$ stratigraphy of the S57 core from the Tarfaya Basin. a) Tsikos et al. (2004), (b) Kolonic et al. (2005), (c) Dickson et al. (2016).

~ -0.09 – 0.85‰ with an average of $0.32 \pm 0.41 \text{‰}$ (2 SD $n = 38$). $\delta^{114}\text{Cd}$ values range from ~ -0.61 – 0.26‰ with an average of $-0.07 \pm 0.37 \text{‰}$ (2 SD $n = 36$). These values are marginally lighter than values observed in the modern (deep) ocean and modern marine sediments (average dissolved $\delta^{114}\text{Cd}$: 0.38 ± 0.07 , 1SD; average dissolved $\delta^{66}\text{Zn}$: 0.49 ± 0.07 , 1SD; compiled by John et al., 2017). The lightest values for both zinc and cadmium are observed during the Plenian Cold Event (unit 2). The heaviest isotope compositions for both elements are found in the stratigraphic interval just post-dating the Plenian Cold Event, during the peak interval of OAE-2.

The average $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ for Cenomanian–Turonian background conditions (unit 1) are -0.10 ± 0.09 and 0.31 ± 0.12 (1 SD, $n=18$) respectively. Average $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values for unit 2 ($\sim$ Plenian Cold Event) are -0.24 ± 0.23 and 0.14 ± 0.18 (1 SD, $n=9$) and for unit 3 (plateau-phase) $0.11 \pm 0.09 \text{‰}$ and 0.45 ± 0.23 (1 SD, $n=11$) respectively.

4.5 Discussion

4.5.1 Chemostratigraphic units

To assess the environmental controls on stratigraphic $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ variations, samples for the Tarfaya core were grouped into three chemostratigraphic units, based mainly on the carbon-isotope stratigraphy. The shading of these different units, as indicated in Figure 4.2, will later be used in cross-plots to compare and contrast metal (isotope) geochemistry for these different intervals (Figure 4.3 and 4.5).

1. In white, samples from before the onset of the carbon-isotope excursion (CIE) and after the plateau-phase. These samples represent background conditions for the Cenomanian–Turonian.
2. In dark grey, samples from an interval approximately coeval with the Plenian Cold Event. The timing of this event, initially recognized by the occurrence of boreal fauna and relatively heavy bulk oxygen-isotope compositions in the English chalk, can be correlated to sections that lack characteristic fossils by

comparison of the carbon-isotope stratigraphy (Gale and Christensen, 1996; Jenkyns et al., 2017). The brief dip in the carbon-isotope curve coincident with the Plenus Cold Event may record a temporary drop in carbon-burial rates and can be used as a correlative tool. Here, this chemostratigraphic unit is extended just beyond the slight dip in the carbon-isotope curve to cover the full interval of lower Mo enrichments, which fits with oxygenation associated with the Plenus Cold Event in several other localities (Jenkyns et al., 2017). High-resolution data from previous studies (Poulton et al., 2015; Goldberg et al., 2016) covers this entire interval and is used later in this study to evaluate trends in more detail (Figure 4.4)

3. In light grey, samples from the CIE interval but prior to the Plenus Cold Event and samples from the plateau-phase of the CIE. This interval represents maximum organic-carbon burial globally.

4.5.2 Controls on Zn and Cd enrichments

Cd (and to a lesser extent Zn) enrichments relative to TOC show distinctly different patterns for the various chemostratigraphic units. In general, Cd concentrations in samples from unit 3 (the plateau phase of OAE 2), are relatively low despite TOC contents of occasionally >20% at some levels. Conversely, Cd concentrations are relatively high for samples from unit 1 (pre- and post-OAE 2), despite generally modest TOC content (<10%). The lowest Cd/TOC ratios are observed for unit 2 (the Plenus Cold Event), which also generally shows the lowest TOC and Cd enrichments. These general patterns are similar, though more muted, for Zn.

However, although low trace-metal/TOC ratios are found for both units 2 and 3 (i.e. samples from the CIE) their isotopic compositions are distinctly different (Figure 4.3C). Samples with low trace-metal/TOC ratios from unit 3 show high $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ whereas lower isotope values are observed for samples with comparable trace-metal/TOC ratios from unit 2. This disparity suggests that different processes caused their degree of enrichment in the different units.

The enrichment of Zn and Cd in the sediment relative to TOC likely mainly depends on the abundance of the dissolved elements and the availability of free H_2S . Trace-metal/TOC ratios of material exported from the surface ocean may be a function of surface-ocean trace-metal availability if their uptake by primary producers is proportional to their dissolved abundances. This ratio can be altered later by the preferential preservation of one over the other, or the presence of metals in other phases in the sediment. For the Tarfaya basin, with highly reducing conditions and low detrital input, sulphides likely present the major other carrier for Zn and Cd. Sulphide formation in sulphidic (pore) waters can lead to the enrichment of Cd or Zn, but only if dissolved metals are available.

In hydrographically restricted and low oxygen modern marine basins, like the Black Sea and Cariaco Basin, dissolved Cd and Zn are nearly depleted below the chemocline (Jacobs and et al., 1987; Tankere et al., 2001; Vance et al., 2016). Such local drawdown has been shown to limit Mo enrichments in the sediments of these basins (Algeo & Lyons, 2006). Mo/TOC ratios in sediments from euxinic basins are proportional to the availability of dissolved Mo, and therefore partly controlled by the degree of hydrographic restriction (Algeo and Lyons, 2006). During times of global expansion of carbon burial and low-oxygen environments, for example OAE 2, trace metal enrichments can also be limited by the large-scale drawdown of marine trace-metal inventories (e.g. Hetzel et al., 2009; Van Bentum, 2009; Owens et al., 2016). Local drawdown of trace-metal inventories due to hydrographic restriction is unlikely for the Tarfaya Basin because of its position in an open marine shelf setting, under an upwelling zone. This open-ocean connection is consistent with the molybdenum-isotope compositions for these sediments, which suggest an abundant supply of Mo (Dickson et al., 2016). However, drawdown of trace metals in the proto-North Atlantic/Tethys region, or globally, might have impacted trace-metal supply to the Tarfaya Basin, if removal into organic-rich sediments outpaced supply.

Low enrichments and heavy isotopic compositions of Cd and Zn during the plateau phase of the CIE (unit 3) may thus be linked to the drawdown of isotopically light Cd and Zn in organic-rich sediment deposits by non-quantitative removal in

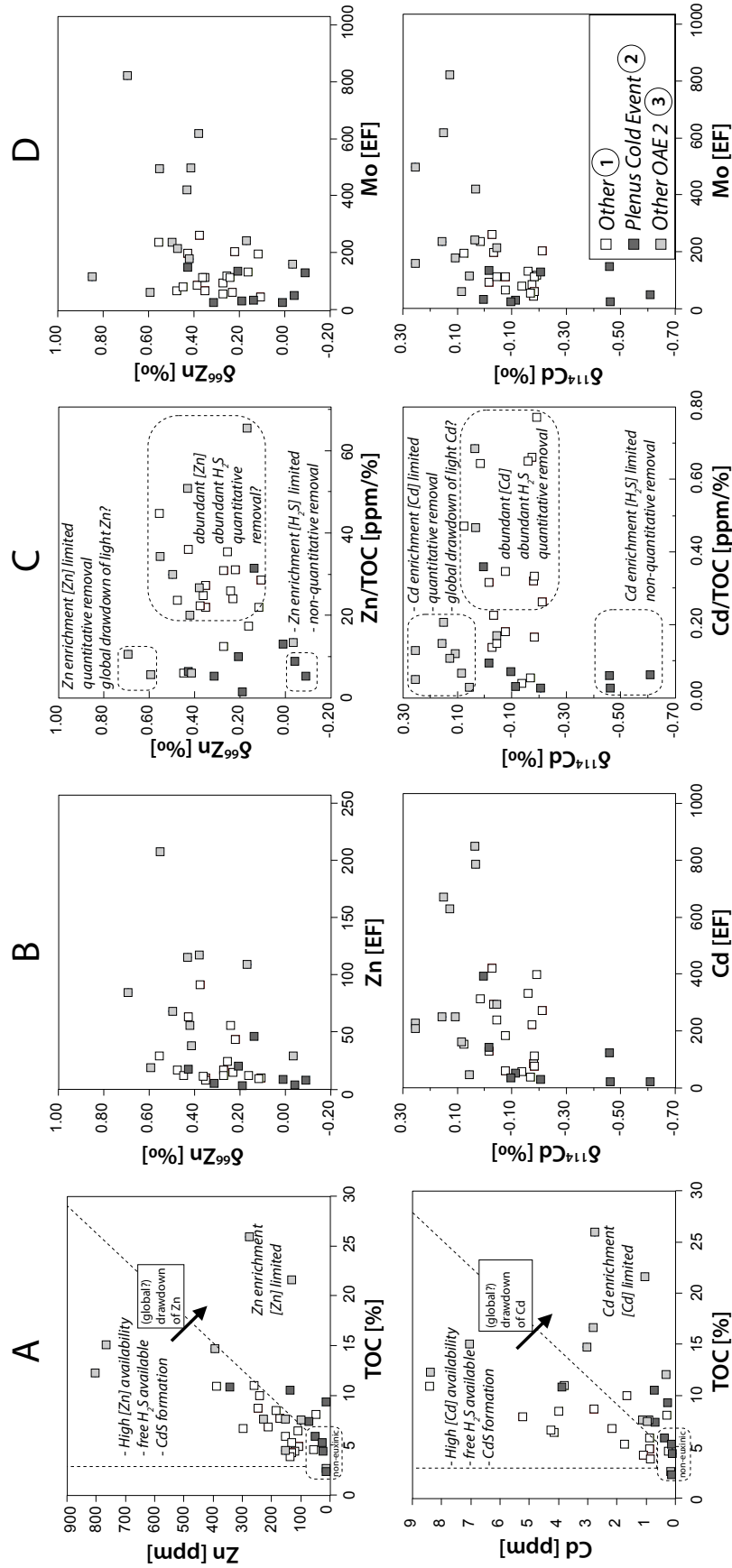


Figure 4.3: Various cross-plots of geochemical parameters from core S57, Tarfaya Basin. The shading represents different stratigraphic intervals as highlighted in Figure 2 and discussed in more detail in the methods section. The $\delta^{13}\text{C}_{\text{org}}$, TOC, and Mo data come from Tsikos et al. (2004), Kolonic et al. (2005), and Dickson et al. (2016) respectively. Enlarged version of plots A and C can be found in Appendix A.

sulphides, globally or around the margins of the proto-North Atlantic. In this case, the enrichment of Cd and Zn was limited by presence of the dissolved elements. Conversely, low enrichments and light isotopic compositions during the Plenus Cold Event (unit 2) may be the result of non-quantitative removal and the preferential uptake of the lighter isotopes. In this case, the enrichment of Cd and Zn was limited by the removal mechanism, i.e. biological uptake and/or sulphide formation were relatively low compared to Cd and Zn availability. As these sediments are from an interval with the lowest Mo enrichments, the lack of sufficient free H_2S for quantitative Cd and Zn removal seems likely, mainly as relatively light $\delta^{114}\text{Cd}$ compositions have previously been observed for more oxygenated conditions as a result of non-quantitative removal (Chapter 3). A similar process may have impacted Zn-isotope compositions for this interval, although the stratigraphic patterns in $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ are considerably different. Addressing this contrast requires a more detailed look at the Plenus Cold Event and surrounding interval.

4.5.3 $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ variability during the Plenus Cold Event

High-resolution Fe-speciation and Mo (-isotope) data from previous studies provide a more detailed look at the impacts of changing redox environments on $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ patterns during the Plenus Cold Event (Figure 4.4; Poulton et al., 2015; Goldberg et al., 2016). The Fe-speciation data show euxinic conditions with brief, cyclically occurring shifts to anoxic ferruginous conditions. Patterns in Mo_{EF} do not vary systematically with the cyclic alternation between euxinic and ferruginous conditions but instead more closely follow trends in TOC content. It has been suggested that very short-lived episodes of euxinia, or the presence of sulphides near the sediment-water interface, can explain the Mo enrichment during ferruginous intervals (Poulton et al., 2015; Goldberg et al., 2016).

The lightest $\delta^{114}\text{Cd}$ values, possibly indicative of non-quantitative removal of Cd in non-euxinic conditions, are not systematically registered in ferruginous intervals; only one of the two perturbations to low $\delta^{114}\text{Cd}$ is coincident with a ferruginous

interval. $\delta^{114}\text{Cd}$ patterns more closely follow trends in Mo_{EF} , with low $\delta^{114}\text{Cd}$ values occurring during intervals of low Mo_{EF} . Absolute $\delta^{114}\text{Cd}$ values for these samples suggest non-quantitative removal of Cd, because they show isotopically very light $\delta^{114}\text{Cd}$ compositions (~ -0.6 to -0.4 ‰). These values are much lighter than ocean inputs and dissolved $\delta^{114}\text{Cd}$ in the modern ocean (Schmitt et al., 2009; Lambelet et al., 2013; Conway and John, 2015). It is therefore unlikely that these values represent seawater conditions, particularly as sinks for heavy Cd in the modern ocean have not been recognised. The other samples of sediments recording the Plenus Cold Event, from intervals with higher Mo_{EF} , may represent seawater compositions and show $\delta^{114}\text{Cd}$ values comparable to Cenomanian–Turonian background conditions (~ -0.1 ‰).

In contrast to $\delta^{114}\text{Cd}$, $\delta^{66}\text{Zn}$ shows a more gradual decrease during the PCE. Non-quantitative removal may also be used to explain the lighter Zn-isotope compositions observed during this interval. However, there is no systematic relationship with $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ or Mo_{EF} , and therefore no apparent local redox control on the decrease in $\delta^{66}\text{Zn}$. The lightest $\delta^{66}\text{Zn}$ values observed (~ 0.0 ‰) are lighter than bulk silicate earth (~ 0.3 ‰, Chen et al., 2013) but not higher than $\delta^{66}\text{Zn}$ estimates for hydrothermal input (~ -0.5 to 0.3 ‰, Conway and John, 2014; Vance et al., 2016). Additionally, several isotopically heavy sinks for Zn have been recognised in the modern ocean, allowing seawater $\delta^{66}\text{Zn}$ values to evolve to lighter compositions than ocean inputs. It is therefore well possible that the observed decrease in $\delta^{66}\text{Zn}$ coincident with the Plenus Cold Event represents a change in $\delta^{66}\text{Zn}_{\text{seawater}}$. However, the true magnitude of this shift cannot be estimated due to the complexities of evaluating the efficiency of Zn removal from seawater into sediments for this interval.

In conclusion, the estimated $\delta^{114}\text{Cd}_{\text{seawater}}$ values for the Plenus Cold Event are constant and similar to background conditions for the Cenomanian–Turonian. By contrast, estimated $\delta^{66}\text{Zn}_{\text{seawater}}$ shows a negative excursion associated with the Plenus Cold Event, which may be as large as -0.5 ‰.

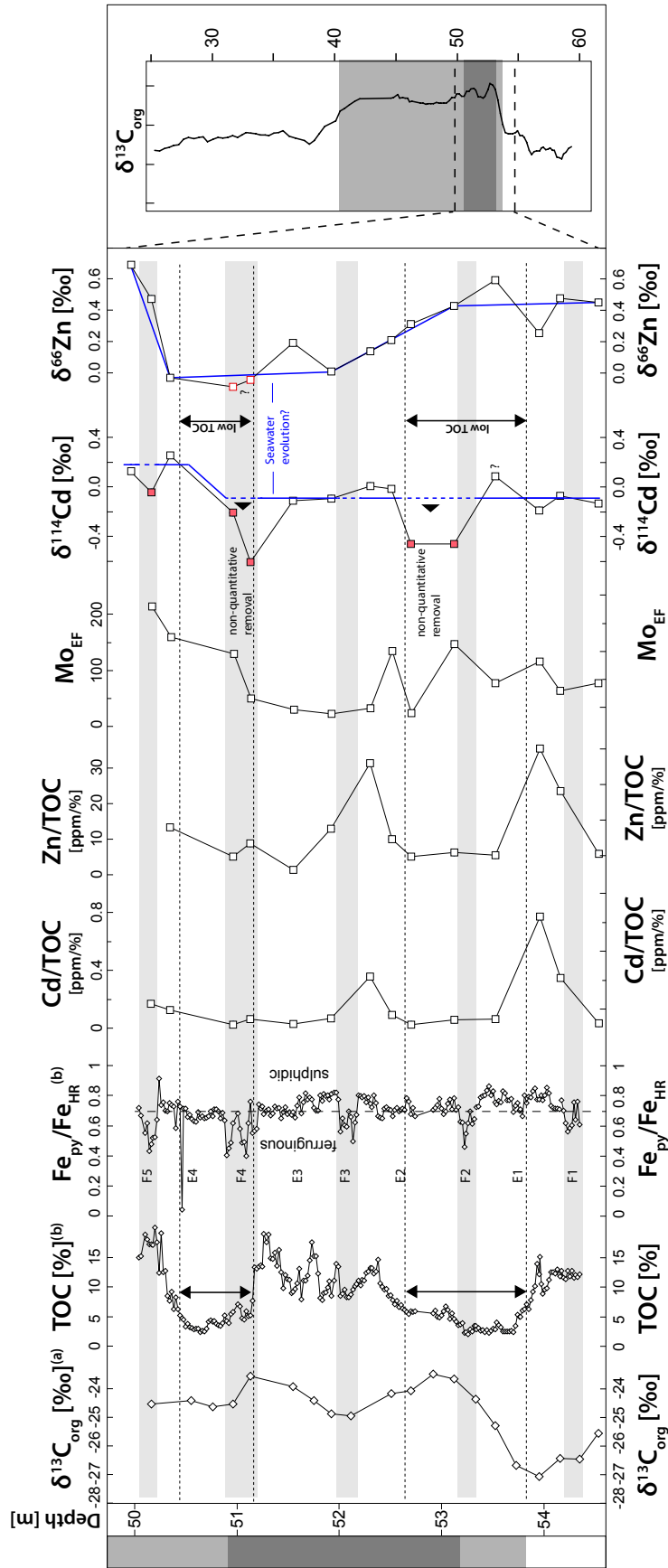


Figure 4.4: Close-up of an interval from the S57 core to compare $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ stratigraphy to high-resolution $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ and Mo(-isotope) data. The blue lines represent proposed reconstruction of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ seawater compositions. Samples marked in red highlight intervals that possibly represent non-quantitative removal of Cd and Zn. See text for discussion. a) Tsikos et al., 2004, (b) Poulton et al., 2015 (c) Goldberg et al., 2016.

4.6 Stratigraphic comparison of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$

The overall similarity in stratigraphic patterns between $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ for samples from core S57 is remarkable. This similarity suggests that local removal mechanisms are similar for Cd and Zn. However, a cross-plot of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$, reveals considerable scatter, even for samples outside of the Plenus Cold Event interval (unit 2). This scatter is indicative of small differences in their (bio)geochemical behaviour in the ocean and in sedimentary environments, which may impact the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ preserved in the sedimentary record. If these differences are sufficiently understood, they may provide complementary information on past changes in ocean chemistry. Despite outstanding questions on the behaviour of Cd and Zn in the modern ocean, several observations have been made that may explain the observed differences in this study.

1. *Surface ocean processes.* Modern ocean dissolved $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ profiles generally vary in different directions, with higher $\delta^{114}\text{Cd}$ and lower $\delta^{66}\text{Zn}$ in the surface ocean, despite similar patterns in concentrations. This difference in surface-ocean cycling may explain contrasting patterns in the sedimentary record, but only if surface-ocean removal was non-quantitative, which would allow the exported material to be isotopically lighter, or heavier, than the deep-water input to the basin. Despite near-quantitative removal of Cd and Zn in most parts of the modern surface ocean, non-quantitative surface-ocean removal should be considered to have had an effect on sediments from the Tarfaya Basin, as it is thought to have represented an active upwelling region. Such a palaeoceanographic configuration may have been particularly relevant with regards to the Plenus Cold Event, for which it has been shown that several trace metals (incl. Zn) were relatively abundant due to the temporary loss in organic-rich sinks, remobilisation of trace-metals from (margin) sediments, and/or the enhanced input from some sort of basalt-seawater interaction (e.g. Snow et al., 2005; Eldrett et al., 2014; Jenkyns et al., 2017, Chapter 2). These processes will be discussed in more detail below.

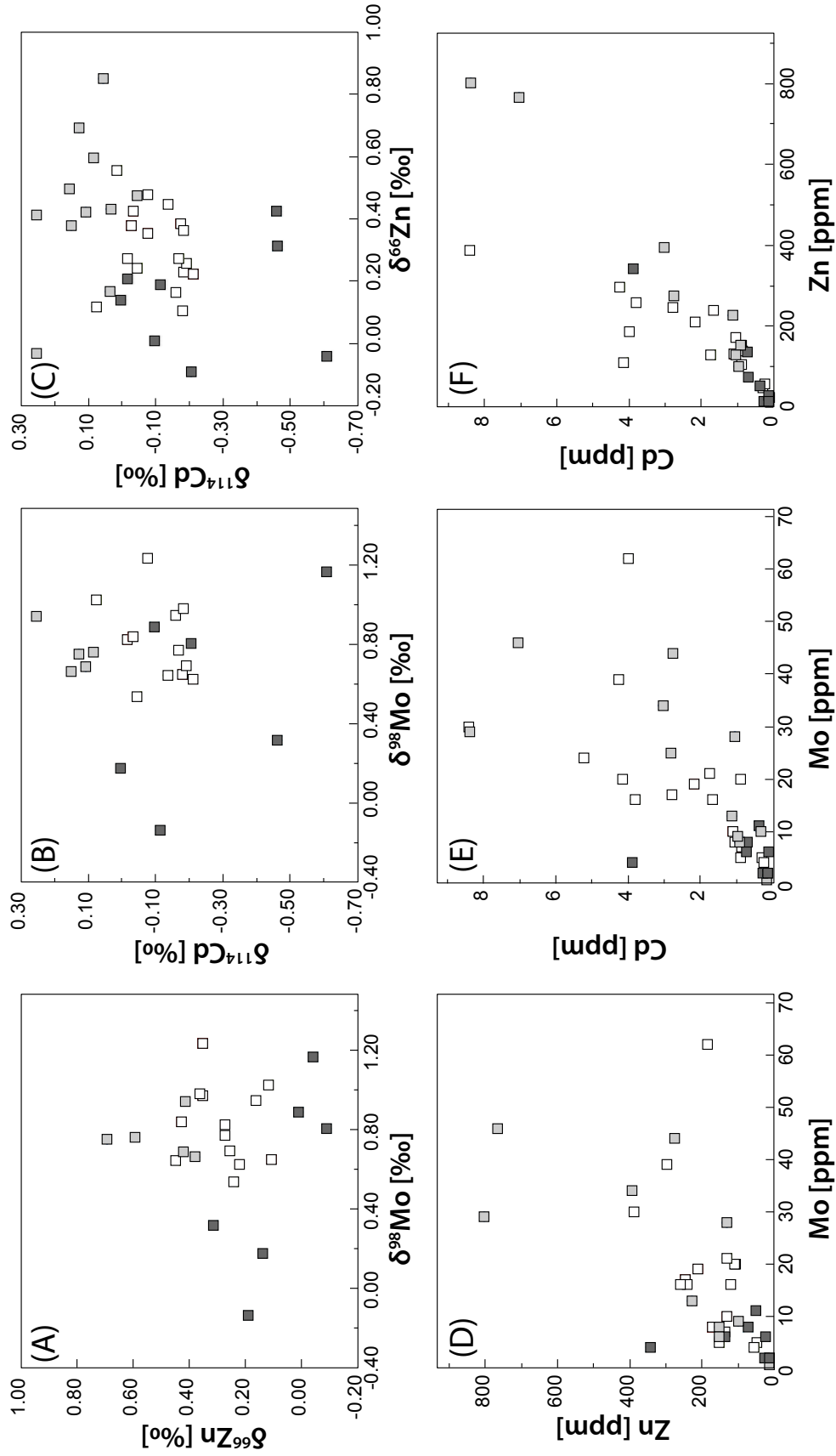


Figure 4.5: Comparison of Cd, Zn, and Mo isotopes and abundances for the Tarfaya S57 core.

