Selenium geochemistry and isotopic composition of sediments from the Cariaco Basin and the Bermuda Rise: a comparison between a restricted basin and the open ocean over the last 500 ka.

Thesis submitted for the degree of Doctor of Philosophy at the University of Leicester

by

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This thesis is in memory of my daddy Tim, who is sorely missed, and my grandpa David, who would have loved to have read this!

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Broad changes in atmospheric oxygen have been identified for the last 4 Ga whereas changes in ocean oxygenation are not as well constrained. Mo isotope ratios have already been suggested as a potential global ocean palaeoredox proxy. However, a shorter oceanic residence time, theoretically greater isotope shifts, and no reliance on free H_2S to alter its isotope composition, suggest Se isotope ratios could be a better global ocean palaeoredox proxy.

The Cariaco Basin, on the Venezuela margin, has been the subject of numerous palaeoceanographic studies. Alternating laminated and non-laminated sediments indicate cyclical changes in water column oxygenation. It is therefore an ideal natural laboratory in which to study these effects on Se isotopes. A comparison with the Bermuda Rise, in the western North Atlantic, over the same time period, allows an evaluation of the spatial variations of sedimentary Se isotope signatures.

Over the last interglacial-glacial transition, laminated (interglacial) sediments from the Cariaco Basin are characterised by high Se (~10 ppm) and high $\delta^{82/76}$ Se (~0.03‰). In contrast, sediments from non-laminated (glacial) sediments have low Se (~0.5 ppm) and negative $\delta^{82/76}$ Se (~-0.97‰). These end members result from two modes of Se cycling. Laminated sediments are dominated by organically-bound Se and low Se/C_{org}. Bioturbated sediments have a higher proportion of authigenic Se and higher Se/C_{org}. Over older interglacial-glacial cycles, the relationship between the two end-members and interglacial-glacial states becomes less clear. Similar end-members to those in the Cariaco Basin exist in the Bermuda Rise except the low $\delta^{82/76}$ Se end-member has lower Se concentrations. As in the Cariaco Basin, variations are controlled by local climate rather than overall interglacial-glacial state. A comparison of the $\delta^{82/76}$ Se values for the two sites show similarities which suggest that Se isotope ratios might not be just recording local changes.

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iii

Table of Contents

Abstract	ii
Acknowledgements	iii
Table of Contents	iv
Chapter 1: Introduction	1
1.1: Background and Rationale	1
1.2: Thesis aims	5
1.3: Thesis outline	6
Chapter 2: The behaviour of Se within the natural environment	8
2.1: Aims and Introduction	8
2.2: Se geochemistry	8
2.2.1: Se cycling within the marine environment	10
2.2.2: External influences on the cycling of Se within a marine	
environment	19
2.3: Se reservoirs and fluxes within the natural environment	20
2.3.1: The continental crust	$\frac{1}{20}$
2.3.2: Igneous and metamorphic rocks	21
2.3.3: Sedimentary rocks	22
2.3.4: Atmospheric Se	24
2.3.5: Plant material	26
2.3.6: Transport pathways and fluxes of Se	26
2.4: Se isotope geochemistry	29
2.4.1: Notation and current standards	29
2.4.2: Isotope systematics	30
2.4.3: Recent applications of Se isotopes	37
2.5: Hypothesis	42
Chapter 3. Analytical Methods and Instrumentation	44
3 1: Introduction	44
3.2. Sample preparation	44
3 3: LECO CS 230 Carbon/Sulphur Determination	45
3.3.1: Sample preparation	45
3.3.2: Instrumental methodology	45
3.4: X-Ray Fluorescence Spectroscopy (XRF)	47
3.4.1: Sample preparation	47
3.4.2: Instrumental methodology	49
3.5: Total Se extraction protocols	56
3.5.1: Parr total HNO ₃ digestion	56
3.5.2: Pilot study $-$ a comparison of acid digestion methods	56
3.5.3: Microwave-assisted HNO ₃ digestion	58
3.6: Se isotope preparation protocols	59
3.6.1: Making Thiol-cotton fibre (TCF)	59
3.6.2: Chemical separation of Se using TCF	60
3.7: Hydride Generation (HG)	62
3.8: Atomic Fluorescence Spectroscopy	63
3.8.1: Background	63
3.8.2: Instrumental methodology	65
3.8.3: Precision and accuracy	65

3.9: HG-MC-ICP-MS	67
3.9.1: Background	67
3.9.2: Instrumental methodology	69
3.9.3: Precision and accuracy	73
·	
Chapter 4: Global climate and the Cariaco Basin over the last 500 ka	76
4.1: Global and regional climate events of the last 500 ka	76
4.1.1: Introduction	76
4.1.2: 500-130 ka	80
4.1.3: The last 130 ka	84
4.1.4: Last Glacial Maximum Interval 23-14.6 ka	89
4.1.5: Bølling-Allerød interval 14.6-13 ka	91
4.1.6: Younger Dryas 13-11 ka	92
4.1.7: Holocene 11 ka to present	93
4 2: Synthesis of history of the Cariaco Basin	94
4.2.1.2. Synthesis of instally of the Canado Basin 4.2.1. Location and Geological setting	94
4.2.2: Sources of sediment to the Cariaco Basin	96
4.2.2. Sources of seament to the Cartaco Dash	00
4.2.5. Carlaco Dasin hydrography A.2.4: Sedimentary record of the Cariaco Basin	103
4.2.5: Basin processes on interplacial glacial timescales	105
4.2.5. Dashi processes on Intergracial-gracial interseates	100
4.2.0. Tectome influence of Cartaco Basin deposition	109
4.5. Carrado Basin as part of the global ocean system $4.2.1$; SDECMAD S ¹⁸ O record	111
4.5.1. SPECIMAP 0 O lecolu $4.2.2$, L DO4 S ¹⁸ O record	111
4.5.2. LKU4 0 U record 4.2.2. Deviations of Caricas Devia S^{18} O record from SDECMAD S^{18} O	114
4.3.3: Deviations of Cariaco Basin 6 ^o 0 record from SPECMAP 6 ^o	110
record	110
Charter 5. Carelandistry of the Caric as Davis	110
Chapter 5: Geochemistry of the Carlaco Basin	119
5.1: Introduction	119
5.2. Chemical parameters of Cariaco Basin water column	120
5.2.1: Data source	120
5.2.2: Oxygen, salinity, temperature	121
5.2.3: Carbon	123
5.2.4: Nutrient and trace metal profiles	128
5.3: Chemical oceanography of the sediments	135
5.3.1: Theory of sedimentary chemical proxies	135
5.3.2: The recent glacial-interglacial transition	136
5.3.3: Interglacial-glacial variations between 100-500 ka	145
Chapter 6: Se in the Cariaco Basin (ODP Leg 165)	151
6.1: Introduction	151
6.2: Sample information	151
6.2.1: Depth-age relationship for site 1002	151
6.2.2: Sample locations for the last 18 ka	152
6.2.3: Sample locations for four glacial-interglacial cycles	155
6.3: Se concentrations in the Cariaco Basin	157
6.3.1: The last glacial-interglacial transition	157
6.3.2: Cycling of Se in the Cariaco Basin during glacial and interglacial	
periods	172
6.3.3: Conclusion	177
6.4: Se concentrations in the Cariaco Basin over four glacial-interglacial cycles	
(MIS 5-12)	177
6.4.1: Variation in Se concentrations	178
6.4.2: Relationships between Se-Fe-Organic C	183
6.4.3: A refined model of Se cycling within the Cariaco Basin	186

6.4.4: Conclusion	189
6.5: $\delta^{82/76}$ Se values over the last glacial-interglacial transition	192
6.5.1: Introduction	192
6.5.2: Variation in $\delta^{82/76}$ Se values	192
6.6: $\delta^{82/76}$ Se values over four glacial-interglacial cycles (MIS 5-12)	202
6.6.1: Variation in $\delta^{8\bar{2}/76}$ Se values	202
6.6.2: Conclusion	210
Chapter 7: Se in the Bermuda Rise (ODP Leg 172)	211
7.1: Introduction	211
7.2: ODP Leg 172-North Atlantic Sediment Drifts	212
7.2.1: Introduction	212
7.3: Site 1063-Northeast Bermuda Rise	215
7.3.1: Introduction and Location	215
7.3.2: Sedimentary sequence	215
7.3.3: Biostratigraphic and palaeomagnetic data	218
7.3.4: Interstitial water chemistry	218
7.4: Sample information	221
7.4.1: Depth-age relationship for site 1063	221
7.4.2: Sample locations	222
7.5: Chemical oceanography of sediments	225
7.5.1: Carbon geochemistry	225
7.5.2: Trace element geochemistry	228
7.6: Se concentrations from the Bermuda Rise over the last 500 ka	237
7.6.1: Glacial-interglacial variations	237
7.6.2: Relationships between Se-Fe-S-Organic C	239
7.6.3: Se cycling at the Bermuda Rise	247
7.6.4: Summary	250
7.7: $\delta^{\delta 2/6}$ Se values from the Bermuda Rise over the last 500 ka	250
7.7.1: Glacial-interglacial variations	250
7.7.2: Comparison of $\delta^{827/6}$ Se values from Cariaco Basin with $\delta^{827/6}$ Se	
values from the Bermuda Rise	256
Chapter 8: Conclusions	260
8.1: Introduction	260
8.2: Hypothesis	260
8.2.1: Mechanisms of Se cycling under anoxic and oxic seawater	260
8.2.2: Isotope fractionation under anoxic and oxic seawater	263
8.2.3: Se isotope ratios are well mixed on geological timescales	264
8.3: Future work	266

Appendix 1 Appendix 2 Appendix 3 Appendix 4 Appendix 5

References

1.1. Background and rationale

Selenium is a redox sensitive element whose behaviour in the natural environment is dependent on the oxygen content. Two gasses dominate Earth's atmosphere: N₂ and O₂. The former is primordial and its presence and atmospheric abundance are not driven by biological processes (Berner 2006). In contrast O₂ is continuously produced biologically via the oxidation of water driven by energy from the Sun. O₂ was almost non-existent in Earth's early atmosphere, it is highly reactive, and has an atmospheric lifetime of ~ 4 Ma (Keeling *et al.* 1993). Despite this short atmospheric lifetime O₂ has constituted between 10-30 % of the atmospheric volume for the past ~500 Ma (Falkowski & Isozaki 2008).

Elemental oxygen (O) is produced by successive ⁴He fusion reactions in hot stars and was delivered to the early Earth chemically bound to other elements. After repeating cycles of heating and cooling, the O reacted with Si and C to form the anions, together with metal cations, that form the major minerals in the mantle and crust, and reacted with H to form water (Holland 1984). The water is then photobiologically split, by algae and cyanobacteria in the ocean and by plants on the land, producing O_2 as the waste product via the following reaction:

$$2H_2O \rightarrow 4e^- + 4H^+ + O_2$$

The free electrons and protons are then used to reduce CO₂ to form organic matter via:

$$CO_2 + 4e^- + 4H^+ \rightarrow (CH_2O) + H_2O$$

A small fraction of this organic matter is then buried in sediments and ultimately tectonically added to continents and subducted deep into the Earth's mantle (Falkowski & Isozaki 2008). Over millennia the reactions above are closely coupled to the reverse process of respiration so that net production of O_2 is virtually zero. In order to achieve a net oxidation of the atmosphere, an imbalance is required between the oxygenic photosynthesis and aerobic respiration over millions of years; hence to generate an oxidised atmosphere more organic matter must have been buried than respired and weathered.

The broad outlines of the oxygenation history of the atmosphere and oceans are reasonably well-known; however, there are still significant gaps in the record, especially for the oxygenation of the oceans (Holland 2006). The last 3.85 Ga of Earths history has been divided into five stages because of changes in the oxygenation of the atmosphere and oceans (Holland 2006). During stage 1 (3.85-2.45 Ga) the atmosphere and oceans were almost entirely anoxic with the possible exception of oxygen oases in the shallow oceans (Holland 2006). During stage 2 (2.45 – 1.85 Ga) atmospheric oxygen levels rose to 0.04 atm, the shallow oceans became mildly oxygenated while the deep oceans remained anoxic. Throughout stage 3 (1.85 - 0.85 Ga) atmospheric oxygen and shallow ocean concentrations did not significantly alter whilst the deep ocean became mildly oxygenated. During stage 4 (0.85-0.54 Ga) atmospheric and shallow ocean oxygen levels rose to ~ 0.2 atm whilst the deep oceans became anoxic during the intense Neoproterozoic ice ages. This boost in atmospheric and shallow ocean O₂, inferred from carbon isotopes, corresponds to the increase in single-celled phytoplankton which would have accelerated the burial of organic matter in marine sediments (Falkowski & Isozaki 2008). Finally, during stage 5 (0.54 Ga – present) atmospheric oxygen levels rose to a maximum of ~ 0.3 atm during the Carboniferous before returning to its current value. The shallow oceans remained oxygenated, while the oxygenation of the deep oceans fluctuated considerably on geologically short time scales. The final rises in O₂

Chapter 1: Introduction

content were due to large amounts of organic carbon being buried as land plants, especially trees and woody material, which had doubled the primary productivity of the planet (Berner 2004).

The current, yet limited, knowledge of oceanic oxygenation suggests the oxygenation history of the deep ocean has been complex over the last 540 Ma. Currently, euxinic settings comprise less than 0.5% of the deep ocean today with the Black Sea and Cariaco Basin the largest and second largest examples respectively (Lyons *et al.* 2009). However, oxygen deficiencies and even euxinia have occurred on the scale of ocean basins as demonstrated by Oceanic Anoxic Events (OAEs). These intervals during the Mesozoic Era are characterised by abundant, widespread, organic-rich black shales (Lyons *et al.* 2009). Similar intervals have occurred throughout the Phanerozoic and links have been suggested between deep sea anoxia and mass extinction, with the Toarcian (Jurassic), the Frasnian/Fammenian (Late Devonian), and the end Permian as prime candidates (Lyons *et al.* 2009). Oxygen deficiencies appear to have dominated the pre-Phanerozoic ocean and are certain to have had an important role in the early diversification of life (Lyons *et al.* 2009).

It appears the evolution and extinction of life are closely linked to the oxygen state of the ocean - the oxygen content of the oceans is connected with the geochemical cycles of carbon and other elements in a complex network of feedbacks. Therefore it is of interest to many groups of researchers, that studies attempting to reconstruct how redox conditions in the oceans and the broader environment have changed with time (Anbar & Gordon 2008), take place. The reconstruction of redox conditions in the ancient oceans is a major challenge in Earth systems science and the subject of many recent studies (Siebert *et al.* 2003)(Pearce *et al.* 2008). Palaeoredox reconstruction can be approached on different scales. A small-scale approach can be extracting chemical

Chapter 1: Introduction

signatures from individual samples that reliably tell us of oxygen conditions in the water column at the time and place the sample was deposited. The global relevance of these samples is then an argument about the connectivity of the basin to the ocean. Less-localised approaches rely on numerical models for large-scale conditions which are based on data from individual locations (Lyons *et al.* 2009). Other large scale approaches rely on geochemical proxies for global seawater, recording shifts that mirror changes in the balance between oxic and anoxic deposition on the largest scale (Lyons *et al.* 2009).

Because many of the environmental properties of interest are not recorded directly in the rock record, they are measured indirectly using geochemical proxies. Metal stable isotopes are emerging as a powerful proxy for palaeoredox reconstructions. Transition metals are suited as palaeoredox proxies because their chemical transformations and speciation are tightly coupled to the presence or absence of O_2 in the environment. Recently, an abundance of studies using Mo (Siebert et al. 2003)(Archer & Vance 2008)(Pearce et al. 2008)and Fe (Rouxel et al. 2005) isotopes have been published. Mo isotopes record the extent of ocean oxygenation directly while Fe isotopes record redox conditions indirectly through their effects on oxygen-sensitive biological processes. Another metal stable isotope system that has been the focus of study more recently is selenium. These studies have been confined to using the redox sensitive behaviour of Se and the Se isotope system (Johnson 2004) to quantify the amount of reduction that has taken place in order to monitor the mobility of contaminants (Clark & Johnson 2008). However, (Wen et al. 2007) measured Se isotope ratios in black shales from China and concluded that their results strongly supported the potential of Se isotopes to be a powerful redox tracer. Several features of Se, compared to Mo, suggest it could be utilised as a palaeoredox proxy - a shorter oceanic residence

time allows rapid changes in ocean oxygenation to be recorded, not requiring free H_2S in seawater to change its isotopic composition allows Se isotopes to be more sensitive to smaller changes in the oxygenation, and theoretical calculations and laboratory measurements both suggest the isotope shifts are expected to be greater.

Many proxies are developed based on observations from the ancient rock record; however, these observations can only be interpreted through comparison with similar observations from modern analogue environments. The Cariaco Basin, off the coast of Venezuela, is well known as a site for intensive palaeoceanographic studies. The alternating laminated and non-laminated sediments indicate the basin has undergone cyclical changes in the oxygenation content of the water column. It is therefore an ideal natural laboratory to study the potential of Se isotopes to vary with changes in oxygen concentrations. Comparisons with open ocean sites might also allow for the global scope of Se isotope ratios to be evaluated.