2. *Sulphide formation and remobilisation from (margin) sediments.* Differences in behaviour under low-oxygen conditions may have impacted sedimentary patterns: locally, by controlling whether removal was quantitative, and/or globally, by affecting the relative size and isotopic compositions of the different sinks. Both Cd and Zn are thought to form their own sulphide phase, rather than being incorporated into pyrite, while equilibrium thermodynamics suggest Zn-sulphide complexes are relatively less stable (Al-Farati and Van den Berg, 1999; Morse and Luther, 1999; Little et al., 2015 and references therein). This geochemical behaviour may be reflected by the fact that Zn appears to be more easily released/remobilised from (margin) sediments. Dissolved $\delta^{66}\text{Zn}$ and $[\text{Zn}]$ patterns from the North Atlantic show signs of the release of isotopically light Zn from continental-margin sediments (Conway and John, 2014). Studies on dissolved $\delta^{114}\text{Cd}$ for the same transect have not revealed any sign of such a process (Conway and John, 2015). Remobilisation of Zn from sediments around margins of the proto-North Atlantic or globally due to oxygenation associated with the Plenus Cold Event may have driven the ocean to lighter Zn-isotope compositions.
3. *Volcanic inputs.* Spikes in trace-metal abundances and their isotopes, predominantly from the Western Interior Seaway, have been linked to mafic input from the Caribbean and High Arctic Large Igneous Provinces (LIPs) during the Plenus Cold Event interval (Snow et al., 2005; Eldrett et al., 2014; Holmden et al., 2016; Scaife et al., in press). As the details of volcanically derived Cd and Zn input are not well constrained, differences in the amount and isotopic composition of input from LIP volcanism may explain differing stratigraphic patterns. Hydrothermal plumes have been shown to be a source of isotopically light Zn, but a sink for isotopically light Cd in the modern ocean (Conway and John, 2014; Conway and John, 2015). Hydrothermal venting or submarine volcanism input could therefore explain low $\delta^{66}\text{Zn}$ values compared to $\delta^{114}\text{Cd}$.

4. *Residence times.* Both Cd and Zn show intermediate residence times in the modern ocean. However, estimates vary and the differences may be high enough to explain the scatter in Figure 4.5C. Differences in residence times could explain generally similar stratigraphic patterns but scatter in $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ cross-plots, as the elements may respond to imposed changes to their geochemical cycles on slightly different time-scales. However, estimates of residence times for Cd and Zn are not currently detailed enough to allow assessment of this effect, especially as they may have been different in the Late Cretaceous.

4.6.1 Comparing different archives for $\delta^{66}\text{Zn}$

A comparison of the $\delta^{66}\text{Zn}$ in organic-rich sediments in this study to time-equivalent $\delta^{66}\text{Zn}$ data from organic-lean carbonates from the English chalk (Chapter 2) is presented in Figure 4.6A. Samples were grouped into different intervals related to principal changes in the C-isotope stratigraphy to allow direct comparison between sites; the averages of the data contained within these intervals are plotted. The comparison between these two very different sedimentary archives from different ocean regions may provide some information on local versus global controls on Zn-isotope patterns and the suitability of these archives for palaeo-environmental reconstructions. General patterns between the two sites are remarkably similar, and show similarities to the C-isotope stratigraphy; absolute values, however, are considerably different.

$\delta^{66}\text{Zn}$ values for Eastbourne are heavier than values found from Tarfaya ($\sim +0.5\text{--}0.8\text{‰}$), which highlights the complexities of reconstructing past $\delta^{66}\text{Zn}$ of seawater. This offset supports considerable ($>0.4\text{‰}$) Zn-isotope partitioning between Late Cretaceous seawater and carbonates as hypothesized earlier (Chapter 2). Conversely, the Tarfaya dataset allows only a minimum estimate of past $\delta^{66}\text{Zn}_{\text{seawater}}$ as, although most samples likely record euxinic conditions, quantitative removal cannot be guaranteed to have taken place.

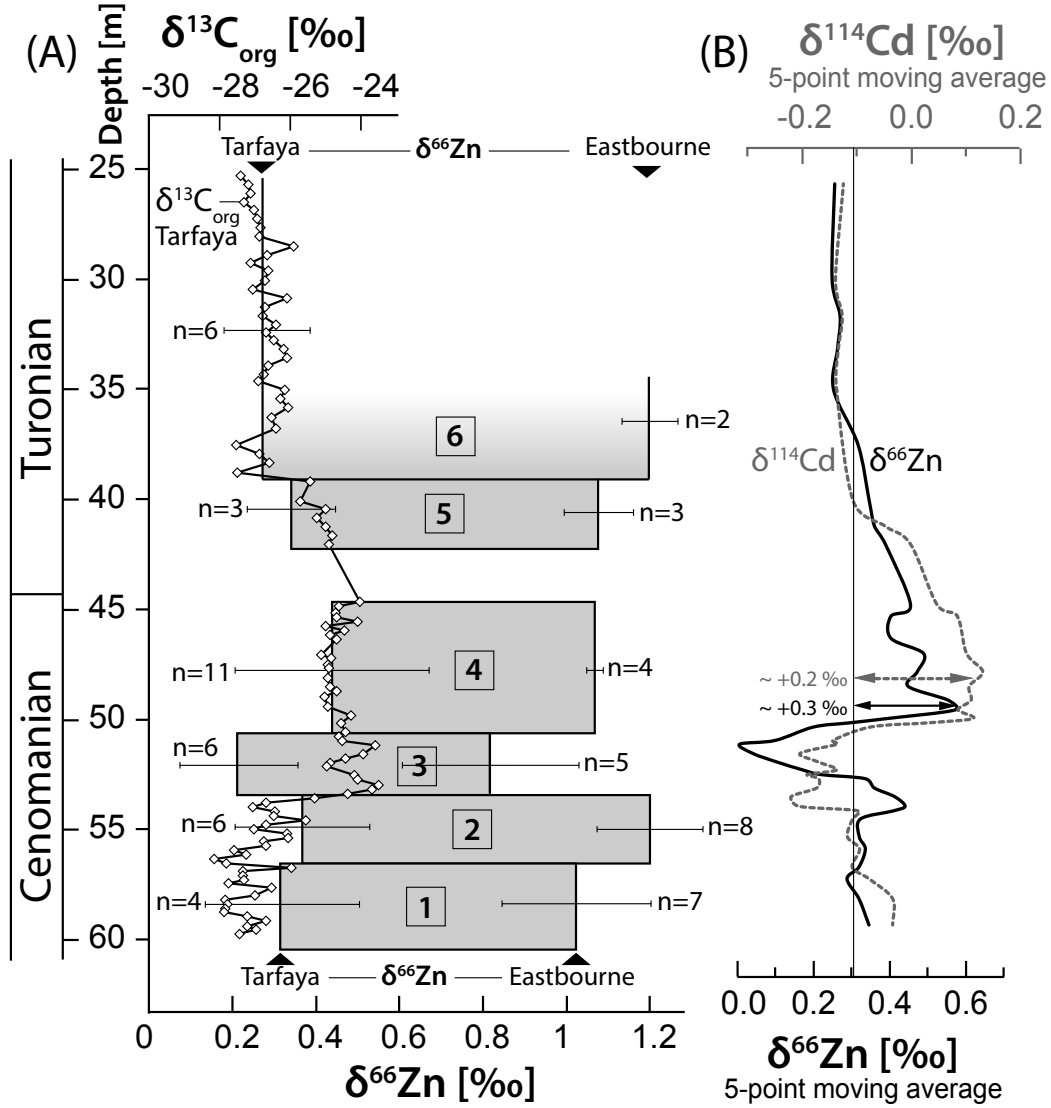


Figure 4.6: (A) Comparison of $\delta^{66}\text{Zn}$ stratigraphy from this study to time-equivalent data from the Eastbourne chalk section (Chapter 2). Averages for different stratigraphic intervals were calculated for both sections and then plotted relative to the $\delta^{13}\text{C}_{\text{org}}$ stratigraphy from the Tarfaya Basin. The numbers refer to different stratigraphic intervals as discussed in the relevant text. (B) 5-point moving averages for $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ from the Tarfaya Basin.

Similarities in the relative stratigraphic patterns for both sites do, however, imply that these trends follow supra-local and possibly global palaeoenvironmental changes. Pre-OAE (section 1 in Figure 4.6B) $\delta^{66}\text{Zn}$ values for both sites are lighter than the average for samples from the build-up (section 2) and plateau (section 4) phases of the OAE. The isotopically lightest values for both sites are observed for the Plenus Cold Event interval (section 3). After the plateau-phase of the OAE (sections 5 and 6) both sites converge, with $\delta^{66}\text{Zn}$ values in Tarfaya returning to pre-OAE values while they remain high at Eastbourne. Data density for this interval is, however, very low in Eastbourne, so the values may not be representative.

4.7 Conclusion

- Apart from short intervals during the Plenus Cold Event, the Tarfaya Basin was euxinic throughout the Cenomanian–Turonian interval based on Fe-speciation, trace metal enrichments and organic biomarkers. Such geochemical conditions suggest near-quantitative removal of Zn and Cd to the sediment has taken place, which thus may provide a minimum estimate of past $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ of seawater. The former location of the Tarfaya Basin, in an upwelling zone, suggests that reconstructions of the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ composition of seawater in the basin represent deep-water conditions and may thus be extrapolated to infer changes on a regional scale.
- A combination of the Cd and Zn abundances, and the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ compositions of the sediment, suggests global drawdown of Cd and Zn resulting from extensive organic-rich sediment burial during the plateau phase of the carbon-isotope excursion that records the OAE. This is associated with an estimated $\sim +0.2$ and $+0.3$ ‰ shift in the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ composition of waters in the Tarfaya Basin and by inference proto-North Atlantic. If the different sinks of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ under varying redox conditions are better constrained, these isotopic shifts can be used to estimate the spatial extent of organic-rich sediment burial during OAE 2.

- Dissolved $\delta^{66}\text{Zn}$ values characteristic of the Plenus Cold Event were isotopically lighter relative to background conditions. However, temporarily non-sulphidic conditions in the basin prevent a quantitative assessment of this isotope shift. Very low $\delta^{114}\text{Cd}$ values ($<-0.4\text{‰}$) observed during the Plenus Cold Event interval are likely the result of non-quantitative removal. The other samples from the Plenus Cold Event interval show similar $\delta^{114}\text{Cd}$ values to Late Cretaceous background conditions, which suggests dissolved $\delta^{114}\text{Cd}$ values at these times may have been similar. This discrepancy between $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ patterns may be the result of enhanced input of light Zn, released from continental-margin sediments or a hydrothermal source.
- Pelagic carbonate (Chalk, Eastbourne) and organic-rich sedimentary (Tarfaya) archives from different oceanic regimes record similar stratigraphic patterns in $\delta^{66}\text{Zn}$ during the Cenomanian–Turonian interval. This similarity implies that common changes in the $\delta^{66}\text{Zn}$ stratigraphy derive from the oceanic dissolved $\delta^{66}\text{Zn}$, and that these archives record supra-regional palaeo-environmental information. However, more work on understanding the Zn-isotope partitioning between water and these different sediment archives is needed to allow reconstructions of absolute $\delta^{66}\text{Zn}_{\text{seawater}}$ values, as there is a significant contrast between the two archives that is hard to explain only by regional differences in $\delta^{66}\text{Zn}_{\text{seawater}}$.
- Despite some outstanding questions and uncertainties, the combined $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ analysis of organic-rich sediments shows potential as an important tool to reconstruct the redox dynamics of past oceans and its impact on (micro)nutrient cycling.

5

A multi-site approach to reconstructing $\delta^{66}\text{Zn}_{\text{ocean}}$ during OAE 2

Contents

5.1	Abstract	81
5.2	Introduction	82
5.2.1	OAE 2 and the Plenus Cold Event	84
5.2.2	Modern ocean Zn cycling	84
5.3	Material and Methods	87
5.3.1	Sites 1260 and 367	87
5.3.2	Furlo	89
5.4	Discussion	89
5.4.1	Nutrification as a trigger for onset OAE	89
5.4.2	Basin-scale controls on $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$	92
5.4.3	A multi-site approach to reconstructing $\delta^{66}\text{Zn}_{\text{seawater}}$	96
5.5	Conclusion	101

5.1 Abstract

Studies on the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ composition of Cenomanian–Turonian sediments have previously revealed patterns associated with changes in global ocean chemistry related to OAE 2, but have also highlighted local environmental controls on these proxies. This study aims to separate local from global controls by focusing on coeval changes in $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ from different marine sediment archives.

Based on a large dataset, an empirical approach to reconstructing Cenomanian–Turonian $\delta^{66}\text{Zn}_{\text{seawater}}$ values is presented by comparison to modern marine sediment equivalents. $\delta^{66}\text{Zn}_{\text{seawater}}$ values are reconstructed for four different intervals. The heaviest $\delta^{66}\text{Zn}_{\text{seawater}}$ values are found during the OAE 2 interval, at times of peak organic-carbon burial globally. Average $\delta^{66}\text{Zn}_{\text{seawater}}$ values of $0.69 \pm 0.06\text{‰}$ for this interval suggest a significantly larger proportion of Zn burial in organic-rich sediments relative to the modern ocean conditions.

The lowest values are found during the Plenus Cold Event, a period of cooling and oxygenation during the OAE 2 interval. Reconstructions suggest an average $\delta^{66}\text{Zn}_{\text{seawater}}$ of $0.48 \pm 0.10\text{‰}$, which may temporarily have been as low as $0.26 \pm 0.12\text{‰}$. These values imply that oxic sinks may have been relatively more abundant during the Plenus Cold Event. Alternatively, these lower values may be explained by a more substantial flux of isotopically light Zn to the ocean, such as Zn released from margin-sediments or hydrothermal vents.

The data presented in this study support a hydrothermal source of light Zn prior to the onset of the carbon-isotope excursion, likely associated with the emplacement of a Large Igneous Province (LIP). This explanation agrees with conceptual and geochemical models that have suggested a role for LIP-driven ocean nutrification as a key driver for the onset of the geochemical change associated with OAEs.

5.2 Introduction

In addition to previous studies (Kunzman et al., 2012; Georgiev et al., 2014; Hohl et al., 2016; John et al., 2017; Liu et al., 2017), Chapters 1 to 4 have highlighted the potential of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ as new palaeoenvironmental tracers. However, these chapters have also emphasized several issues that complicate extrapolating findings from a single site to address global ocean chemistry change.

Chapter 2 has revealed that marine carbonates of Cenomanian–Turonian age from different marine basins show similar stratigraphic $\delta^{66}\text{Zn}$ patterns. These common $\delta^{66}\text{Zn}$ patterns are likely associated with global environmental change. The lack of sufficient understanding of surface-ocean Zn cycling and the Zn-isotope

partitioning between carbonates and seawater prevents a direct comparison with modern conditions and thereby a true advance in our understanding of environmental conditions during Oceanic Anoxic Event 2 (OAE 2).

Subsequently, Chapter 4 has shown how organic-rich sediments may also be suitable archives for global $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ signals and has revealed similar patterns to those found in the carbonate sequences, strengthening the case for a global environmental control. However, local redox/environmental conditions have been demonstrated to have a potentially substantial impact on the $\delta^{114}\text{Cd}$ (Chapter 3) (and $\delta^{66}\text{Zn}$, Appendix A) of organic-rich marine sediments in specific marine settings. Separating local from global controls on the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ composition of the sedimentary records is of key importance for palaeoenvironmental interpretations based on these proxies. With the current understanding of Zn and Cd isotope cycling, local effects are hard to quantify, and seawater reconstructions based on a single core and/or marine sediment archive are therefore associated with significant uncertainties. As a result, several questions surrounding the OAE 2 interval remain, including:

1. Can the comparison of multi-site records of Zn and Cd isotopes help to identify ‘local’ artifacts on the isotope data, and thus highlight global signatures derived from global Zn/Cd cycle changes?
2. Can these comparisons be used to test the hypothesis that volcanic activity and redox changes drove changes in the Zn and Cd cycles during OAE-2?

One way to work towards more robust Zn and Cd seawater isotope estimates, which might allow answering these questions, may be the study of several time-equivalent sections, from various marine basins with a range of hydrographic characteristics, and with different local environmental conditions. Comparing the isotope composition of several cores and sections to that of modern marine equivalents and their relation to modern seawater isotope compositions may allow the reconstruction of past seawater compositions. Here, this approach is explored by comparing the Zn-isotope composition from six sedimentary successions that cover the Cenomanian–Turonian

interval. These records are also compared to $\delta^{66}\text{Zn}$ data from modern sediments from the Black Sea, the Peru Margin, various other margin sediments, and Quaternary carbonates (Pichat et al., 2003; Little et al., 2016; Vance et al., 2016).

5.2.1 OAE 2 and the Plenus Cold Event

Oceanic anoxic events (OAEs) in the Mesozoic Era are characterised by the widespread burial of organic-rich marine sediments and are associated with a range of environmental and geochemical change (e.g. Schlanger and Jenkyns, 1976; Jenkyns, 2010). OAE 2, of Late Cretaceous Cenomanian–Turonian age (~ 94 Ma), represents one of the most extreme and best-studied examples (Meyers et al., 2012). Large Igneous Province (LIP) volcanism is thought to have been the primary driver for the onset of the event, leading to ocean nutrification and global warming that would have stimulated the expansion of low-oxygen marine environments and burial of organic-rich sediments, amongst several other perturbations to ocean chemistry (e.g. Forster et al., 2007; Turgeon and Creaser, 2008; Jenkyns, 2010).

However, environmental conditions were not uniform during OAE 2. In particular, the Plenus Cold Event represents a period of cooling and was associated with major geochemical change (Gale and Christensen, 1996; Jenkyns et al., 2017). Reconstructing the global impact of these more dynamic changes in ocean (redox) chemistry requires isotopic tracers with sufficiently short residence times. Chapters 2 and 4 have shown that $\delta^{114}\text{Cd}$, and particularly $\delta^{66}\text{Zn}$, have the potential to reconstruct these more rapid environmental changes. The focus in this chapter is on Zn, as better constraints on the global isotopic mass balance from the modern ocean are available compared to Cd.

5.2.2 Modern ocean Zn cycling

Zn-isotope cycling and the isotopic mass balance of the modern ocean have been discussed in more detail in Chapter 1. Studies on the dissolved $\delta^{66}\text{Zn}$ of the modern ocean have revealed complex patterns in the surface ocean for which various explanations have been put forward (e.g. John and Conway, 2014; Conway and John,

2014; Vance et al., 2017). The incomplete understanding of surface-ocean Zn-isotope cycling in the modern ocean presents challenges for the interpretation of Zn-isotope data from ancient marine sediment archives. However, the $\delta^{66}\text{Zn}$ composition of modern marine sediments and their relation to the average deep-ocean isotope composition (and ocean inputs) show a much clearer picture (Figure 5.1A).

The weighted mean of riverine $\delta^{66}\text{Zn}$ input to the modern ocean is $\sim 0.33\text{‰}$, within error margin of estimates for the bulk silicate earth composition ($0.28 \pm 0.05\text{‰}$, 2 SD) (Chen et al., 2013; Little et al., 2014). The flux and isotopic composition of hydrothermal input are heavily debated, but if significant in size, isotopically similar or lighter than riverine input (Chapter 1). Open ocean oxic sinks for Zn are on average $\sim +0.4\text{‰}$ heavier than the average ocean composition (Pichat et al., 2003; Andersen et al., 2011; Little et al., 2014). Organic-rich margin sediments represent the main sink for light Zn and are $-0.4\text{--}0.6\text{‰}$ lighter than the average ocean composition (Little et al., 2016). Sediments underlying the highly restricted, euxinic deep waters of the Black Sea show $\delta^{66}\text{Zn}$ values of $\sim 0.5\text{‰}$ on average, identical to the average ocean composition as a result of near-quantitative removal (Vance et al., 2016).

The relative proportion of removal between these different marine sediments sets the average modern ocean composition at $\sim 0.5\text{‰}$ (e.g. Conway and John, 2014 or compilations by Vance et al., 2016; John et al., 2017). Any change in the relative proportion of ocean outputs or the isotopic composition of inputs to the ocean may alter the seawater composition. Assuming constant ocean inputs equal to modern values of $\sim 0.3\text{‰}$ and constant isotope fractionation factors between seawater and known Zn outputs, ocean compositions may vary between ~ -0.1 and $+0.8\text{‰}$, where $\sim -0.1\text{‰}$ represents exclusively oxic sinks, and $+0.8\text{‰}$ exclusively organic-rich sinks (Figure 5.1B). This range in $\delta^{66}\text{Zn}$ may be lighter during intervals of substantial input of isotopically light Zn, possibly from margin sediments or hydrothermal sources, which could alter the average isotopic composition of ocean inputs.