1.2. Thesis aims

The aims of this thesis are:

- Introduce and evaluate the potential for Se isotope ratios to be used as a new palaeoredox indicator and discuss the potential for the Cariaco Basin to be a suitable location for testing this hypothesis.
- Describe and interpret Se concentrations and Se isotope ratios from the Cariaco Basin over the last glacial-interglacial transition with reference to Se cycling under different water column conditions.
- Investigate using Se concentrations and Se isotope ratios if similar processes to the last glacial-interglacial transition are operating over multiple glacial-interglacial cycles.

Chapter 1: Introduction

- Describe and interpret Se concentrations and Se isotope ratios from an open ocean location, and investigate if a relationship exists between the isotope ratios of the Cariaco Basin and the open ocean.
- Decide on the capability of Se isotope ratios to act as a new palaeoredox proxy

1.3. Thesis outline

This thesis describes and interprets Se concentrations and Se isotope ratios in marine sediments over the last 500 ka from the Cariaco Basin and the Bermuda Rise.

Selenium is an element which exists in many environments at varying concentrations as a result of its geochemical behaviour. This behaviour also governs the isotope systematics of Se. *Chapter 2* outlines the key characteristics of the geochemistry of Se, describes the various reservoirs in which Se is found, identifies the major transport fluxes which distribute Se among these various reservoirs, and outlines the main isotope fractionation mechanisms of Se. A hypothesis is then proposed about the use of Se isotopes as a palaeoroedox proxy.

Due to low natural concentrations in most rocks, standard analytical techniques can not be used to measure either Se abundances or Se isotope ratios. *Chapter 3* describes the analytical procedures used in this thesis to extract, concentrate, and measure Se concentrations and Se isotope ratios. There is also a brief description of the instrumentation used and an estimation of the precision and accuracy of our analyses.

Over the last 500 ka, the key features of the Earths climate are the glacialinterglacial cycles which are documented through microfossil δ^{18} O changes at a periodicity of ~100 ka. The Cariaco Basin has been studied intensively and a large geochemical dataset exists which supplements the Se data collected in this project and provides a detailed geochemical context for these Se data. *Chapter 4* summarizes the global climatic events which occurred in the last 500 ka and introduces regional climate

events which have affected the Cariaco Basin. This is followed by a detailed synopsis of the oceanographic conditions, sedimentation, and local tectonic influences on the basin. The degree of connectivity between the Cariaco Basin and the open ocean is also demonstrated. In order to interpret past basin conditions, an understanding of the present basin is required. *Chapter 5* describes the current water column chemistry within the Cariaco Basin and reviews the existing sediment geochemical data and the constraints they place on conditions in the Cariaco Basin over the last 500 ka.

Chapter 6 describes, analyses, and interprets the Se concentration and Se isotope measurements from sediments within the Cariaco Basin over the last glacial-interglacial transition and over four glacial-interglacial cycles. Key differences in the cycling of Se under different water column oxygen concentrations are outlined and models of Se cycling within the Cariaco Basin are constructed. Two Se isotope end-members are suggested to exist in the Cariaco Basin; Se isotope ratios of our sediment samples are interpreted using these end members and the different behaviours of Se under changing water column conditions.

Comparing the Se isotope ratios from Cariaco Basin sediments with isotope ratios from open ocean sediments is one method of illustrating the possible global nature of Se isotope ratios. *Chapter 7* reports Se concentrations and Se isotope ratios from the Bermuda Rise, an open ocean environment within the North Atlantic. The Se isotope ratios from both locations are then compared to identify similar isotope features. New geochemical data are also examined to provide constraints on the conditions of the water column over the last 500 ka. *Chapter 8* synthesises the observations and conclusions from chapters 6 and 7 into a discussion about the potential for Se isotope ratios to be adopted as a new palaeoceanographic redox proxy.

Chapter 2: The behaviour of Se within the natural environment

2.1. Aims and Introduction

Selenium exists in atmospheric, marine and terrestrial environments, where it is transported and transformed via different chemical and physical pathways. The aim of this chapter is to provide an overview of the current literature concerning the chemical and environmental behaviour of Se. This chapter will describe the geochemistry of Se including the redox conditions of the four main valence states, illustrate the behaviour of Se within a marine environment, and show the importance of atmospheric inputs to the Se budget of the equatorial Atlantic. The reservoirs of Se and transport fluxes which exist in the natural environment, as a result of the geochemical behaviour of Se, will then be outlined. A description of the various experimentally determined Se isotope fractionations for different reactions will be given and the recent applications of selenium isotopes in the natural environment outlined. Finally, a number of hypotheses will be described which form the basis of this study.

2.2. Se geochemistry

Selenium is a non-metal in group 6 below sulphur and above tellurium and in period 4 between arsenic and bromine. It has an atomic number of 34 and an atomic mass of 78.86 g mol⁻¹. The Swedish scientist Jons Jacob Berzelius discovered selenium in 1817 as an impurity in sulphuric acid produced in a Swedish factory. Zero-valent selenium occurs in three distinct forms: a non-crystalline grey metal, a deep red to black powder, and as red crystals. Its electron configuration is [Ar] $4s^2 3d^{10} 4p^4$ with an electron arrangement 2, 8, 18, 6. The chemical behaviour of Se depends strongly on redox reactions (Elrashidi *et al.* 1987), which change the oxidation state of selenium to and from its four stable valences: -2, 0, +4, and +6. (Table 2.1). Se(IV) and Se(VI) are the most common inorganic dissolved forms of Se and both are present in seawater. Bacteria use Se(VI) and Se(IV) as electron acceptors (Switzer Blum *et al.* 1998), and uptake of Se(VI) and Se(IV) by phytoplankton causes Se concentrations to decrease in near surface marine waters. Natural redox reactions involving selenium are both biologically and abiotically mediated with the latter being less important because their rates are small in most cases (Tokunaga *et al.* 1991).

Oxidation state	-II	0	IV	VI
Speciation	Selenide/Organo-selenium	Elemental Selenium	Biselenite + Selenite	Selenate
Formulae	HSe ⁻ , Se ²⁻ , R-Se-R	Se (0)	$HSeO_3^-$, SeO_3^{2-}	$\mathrm{SeO_4}^{2-}$
Comments	Exists as insoluble selenide minerals; substituted for S in sulphide minerals; organo-Se compounds formed by biological reduction of oxidised forms	Primary product of Se- reducing microbes in anoxic environments; stable and insoluble in moderately reducing environments	Highly soluble; ex in solution; adsort positively charged mineral surfaces, o Se(IV).	tists as ions bed to l oxide especially

Table 2.1: Speciation of selenium (Kulp & Pratt 2004)

Under oxidising conditions in seawater, Se(VI) is the thermodynamically favoured species and forms the selenate ion (SeO₄²⁻) (Fig 2.1), which is very soluble and not very adsorbing (Neal & Sposito 1989). Under mildly reducing conditions, (Eh = 300-500 mV at ph 7) Se(VI) may be reduced to Se(IV) which forms the highly soluble selenite (SeO₃²⁻) and biselenite (HSeO₃⁻) anions, which adsorb strongly onto Fe- and Aloxides (Bar-Yosef & Meek 1987). Under moderately reducing conditions, Se(IV) reduces to Se(0), an insoluble non-metallic solid that is very resistant to re-oxidation (Fig 2.1). Thermodynamic calculations suggest that if metals such as Cu, Pb, Cd, and Hg are present then metal selenides, with Se in the –II valence state, will be formed instead of Se (0) (Elrashidi *et al.* 1987). Under strongly reducing conditions, the final stage is a complete reduction to Se(-II), as the thermodynamically stable HSe⁻ ion (Elrashidi *et al.* 1987) (Fig 2.1).

Se has some chemical similarities to S because of their position in the same group in the periodic table. However, their redox speciation is different enough so that decoupling of Se from S can occur (Fig 2.1). Under moderately reducing conditions, Se is stable as either Se(IV) or Se(0), whereas S (IV) is not stable in the natural environment and S(0) is stable only under a restricted set of conditions (Fig 2.1). Additionally, Se is concentrated more by living organisms than S is and this also leads to decoupling of Se and S (Johnson & Bullen 2004).



Figure 2.1: Eh-pH stability diagram for aqueous Se (left) and S (right) species. Oxic waters plot just below the uppermost diagonal line and conditions are increasingly reducing with decreasing Eh. $S=10^{-3}$ M (~32 ppm); Se = 10^{-6} M (~80 ppb) (Brookins 1988)

2.2.1. Se cycling within the marine environment

In order to investigate the suitability of sedimentary Se to act as a palaeoredox proxy for ocean oxygenation it is necessary to understand the cycling of Se within the water column before it is incorporated into the sediments. This section outlines the behaviour of dissolved and particulate selenium in the ocean environment under different oxygen concentrations.