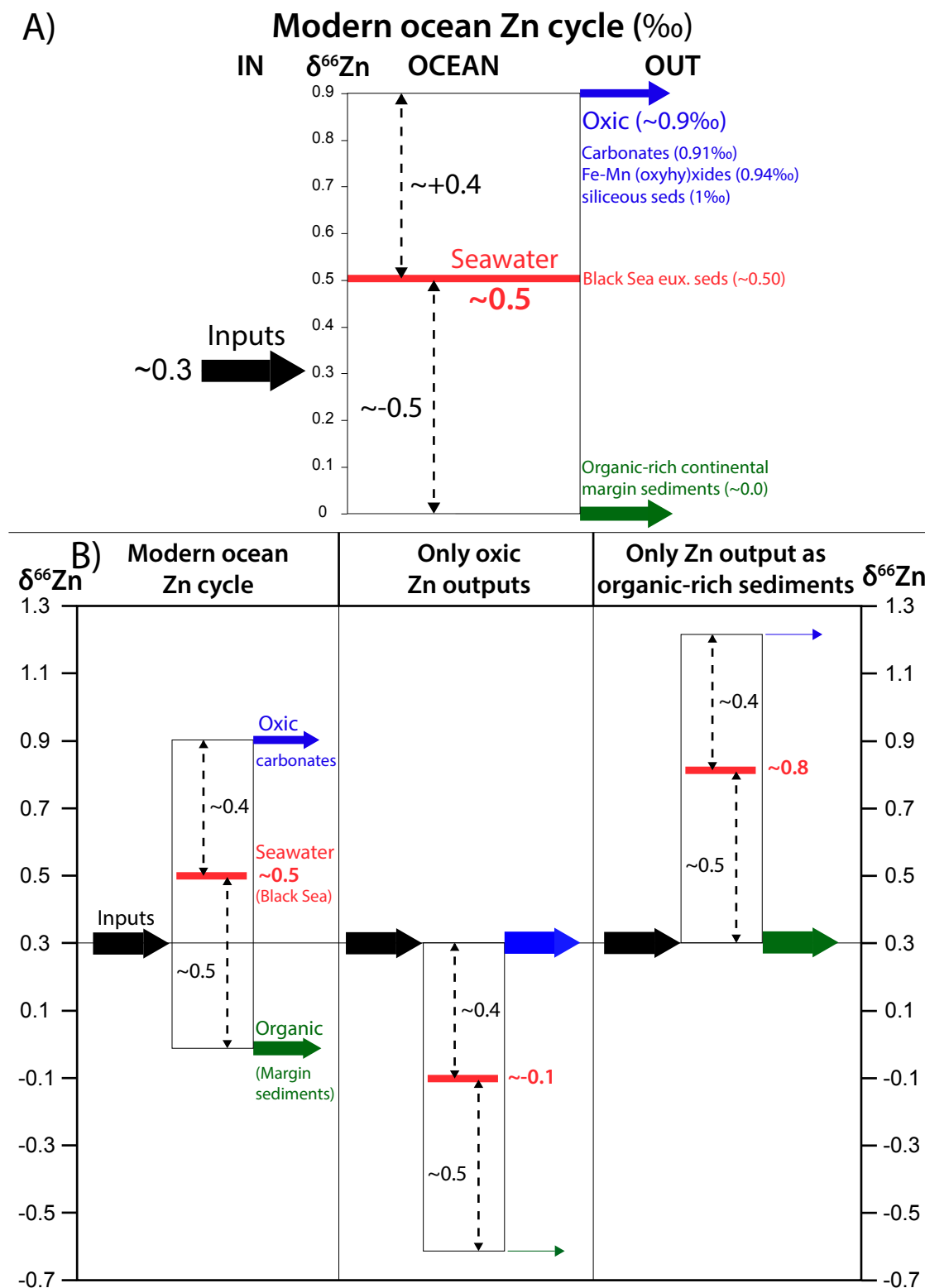


Figure 5.1: A) Simplified summary of the modern ocean Zn cycle. Modified from Vance et al. (2016). B) Hypothetical limits of global isotopic mass balance for Zn representing exclusive Zn burial in oxic or organic-rich continental margin sediments, assuming isotope fractionation between these sinks and seawater as found for the modern ocean.

5.3 Material and Methods

This study focuses on core and outcrop material from 8 different sites (Figure 5.2). The Eastbourne and Raia del Pedale (Chapter 2), Iona-1 and Innes-1 (Chapter 3) and Tarfaya (Chapter 4) sites and their geochemical characteristics have all been discussed in more detail previously. Here, data from three more sites are discussed: DSDP site 367 (Cape Verde Basin), ODP site 1260 (Demerara Rise), and a disused quarry outcrop near Furlo, Italy (Marche-Umbria region). The $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ data for these individual sites and other more specific geochemical characteristics are discussed in more detail in the supplementary information to this chapter. For all new sites, analytical methods were identical to those applied to the other organic-rich sediments and based on a partial shale digestion using inverse aqua regia to preferentially target the authigenic shale component (Chapter 1, Xu et al., 2012)

5.3.1 Sites 1260 and 367

During the Cenomanian–Turonian, sites 1260 and 367 were both located in the equatorial proto-North Atlantic, an area where reducing conditions were most extreme. Here, euxinic conditions were frequent and prolonged, likely stimulated by stratified waters as a result of the high temperatures and palaeogeography of narrow oceans and epicontinental seas, as well as high carbon fluxes from zones of upwelling and high primary productivity (Jenkyns, 2010; Trabucho Alexandre et al., 2010). Evidence from biomarker data suggests euxinia reached into the photic zone (Sinninghe-Damsté and Koster, 1998; Kuypers et al., 2002; van Bentum et al., 2009), which may have aided the extreme removal and temporary drawdown of trace elements in this region (Hetzl et al., 2009; van Bentum et al., 2009; Westermann et al., 2014; Dickson et al., 2016; Owens et al., 2016). High-resolution Mo-isotope stratigraphy reveals cyclic changes in $\delta^{98}\text{Mo}$ for DSDP site 367 during the OAE 2 interval, where the intervals with highest $\delta^{98}\text{Mo}$ approach seawater compositions due to near-quantitative removal (Dickson et al., 2016; Dickson, 2017). More detailed chemostratigraphic and geochemical information is provided in Appendix A.

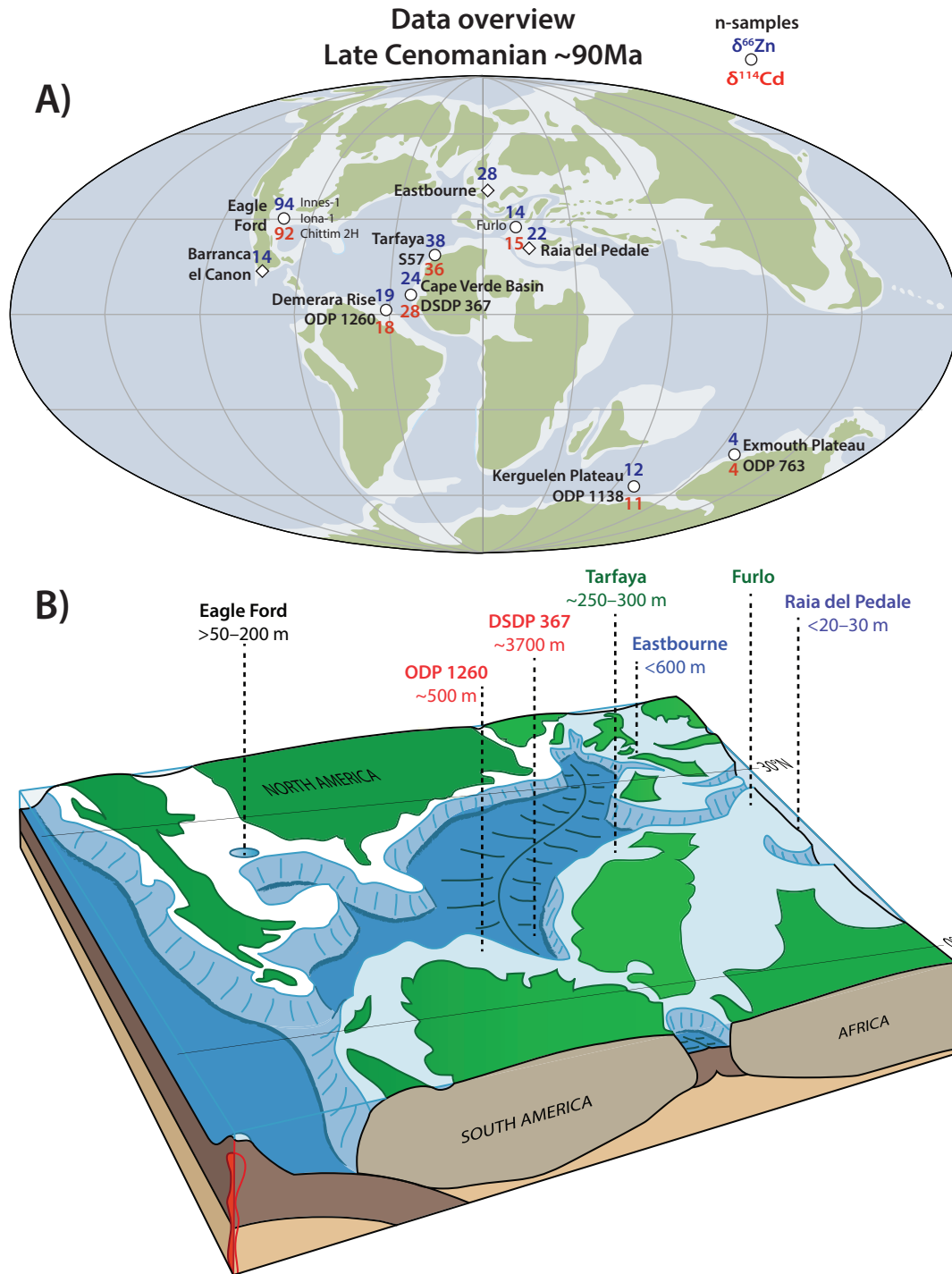


Figure 5.2: (A) Palaeogeographical reconstruction for the Cenomanian–Turonian Boundary interval (~ 90 Ma) with approximate study locations. Courtesy of Lauren O’Connor, modified from Jarvis et al. (2011). The blue and red numbers indicate the number of $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ samples analysed respectively. (B) Hydrographic reconstruction of proto-North Atlantic region and bordering seas/oceans with approximate site locations. Modified from Trabucho-Alexandre et al. (2010). Sources of palaeo-water-depth estimates, as given below the site names, are as follows: Eagle Ford, Eldrett et al. (2014; 2015b); ODP 1260, Friedrich et al. (2009); DSDP site 367, Dickson et al., 2016; Tarfaya Basin, Kolonic et al. (2005); Eastbourne, Hancock (1975)

5.3.2 Furlo

The Furlo section hosts pelagic continental-margin deposits, with dominantly carbonate rocks before and after the OAE 2 interval, and laminated organic-rich sediments and radiolarian sands during the event interval, locally known as the Bonarelli Level (Turgeon & Brumsack, 2006; Jenkyns et al., 2007). Data presented here from before the OAE interval come from thin (millimetre to centimetre) organic-rich black shales that are intercalated between the carbonate rocks. Fe-speciation and trace metal geochemistry for this section suggest that these pre-OAE interval black-shales were deposited in anoxic ferruginous conditions while during the OAE 2 interval redox conditions were euxinic (Owens et al., 2017).

$\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ data from three other cores will briefly be mentioned: the Chittim core, hosting Cenomanian sediments from the deepest part of the Maverick Basin (Eagle Ford Fm, Scaife et al., 2017), and ODP sites 763 (Exmouth Plateau) and 1138 (Kerguelen Plateau, Dickson et al., 2017) providing Cenomanian–Turonian boundary interval sediments from the Southern Hemisphere. More detailed chemostratigraphic and geochemical information is provided in Appendix A.

5.4 Discussion

5.4.1 Nutrification as a trigger for onset OAE

Large Igneous Provinces and ocean nutrification

Conceptual models for OAE formation include nutrification of the surface ocean as a key mechanism in the chain of feedback processes that eventually leads to the enhanced burial of organic-rich sediments (e.g. Jenkyns, 2010). Evidence for nutrification might manifest itself in the $\delta^{66}\text{Zn}$ and/or $\delta^{114}\text{Cd}$ stratigraphy if it was associated with a shift in the average isotopic composition of ocean inputs. Alternatively, enhanced input of Cd/Zn may alter seawater compositions indirectly, if it impacted the relative proportion of isotopically different sinks for Cd and Zn, for example by stimulating primary productivity or allowing more non-quantitative removal of Cd/Zn. The effect ocean nutrification may have had on the $\delta^{66}\text{Zn}$ and/or

$\delta^{114}\text{Cd}$ composition of past seawater would in turn impact the isotopic composition of the different marine sediment archives.

Large Igneous Province (LIP) volcanism is generally thought to be the key initial driver for the onset of processes associated with the OAE 2 interval (Adams et al., 2010; Jenkyns, 2010; Scaife et al., 2017). Os-isotope stratigraphy comprises the most substantial evidence for this theory as an unradiogenic shift in Os-isotopes is found in many localities and pre-dates the onset of the positive C-isotope excursion (Turgeon and Creaser, 2008; Du Vivier et al., 2014; 2015). This magmatic episode led to the enhanced input of various (trace) elements to the ocean, as evidenced from trace metal anomalies (Snow et al., 2005), thereby providing more nutrient-rich conditions for primary producers. The enhanced input of trace elements may have happened directly, by enhanced basalt seawater interaction and/or indirectly through enhanced silicate weathering and/or an intensified hydrological cycle caused by volcanically-induced greenhouse warming (Pogge von Strandmann et al., 2013; Van Helmond et al. 2013; Jenkyns et al., 2017).

$\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ in relation to Large Igneous Province volcanism

Analysis of a variety of volcanic rocks suggests that magmatic differentiation does not cause significant Zn-isotope fractionation and estimates for the $\delta^{66}\text{Zn}$ composition of bulk silicate earth ($0.28 \pm 0.05\text{‰}$, 2s.d.) are within error margin of riverine and aeolian dust ocean inputs (Chen et al., 2013). Direct enhanced input of average bulk silicate earth material, by emplacement of a LIP, may therefore not be expected to significantly shift the average Zn-isotope composition of ocean inputs. Estimates for the isotopic composition of hydrothermal Zn input vary but are either similar or isotopically lighter than riverine inputs (see Chapter 1).

There are no published observations that suggest a magmatic episode would lead to a significant change in the average $\delta^{114}\text{Cd}$ of ocean inputs compared to today (Chapter 1). Data for Cd, however, are very sparse so some effect cannot be excluded. Enhanced Zn input caused by a magmatic episode may lead to a significant change

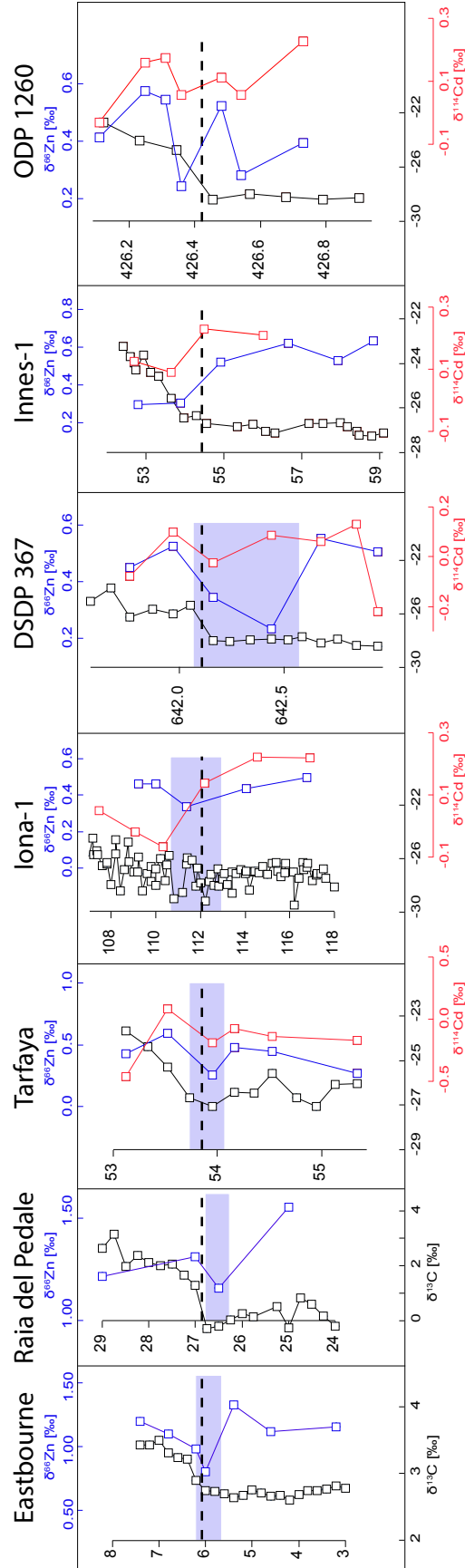


Figure 5.3: Multi-site comparison of $\delta^{13}\text{C}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphy for the interval around the onset of the carbon-isotope excursion (CIE) associated with OAE 2. Black horizontal dashed lines represent the approximate onset of the CIE, based on the $\delta^{13}\text{C}$ stratigraphy. The blue horizontal bands highlight intervals anomalously low $\delta^{66}\text{Zn}$ compositions.

in the average $\delta^{66}\text{Zn}$ of ocean inputs, but likely only if hydrothermal Zn input presents a significant source of Zn relative to other inputs.

Stratigraphic $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ patterns around the onset of the OAE 2 interval

A brief perturbation to lower $\delta^{66}\text{Zn}$ values just prior to the onset of the OAE 2 interval in the Eastbourne chalk has been linked to the input of isotopically light Zn from hydrothermal fluids associated with LIP emplacement (Chapter 2). In order to explore this hypothesis and its relevance, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ patterns for the interval around the onset of OAE 2 are compared for multiple sites (Figure 5.3). This brief perturbation to low $\delta^{66}\text{Zn}$ prior to the onset of the CIE can be observed in several locations from different archives with a wide spatial distribution and varying local environmental conditions (Eastbourne, DSDP 367, Tarfaya, and to a lesser extent Iona-1 and Raia del Pedale). This observation may be taken to provide evidence for a substantial input flux of isotopically light Zn at this time.

Apart from the Tarfaya basin, $\delta^{114}\text{Cd}$ patterns do not reveal a similar transition during this interval. This observation would be consistent with a hydrothermal source for isotopically light Zn, which is not expected to be associated with the enhanced input of isotopically light Cd, based on current knowledge. However, the data resolution is low relative to the apparently short duration of the perturbation. Better characterisation of hydrothermal Cd and Zn input and higher data resolution are needed to confirm observations and establish the magnitude of the $\delta^{66}\text{Zn}$ excursion, which can lead to a more quantitative assessment of the underlying mechanisms.

5.4.2 Basin-scale controls on $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$

Despite a lot of scatter, a generally positive trend is observed in a cross-plot between $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$, as may be expected considering some of the shared geochemical characteristics of these elements (Figure 5.4). Interestingly, this positive relationship is observed across different sites, and most scatter actually appears to be associated with variation for the individual sites separately, rather than result from differences between sites.

The three Eagle Ford sites (Iona-1, Innes-1, Chittim) display the heaviest $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions, closely followed by DSDP site 367 (Cape Verde Basin) and ODP site 1260 (Demerara Rise). On average, isotopically lighter values are observed for sediments from the Tarfaya Basin, Furlo, and ODP site 763. Lowest $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values are found for site 1138. Apart from the Eagle Ford cores (i.e. Innes-1, Iona-1, Chittim H2H), which will be discussed later, this typical distribution appears to generally follow local redox and hydrographic conditions.

Sites 367 and 1260, from the equatorial proto-Atlantic region, feature dominantly euxinic conditions and a relatively restricted palaeogeography, allowing severe drawdown of trace metal inventories (Hetzl et al., 2009; van Bentum et al., 2009; Westermann et al., 2014; Dickson et al., 2016; Owens et al., 2016). These particular environmental conditions likely result in near-quantitative removal of trace elements to the sediment, and therefore high $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$, as have been previously observed for Zn in the modern Black Sea (Vance et al., 2016).

Sediments from the Tarfaya and Furlo sites were also mainly deposited under euxinic conditions, but do show brief perturbations to anoxic ferruginous conditions (Poulton et al., 2015; Owens et al., 2017). Also, euxinia for these sites may have been less persistent and/or largely been limited to bottom waters, as evidenced by comparatively lower abundances of biomarkers for photic zone euxinia (Van Bentum, 2009; Poulton et al., 2015). Additionally, the palaeogeographic setting of the Tarfaya and Furlo sites provides a better connection to the open ocean, which allows a higher influx of trace elements, particularly for the Tarfaya Basin, which is positioned in an area of upwelling (Kolonic et al., 2005; Owens et al., 2016). Severe local drawdown of trace element inventories is therefore less likely for these sites, which allows non-quantitative removal and lower $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values.

Finally, sediments from ODP site 1138 show on average the lowest $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions for all studied sites. Mo-U and Mo-TOC co-variations for this site suggest open-marine conditions and mostly suboxic–anoxic bottom water conditions (Algeo & Lyons, 2006; Algeo & Tribovillard, 2009; Dickson et al., 2017). These conditions can lead to the non-quantitative removal of Cd and Zn, and

therefore lower $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ of bulk sediments. An additional factor that may result in lower $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ ratios is the location of site 1138 away from the proto-Atlantic–Tethyan region, where most other sites are placed. The drawdown of trace elements in the Atlantic/Tethys and the restricted nature of these ocean basins may lead to spatial differences in dissolved seawater isotope compositions, with possibly higher values found in Atlantic/Tethyan waters due to the drawdown of the lighter isotopes.

However, in general, the dominant control on the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ contrast between sites is likely the degree of anoxia and hydrographic restriction. Highly restricted and euxinic sites represent quantitative removal and result in higher $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$, whereas basins with suboxic-anoxic water and free water exchange with the open ocean represent non-quantitative removal and lower isotope compositions, similar to observations for $\delta^{66}\text{Zn}$ from the modern ocean (Little et al., 2016; Vance et al., 2016).

The Eagle Ford cores present a major exception to this trend, which may be due to temporal changes in $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ and/or local basin controls. The Maverick Basin deposits cover time intervals from the Early Cenomanian to the Late Turonian for the Innes-1 and Iona-1 cores, and exclusively Turonian for the Chittim 2H core (Eldrett et al., 2017; Scaife et al., 2017). As a result, they are not directly time-equivalent to the other sites presented in the compilation, for which the data are largely limited to the Cenomanian–Turonian boundary interval. For the Eagle Ford sites, the heaviest $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ are found during the (Early) Cenomanian (Chapter 3; Supplementary Info).

Comparison to the other sites suggests there may be a temporal change in global seawater compositions from the Middle Cenomanian to the Early Turonian, as has been suggested to impact local seawater compositions (Chapter 3), which would explain the relatively high $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values found for the Eagle Ford cores compared to other settings. However, considering the anomalous behaviour of the Maverick Basin compared to global carbon-burial patterns and the specific characteristics of this basin, findings for this site cannot be extrapolated to global

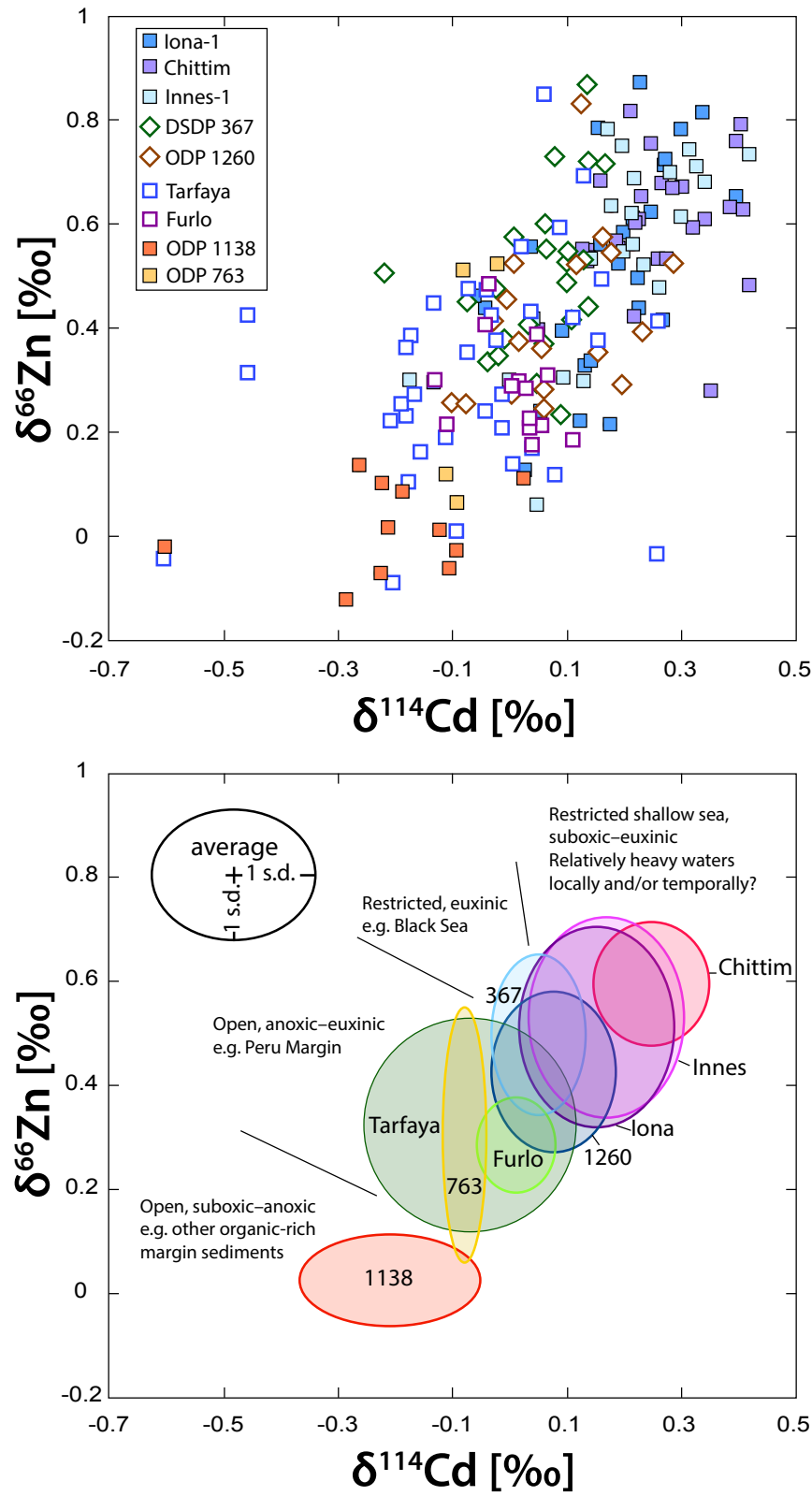


Figure 5.4: Cross-plots of $\delta^{66}\text{Zn}$ versus $\delta^{114}\text{Cd}$ values for multiple sites with Cenomanian–Turonian organic-rich mudrocks. All data is plotted stratigraphically in Appendix A

relevance (Eldrett et al., 2014, Chapter 3). Studies on other stratigraphically expanded sections from different marine basins are needed to address temporal $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ variations beyond the Cenomanian–Turonian boundary interval.

An alternative explanation for the relatively high $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values for the Eagle Ford may be the position of the Maverick basin in the shallow seas of the Western-Interior Seaway. This particular hydrographic setting may result in a relatively higher influx of surface waters into the basin, which are characterised by higher $\delta^{114}\text{Cd}$ values in the modern ocean. However, $\delta^{66}\text{Zn}$ values of surface waters in the modern ocean are generally lower than found for the deep ocean, so surface water inflow to the Maverick Basin cannot directly explain the comparatively high $\delta^{66}\text{Zn}$ values for sediments from this basin.

5.4.3 A multi-site approach to reconstructing $\delta^{66}\text{Zn}_{\text{seawater}}$

The distinct isotope composition of different modern marine sediments and minerals and their relation to modern ocean compositions may allow an empirical reconstruction of past seawater compositions. Carbonate sediments from the Eastbourne and Raia del Pedale sites have a (near-)modern equivalent in the glacial–interglacial carbonates (Pichat et al., 2003). Both the Eastbourne chalk and the glacial–interglacial carbonates mainly consist of coccoliths and are thus directly comparable. The Raia del Pedale shallow-water carbonates show slightly heavier $\delta^{66}\text{Zn}$ than the coccolith-dominated Eastbourne chalk, which may represent a slight diagenetic difference, as has been observed for uranium-isotopes (Clarkson et al., paper under review).

Deposits from the Tarfaya and Furlo sections are comparable to sediments from the modern Peru Margin, as they all feature ferruginous to euxinic conditions and a good connection to the open ocean. Most other modern marine margin sediments with lower $\delta^{66}\text{Zn}$ are generally deposited under more oxygenated conditions, and therefore less comparable to sediments from the Tarfaya and Furlo sites (Little et al., 2016). ODP site 1260 and DSDP site 367 are taken as equivalents to the Black Sea sediments due to the restricted nature of the southern Proto-North

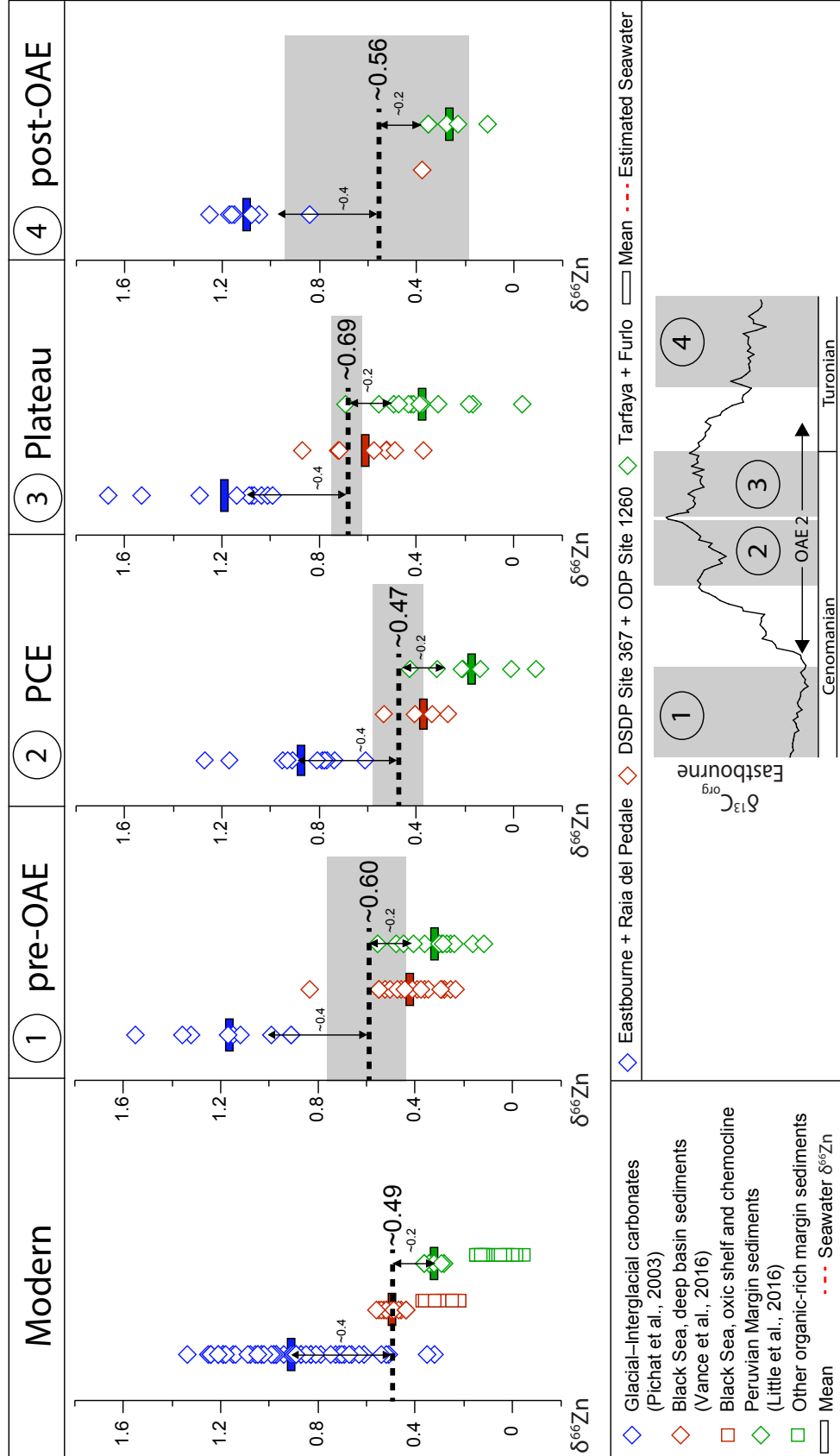


Figure 5.5: A multi-site approach to reconstructing $\delta^{66}\text{Zn}_{\text{seawater}}$ of different time intervals from the Cenomanian–Turonian boundary interval by comparison to modern equivalents. The four different time intervals (pre-OAE, Plenus Cold Event (PCE), plateau-phase, post-OAE) correspond to recognised features in the C-isotope stratigraphy as illustrated on the reference curve from the Eastbourne chalk. Only samples with $\text{Zn}_{\text{EF}} > 5$ were included to limit any impact from varying proportions of detrital Zn.

Atlantic basin, highly reducing conditions and evidence for local drawdown of trace elements. In order to reconstruct the temporal evolution of $\delta^{66}\text{Zn}_{\text{seawater}}$ for the Late Cretaceous, four different stratigraphic units are established and compared, as identified by the C-isotope stratigraphy: a pre-OAE interval, the Plenus Cold Event interval, sediments from the ‘plateau-phase’ of the OAE interval, and the interval after the CIE (Figure 5.5).

Based on the $\delta^{66}\text{Zn}$ composition for these different sites and comparison to their modern equivalents, past seawater $\delta^{66}\text{Zn}$ can be estimated (Fig 5). Magnitudes of Zn-isotope partitioning between sediment archives and seawater of $\sim +0.4\text{‰}$ for carbonates, $\sim -0.2\text{‰}$ for Peru Margin sediments, and 0‰ for Black Sea sediments, as observed in the modern ocean, are taken and applied to their respective Cenomanian–Turonian equivalents to reconstruct seawater compositions. $\delta^{66}\text{Zn}_{\text{seawater}}$ compositions for each of the different intervals are estimated by taking the average of: 1) average $\delta^{66}\text{Zn}$ for Eastbourne -0.4‰ ; 2) the 3rd quartile of the $\delta^{66}\text{Zn}$ data for sites 367 and 1260; 3) the 3rd quartile of the $\delta^{66}\text{Zn}$ data for the Tarfaya and Furlo sites $+0.2\text{‰}$ (Figure 5.5). For the carbonates focus is only on samples from the Eastbourne site as this site is most comparable to the Quaternary carbonates by Pichat et al. (2003); isotope fractionation between seawater and Raia del Pedale sediments is likely higher than $+0.4\text{‰}$ (Chapter 2). For the different organic-rich sediments the 3rd quartiles (Q3) are taken, rather than the average. This approach is meant to correct for temporarily non-euxinic conditions and therefore a possibly larger offset between seawater and sediments than for the modern ocean equivalents being used, where redox conditions are better constrained. The error bars on the $\delta^{66}\text{Zn}_{\text{seawater}}$ reconstructions represent two standard deviations from the average of the three different inputs to the reconstructions.

Generally, this approach results in values comparable values to those found in the modern ocean ($\sim 0.49\text{‰}$) but also reveals significant stratigraphic differences. Reconstructed $\delta^{66}\text{Zn}_{\text{seawater}}$ values are $0.60 \pm 0.16\text{‰}$ (pre-OAE), $0.48 \pm 0.10\text{‰}$ (Plenus Cold Event), $0.69 \pm 0.06\text{‰}$ (Plateau-phase), and $0.56 \pm 0.38\text{‰}$ (post OAE) for the different intervals. This implies that during peak organic-carbon burial

globally (Plateau-phase) the average isotopic composition global ocean was $\sim 0.2\text{‰}$ higher than today and during the Plenus Cold Event interval. These differences may be related to changes in the relative proportion of the ocean outputs (and inputs), which will be further explored later.

However, the problem with this approach is that by taking average and Q3 values for $\delta^{66}\text{Zn}$ compositions of the different intervals, possible evolution of $\delta^{66}\text{Zn}_{\text{seawater}}$ within an interval is ignored. This may be particularly problematic for the Plenus Cold Event, where variations of up to $\sim 0.6\text{‰}$ are observed within a single stratigraphic interval (Chapter 4). The approach used above may therefore not illustrate the full extent of $\delta^{66}\text{Zn}_{\text{seawater}}$ change during this interval. In order to estimate the maximum range of $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the Cenomanian–Turonian, minimum $\delta^{66}\text{Zn}$ values are estimated for the Plenus Cold Event interval (where on average the lowest $\delta^{66}\text{Zn}$ compositions are found). During the Plenus Cold Event, $\delta^{66}\text{Zn}$ ratios go down to ~ -0.0 , 0.30 , and 0.67‰ for sediments from the Tarfaya basin (Chapter 3), sites 367 and 1260 combined (Appendix A), and Eastbourne (Chapter 2) sites respectively. Adjusted for isotope fractionation associated with these different marine sediment archives (i.e. $+0.2\text{‰}$ for Tarfaya, -0.4‰ for Eastbourne), this suggests $\delta^{66}\text{Zn}_{\text{seawater}}$ values may have been as low as $\sim 0.26 \pm 0.12\text{‰}$ during the Plenus Cold Event.

As the seawater $\delta^{66}\text{Zn}$ composition is set by the average ocean input composition and the relative proportion of the different Zn sinks, these $\delta^{66}\text{Zn}_{\text{seawater}}$ may be used to estimate relative sizes of Zn outputs if assumptions are made on the average ocean input $\delta^{66}\text{Zn}$ composition. This estimate does not include near-quantitative removal of Zn in highly euxinic, restricted basins, as the $\delta^{66}\text{Zn}$ of this sink is indistinguishable from average ocean compositions. These are therefore minimum estimates of the true proportional removal of Zn in organic-rich sediments. Assuming steady-state conditions and an average $\delta^{66}\text{Zn}$ composition of ocean inputs 0.3‰ the estimated proportion of Zn removal into organic-rich sediments during peak-organic carbon burial in the ‘plateau-phase’ of the OAE interval is $>87\%$ (Figure 5.6).

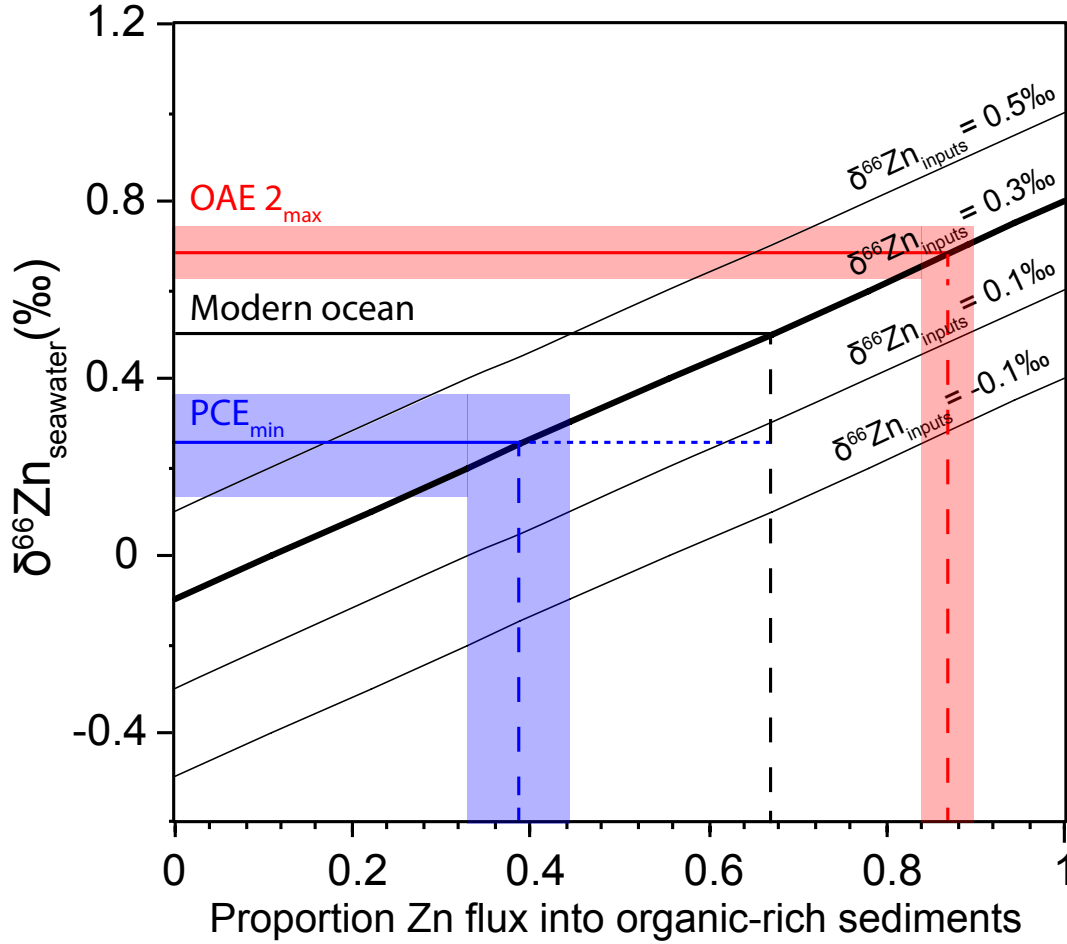


Figure 5.6: Simplified mass-balance Zn model for different seawater isotope compositions and average ocean input $\delta^{66}\text{Zn}$ values at steady state conditions (size and isotopic composition of ocean inputs equal that of ocean outputs). The $\delta^{66}\text{Zn}$ composition of seawater is a function of the relative proportion of the different ocean outputs (oxic sinks $\approx +0.4 \text{‰}$; organic-rich sediments $\approx -0.5 \text{‰}$ relative to seawater) and the average $\delta^{66}\text{Zn}$ composition of ocean inputs ($\sim 0.3\text{‰}$ for the modern ocean). Reconstructed $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the Cenomanian–Turonian can thus be used to estimate the relative proportion of organic-rich sinks for Zn if the $\delta^{66}\text{Zn}$ of ocean inputs is assumed to be equal to the modern ocean. The isotopic mass balance is as follows: $\delta^{66}\text{Zn}_{\text{input}} * F_{\text{input}} = \delta^{66}\text{Zn}_{\text{oxic}} * F_{\text{oxic}} + \delta^{66}\text{Zn}_{\text{oxic}} * F_{\text{euxinic}} + \delta^{66}\text{Zn}_{\text{organics}} * F_{\text{organics}}$. This is simplified here by including the euxinic sink in the organic-rich sediment sink and writing the output fluxes proportionally: $\delta^{66}\text{Zn}_{\text{input}} = \delta^{66}\text{Zn}_{\text{oxic}} * f + \delta^{66}\text{Zn}_{\text{organics}} * (1-f)$. Due to this last simplification, the true proportional removal of Zn in organic-rich sediments is higher than these estimates, which provide a minimum limit only. This is because the $\delta^{66}\text{Zn}_{\text{organics}}$ now include sediments with near-quantitative removal of Zn, and thus higher $\delta^{66}\text{Zn}$ than estimated here. The OAE 2-max and PCE-min represent reconstructed $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the plateau-phase and minimum $\delta^{66}\text{Zn}_{\text{seawater}}$ estimates for the Plenus Cold Event respectively plotted to represent the maximum observed range in $\delta^{66}\text{Zn}_{\text{seawater}}$

Minimum $\delta^{66}\text{Zn}_{\text{seawater}}$ estimates of $\sim 0.26\text{‰}$, found during the Plenus Cold Event interval equate to a proportional burial of Zn into organic-rich sediments of $>39\%$, compared to $>67\%$ estimated for the modern ocean and background Cenomanian–Turonian conditions. Alternatively, the proportion of Zn burial during the PCE event may have been similar to modern ocean conditions if the average Zn-isotope composition of ocean input was significantly lighter ($<0.1\text{‰}$) than for the modern ocean, for example as a result of more substantial Zn input from hydrothermal vents or Zn remobilised from previously buried organic-rich sediments (Figure 5.6).