The depth profiles from the North and South Pacific Oceans show the existence of three dissolved Se species: Se(IV), selenate, and organic selenide (Fig 2.2). Total dissolved selenium increases constantly with depth through the water column reaching a maximum concentration of ~2.3 nmol kg⁻¹ at 3 km depth (Fig 2.2).



Figure 2.2: Depth profiles of dissolved Se species from VERTEX II site in the eastern tropical North Pacific Ocean (Cutter & Bruland 1984). Shaded area indicates a suboxic zone with oxygen levels <10 μ mol litre⁻¹. Below 1750 m, organic selenide is not detected.

In surface waters Se(IV) and selenate concentrations are uniformly low because of the nutrient role of Se in the oceans. Phytoplankton utilise nutrients such as phosphate, nitrate, and silicate in the euphotic zone and as the phytoplankton grow, trace elements such as selenium which are needed for biosynthesis are also extracted from the water (Chester 2000). Se is essential to most phytoplankton at low concentrations (0.1 to 100 nM) but higher concentrations can be toxic (Doblin *et al.* 1999 and refs therein). Studies on the uptake of Se into algal cells have shown that selenium is incorporated into various biochemical compounds such as amino acids, proteins and lipids (Doblin *et al.* 1999). Selenium has multiple roles in cell function: One study suggests selenium is important in cell division processes and maintaining internal cell membrane integrity (Doucette *et al.* 1987) while another suggests it is an essential part of enzymes involved in protecting cells against the destructive effects of H_2O_2 (Overbaugh & Fall 1982; Price & Harrison 1988).

Selenate concentrations increase rapidly downwards over the top 125 m because of replenishment at depth via decay of organic matter, enhanced upwelling and vertical mixing of selenium-rich sub-surface waters. However, Se(IV) concentrations are kept low because Se(IV) species are taken up preferentially by living organisms in the marine environment and are converted into organic selenides, which are the biochemically functional form (Wake et al. 2004). Organic selenides make up ~80% of the total dissolved selenium at the surface; the organic selenide maximum coincides with the maximum in primary productivity and dissolved free amino acids from the breakdown of planktonic debris (Cutter & Bruland 1984). The Se profiles highlight a further distinction between Se and S: Se shows bio-intermediate behaviour in seawater, as it is completely removed from surface waters by marine productivity, while S shows conservative behaviour with constant concentration relative to salinity because biological uptake is weak relative to the high concentrations in sea water (Chester 2000). Deep ocean waters are enriched in both Se(IV) and selenate, while organic selenide decreases to effectively zero (Fig 2.2). The presence of Se(IV) in deep oxic ocean waters is thermodynamically unstable, it is suggested that Se(IV) might be an intermediate product formed during the oxidation of organic Se compounds (Cutter & Bruland 1984). The strong affinity for Se(IV) to adsorb onto Fe and Mn oxy-hydroxides in the water column and at the sediment-water interface (Balistrieri & Chao 1990) also draws down Se(IV) to the ocean floor. Between 150 and 600 m there is a suboxic zone

where dissolved oxygen levels are less than 10 μ mol L⁻¹. This zone is well defined as a region where complete iodate reduction and denitrification is taking place (Cutter & Bruland, 1984). At the top of the suboxic zone, organic selenide concentrations increase to a secondary maximum and Se(IV) concentrations decrease (Fig 2.2).

Fluxes of particulate selenium, carbon and nitrogen, collected in sediment traps, decrease with depth at the VERTEX II site (Fig 2.2, Table 2.2). The decrease in carbon and nitrogen concentrations and increase in C: N ratios indicate that the falling material becomes more refractory with depth as the labile organic material is selectively removed. The selenium speciation for the 50 m trap shows that only 9.5% of the total selenium flux from the mixed layer is Se(IV) and Se(VI) (Table 2.2) confirming that Se(IV) and Se(VI) are taken up by organic matter in the euphotic zone and are transported to deeper waters as organic selenides.

Depth (m)	Total Se (nmol g ⁻¹)	Total Se flux (µmol m ⁻² yr ⁻¹)	Total C	Organic C	Total N	C:N
				%		
50	1.69	1.40	30.1	23.5	5.72	5.26
	(0.07 as +4)					
	(0.09 as +6)					
100	2.98	0.98	29.1	24.4	5.32	5.47
470	6.17	0.94	18.7	14.5	2.10	8.90
970	3.64	0.44	18.1	11.5	2.02	8.96

Table 2.2: VERTEX II sediment trap data for selenium, carbon, and nitrogen (Cutter & Bruland 1984).

Cutter and Bruland (1984) used these selenium data from the VERTEX II site (Fig 2.2, Table 2.2) to produce a biogeochemical cycle of selenium in the marine environment. This cycle includes selective uptake and reductive incorporation into biogenic material of dissolved Se(VI) and Se(IV). Selenium is then delivered to the deep ocean as particulate organic selenide, where a multistep regeneration of this particulate selenium back to the dissolved Se(IV) and Se(VI) species occurs. In addition kinetic effects are vital to the existence of thermodynamically unstable organic selenide species and Se(IV) which are produced in the multistep regeneration process (Fig 2.3).

The first step in the regeneration of selenium from biogenic particles appears to be the production of dissolved organic selenide. The rate of this reaction is biologically controlled and regeneration experiments suggest it is fast (> 0.2 d^{-1}) (Cutter, 1982). Although organic selenide is a regeneration intermediate, it is not expected to be present at significant levels in oxic waters due to its thermodynamic instability. However, organic selenide can be found if its production rate (through regeneration) is fast or its removal rate (by uptake or oxidation) is slow. In the deeper waters oxygen consumption rates are low. Therefore regeneration rates and the production of organic selenide are greatly reduced, resulting in non-detectable levels of organic selenide. However there is the secondary organic selenide peak in the suboxic zone at 350 m (Fig 2.2). It is possible the lower oxygen levels in this zone stabilised the organic selenide, stopping its oxidation to Se(IV) (Cutter & Bruland 1984). The second regenerative step involves the production of Se(IV) by the abiotic or biotic oxidation of dissolved organic selenide species. This reaction is seen to be pseudo-first order for dissolved organic selenide in surface and deep waters due to the excess of oxygen relative to organic selenide (Cutter & Bruland 1984). However in the suboxic zone the low oxygen concentration slows down the selenium multistep regeneration process resulting in the Se(IV) minimum (Fig 2.2). The rest of the profile shows the ubiquitous presence of Se(IV) despite its thermodynamic instability. The final step in the regeneration process is the oxidation of Se(IV) to selenate, the thermodynamically stable form of selenium in oxic waters. For the same reasons given in the discussion of the organic selenide oxidation reaction rate, the oxidation of Se(IV) to selenate can also be assumed to be pseudo-first order (Cutter & Bruland 1984). The rate of this reaction affects the concentrations of both Se(IV) and

selenate. The mean life of Se(IV) in the deep sea with respect to oxidation was calculated as 1,150 years (Cutter & Bruland 1984). With an average residence time of water in the deep ocean being 1,600 years, this mean life explains the presence of Se(IV) in the deep ocean.



Figure 2.3: Schematic diagram of the biogeochemical cycling of Se in the marine environment. Se(IV) is present as $SeO_3^{2^-}$ and Se(VI) as $SeO_4^{2^-}$. The dominant species in each region are indicated by bold font [from (Wake *et al.* 2004) and refs therein].

Profiles of dissolved selenium species have been measured within the Orca Basin, an intra-slope depression covering about 400 km² on the continental slope in the northwestern Gulf of Mexico (Takayanagi & Wong 1985). Down to 2000 m the profiles of the Orca Basin are similar (Fig 2.4) to those measured in the Pacific Ocean (Fig 2.2) and are consistent with the model for the multistep regeneration of selenium in the oceans previously described (Fig 2.3).



Figure 2.4: Vertical profiles of organic selenium, Se(IV) and Se(VI) from the Orca Basin. The redox change occurs at 2,235 m (Takayanagi & Wong 1985). Anoxic – oxic interface occurs between 2080 - 2235 m.

However, where the Orca Basin profiles differ from the Pacific profiles (Fig 2.2), is anoxic conditions exist in the water column below 2,080 m and this affects the selenium speciation accordingly. The reason for this oxygen decrease is a large salinity increase between 2,150 and 2,235 m from ~36.2‰ to ~260‰ due to the dissolution of evaporite deposits from the surrounding slopes (Takayanagi & Wong 1985). The extreme vertical stratification resulting from this strong halocline allows anoxic hypersaline brine to accumulate below 2,235 m. Within the oxic-anoxic interface, the concentration of Se(VI) decreases downwards to undetectable levels reflecting the increasing reducing conditions (Fig 2.4). At the same time, Se(IV) increases initially below the oxic-anoxic interface and is the dominant selenium species at about 2180 m depth. The Se(IV) concentration then decreases rapidly towards the bottom of the suboxic zone (Fig 2.4) suggesting Se(IV) might have been converted to either a

particulate form or to another dissolved Se species. Se(IV) may be converted to a particulate form by reduction to the elemental state, Se(0), by formation of a metal selenide (Cutter, 1982), or by adsorption onto solid phases (Takayanagi & Wong 1985). In the suboxic zone the organic selenium concentration increases substantially from undetectable levels to 0.49 nmole kg⁻¹ and continues to increase in the anoxic brine to a maximum of 2.6 nmole kg⁻¹ (Fig 2.4). This increase is probably a result of the decomposition of organic matter *in situ* in the water column and/or in the sediments followed by diffusion into the water column (Takayanagi & Wong 1985).

Dissolved Se species have also been measured in the Saanich Inlet, an intermittently anoxic fjord, located on the southeastern portion of Vancouver Island, Canada (Cutter, 1982). The total dissolved selenium and Se(IV) profiles above 1000 m resemble those of the previously described oceanic profiles. However, Se(VI) does not show a mid-depth maximum; instead Se(VI) decreases constantly downwards until the O₂-H₂S interface. Below the O₂-H₂S interface, the Se speciation is similar to that of the Orca Basin with organic selenide the dominant species (Fig 2.5). According to thermodynamic predictions hydrogen selenide concentrations should be high in the anoxic zone. However, H₂Se concentrations are near the limit of detection in the Saanich Inlet (Fig 2.5). This might be because the conditions are not reducing enough and organic selenide is the final step in the regeneration cycle. These profiles indicate a similar biogeochemical cycle to that previously described (Fig 2.3). The extent of the regeneration within the Saanich Inlet depends on the oxygen content of the water dissolved organic selenide is stable under anoxic conditions and so regeneration would only proceed to this step. Correspondingly, the production of Se(IV) and Se(VI) by the oxidation of organic selenide would be the final regeneration step in the oxic waters (Cutter, 1982).



Figure 2.5: Profiles of dissolved Se species in the Saanich Inlet: (a) Se(IV), Se(VI), and total dissolved selenium; (b) organic selenide and hydrogen selenide. Waters above 110 m are oxic. The oxic-suboxic interface is at 110 m - the suboxic zone is characterised by O_2 concentrations <10 μ M and nitrate reduction. The suboxic-anoxic interface is at 175 m. (Cutter, 1982)

Only a fraction of the total biological productivity in surface waters of the ocean is recorded in the concentrations of organic matter in modern sediments and sedimentary rocks. Phytoplankton biomass that is lost from the efficient recycling operation in the upper water column (euphotic zone) is called export productivity; this material is then delivered to the sediment-water interface following additional degradation through the water column. Under normal marine conditions, only ~10% of the total productivity leaves the euphotic zone (Chester 2000). Despite the efficient recycling mechanism at the surface, the delivery of export productivity to the sediment-water interface and the final C burial flux are generally proportional to surface water total productivity (Tribovillard *et al.* 2006). In oxic seawater, the downward particulate organic Se flux decreases with depth due to the liberation and re-oxidation of the

organic selenides to Se(IV) and Se(VI). Therefore in deep ocean sediments an important pathway of Se uptake into the sediment is authigenic reduction of Se(IV) to Se(0) immediately after the sediments become post-oxic (Thomson *et al.* 2001). In addition to these authigenic enrichments, (Piper, 1994) stressed the probable importance of an enhanced elemental supply to the sediments associated with settling organic C in marine settings with a high productivity. In contrast, under anoxic seawater the re-oxidation of organic selenides does not take place, and accumulation of particulate organic Se will represent the dominant Se flux into the sediment.

2.2.2. External influences on the cycling of Se within a marine environment

The selenium cycle in the ocean has largely been studied in mid-latitude sites, primarily far away from strong allochthonous inputs, e.g. North Pacific Central Gyre (Cutter & Bruland 1984), where the concentrations and speciation of Se are controlled by *in situ* processes (see section 2.2.1). Data from the equatorial and western Atlantic demonstrates that external inputs can profoundly influence the speciation and concentration patterns that result from this *in situ* cycle. One such example of external forcing on the selenium cycle is the dilution effect of the Amazon River discharge into the Atlantic on selenium concentrations (Cutter & Cutter 2001). Total Se concentration data on a transect along the eastern coast of South America were relatively constant, ranging between 0.61 ± 0.04 nM to 0.74 ± 0.19 nM, with the exception of Se concentrations measured from within the Amazon plume which dropped to 0.36 ± 0.01 nM. The measured values outside the Amazon plume are similar to Se concentrations measured in the eastern Atlantic $[0.58 \pm 0.07 \text{ nM} - (\text{Cutter & Cutter 1995})]$ but are elevated with respect to northern Atlantic values $[0.49 \pm 0.08 \text{ nM} - (\text{Cutter & Cutter})]$ 1998)]. Therefore the Amazon plume concentrations show a strong departure from the norm, demonstrating the significant spatial influence of these low dissolved Se waters.

This Amazon discharge is unique for the equatorial Atlantic but the importance of atmospheric selenium inputs to the surface ocean budgets has been discussed and quantified by a number of studies (Cutter & Cutter 2001) and refs therein]. For the north Pacific, atmospheric fluxes of Se exceeded fluxes from upwelling (Cutter & Bruland 1984). In the equatorial Atlantic a link was established between high particulate Al concentrations, a tracer for atmospheric materials originating in North Africa, and high surface Se(IV) concentrations (rainwater is enriched in Se(IV) relative to ocean surface waters - (Cutter & Church 1986). These air masses originating from North Africa are then further enriched when they mix with air masses from Europe which contain high Se concentrations from fossil fuel combustion processes (Arimoto *et al.* 1991; Arimoto *et al.* 1995). For the area in the Atlantic between 2°S and 8°N, a total atmospheric flux of 8.9-10.9 x 10^6 mol Se yr⁻¹ was calculated. In comparison the riverine input to the Equatorial Atlantic is 1.6×10^6 mol Se yr⁻¹. Therefore the riverine input is only 16% of the atmospheric flux and atmospheric Se inputs are an important external influence in the cycling of Se in the surface western and equatorial Atlantic.

2.3. Se reservoirs and fluxes within the natural environment

2.3.1. The continental crust

Selenium is a trace element with a complex geochemical cycle and exhibits a wide range of concentrations amongst its various reservoirs. Bulk continental crust contains ~0.12 ppm (Gao *et al.* 1998; Wedepohl, 1995). This is not evenly distributed within the crust – averages of the upper, middle, and lower crust from central east China craton are 0.15 ± 0.01 ppm, 0.06 ± 0.01 ppm, and 0.12 ± 0.01 ppm respectively (Gao *et al.* 1998).

2.3.2. Igneous and Metamorphic rocks

Selenium is not uniformly distributed in rocks formed by magmatic processes (Fig 2.6). Se concentrations are low in ultrabasic rocks (SiO₂ < 44%) (Malisa, 2001). Se concentrations are increased during magmatic differentiation and are highest in basic rocks (SiO₂ = 44-51%). High aluminium basalts and tholeiite basalts tend to have higher Se concentrations than in olivine basalt (Tamari *et al.* 1990). Se concentrations decrease again in intermediate rocks (SiO₂ = 51-65%) and are at their lowest in acid rocks, syenites, and alkaline rocks (SiO₂ > 65%). Within these individual groups, Se contents are typically higher in iron-rich rocks (Malisa, 2001). Tamari *et al.* (1990) show that Se concentrations in igneous rocks has a log-normal distribution with a geometric mean of 8.6 ng g⁻¹ (n=115). The main Se reservoirs in igneous rocks are the feldspar minerals (3.6-149 ppb) compared to quartz (0.6-6.4 ppb) and mica (2.4-14.8 ppb) (Tamari *et al.* 1990) (Fig 2.6).



Figure 2.6: Geometric means and ranges of Se concentrations in various igneous rocks and rock-forming minerals (Tamari *et al.* 1990).

Little recent data are available for Se concentrations in metamorphic rocks. A comparison of metamorphic rocks with sedimentary rocks and sediments shows that selenium content decreases with increasing metamorphism (Malisa, 2001) (Table 2.3). Assuming there has been no loss of volatile Se during metamorphism, the typical Se concentrations of the precursor sediments will be reflected in the metamorphic equivalents. The high Se values in these organic rich meta-sediments suggest that the large selenium concentrations found in the precursor anoxic sediments are not obliterated by metamorphism.