5.5 Conclusion

- The data in this study support a perturbation to ocean Zn chemistry prior to the onset of the carbon-isotope excursion, likely resulting from some sort of enhanced basalt-seawater interaction by LIP emplacement. Enhanced hydrothermal input of micronutrient Zn, and likely other (micro)nutrients, as a result of this perturbation to ocean chemistry, provides support for nutrification of the (surface) ocean as one of the key triggers for the onset of OAE formation. Future work should focus on increasing data resolution and characterisation of hydrothermal Zn input to provide a definitive and more quantitative assessment of the perturbation to the Zn cycle, and by extrapolation that of other (micro)nutrients.
- A cross-plot of $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ data, from nine different cores/sections with organic-rich sediments of Cenomanian–Turonian age, reveals a largely similar control on the two isotope systems. Except for material from the Eagle Ford Fm, a large part of the variation observed in this dataset can be related to local hydrographic and (redox) environment conditions. The highest $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values are generally found for sediments from hydrographically restricted marine basins with dominantly euxinic waters, allowing near-quantitative removal of trace elements to the sediments. $\delta^{66}\text{Zn}$

and $\delta^{114}\text{Cd}$ values become progressively lighter in more open and relatively more oxygen-rich depositional conditions.

- The characteristic compositions of zinc different sedimentary and mineral phases in the modern ocean establish an empirical framework for interpreting Zn-isotopes in ancient marine sediments. This new approach allows a first reconstruction of $\delta^{66}\text{Zn}_{\text{seawater}}$ for the Cenomanian–Turonian interval, by utilizing multiple sites and different marine archives, thereby limiting uncertainties associated with observations from a single site/archive.
- Reconstructed $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the Cenomanian–Turonian reveal temporal changes that can be linked to key intervals of palaeoenvironmental change and, more specifically, the spatial expansion and contraction of organic-rich sediment burial. These changes in $\delta^{66}\text{Zn}_{\text{seawater}}$ can be attributed to large-scale variability in redox conditions, revealing a more dynamic ocean redox chemistry during OAE 2 than is often considered.
- Average $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the Plenus Cold Event interval are estimated at $0.48 \pm 0.10\text{‰}$, with a minimum of $\sim 0.26 \pm 0.12\text{‰}$. This reconstruction suggests that the proportion of Zn removed into organic-rich sediments relative to oxic sinks during the Plenus Cold Event was lower ($>39\%$) than estimated for the modern ocean ($>67\%$). Alternatively, this difference may be explained by the input of isotopically light Zn from hydrothermal fluids or remobilised from previously buried organic-rich (margin) sediments in response to ocean oxygenation during the Plenus Cold Event.
- $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the ‘plateau-phase’ of the OAE interval, an interval of peak organic-carbon burial, average $0.69 \pm 0.06\text{‰}$. These values imply that at peak organic-carbon burial globally, nearly all Zn output ($>87\%$) from the ocean was into organic-rich sediments.

6

Conclusion

Contents

6.1	Summary and impact	104
6.1.1	Zn and Cd isotopes in organic-rich mud rocks	104
6.1.2	Global change in ocean $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ on geological timescales	105
6.1.3	Impacts on marine Zn- and Cd-isotope systematics	106
6.1.4	Insights into palaeoenvironmental change associated with OAE 2	106
6.2	Future studies	107
6.2.1	Characterising sources, sinks, and internal cycling in the modern ocean	108
6.2.2	Constraining isotope fractionation factors	108
6.2.3	Phase-specific isotope analysis	108
6.2.4	Palaeoenvironmental studies	109
6.3	Outlook	109

Previous studies on the Zn- and Cd- isotope cycling in the modern ocean have suggested Cd and Zn may preserve valuable information on past redox and/or nutrient conditions if primary signals are preserved in the sedimentary record. This study has explored the use of Zn- and Cd-isotopes as new palaeo-ocean chemistry proxies by using the Late Cretaceous Cenomanian–Turonian Oceanic Anoxic Event 2 (OAE 2, ~ 94 Ma) as a case study. This stratigraphic interval represents a major perturbation to ocean chemistry and environments, and is associated with the spread

of low-oxygen marine environments and enhanced burial of organic-rich sediments.

Chapters two to five have presented the first $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ data for Cenomanian–Turonian aged carbonate and organic-rich sedimentary deposits. As such, this study presents an important advance in efforts to explore $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ as novel palaeoenvironmental tracers. The new data presented in this study have confirmed the potential of these elements and their isotopes as proxies for past ocean chemistry, but have also highlighted several issues and gaps in our current understanding.

6.1 Summary and impact

6.1.1 Zn and Cd isotopes in organic-rich mud rocks

This study presents the first evidence for stratigraphic variations in $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ in organic-rich mudrocks. Zn- and Cd-isotope values observed in this study are largely within the range of values found for natural Earth surface materials, thereby showing no sign of severe diagenetic or catagenic alteration. Absolute isotope values and stratigraphic trends are reproducible between cores within close geographical proximity. Importantly, stratigraphic isotopic variations occur during key intervals of local and global palaeoenvironmental change, as established by previously published interpretations. Together, this suggests that the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions of organic-rich mudrocks preserve valuable palaeoenvironmental information.

High $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values were commonly found for sediments deposited in euxinic environments, whereas lower ratios are mostly found for sediments formed in more oxygenated conditions. It is proposed here that these trends are largely due to varying proportions of sulphide-formation, where non-quantitative removal in more oxygenated conditions results in lower isotope values. This conceptual model has previously been used to explain $\delta^{66}\text{Zn}$ values of modern organic-rich marine sediments (Little et al., 2016; Vance et al., 2016). Data presented in this study suggest a similar mechanism controls the Zn- and Cd-isotope of composition organic-rich mudrocks.

Most of the variation in $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ found in this study can be attributed to such different local environmental conditions between sites, as illustrated by a

$\delta^{66}\text{Zn}$ versus $\delta^{114}\text{Cd}$ cross-plot for all the studied sections. These spatial variations can largely be ascribed to differences in the proportion of sulphide formation and varying degrees of hydrographic restriction. An impact from variable biological uptake/nutrient utilisation rates cannot be excluded but, a biological control seems of second order importance to the variation observed in this dataset. The data therefore suggest that these proxies may be used as an indicator for environmental conditions related to ocean redox chemistry, rather than nutrient dynamics.

6.1.2 Global change in ocean $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ on geological timescales

Coeval changes in $\delta^{66}\text{Zn}$ are found in various organic-rich mudrocks and marine carbonate successions across key intervals of global palaeoenvironmental change. Such stratigraphic patterns therefore more likely represent perturbations to the $\delta^{66}\text{Zn}$ (and $\delta^{114}\text{Cd}$) composition of the ocean globally, associated with global changes in ocean chemistry and environments. As such, this study provides the first multi-site evidence for global ocean change in $\delta^{66}\text{Zn}$ (and $\delta^{114}\text{Cd}$) in the geological past.

Linking $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ of marine sediments to changes in the global cycling of these elements requires the consideration and correction of local environmental controls. This study presents several suggestions for the reconstruction of past seawater compositions. Because $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ of sediments deposited in euxinic marine basins are thought to represent seawater compositions, a focus on only such sediments can provide estimates for temporal variability in ocean isotope values (Chapter 3). Alternatively, established isotope fractionation factors between seawater and marine sediments may be applied to equivalents from the sedimentary record to reconstruct ancient seawater isotope compositions. This approach becomes more robust when different marine sediment archives are used (Chapter 5). Although these reconstructions are associated with considerable uncertainties, estimated seawater values for the Cenomanian–Turonian are similar to those observed in the modern ocean and within sensible limits. Growing understanding of the isotope systematics for these two elements in the modern ocean will improve future estimates

and increase applicability of these systems in palaeoenvironmental studies. One of the main challenges for the further development of these proxies will be separating local from global controls on the Zn- and Cd-isotope composition of the sediment.

Reconstructed $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the Cenomanian–Turonian identify significant changes associated with known intervals of global changes in anoxia and carbon-burial. The highest values are found during the main 'plateau-phase' of the OAE, an interval of peak organic-carbon burial globally. $\delta^{114}\text{Cd}_{\text{seawater}}$ values can not be reconstructed in the same detail, but initial results suggest similar patterns to Zn. This observation implies that $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values from the sedimentary record respond to global changes in organic-carbon burial and that such conditions are associated with the burial of isotopically light Zn and Cd.

6.1.3 Impacts on marine Zn- and Cd-isotope systematics

In contrast to dissolved $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ from the modern ocean (Chapter 1), a positive relationship is observed between $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ for all data on organic-rich mudrocks generated in this study (Chapter 5). The discrepancy between the Zn-Cd relationship for modern ocean waters and ancient seafloor sediments implies that mechanisms controlling the internal cycling of Zn and Cd in the modern ocean are not the dominant factors affecting the isotope composition of this sedimentary archive, at least not for the Late Cretaceous. It is more likely that coeval variability in $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ of the sedimentary record is caused by similarities in global isotopic mass balance characteristics and behaviour during early diagenesis and/or in low-oxygen conditions (i.e. sulphide formation). It could be postulated that the Cd-isotope compositions of modern marine sediments, which still have to be explored, are thus likely to show similar patterns to the more established Zn-isotope cycle.

6.1.4 Insights into palaeoenvironmental change associated with OAE 2

Despite the uncertainties that come with the reconstruction of past environments based on relatively new proxies, some interesting trends were observed in this

study that may impact our understanding of changing environments associated with the OAE 2 interval. Brief intervals of lower $\delta^{66}\text{Zn}$ values, observed just prior to onset of the positive carbon-isotope excursion may be related to enhanced volcanic/hydrothermal input of Zn. This observation would support geochemical and conceptual models that have argued for volcanically driven ocean nutrification as a trigger for increased carbon burial. Further work should aim to increase the data resolution for this interval to test this theory.

Additionally, this study highlights the Plenus Cold Event interval as a period of substantial change in global ocean chemistry. The implication of this finding is that ocean environmental conditions during the OAE 2 interval were more dynamic than considered in many conceptual and geochemical models, which may have implications for our thinking on climate feedback mechanisms in the ocean-atmosphere system of the Late Cretaceous. $\delta^{66}\text{Zn}_{\text{seawater}}$ reconstructions as presented in this study reveal the highest proportion of Zn burial in organic-rich sediments during the plateau-phase of the CIE, whereas the lowest proportion is found during the Plenus Cold Event. Quantifying such changes more accurately and precisely requires better constraints on the isotopic mass balances of Zn and Cd in the modern ocean.

6.2 Future studies

The data presented in this study confirm the potential of these two isotope systems as new palaeoenvironmental tracers. However, the value of application in palaeoenvironmental studies is currently still limited, largely due to a lack of constraints and gaps in our understanding of these systems in the modern ocean. One of the main outcomes of this study is to provide incentive and encouragement for the further study of $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ in the modern ocean and sediments, and in laboratory environments, to ultimately provide better constraints for the use as palaeoenvironmental tracers.

6.2.1 Characterising sources, sinks, and internal cycling in the modern ocean

The Zn-isotope mass balance is reasonably well established compared to the Cd-isotope system, where better constraints are still needed for most ocean inputs and outputs. Specifically from this study it follows that a closer look at pore- and bottom-water isotope systematics for both elements is needed. High $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ would be expected in pore waters just above the sulphate-reduction front, if the proposed conceptual model of isotope fractionation with non-quantitative sulphide formation (Chapter 3) were accurate. From this study it also follows that constraining hydrothermal fluxes and isotope compositions to address past changes in global isotopic mass balance of Cd and Zn and move towards a more quantitative assessment of observed changes in the global isotopic mass balance of past oceans.

6.2.2 Constraining isotope fractionation factors

Laboratory experiments including culture and precipitation studies may be used to (further) constrain the controls on Zn and Cd-isotope systematics for a variety of processes. Specifically, Zn isotope fractionation associated with incorporation into marine carbonates still causes considerable uncertainty for palaeoenvironmental applications. For both Zn and Cd, isotope fractionation factors for a variety of marine primary producers still need to be constrained. Finally, a closer look at the impact of early diagenetic processes on Zn- and Cd-isotope systematics is needed to test the proposed conceptual models.

6.2.3 Phase-specific isotope analysis

Physically or chemically separating different sediment phases for more specific isotope analysis may be very beneficial for future palaeoenvironmental studies. For example, phase specific metal-isotope analysis may help to separate local from global controls on $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values of the sediment if phases can be isolated that are specific to deep or surface water isotope compositions. If possible, this might allow addressing variations in past vertical gradients in seawater $\delta^{114}\text{Cd}$,

which could be linked to nutrient utilisation and primary productivity. This type of development will be partly dependent on analytical advances. If measurements on smaller quantities of Zn and Cd are feasible, this may allow isotope analysis of for example specific foraminifera, similar to the development of for example the C- and O-isotope proxies over the last decades.

6.2.4 Palaeoenvironmental studies

Future palaeoenvironmental studies should focus on utilising the relatively short residence times of these tracers and perform high-resolution analysis on key intervals of past environmental change. Obvious study subjects are other periods of enhanced carbon-burial and/or extinction intervals, particularly those associated with ocean (de-)oxygenation; for example the Great Oxidation Event, Permian–Triassic boundary event, Toarcian and Early Aptian Oceanic Anoxic Events, and the Paleocene–Eocene Thermal Maximum. For the further development of these proxies it would also be interesting to study more recent intervals of temporarily enhanced organic-carbon burial, for example Mediterranean sapropels. Here, environmental conditions are better constrained, and such studies may therefore act as a case study for $\delta^{66}\text{Zn}$ - and/or $\delta^{114}\text{Cd}$ -based palaeoenvironmental reconstructions further back in geological history.

6.3 Outlook

Ultimately, this study provides compelling evidence for local and global environmental controls on the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ of ancient marine sediments deposited during the OAE 2 interval. It suggests that, with a growing understanding of Zn and Cd cycling in the modern ocean and sedimentary environments, the $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ composition of marine sediments provides a valuable tool for future palaeoenvironmental studies, specifically those addressing global ocean redox change on timescales of 10^3 – 10^5 years.

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Appendices



Supplementary Figures

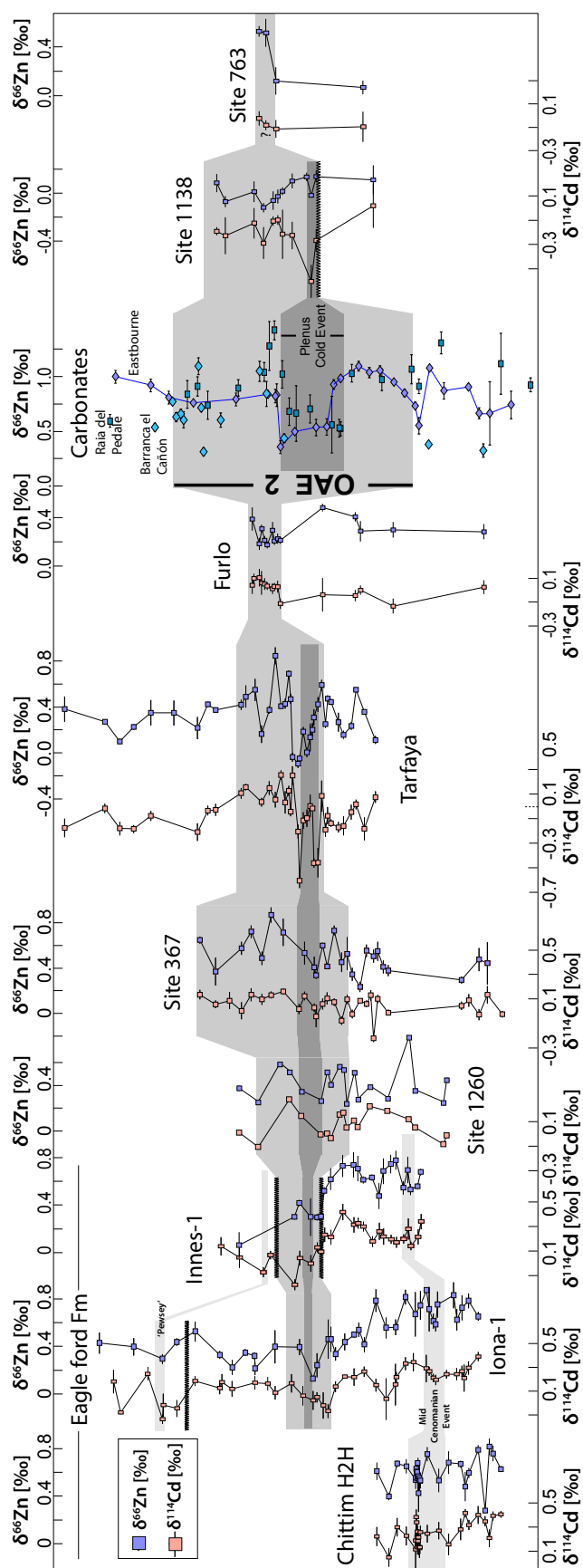


Figure A.1: All presented data plotted stratigraphically. Stratigraphic correlations based on published work (Tsikos et al., 2004; Jenkyns et al., 2008; Parente et al., 2008; Elrick et al., 2009; Dickson et al., 2016, 2017b; Eldrett et al., 2017; Scaife et al., 2017)

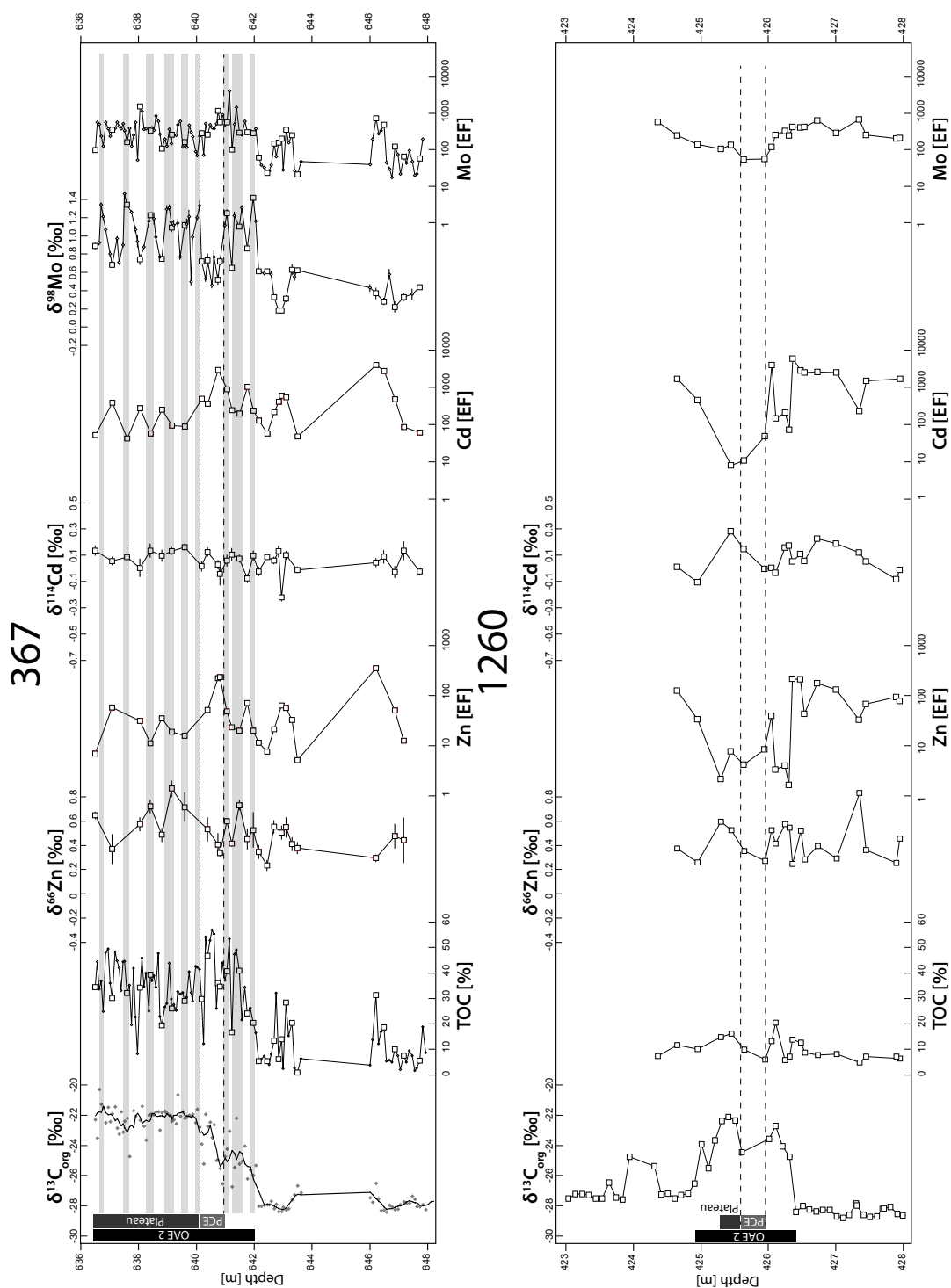


Figure A.2: $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphy for DSDP site 367 (Cape Verde Basin) and ODP site 1260 (Demerara Rise) from the Late Cretaceous Cenomanian–Turonian interval. The grey horizontal bands represent cycles of more restricted basinal condition that have led to drawdown of trace elements, as recognised from the Mo-isotope stratigraphy (Dickson et al., 2016).

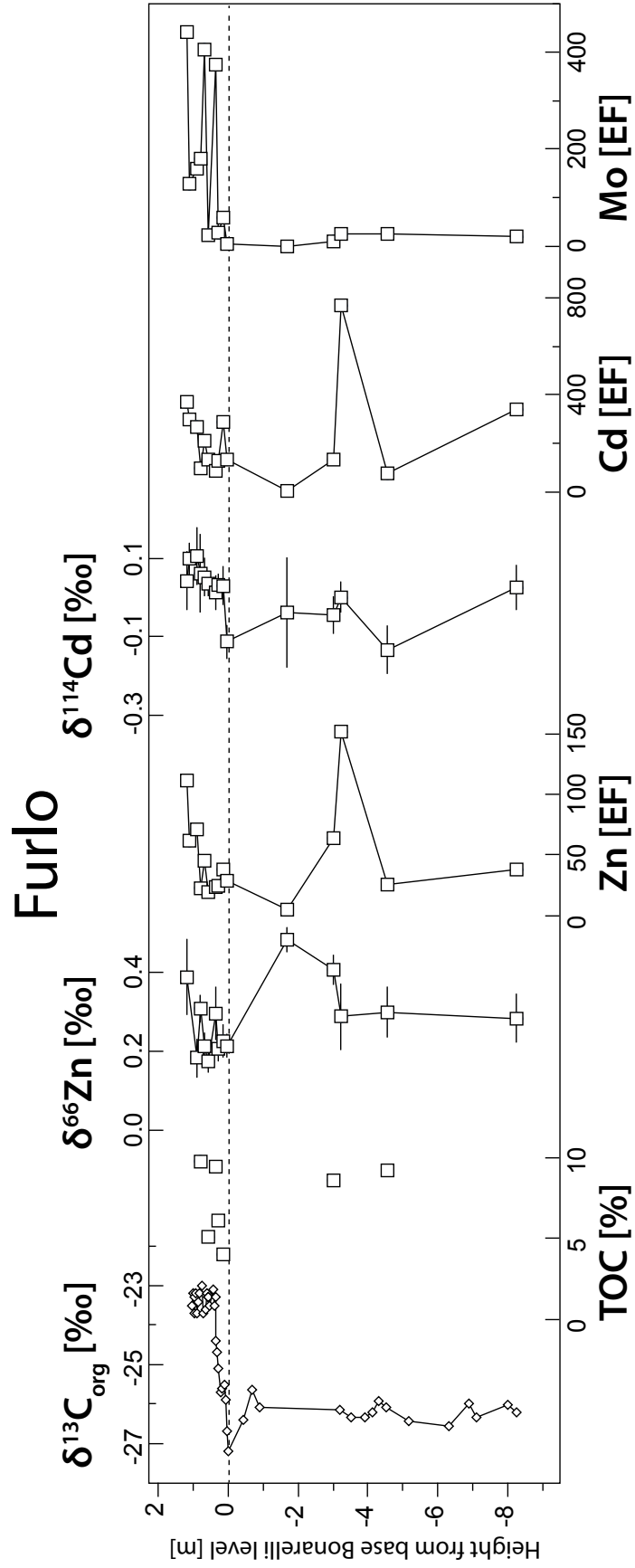


Figure A.3: $\delta^{66}Zn$ and $\delta^{114}Cd$ stratigraphy for the disused quarry outcrop near Furlo, Italy (e.g. Owens et al., 2017). Pre-event samples are from thin layers of shales intercalated between the carbonate sequence.