Rock type	Arithmetic mean (ppb)	Range (ppb)	n
Gneiss	62	320-<20	35
Quartzite	43	125-<20	8
Conglomerate	120	200-40	4
Mica schist	190	310-61	6
Black schist	9900	37000-570	8
Amphibolite	240	420-93	6
Metavolcanics	36	100-<20	10

Table 2.3: Se concentration data for metamorphic rocks (Koljonen, 1973)

2.3.3. Sedimentary rocks

A survey of 46 sedimentary rocks provided a geometric mean concentration of 86 ppb (Tamari *et al.* 1990). High amounts of selenium were found in mudstones and shales compared to sandstones, tuffs, and carbonate rocks (Figure 2.7). The cause of these high Se concentrations in sedimentary rocks is abundant organic material (Tamari *et al.* 1990). A Lower Aptian sequence in which a "fish shale" horizon formed under anoxic, stagnant sedimentation averages 11.1 ppm, and the underlying anoxic-suboxic dark claystones and paper shales average 3.47 and 10.5 ppm respectively (Hild & Brumsack 1998) (Fig 2.7). In contrast, the overlying oxic marls contain 0.48 ppm Se (Hild & Brumsack 1998). Carbonaceous shales from the Yutangba selenium deposit in Hubei, China have Se concentrations ranging from 28 to 4646 ppm, though the highest

1.0E+07 Geometric Mean 1.0E+06 Se concentration (ppb) 1.0E+05 1.0E+04 1.0E+03 1.0E+02 1.0E+01 1.0E+00 River and lake sediment ^bCarbonaceous shales/cherts ^fFreshwater evaporites dCoal Shale Sandstone °Coal Mudstone Tuff Carbonates Deep sea sediment ^aFish shale (an) ^aClaystones (an) ^aPaper shales (an) ^aOxic marls Carbonate ooze Tamari et al. (1990)

concentrations are probably caused by weathering-related enrichment (Wen et al. 2007)

(Fig 2.7).

Figure 2.7: Geometric means and ranges of Se concentrations in various sedimentary rocks. Data from: ^a(Hild & Brumsack 1998); ^b(Wen *et al.* 2007); ^c(Coleman *et al.* 1993); ^d(Li & Tang 1996); ^e(Thomson *et al.* 2001); ^f(Ong *et al.* 1997). (an) = anoxic.

Coal contains high concentrations of Se with a mean concentration of 1.7 ppm (Fig 2.7); Se in coal occurs in several forms, but is chiefly associated with the organic fraction, probably substituting for organic sulphur (Coleman *et al.* 1993). Even greater Se concentrations were found in 488 samples of coal from Hubei province, China (Li & Tang 1996). Overall these Se values ranged from 0.11-347 ppm, averaging 10.15 ppm (Fig 2.7). Three types of coal were analysed and the average contents of chert-rich "stony" coal (median = 42.06 ppm) were 4-5 times higher than in bituminous (range 1-48.3 ppm, median = 9.22 ppm) and "white" coal (range 0.11-59.3 ppm, median = 7.82 ppm) (Li & Tang 1996). Another study, in western Hubei, found the median of 129

"stony" coal samples to be much higher at 143.9 ppm, with the highest Se concentration measured at 1150 ppm (Mao *et al.* 1990).

Accurate Se concentration measurements within carbonates are not numerous. Tamari *et al.* (1990) report a range for 6 carbonate rocks (including one marble) of 2.2-44.3 ppb, with a mean of 12.4 ppb. More recently, Thompson *et al.* (2001) reported Se concentrations for carbonate ooze (79 wt% CaCO₃) of ~400 ppb total Se (Fig 2.7).

Evaporites concentrate Se weakly (above the crustal average). Typical Se concentrations in freshwater evaporites from the San Joaquin Valley, California are 0.3-0.5 ppm but can reach as high as 33.2 ppm (Ong *et al.* 1997) (Fig 2.7). Se concentrations of two evaporite salt samples from the San Joaquin Valley are much greater – 5.61 and 5.67 ppm (Herbel *et al.* 2002). There are no available data for marine evaporites. With such a low seawater Se concentration and the preference of dissolved Se species to either absorb or adsorb onto iron oxyhydroxides or be taken up into phytoplankton, the Se content of marine evaporites is thought to be low. Data for sandstones are scarce - Tamari et al. (1990) give a range of 2.8-593 ppb (n=6) with an arithmetic mean of 117 ppb (Fig 2.7).

2.3.4. Atmospheric Se

Common atmospheric volatile Se compounds include dimethyl selenide (DMSe), dimethyl diselenide (DMDSe), and methyl selenol (MeSeH) (Amouroux & Donard 1996). In both surface ocean waters and the atmosphere, DMSe is found to be the major volatile compound with additional significant amounts of DMDSe and MeSeH (Table 2.4). Assuming the mass of the atmosphere to be 5.3×10^{15} t (Holser & Kaplan 1966), and the total atmospheric Se concentration to be 1.4 pmol m⁻³ (Table 2.4), the mass of Se in the atmosphere is 486 t. More recent estimates of volatile Se concentrations from surface waters of the North Atlantic Ocean confirm the presence of

DMSe, DMDSe and one other volatile compound, DMSeS (dimethyl selenyl sulphide) (Amouroux *et al.* 2001). DMSe and DMSeS represent the two major volatile species in the North Atlantic surface waters with DMSe accounting for ~50% of the total volatile Se, a comparable distribution to that observed in the eastern Mediterranean (Amouroux & Donard 1996; Amouroux *et al.* 2001).

Table 2.4: Speciation of volatile Se compounds in marine water and air from the northeastern Mediterranean (Amouroux & Donard 1996)

	Wat	ter	Air	
	Mean	Range	Mean	Range
DMSe (pmol m ⁻³)	209 ± 83	60-636	0.6 ± 0.2	0.3-1.2
DMDSe (pmol m ⁻³ as Se)	116 ± 40	71-259	0.4 ± 0.1	0.3-0.6
MeSeH (pmol m ⁻³)	83 ± 27	60-158	0.5 ± 0.2	0.3-0.8
^a TVSe (pmol m ⁻³)	409 ± 127	248-955	1.4 ± 0.3	0.9-2.0

^aTVSe = DMSe + DMDSe + MeSeH, as Se

The amount of Se cycled through the troposphere annually is estimated to be between 15,000 and 27,000 tons (Mosher & Duce 1987). Selenium is emitted into the atmosphere from a variety of natural and anthropogenic sources with the former accounting for between 50-65% of the total emissions (Mosher & Duce 1987). Natural sources of Se include the products of crustal weathering (wind blown soil and dust), volcanoes, sea salt, and the continental and marine biospheres. Since the industrial revolution, anthropogenic emissions have increased greatly compared to natural sources (Wen & Carignan 2007). Anthropogenic sources comprise combustion (coal, oil, wood, biomass), nonferrous metal smelting, manufacturing, and utilisation of agricultural products (Mosher & Duce 1987). Once emitted into the atmosphere, Se undergoes physical and photochemical processes and/or interactions. The residence time of these volatile organo-selenium compounds (Table 2.4) in the atmosphere is ~12 days which means Se is well-mixed at the ocean and land surface (Cutter & Cutter 2001). This is comparable to studies which suggest that Se has an atmospheric residence time of 1 (for

wet deposition) to 4 weeks (for dry deposition) (Ranville *et al.* 2010 and refs. therin). This is much faster than estimates of residence times for Se in the oceans. Whitfield & Turner (1987) estimated the residence time of Se in the oceans to be $\sim 10^4$ years while Haygarth (1994) estimated the residence time of Se to be 70 years in the mixed layer and 1100 years in the deep layer. Cutter & Bruland (1984) approximated surface water residence times of Se(IV) and Se(VI) as <0.1 years and 2.6 years while sediment trap data indicated the residence time of total selenium in the mixed layer to be \sim 39 years. More recently, Cutter & Cutter (1998) estimated a residence of time for organic selenide in the oceans as being 10.3 years.

2.3.5. Plant material

Terrestrial plants use both Se(IV) and selenate, but they appear to absorb selenate preferentially (Barceloux, 1999) whereas phytoplankton take up nearly all the dissolved Se(IV) and selenate in surface seawater, with a preference for Se(IV) (Cutter & Bruland 1984). The uptake of selenium by plants is reduced when the soils are acidic and when complexation, frequently with iron or aluminium, occurs (Rayman, 2000). Studies have shown that plants can concentrate Se from the environment. Aquatic plants grown in 2.5 ppb Se solutions had dry matter Se concentrations of 0.3 to 1 ppm, an increase in concentration up to 400x (Ornes *et al.* 1991).

2.3.6. Transport pathways and fluxes of Se

Se exists in the atmospheric, marine, and terrestrial environments where it is transported via different chemical and physical pathways (Table 2.5) resulting in a distribution of Se which is inhomogenous (see section 2.2). In particular, elevated levels of Se in the aquatic environment and in terrestrial plants such as lichen and mosses remote from anthropogenic sources have been documented, indicating that atmospheric deposition may be an important flux of Se (Wen & Carignan 2007). The atmosphere

represents the major natural input of Se to the land surface globally, via wet and dry deposition (Table 2.5). From global budget assessments, marine environments are presumed to be the major source of Se to the atmosphere, accounting for between 50 and 60% of global emissions (Amouroux & Donard 1996; Mosher & Duce 1987) (Table 2.5; figure 2.8).

Source	Flux 10 ⁹ g Se yr ⁻¹	Data source ^a
Land to atmosphere	7.14-10.88	
Coal burning	3	MD
Oil, fuelwood, biomass and incineration	1.09	MD
Smelting & refining	1.71	MD
Manufacturing	0.24	MD
Dust & volcanoes	0.4-1.24	MD
Continental biosphere	0.7-3.6	MD
Ocean to atmosphere	8.04-16.4	
Sea salt	0.04-0.4	MD
Marine biosphere	8-16	MD,
Total to atmosphere	15.18-27.28	MD
Atmosphere to ocean ^b	10.12-18.19	
Atmosphere to land ^b	5.06-9.09	
Land to ocean	6.24-7.03	
Fluvial	6.24	VD
Hydrothermal	0-0.79	VD
Ocean to land	6.24-7.03	
Authigenesis	3.6	Thomson
Biogenic sediment ^c	2.64-3.43	

Table 2.5: Compilation of Se flux estimates between the land, ocean, and atmosphere

^aMD =(Mosher & Duce 1987), VD = (Von Damm *et al.* 1985), Thomson =(Thomson *et al.* 2001).

^bEarth is $^{2}/_{3}$ ocean and $^{1}/_{3}$ land and assuming a closed system and mass balance, these values are a proportion of the total flux to the atmosphere from the ocean and land.

^cThis is the remainder of the ocean to land flux so that the inputs are balanced.



Figure 2.8: The main reservoirs of Se and the flux of Se between the reservoirs which make up the Se cycle in the natural environment. The oceanic reservoir is represented by 1 mm², the continental reservoir is 10,000 mm², and the atmospheric reservoir is 1μ m² but this is too small to show on the diagram. The width of the flux arrows in cm represents ¼ of the flux value (in 10⁹ g Se yr⁻¹). Values for the fluxes are taken from table 2.5. Continental mass of Se assumes an average Se concentration of 0.12 ppm and a mass of bulk continental crust of 2.13 x 10⁹ t (Wedepohl, 1995). Oceanic mass of Se assumes an average Se concentration of 0.17 ppb (Cutter & Bruland 1984) and an oceanic mass of 1406 x 10¹⁵ t. Atmospheric mass of Se is calculated in the text.

2.4. Se isotope geochemistry

Selenium has six naturally occurring isotopes (Table 2.6), five of which are stable: ⁷⁴Se, ⁷⁶Se, ⁷⁷Se, ⁷⁸Se, and ⁸⁰Se. ⁸²Se has a very long half-life (~10²⁰ years) and is therefore considered stable. Because of the chemical similarities between Se and S, sulphate and selenate reduction may be expected to have some common isotope systematics, as reduction of these oxyanions involves a transfer of multiple electrons and re-arrangement of the oxygens bonded to the S or Se (Johnson & Bullen 2004). Sulphate reduction converts S (VI), as SO_4^{2-} , to S (-II) as H_2S or HS^- . The reduction is bacterially-driven in nature and several studies have revealed a strong variability in the isotopic fractionation (Johnson & Bullen 2004) and refs therein). The fractionation appears to depend on the microbial species and on the metabolic state of an individual species (Kaplan & Rittenberg 1964). Abiotic sulphate reduction also occurs but, at Earth surface temperatures, is kinetically sluggish in the absence of enzymes or catalysts (Johnson & Bullen 2004). The body of research on isotopic fractionation caused by sulphate reduction provides insight into selenate and Se(IV) reduction. Like sulphur, Se oxyanion reduction is microbially mediated at Earth surface conditions but abiotic reactions may have a greater role in some transformations (Johnson & Bullen 2004).

	⁷⁴ Se	⁷⁶ Se	⁷⁷ Se	⁷⁸ Se	⁸⁰ Se	⁸² Se
Natural Se	0.889	9.366	7.635	23.772	49.607	8.731

Table 2.6: Isotopic composition of natural Se (atom %) (Johnson & Bullen 2004)

2.4.1. Notation and current standards

A number of Se isotope ratios have been reported in the literature, including $\delta^{82/76}$ Se (Layton-Matthews *et al.* 2006), $\delta^{82/77}$ Se (Rouxel *et al.* 2002), $\delta^{82/78}$ Se (Rouxel *et al.* 2004a), $\delta^{80/76}$ Se (Herbel *et al.* 2002), and $\delta^{78/76}$ Se (Clark & Johnson 2008). Data in this study are reported using $\delta^{82/76}$ Se, as per mil deviations of Se relative to NIST SRM
3149 and any data reported using other ratios have been converted to $\delta^{82/76}$ Se for consistency:

_____ (‰)

Se isotope delta values have been reported relative to a number of standards including NIST SRM 3149 (Clark & Johnson 2008), MERCK (Rouxel *et al.* 2002; Rouxel *et al.* 2004a), MH-495 (Herbel *et al.* 2002; Johnson *et al.* 2000) and CRPG (Rouxel *et al.* 2002). After discussion at international workshops on isotope reference standards it was decided to use NIST SRM 3149 as the standard (Carignan & Wen 2007). NIST SRM 3149 is an intermediate purity Se solution (HNO₃ matrix) sold as a 10,000 ppm concentration standard (Johnson & Bullen 2004). Carignan and Wen (2007) reported the compostion of MERCK, MH-495, and CRPG relative to NIST SRM 3149 (Table 2.7).

Table 2.7: Mean isotopic composition of MERCK, CRPG, and MH-495 Se solutions against the NIST 3149 Se (Carignan & Wen 2007)

Sample	n	^{82/76} Se (‰)	^{82/77} Se (‰)	^{82/78} Se (‰)
NIST 3149		0	0	0
MERCK	16	1.54 ± 0.20	1.36 ± 0.20	1.03 ± 0.20
CRPG	5	-2.01 ± 0.15	$\textbf{-1.70} \pm 0.15$	$\textbf{-1.36} \pm 0.22$
MH-495	2	-3.04 ± 0.50	$\textbf{-2.48} \pm 0.45$	-2.01 ± 0.45

2.4.2. Isotope systematics

All Se isotope fractionations described in this section are assumed to be kinetically controlled. The basic principles of kinetic isotope fractionation can be understood with reference to kinetic theory. For elementary or single-step reactions, lighter isotopes usually have greater rate constants because the activation energies are less than those of heavier isotopes, e.g. the breakage of one of the four S-O bonds in SO_4^{2-} is an important isotope fractionating reaction step during sulphate reduction, and this breakage requires less energy for ³²S than for ³⁴S (Harrison & Thode 1957). When isotopes are fractionated kinetically during chemical reactions, the isotope ratio shift of the products relative to the reactants often depends on the reaction mechanisms. The chemical reactions between Se species mostly involve multiple steps and there might be multiple pathways by which a chemical transformation can occur. For example the reduction of Se(IV) to Se(0) could proceed via a simple abiotic reaction or via uptake of HSeO₃⁻ by a plant, reduction to Se(-II), incorporation into amino acids, death and decay of the plant, release of the Se(-II), and oxidation to Se(0). The overall transformation is the same but the two reaction pathways differ greatly and the overall isotopic fractionation might be greatly different.

Isotopic fractionation induced by various processes is quantified using a fractionation factor (α):

where R_{react} and $R_{inst prod}$ are the isotope ratios of the reactant pool and the instantaneous reaction product respectively, at one instant in time (Scott *et al.* 2004). This quantity is often expressed using a more convenient form:

$$\varepsilon \equiv (\alpha - l) \times 1000\%$$

This parameter is convenient because ε is, to a close approximation, equal to the difference in delta values of the reaction product and reactant:

$$\varepsilon \approx \delta_{(reactant)}$$
 - $\delta_{(instantaneous product)}$

Variations in Se-isotope ratios in nature and kinetic isotope fractionation during Se(VI) reduction were demonstrated in pioneering work by (Krouse & Thode 1962). This early study demonstrated similarities between Se isotope systematics and those of S but, as with the geochemistry, there are important differences between the two elements. Sulphate reduction to sulphide is treated as a one-step process, but selenium reduction can proceed stepwise with Se(IV) and Se(0) as stable intermediates. Therefore there are three distinct steps for Se reduction, each with a thermodynamically stable product, and the redox conditions determine the final product. Because each Se species is stable and individually important, Se isotope fractionation for each of the reduction/ oxidation steps must be studied (Johnson, 2004).