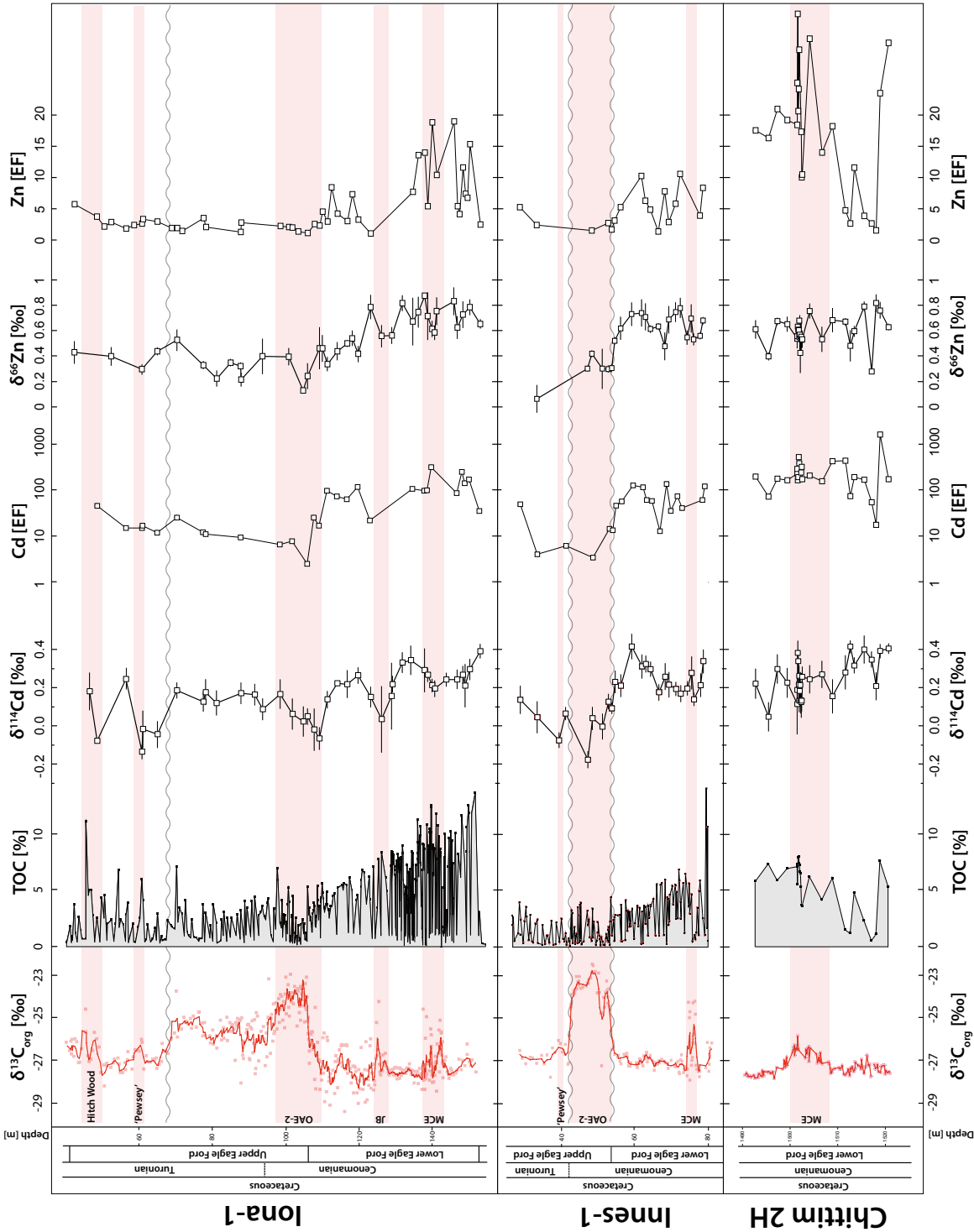


Figure A.4: $\delta^{66}Zn$ and $\delta^{114}Cd$ stratigraphy for the Innes-1, Iona-1 and Chittim 2H cores from the Maverick Basin (Eagle Ford Fm).

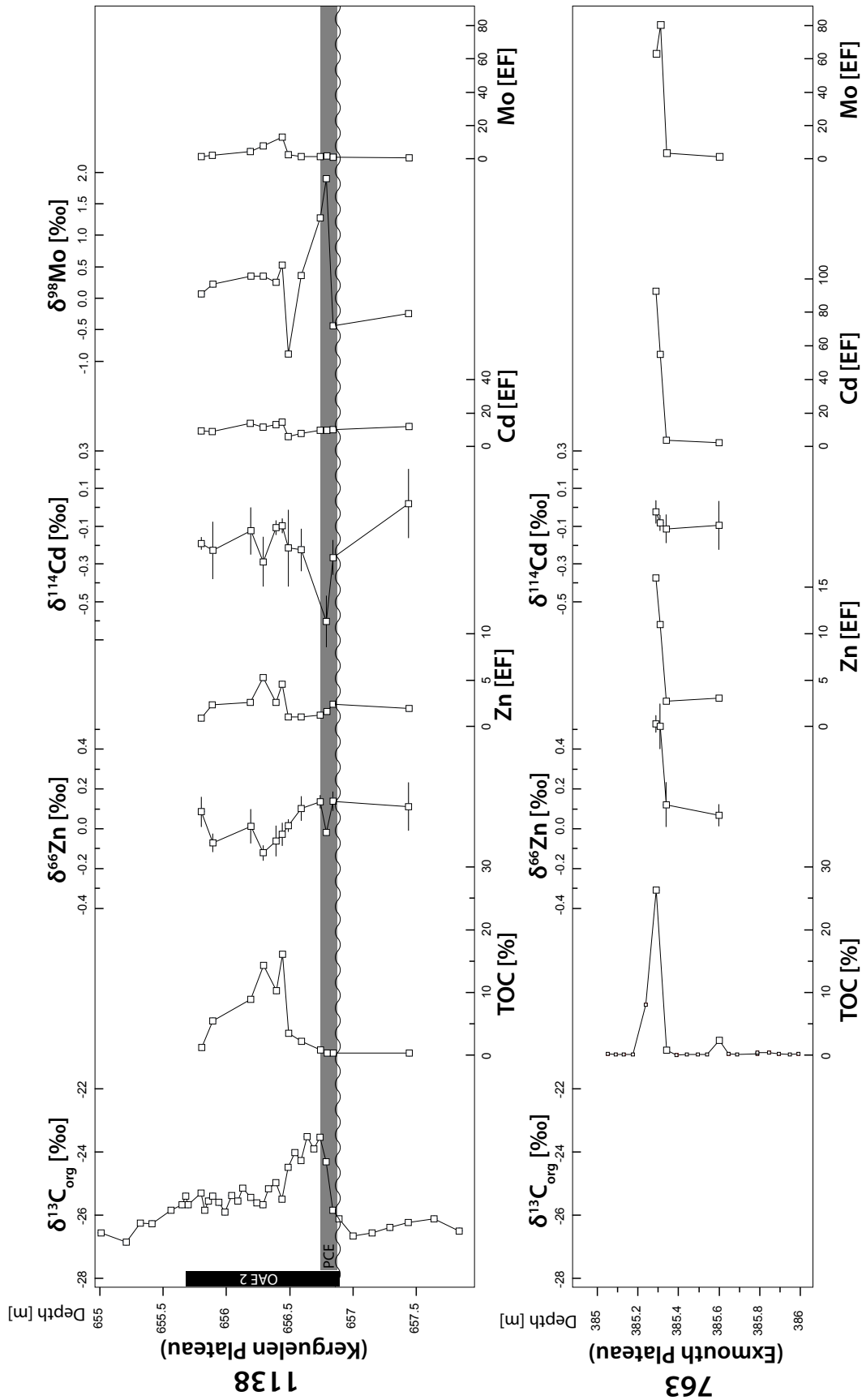


Figure A.5: $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ stratigraphy for ODP sites 763 (Exmouth Plateau) 1138 (Kerguelen Plateau).

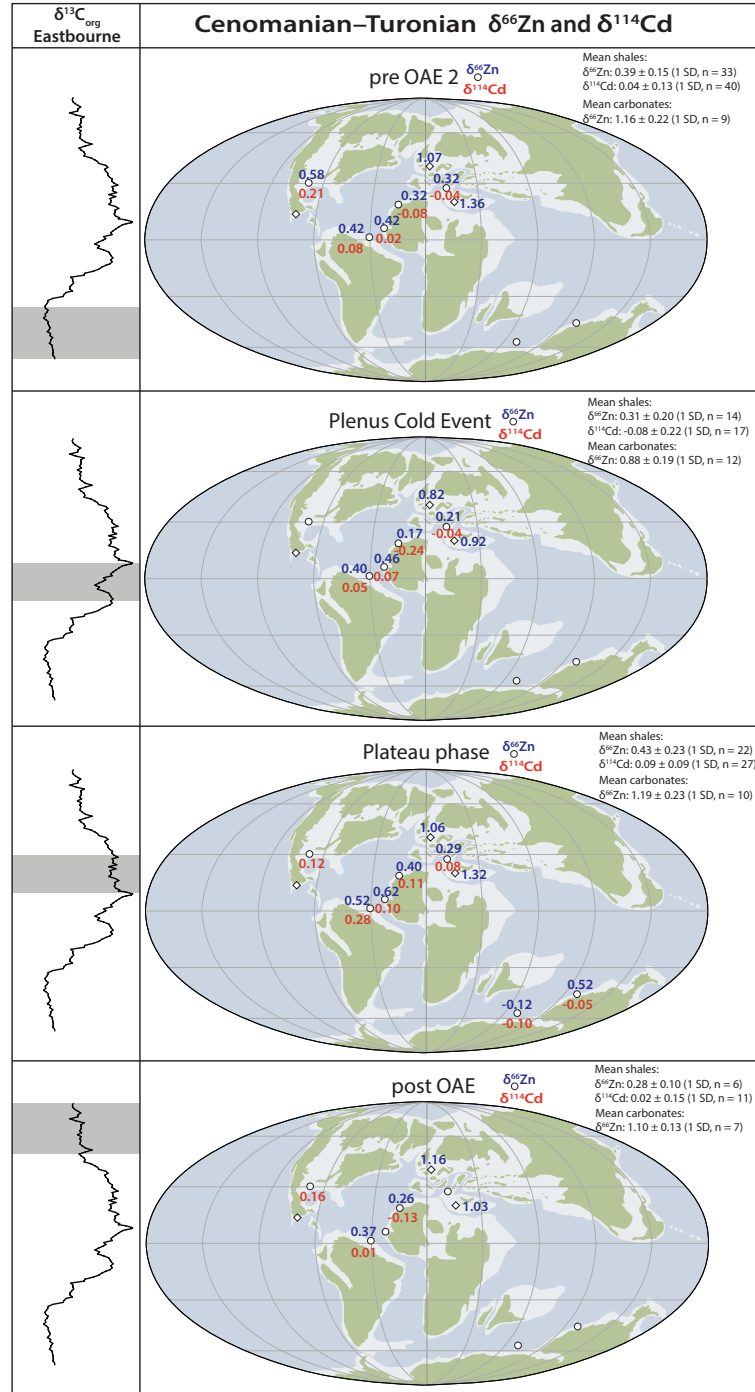


Figure A.6: Geographical distribution of $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ compositions for four different time intervals associated with the Cenomanian–Turonian Boundary Event. The numbers relate to the average $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ values for each site per time interval as correlated by the C-isotope stratigraphy. Relevant time intervals are indicated on the left relative to the $\delta^{66}\text{Zn}$ and $\delta^{13}\text{C}$ curve for the Eastbourne chalk reference section. Quoted $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ average only include samples with enrichment factors (relative to upper continental crust, Rudnick and Gao, 2003) of >5 , to exclude effects by varying proportions of lithogenic material.

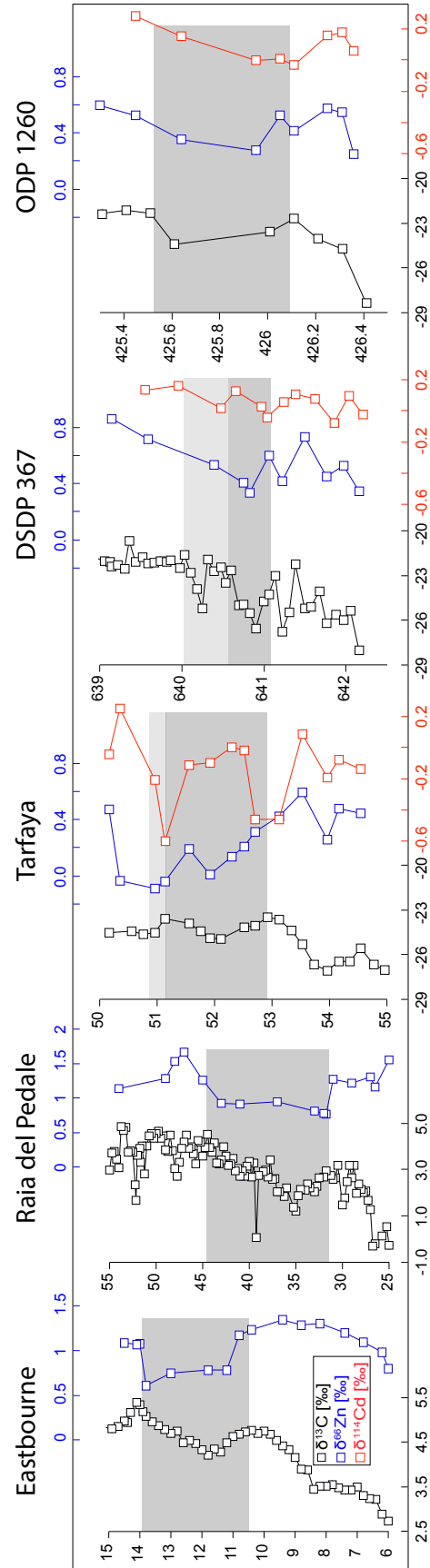


Figure A.7: Multi-site comparison of $\delta^{13}\text{Cd}$, $\delta^{66}\text{Zn}$, and $\delta^{114}\text{Cd}$ stratigraphy for the time interval surrounding the Plenius Cold Event, a period of (northern hemisphere) cooling and ocean deoxygenation.

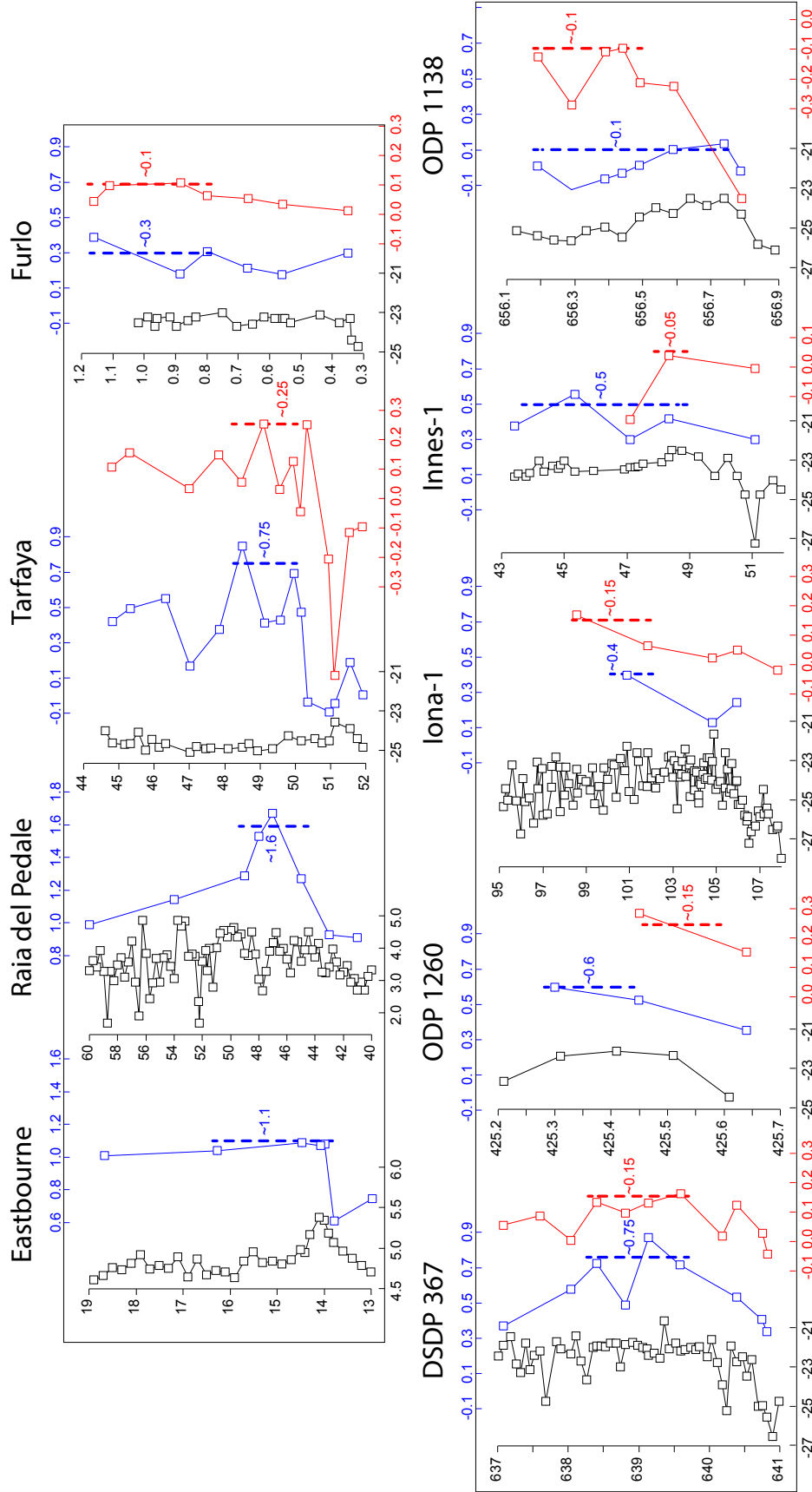


Figure A.8: Multi-site comparison of $\delta^{13}\text{Cd}$, $\delta^{66}\text{Zn}$, and $\delta^{114}\text{Cd}$ stratigraphy for the time interval surrounding the 'plateau-phase' of the OAE 2 interval, as evidenced from the $\delta^{13}\text{Cd}$ stratigraphy.

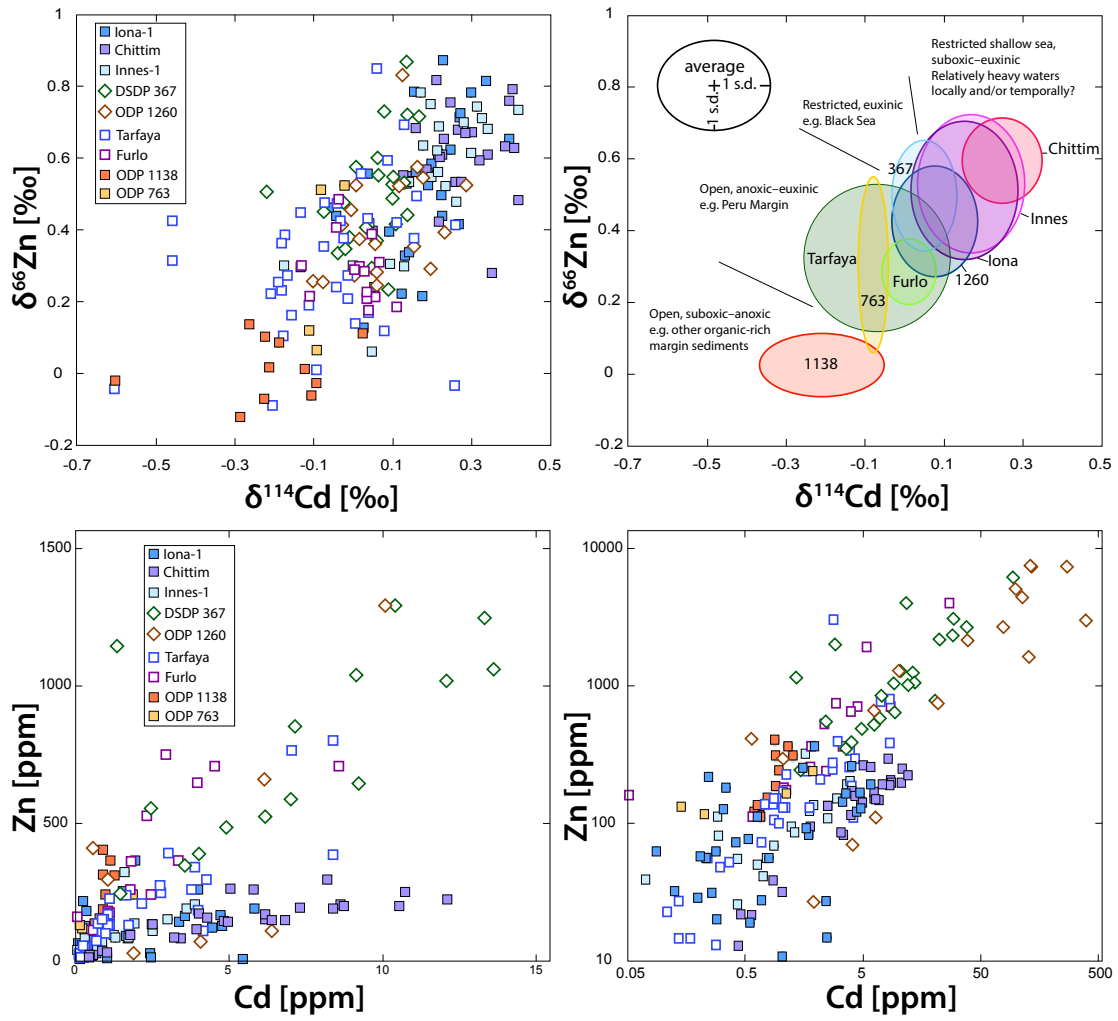


Figure A.9: Compilation of $\delta^{13}\text{Cd}$, $\delta^{66}\text{Zn}$, and Cd and Zn abundances for the studied mudrocks.

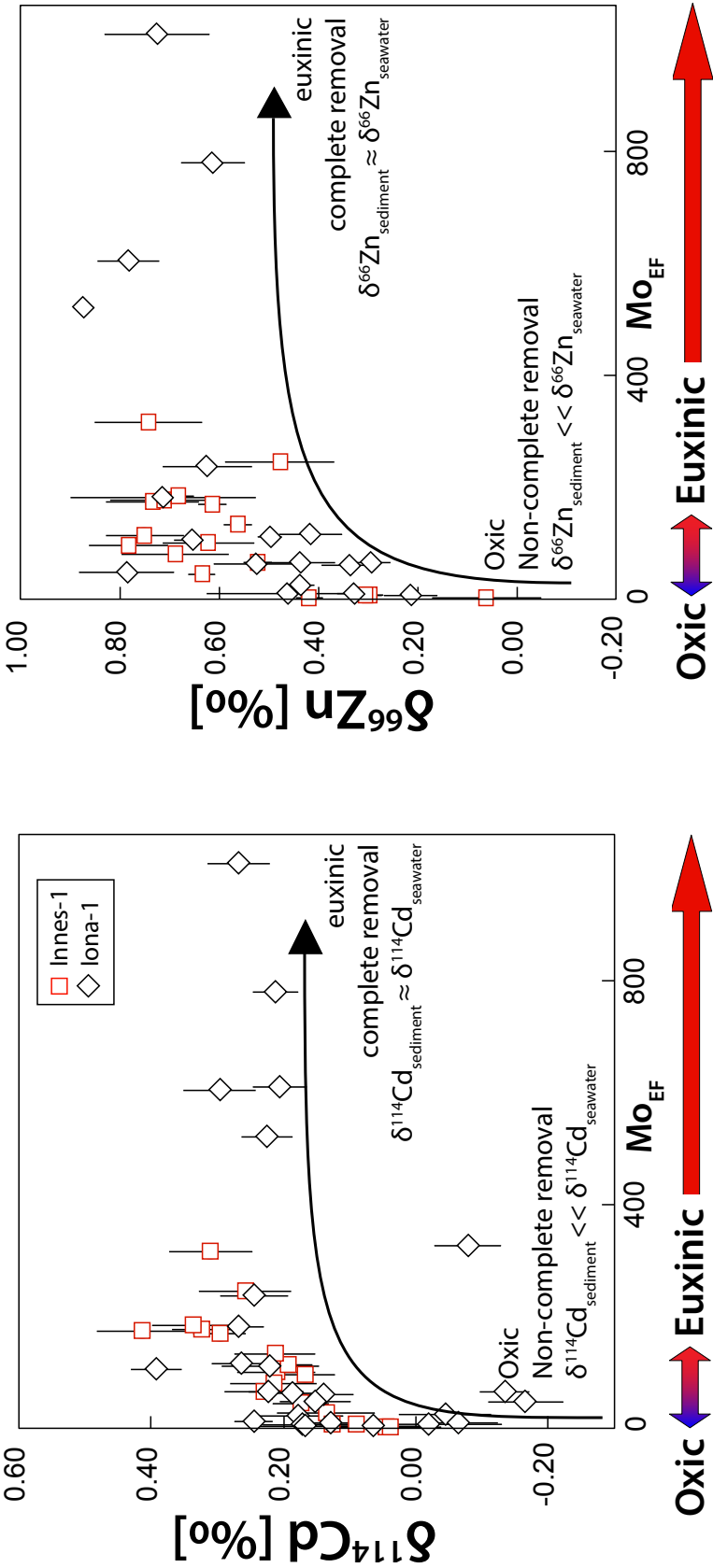


Figure A.10: $\delta^{133}Cd$ and $\delta^{66}Zn$ relative to Mo-enrichment factors for the Innes-1 and Iona-1 (Eagle Ford) cores

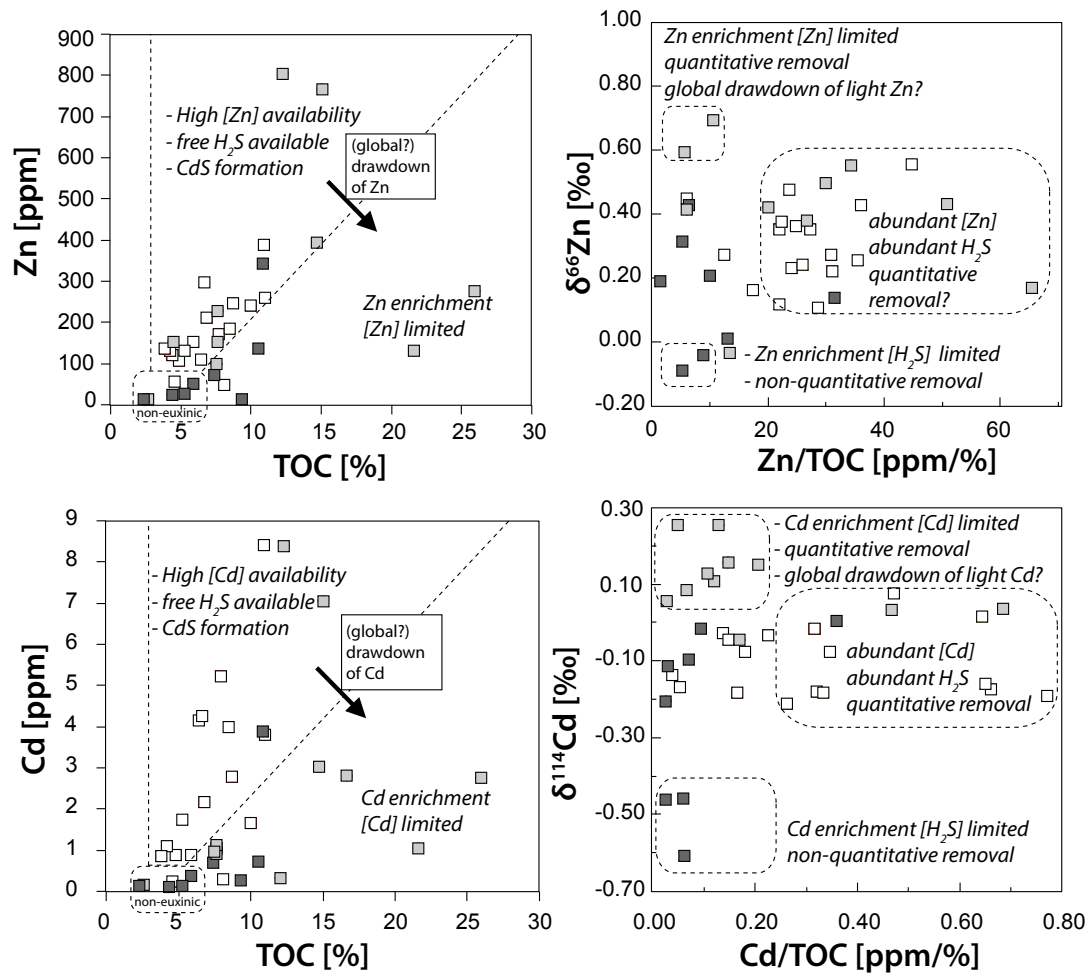


Figure A.11: Enlarged version of Figure 4.3, with data from the Tarfaya S-57 core

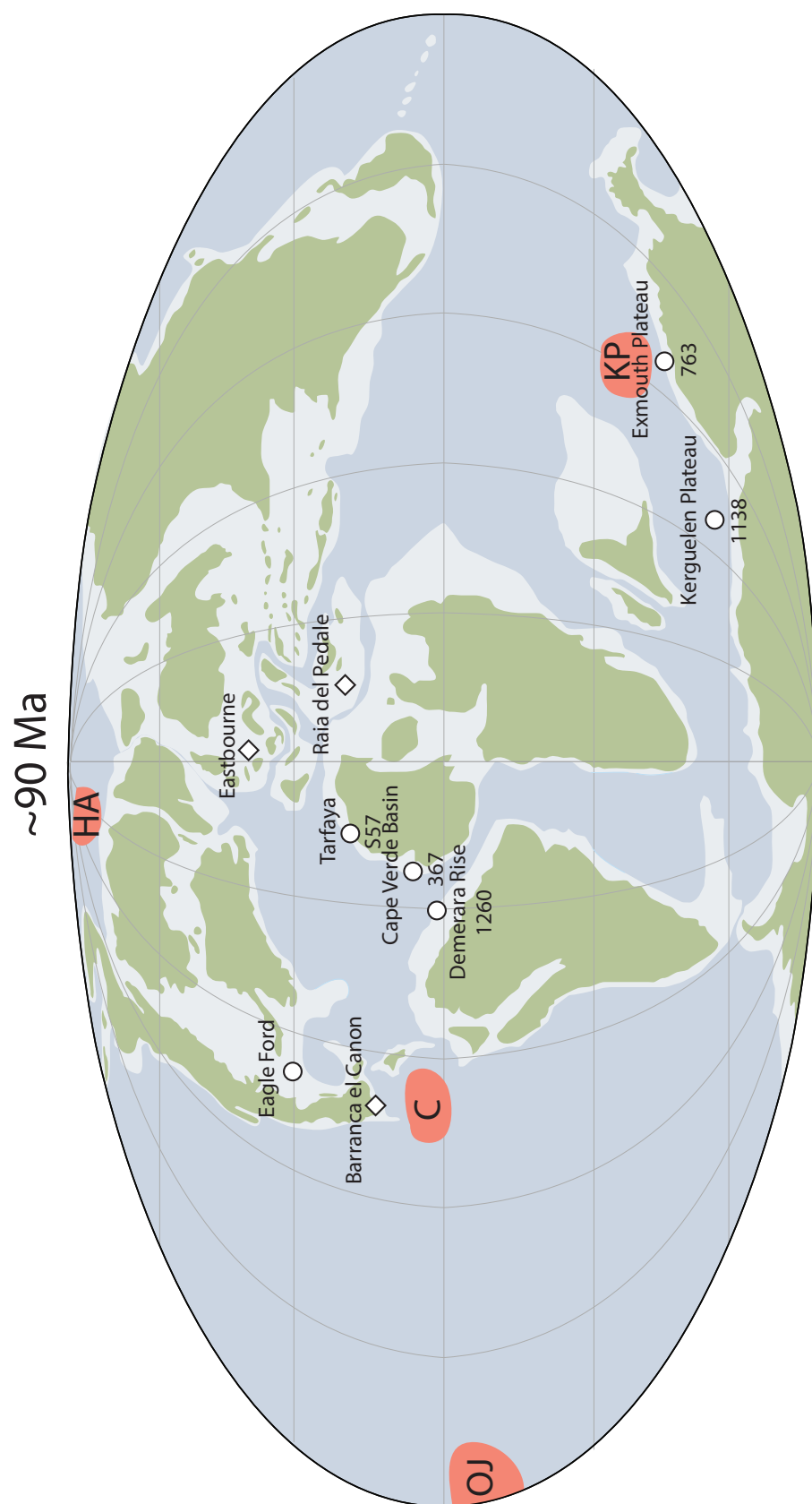


Figure A.12: Palaeogeographical reconstruction of 90Ma, including approximate study locations and locations of Large Igneous Provinces, modified from Jarvis et al. (2011), courtesy of Lauren 'O Connor

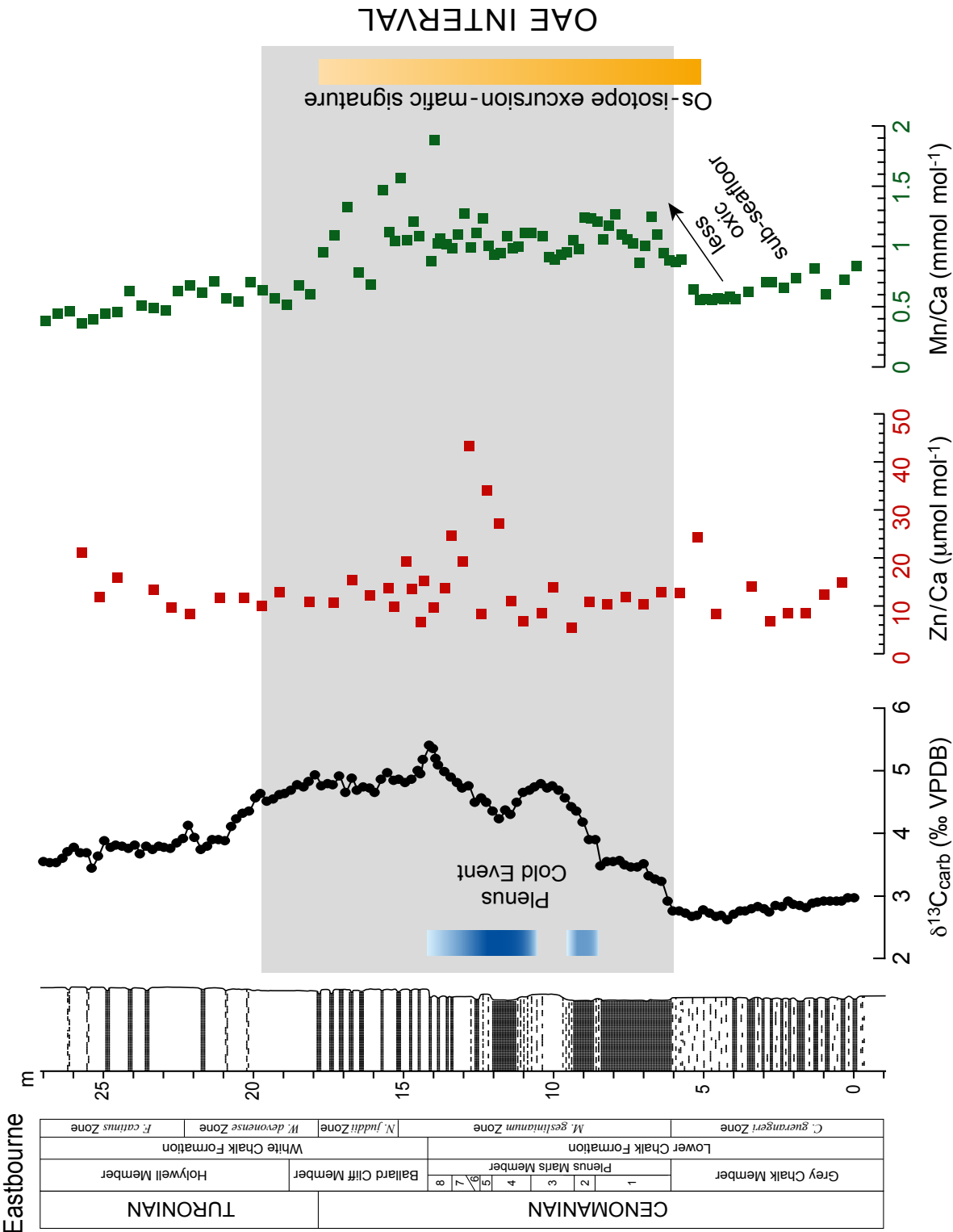


Figure A.13: Mn/Ca ratios for the Eastbourne section

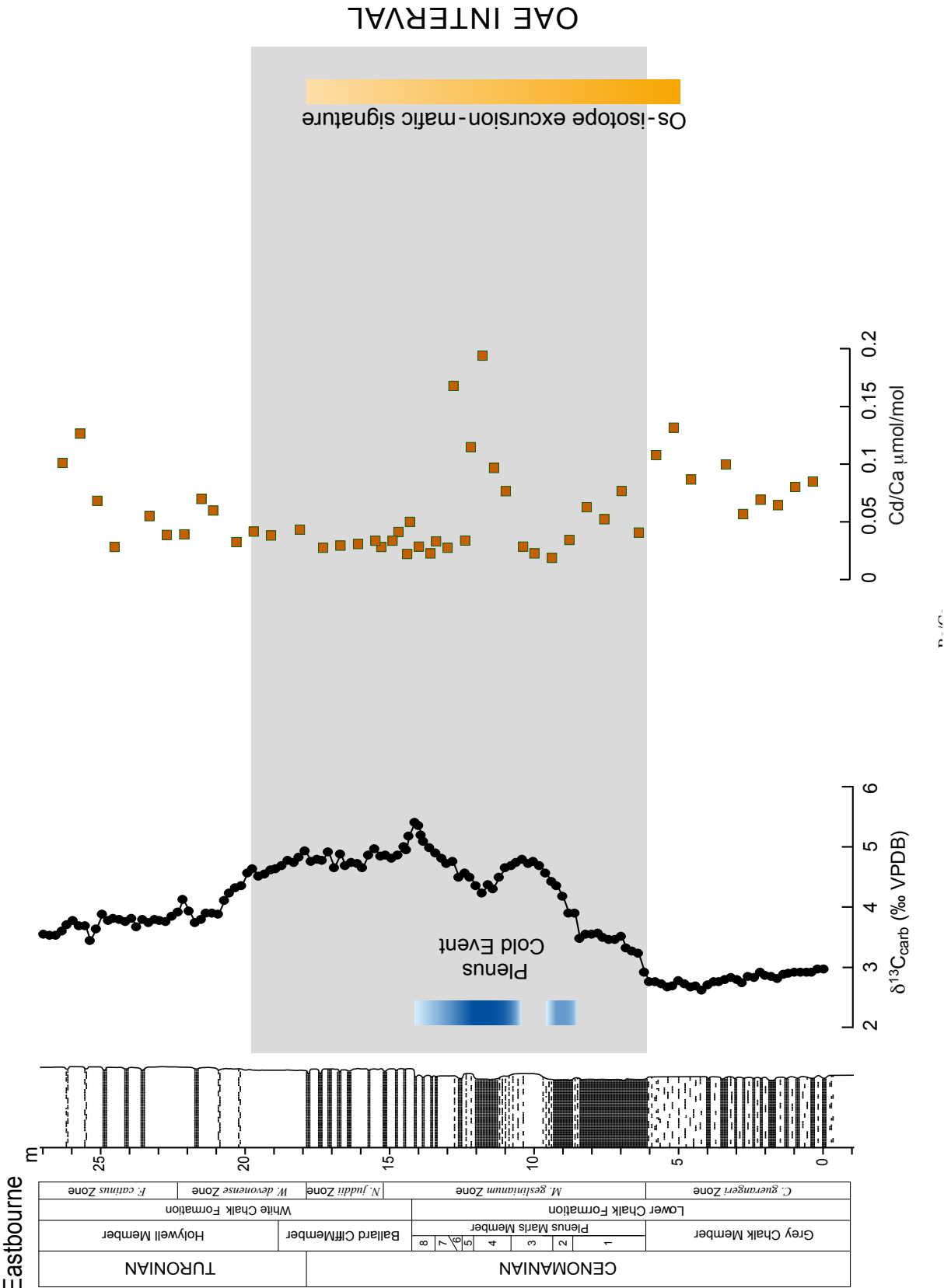


Figure A.14: Cd/Ca ratios for the Eastbourne section

B

Data tables

Site	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
1138	655.80	-25.31	1.21	-0.19	0.03		8.98	0.09	0.08	50.96	0.93
1138	655.89	-25.40	5.45	-0.23	0.15		8.76	-0.07	0.05	181.43	2.37
1138	656.19	-25.43	8.87	-0.12	0.12		13.71	0.01	0.09	180.79	2.62
1138	656.29	-25.67	14.33	-0.29	0.13		11.45	-0.12	0.04	306.45	5.26
1138	656.39	-24.97	10.29	-0.11	0.04		12.72	-0.06	0.08	175.91	2.63
1138	656.44	-25.50	16.10	-0.10	0.04		14.25	-0.03	0.06	229.98	4.57
1138	656.49	-24.48	3.43	-0.21	0.20		5.82	0.02	0.03	81.59	1.07
1138	656.59	-24.27	2.19	-0.23	0.11		7.67	0.10	0.06	78.82	1.07
1138	656.74	-23.54	0.79				9.42	0.14	0.03	89.88	1.25
1138	656.79	-24.32	0.29	-0.60	0.14		9.34	-0.02	0.02	85.43	1.60
1138	656.84	-25.85	0.31	-0.27	0.09		9.69	0.14	0.05	118.29	2.42
1138	657.44	-26.22	0.33	0.02	0.18		11.69	0.11	0.12	96.69	1.96

Site	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
763	385.29		26.36	-0.03	0.06	1.88	92.75	0.52	0.04	241.53	16.02
763	385.31			-0.08	0.04	1.12	55.04	0.51	0.11	165.37	10.95
763	385.34		0.84	-0.11	0.08	0.22	3.89	0.12	0.11	117.50	2.73
763	385.60		2.37	-0.10	0.13	0.14	2.44	0.07	0.06	131.72	3.03

Site	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
Furlo	1.16			0.04	0.07	2.33	368.69	0.39	0.10	526.68	111.86
Furlo	1.11			0.10	0.04	4.53	296.93			707.13	62.27
Furlo	0.89			0.11	0.07	1.18	173.65	0.18	0.05	362.69	71.59
Furlo	0.80		9.77	0.06	0.10	1.06	98.55	0.31	0.04	182.25	22.78
Furlo	0.67			0.05	0.05	1.11	210.89	0.21	0.04	175.90	44.78
Furlo	0.56		5.10	0.04	0.03	3.34	135.18	0.18	0.03	364.22	19.80
Furlo	0.35		9.42	0.01	0.04	0.57	87.56	0.30	0.07	112.75	23.19
Furlo	0.28		6.10	0.03	0.03	1.77	125.71	0.21	0.03	258.73	24.66
Furlo	0.15		4.04	0.03	0.05	2.45	288.95	0.23	0.04	241.92	38.38
Furlo	0.04			-0.11	0.04	3.96	132.04	0.22	0.03	648.01	29.03
Furlo	-1.68			-0.04	0.14	0.05	1.12	0.48	0.03	160.98	4.68
Furlo	-3.01		8.60	-0.04	0.05	5.40	134.18	0.41	0.04	1917.92	64.07
Furlo	-3.22			0.00	0.04	27.26	772.01	0.29	0.08	3981.95	151.47
Furlo	-4.55			-0.13	0.06	2.95	75.64	0.30	0.07	750.28	25.83
Furlo	-8.24			0.03	0.06	8.58	341.93	0.29	0.06	709.41	37.98

Core Number	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
S57-Tarfaya	25.69	-27.19	7.91	-0.18	0.08	5.22	221.22	0.39	0.11		0.00
S57-Tarfaya	30.04	-26.72	6.82	-0.02	0.04	2.16	128.97	0.27	0.02	210.34	16.90
S57-Tarfaya	31.67	-26.79	8.67	-0.18	0.05	2.78	83.12	0.11	0.02	247.33	9.94
S57-Tarfaya	33.16	-26.20	9.96	-0.18	0.03	1.65	75.70	0.23	0.02	240.24	14.76
S57-Tarfaya	35.03	-26.15	4.84	-0.08	0.04	0.88	59.48	0.35	0.11	105.75	9.64
S57-Tarfaya	37.52	-27.55	4.39					0.35	0.11	119.84	7.89
S57-Tarfaya	40.07	-25.73	4.20	-0.21	0.07	1.10	272.77	0.22	0.10	130.85	43.58
S57-Tarfaya	41.22	-24.98	3.82	-0.03	0.04	0.86	293.27	0.43	0.02	137.85	63.37
S57-Tarfaya	42.04	-24.89	7.66	-0.03	0.05	1.05	419.37	0.38	0.02	171.05	91.43
S57-Tarfaya	44.81	-24.63	7.63	0.11	0.04	0.92	249.38	0.42	0.05	153.12	55.86
S57-Tarfaya	45.32	-24.67	7.59	0.16	0.03	1.12	248.59	0.49	0.10	227.83	68.01
S57-Tarfaya	46.32	-24.68	4.49					0.55	0.10	153.56	207.61
S57-Tarfaya	47.01	-25.12	12.28	0.04	0.03	8.40	850.04	0.17	0.08	802.74	109.17
S57-Tarfaya	47.84		14.70	0.15	0.06	3.02	671.53	0.38	0.03	393.84	117.56
S57-Tarfaya	48.50	-24.88	12.04	0.06	0.06	0.32	44.94	0.85	0.07		0.00
S57-Tarfaya	49.13		21.58	0.26	0.04	1.05	226.40	0.41	0.03	130.12	37.86
S57-Tarfaya	49.57		15.05	0.03	0.09	7.03	786.47	0.43	0.04	766.21	115.10
S57-Tarfaya	49.96		25.93	0.13	0.04	2.76	629.81	0.69	0.03	274.71	84.19
S57-Tarfaya	50.16	-24.54	16.61	-0.04	0.04	2.82	294.58	0.47	0.04	3056.90	428.41
S57-Tarfaya	50.35		7.51	0.25	0.08	0.96	208.77	-0.03	0.04	100.07	29.11
S57-Tarfaya	50.96	-24.53	4.37	-0.21	0.06	0.11	28.72	-0.09	0.04	22.87	8.09
S57-Tarfaya	51.13	-23.57	5.88	-0.61	0.06	0.36	20.13	-0.04	0.03	52.14	3.87
S57-Tarfaya	51.55	-23.93	9.31	-0.11	0.07	0.28	51.39	0.19	0.04	13.06	3.23
S57-Tarfaya	51.92	-24.88	10.51	-0.10	0.07	0.73	33.85	0.01	0.04	137.43	8.51
S57-Tarfaya	52.30		10.84	0.00	0.09	3.89	391.22	0.14	0.12	341.72	46.20
S57-Tarfaya	52.51	-24.17	7.37	-0.02	0.05	0.68	141.10	0.21	0.06	73.51	20.35
S57-Tarfaya	52.70	-24.08	5.28	-0.46	0.04	0.14	20.47	0.31	0.07	27.45	5.53
S57-Tarfaya	53.12	-23.67	2.31	-0.46	0.12	0.14	121.92	0.43	0.06	14.63	17.70
S57-Tarfaya	53.52	-25.30	2.61	0.08	0.13	0.17	161.59	0.59	0.05	14.53	18.56
S57-Tarfaya	53.96	-27.07	10.91	-0.19	0.05	8.40	397.19	0.26	0.03	387.13	24.58
S57-Tarfaya	54.16	-26.44	10.96	-0.08	0.07	3.79	184.33	0.48	0.03	258.85	16.90
S57-Tarfaya	54.53	-25.56	8.09	-0.14	0.03	0.30	57.97	0.45	0.03	48.24	12.32
S57-Tarfaya	55.34	-26.05	4.56	-0.17	0.04	0.24	38.67	0.27	0.08	56.44	12.24
S57-Tarfaya	55.90	-27.60	6.39	-0.16	0.08	4.15	330.60	0.16	0.03	110.91	11.86
S57-Tarfaya	56.72	-25.96	5.87	-0.05	0.06	0.87	237.23	0.24	0.03	152.56	55.66
S57-Tarfaya	57.25	-27.32	6.62	0.02	0.04	4.26	314.05	0.56	0.07	296.40	29.36
S57-Tarfaya	58.16	-27.85	5.24	-0.18	0.09	1.74	112.48	0.36	0.03	129.85	11.26
S57-Tarfaya	59.35	-27.24	8.49	0.08	0.05	4.00	153.01	0.12	0.04	186.06	9.57

Site Number	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
367	637.08	-21.91	30.20	0.06	0.03	11.70	386.51	0.37	0.12	4015.55	178.12
367	637.60	-22.20	31.12	0.09	0.07	1.35	42.01			1143.44	47.62
367	638.04	-22.33	34.18	0.00	0.07	4.90	279.27	0.57	0.06	486.95	37.27
367	638.40	-21.93	38.16	0.14	0.05	1.46	57.10	0.72	0.05	245.28	12.85
367	638.81	-21.86	19.37	0.10	0.05	10.42	249.32	0.49	0.06	1290.92	41.48
367	639.14	-22.42	25.70	0.13	0.03	2.90	93.03	0.87	0.07	1991.57	85.97
367	639.59	-22.21	28.59	0.16	0.03	2.45	89.40	0.72	0.12	553.63	27.16
367	640.18	-23.91	29.24	0.02	0.04	13.32	500.47			1247.34	62.96
367	640.39	-22.73	45.99	0.13	0.04	9.15	366.93	0.53	0.10	1038.59	55.95
367	640.75	-24.97	35.15	0.03	0.04	94.60	2904.56	0.41	0.09	6196.64	255.56
367	640.82	-25.54	33.82	-0.04	0.09			0.33	0.03	5706.36	231.17
367	641.06	-24.25	39.95	0.06	0.05	20.57	874.85	0.60	0.03	780.35	44.58
367	641.22	-26.75	15.81	0.11	0.05	13.63	244.20	0.42	0.03	1059.65	25.50
367	641.49	-25.22	40.15	0.07	0.03	6.19	193.95	0.73	0.04	525.31	22.11
367	641.76	-26.21	23.07	-0.08	0.03	38.18	1018.35	0.45	0.09	2678.27	95.96
367	641.97	-25.98	19.27	0.10	0.04	9.24	237.63	0.53	0.15	646.19	22.32
367	642.16	-28.01	5.64	-0.02	0.04	7.01	129.36	0.35	0.06	586.80	14.55
367	642.44	-27.91	4.27	0.09	0.02	4.01	57.23	0.23	0.05	390.71	7.49
367	642.68	-28.19	13.54	0.06	0.03	12.07	218.14	0.55	0.06	1019.35	24.74
367	642.85	-28.37	6.37	0.13	0.04	17.27	415.91				
367	642.95	-28.38	14.29	-0.22	0.03	22.30	599.21	0.51	0.06	2167.99	78.27
367	643.10	-28.29	27.24	0.10	0.03	29.17	536.64	0.55	0.08	2329.39	57.56
367	643.31	-27.59	19.30					0.41	0.06	2776.50	35.30
367	643.49	-26.69	1.11	-0.01	0.03	3.57	47.06	0.38	0.05	348.55	6.17
367	646.21	-26.50	31.38	0.05	0.03	144.27	3993.18	0.29	0.03	11532.02	428.77
367	646.48	-28.29	18.81	0.09	0.05	91.26	2747.31			10355.90	418.76
367	646.86	-28.25	10.20	-0.03	0.05	29.63	471.67	0.48	0.10	3084.95	65.97
367	647.17	-27.72	7.71	0.13	0.07	7.15	85.22	0.44	0.19	853.60	13.67
367	647.73	-28.07	5.71	-0.02	0.03	5.08	60.42				

Site Number	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
1260	424.36		7.50								
1260	424.65		11.80	0.01	0.04	133.94	1712.51	0.37	0.05	7404.30	127.17
1260	424.95		10.20	-0.10	0.04	38.58	448.17	0.26	0.03	2158.00	33.67
1260	425.30		15.00					0.60	0.09	73.81	2.19
1260	425.45		16.20	0.28	0.05	0.56	7.97	0.52	0.08	411.12	7.85
1260	425.64		10.10	0.15	0.07	1.05	11.00	0.35	0.20	297.15	4.19
1260	425.95		6.10	0.00	0.04	10.08	49.08	0.27	0.16	1290.97	8.44
1260	426.05		13.30	0.01	0.05	395.96	3962.77	0.52	0.07	2992.65	40.23
1260	426.11		20.50	-0.03	0.05	6.39	145.73	0.41	0.06	110.77	3.39
1260	426.25		5.90	0.16	0.05	1.90	208.69	0.57	0.05	26.95	3.99
1260	426.31		7.40	0.18	0.03	4.07	72.30	0.55	0.05	69.63	1.66
1260	426.36		13.90	0.06	0.04	272.61	5953.65	0.25	0.07	7364.21	216.04
1260	426.48		12.70	0.11	0.04	133.51	2834.72	0.52	0.07	7427.60	211.84
1260	426.54		8.80	0.06	0.03	127.59	2548.10	0.28	0.05	1628.13	43.68
1260	426.73		7.90	0.23	0.03	99.21	2579.17	0.39	0.04	5043.62	176.14
1260	427.01		8.20	0.19	0.02	112.14	2484.15	0.29	0.10	4407.52	131.15
1260	427.35		5.00	0.12	0.03	6.17	231.22	0.83	0.09	660.47	33.26
1260	427.45		7.40	0.05	0.04	77.97	1480.49	0.36	0.16	2679.62	68.34
1260	427.95		6.50	-0.01	0.09	21.50	1690.32	0.46	0.09	750.83	79.29
1260	427.90		7.30	-0.08	0.04			0.25	0.18	4090.80	94.42

Core Number	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
Chittim H2H	1492.72		5.79	0.22	0.08	4.83	192.76	0.61	0.07		17.57
Chittim H2H	1495.41		7.30	0.05	0.08	2.51	70.43	0.40	0.03		16.33
Chittim H2H	1497.27		5.84	0.30	0.08	4.03	176.13	0.67	0.03		20.92
Chittim H2H	1499.33		6.89	0.23	0.08	4.29	161.97	0.65	0.06		19.17
Chittim H2H	1501.42		7.08	0.11	0.16	6.17	223.11	0.54	0.07		18.42
Chittim H2H	1501.49		7.27	0.19	0.06	8.64	283.34	0.55	0.03		25.19
Chittim H2H	1501.59		5.53	0.38	0.07	8.20	159.76	0.63	0.03		36.15
Chittim H2H	1501.68		7.89	0.34	0.06	6.17	186.96	0.61	0.03		20.64
Chittim H2H	1501.76		7.84	0.22	0.07	10.56	510.20	0.60	0.03		24.20
Chittim H2H	1501.84		8.00	0.26	0.06	10.75	375.78	0.68	0.02		30.45
Chittim H2H	1501.93		7.34	0.13	0.06	12.12		0.55	0.03		
Chittim H2H	1502.02		7.18	0.18	0.06	8.75		0.57	0.16		
Chittim H2H	1502.09		6.60	0.21	0.07	8.40		0.42	0.16		
Chittim H2H	1502.18		6.44	0.13	0.07	6.82		0.54	0.12		
Chittim H2H	1502.34		5.28	0.12	0.08	4.98	238.10	0.55	0.12		17.34
Chittim H2H	1502.38		3.70	0.13	0.06	3.43	316.55	0.53	0.07		10.06
Chittim H2H	1502.51		3.54	0.26	0.06	3.22	171.44	0.53	0.07		10.46
Chittim H2H	1504.05		6.20	0.24	0.07	5.06	205.21	0.76	0.06		32.17
Chittim H2H	1506.63		4.16	0.27	0.07	3.94	154.21	0.53	0.10		14.03
Chittim H2H	1508.85		6.08	0.15	0.09	6.41	419.67	0.68	0.10		18.25
Chittim H2H	1511.55		1.52	0.28	0.09	0.86	426.53	0.67	0.03		4.72
Chittim H2H	1512.59		1.19	0.41	0.03	0.57	73.13	0.48	0.12		2.61
Chittim H2H	1513.41		4.78	0.32	0.04	1.78	188.92	0.59	0.04		11.58
Chittim H2H	1515.49		2.29	0.40	0.07	1.03	164.52	0.79	0.04		3.88
Chittim H2H	1517.04		0.57	0.35	0.04	0.46	52.91	0.28			2.65
Chittim H2H	1518.00		1.08	0.21	0.07	0.44	17.33	0.82	0.07		1.57
Chittim H2H	1518.84		7.57	0.39	0.04	7.32	1589.33	0.76	0.07		23.55
Chittim H2H	1520.65		5.27	0.41	0.03	5.80	168.23	0.63	0.03		31.54

Core Number	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
Iona-1	42.53	-26.86	3.71					0.43	0.09		5.68
Iona-1	46.65	-27.10	4.99	0.18	0.04	1.72					
Iona-1	48.70	-26.05	2.58	-0.08	0.05	0.46	44.84				3.74
Iona-1	52.57	-27.38	2.38					0.40	0.07		2.86
Iona-1	56.61	-27.49	2.81	0.24	0.03	0.79	14.83				1.84
Iona-1	60.93	-26.07	5.97	-0.13	0.04	0.55	14.71	0.29	0.04		2.63
Iona-1	61.14	-26.22	4.11	-0.17	0.06	0.42	16.52				3.31
Iona-1	65.12	-27.45	2.91	-0.04	0.07	0.28	11.63	0.44	0.03		2.94
Iona-1	70.45	-23.82	7.14	0.19	0.04	0.69	25.11	0.53	0.08		1.87
Iona-1	77.60	-25.91	3.77	0.13	0.05	0.26	11.86	0.33	0.03		3.45
Iona-1	78.28	-25.89	2.96	0.18	0.07	0.23	10.87				2.02
Iona-1	81.25	-25.90	1.50	0.12	0.07	0.13		0.22	0.06	48.33	
Iona-1	85.02	-25.55	0.57					0.35	0.03	25.76	
Iona-1	87.74	-25.09	0.65					0.32	0.03		1.29
Iona-1	87.88	-25.73	3.16	0.17	0.06	0.28	9.19	0.21	0.05		2.73
Iona-1	91.56	-25.41	0.48	0.16	0.09	0.09			0.04		
Iona-1	93.76	-25.16	2.60	0.09	0.06	0.15		0.40	0.14	51.64	
Iona-1	98.56	-23.44	2.12	0.17	0.08	0.14	6.49				2.18
Iona-1	100.90	-22.26	5.28					0.40	0.07		2.04
Iona-1	101.83	-22.61	2.72	0.06	0.08	0.20	7.59				1.97
Iona-1	104.83	-23.02	1.68	0.02	0.08	0.13		0.13	0.04		
Iona-1	105.96	-24.01	0.51	0.05	0.04	0.03	2.44	0.24	0.10		1.07
Iona-1	107.82	-26.32	3.88	-0.02	0.11	1.04	24.73		0.07		2.49
Iona-1	109.22	-25.90	3.62	-0.07	0.06	0.53	16.67	0.46	0.17	220.11	2.31
Iona-1	110.01	-26.79	5.55					0.46	0.11		4.48
Iona-1	111.36	-26.43	4.83	0.14	0.05	3.38	96.94	0.34	0.06		2.88
Iona-1	112.45	-27.19	3.55						0.04		8.39
Iona-1	114.04	-26.94	1.09	0.22	0.03	0.64	72.87	0.44	0.07		4.21
Iona-1	116.76	-26.64	5.43	0.22	0.07	2.42	62.45	0.50	0.02		3.00
Iona-1	118.16	-26.92	5.02					0.54	0.06		7.29
Iona-1	119.77	-27.32	4.53	0.26	0.04	4.45	117.91	0.42	0.06		3.27
Iona-1	123.14	-27.10	4.14	0.15	0.05	1.64	21.45	0.79	0.10		1.01
Iona-1	126.10	-27.36	0.75	0.03	0.17	0.21		0.56	0.09	14.83	
Iona-1	128.88	-27.45	5.61	0.16	0.17	2.45		0.56	0.07	127.10	
Iona-1	129.11	-27.39	0.94	0.22	0.04	0.33					
Iona-1	131.74	-27.40	1.37	0.33	0.05	0.50		0.82	0.06	24.69	
Iona-1	134.05			0.35	0.08						
Iona-1	134.65	-27.45	1.52			0.40	106.05	0.67	0.19		7.71

Core Number	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
lona-1	136.14	-27.64	11.29					0.75	0.12		13.55
lona-1	137.85	-27.35	9.04	0.22	0.04	1.55	95.50	0.87	0.02		13.97
lona-1	138.65	-27.47	10.83	0.27	0.04	4.73	99.44	0.71	0.19		5.41
lona-1	139.86	-26.42	12.54	0.21	0.03	5.83	314.33	0.61	0.06		18.81
lona-1	140.59		8.45	0.19	0.04	3.99		0.58	0.06	192.36	
lona-1	141.15	-27.13	11.78					0.75	0.11		10.41
lona-1	143.73	-26.80	0.82	0.24	0.04	0.24			0.03		
lona-1	145.75	-27.75	7.38					0.83	0.11		18.91
lona-1	146.70	-27.52	0.99	0.24	0.05	0.34	86.17	0.62	0.09		5.36
lona-1	147.23	-26.99	8.21					0.28			4.12
lona-1	148.23	-27.06	11.65	0.27	0.05	4.77	250.76	0.73	0.11		11.59
lona-1	148.90	-27.30	7.30	0.21	0.04	3.58	141.19				7.33
lona-1	149.49	-26.78	0.39						0.09		6.73
lona-1	150.15	-27.15	12.56	0.30	0.06	5.44	170.22	0.78	0.06		15.32
lona-1	152.97	-25.98	3.16	0.39	0.04	1.94	34.57	0.65	0.04		2.48

Core Number	Depth [m]	d13Corg	TOC	d114Cd	2 s.e. Cd	[Cd] ID	[Cd] EF	d66Zn	2 s.e. Zn	[Zn] ID	[Zn] EF
Innes-1	28.71	-26.50	2.38	0.14	0.07	1.23	49.13		0.11	95.40	5.11
Innes-1	31.52	-26.83	1.22					0.12	0.07	80.61	
Innes-1	33.30	-27.12	2.42	0.04	0.08	0.29	4.31	0.06	0.11	111.58	2.24
Innes-1	39.29	-26.04	0.42	-0.08	0.04					9.42	
Innes-1	41.04	-26.69	1.20	0.06	0.03						
Innes-1	43.42	-23.84	1.75					0.38	0.03	58.94	
Innes-1	45.33	-23.60	0.21					0.56	0.18	11.62	
Innes-1	47.10	-23.35	1.94	-0.18	0.05	0.07		0.30	0.02	39.28	
Innes-1	48.33	-22.87	3.35	0.04	0.06	0.30	3.77	0.42	0.03	81.34	1.39
Innes-1	51.08	-27.23	0.46	0.00	0.07	0.14		0.30	0.16		
Innes-1	52.70	-23.99	1.74	0.13	0.04	0.43	14.89	0.30	0.03	55.00	2.56
Innes-1	53.65	-25.58	0.98	0.09	0.03	0.63	14.22	0.30	0.03	50.36	1.52
Innes-1	54.55	-26.70	2.82	0.23	0.06	1.72	45.36	0.52	0.03	84.83	3.01
Innes-1	56.08	-27.03	3.71	0.21	0.06	1.76	53.90	0.62	0.09	124.12	5.12
Innes-1	57.18	-26.69	0.62					0.53	0.04	34.62	
Innes-1	57.98	-26.65	2.98					0.63	0.20	126.50	
Innes-1	59.10	-27.10	3.36	0.41	0.07	1.25	102.93	0.73	0.09		
Innes-1	61.83	-26.94	3.11	0.31	0.06	0.75	101.90	0.74	0.11	55.74	10.14
Innes-1	62.88	-26.88	3.54	0.32	0.05	0.88	58.41	0.71	0.11	69.10	6.19
Innes-1	64.23	-26.83	3.68	0.30	0.04	1.30	52.78	0.61	0.03	86.67	4.72
Innes-1	66.45	-27.16	1.00	0.17	0.04	0.13	14.95	0.63	0.03	8.20	1.25
Innes-1	68.15	-27.01	5.95	0.26	0.07	2.51	131.08	0.48	0.11	109.13	7.65
Innes-1	69.27	-27.34	2.29	0.21	0.07	0.43	34.00	0.69	0.11	25.74	2.75
Innes-1	71.08		2.47	0.19	0.04	0.71	72.26	0.75	0.08	41.40	5.67
Innes-1	72.43		3.99	0.17	0.05	1.61	38.79	0.78	0.08	322.97	10.46
Innes-1	74.21			0.20	0.04	2.49		0.55	0.06	134.71	
Innes-1	74.63	-27.40	3.58					0.62	0.07	96.27	
Innes-1	75.40	-26.59	4.64	0.28	0.09	3.63		0.70	0.11	191.95	
Innes-1	76.04			0.14	0.03	1.91		0.53	0.05	135.68	
Innes-1	77.82			0.21	0.06	3.00	55.87	0.56	0.03	152.05	3.81
Innes-1	78.56			0.34	0.06	3.88	115.81	0.68	0.03	204.97	8.22