The isotope geochemistry of Se is complex because it involves several inorganic oxidation states and organic forms, kinetic isotope effects, and microbial action. However, only Se reduction reactions, whether abiotic or bacterially-mediated, result in a significant negative isotope fractionation so that the reduced product is preferentially enriched in the light isotopes (Johnson, 2004). In contrast, adsorption reactions, reactions between organic molecules, and oxidation and assimilatory reactions all appear to have a negligible effect on Se isotope ratios (Johnson, 2004) (Fig 2.9, table 2.8).



Figure 2.9: Summary of Se isotope systematics. Arrows represent reactions between Se species, which are given in bold. Isotopic fractionation for each reaction is given in the box attached to the arrow, and in each case, lighter isotopes are enriched in the reaction products. "?" indicates an estimated or preliminary value. From (Johnson, 2004).

(0/)

(0/)

			8 (‰)	8 (%)
Reference	Transformation	Reacting Agent	^{80/76} Se	^{82/76} Se
(Rees & Thode 1966)	Se(VI) to Se(IV)	HCl, 25°C	12*	18
(Johnson & Bullen 2003)		Green rust	7.4	11.1*
(Ellis et al. 2003)		Sediment slurry (microbial)	2.8	4.2*
(Herbel et al. 2000)		Bacterial cultures	1.1 to 4.8	1.7 to 7.2*
(Krouse & Thode 1962),	Se(IV) To Se (0)			
(Rees & Thode 1966),		NULOU ar accertic acid	10 4+ 12*	15 to 10
(Webster, 1972), (Rashid		NH_2OH or ascorbic acid	10 to 15*	15 to 19
& Krouse 1985)				
(Ellis et al. 2003)		Sediment slurry (microbial)	5.6	8.4*
(Herbel et al. 2000)		Bacterial cultures	6.0 to 9.1	9.0 to 13.7*
(Johnson, 2004)	Se(IV) to Se(VI)	$NaOH + H_2O_2$	< 0.2	<0.5*
(Johnson et al. 1999)	Se (0) oxidation	Incubated soil	< 0.3	<0.5*
(Herbel et al. 2002)	Plant uptake	Wetland plants	<1.0	<1.5*
(Hagiwara, 2000)	Algal uptake	C. reinhardtii	1.0 to 2.6	1.5 to 3.9*
(Johnson et al. 1999)	Se volatilisation	Cyanobacteria	<1.1	<1.7*
		Soil (microbes)	<0.6	<0.9*
	Se(IV) adsorption	Fe(OH) ₃ 'nH ₂ O	0.5	0.8*

Table 2.8: A summary of kinetic isotopic fractionations caused by Se transformations (From (Johnson & Bullen 2004).

*Converted to or from ^{80/76}Se using the relation: $\varepsilon_{80/76} = \frac{2}{3}\varepsilon_{82/76}$.

Se(VI) reduction: abiotic

Early studies by Rees and Thode (1966) reduced Se(VI) to Se(IV) at room temperature using ~8M HCl and obtained an epsilon value ($\varepsilon_{Se(VI)-Se(IV)}$) of 18‰. However, these results were complicated because the Se(IV) product was recovered by reduction to Se(0) and some back-reaction may have occurred (Rees & Thode 1966). In recent experiments (Johnson *et al.* 1999) Se(VI) was reduced by 4M HCl at 70°C which resulted in a fractionation factor of ~8.25 ± 0.45‰. One experiment which is more relevant to natural conditions was the reduction of Se(VI) to Se(IV) by "green rust" which produced a fractionation factor of 11.1 ± 0.3‰. The reduction by green rust is a two-step process and, assuming the second step of transferring electrons from the green rust to reduce the Se(VI) to Se(IV) produces the main kinetic isotope fractionation, the first diffusion step is the rate-limiting step. Therefore the overall kinetic isotope effect should be lower than the single step reduction process. This is the case as the two step value is \sim 7.4‰ compared to \sim 12‰ measured using strong HCl (Johnson & Bullen 2004).

Se(VI) reduction: microbial

The microbially-induced isotope fractionations for Se(VI) - Se(IV) reduction are smaller than those produced abiotically and range between 1.7 to 7.2‰ (Table 2.8). Microbial experiments by Herbel et al. (2000) suggested that the amount of isotopic fractionation depends on the bacterial species and metabolic state of those bacteria. In these experiments the concentrations of Se(VI) and electron donor were greater than would be found in most environments and so the results are not directly translatable to the natural environment. Herbel et al. (2000) speculated that under more natural conditions, the isotopic fractionation would be closer to 7.5‰. In order to approximate a natural wetland setting, reduction of Se(VI) with anaerobic slurries was carried out (Ellis et al. 2003). Three experiments were set up to investigate the effect of selenium concentration and sediment type on the isotopic fractionation. Starting Se concentrations for estuarine sediment experiments were 100 µmol L⁻¹ and 240 nmol L⁻¹ and for wetland sediment the initial Se concentration was 460 nmol L⁻¹. Regardless of differences in sediment type and Se concentration, $\varepsilon_{Se(VI)-Se(IV)}$ varied little, from 3.9% to 4.7‰. Therefore even at low Se concentrations, isotope fractionations still occur. Abiotic reduction of Se(VI) appears to induce greater isotopic fractionation than microbial reduction. Providing more studies are carried out to confirm this, it might be

possible to distinguish between microbial and abiotic Se(VI) reduction in natural settings using the size of Se isotope fractionation (Johnson & Bullen 2004).

Se(IV) reduction: abiotic

Reduction of Se(IV) can take place using mild reducing agents, e.g. ascorbic acid, and without a catalyst; presumably there are many naturally occurring organic reducing agents which can also reduce Se(IV) to Se(0). The ranges in isotopic fractionations are similar to those for abiotic reduction of Se(VI) to Se(IV) (Table 2.8). As with the reduction of Se(VI) to Se(IV), the reduction of Se(IV) to Se(0) is a two-step process with kinetic isotope effects of 7.2‰ and 19.8‰ for the first and second steps respectively (Rashid & Krouse 1985).

Se(IV) reduction: microbial

Se isotope fractionation occurring during microbial reduction of Se(IV) to Se(0) is greater than that occurring during microbial-induced reduction of Se(VI) to Se(IV) (Table 2.8). Similarly with the Se(VI) reduction experiments the isotopic fractionation was small in the initial stages (~1‰) and then increased to between 11.85 and 13.7‰ for the middle to latter stages (Herbel *et al.* 2000). Ellis *et al.* (2003) obtained fractionation factors for Se(IV) reduction of 8.25 to 8.55‰ (Table 2.8) using the same experimental parameters for Se(VI) reduction. As with the Se(VI) reduction experiments in this study, there was no apparent dependence on Se concentration or sediment type, but the number of experiments was small (Johnson & Bullen 2004). In comparison to Se(VI) reduction, the range of microbially-induced Se(IV) reduction overlaps with the range observed for abiotic Se(IV) reduction (Table 2.8). This suggests a fundamental difference between Se(IV) and Se(VI) reduction in which microbial Se isotope fractionation is much smaller than abiotic reduction (Johnson & Bullen 2004).

Se oxidation

Results of experiments suggest that oxidation of Se(IV) to Se(VI) does not fractionate Se isotope measurably (Johnson, 2004) (Table 2.8). The oxidation of Se(0) is unlikely to involve an isotopic fractionation - if solid Se(0) is consumed by an oxidation reaction, any kinetic isotope effect is ultimately negated by mass balance effects (Johnson & Bullen 2004). No experiments have been completed to determine isotopic shifts of Se(-II) oxidation but the S isotope literature suggest they should be small (Canfield, 2001).

Plant uptake

Assimilation of Se(VI) and Se(IV) by algae appears to induce a small enrichment in the lighter isotopes (1.5 to 3.9%; table 2.8). No consistent difference was found in the fractionation between the results of the Se(VI) and Se(IV) assimilation experiments (Hagiwara, 2000). However, the Se concentrations of these experiments was >1.5 µmol L⁻¹, and although the algal assimilation isotope effect is significant, in Se-poor waters the effect may be different because, as described previously, Se is scavenged as a nutrient and occurs at very low concentrations in surface waters (Johnson & Bullen 2004). The isotopic composition of macrophytes from an artificial wetland receiving water with ~320 nmol L⁻¹ Se(VI) showed very little variation (0.78‰ total range; mean = 1.11‰) in isotope ratios (Herbel *et al.* 2002). With little evidence suggesting Se isotopes fractionate during assimilation, the compositions of plant tissues should reflect the soil solutions from which the plants grew.

Volatilisation

The Se isotope fractionation of volatilised Se, presumably as alkylselenides, was measured from cyanobacterial mats and incubated soils (Johnson *et al.* 1999). The results from the cyanobacteria showed no measurable difference between the volatilised Se and the growth medium and the soil volatilisation experiments were all within 0.9‰ of the total Se in the soil. Both these experiments suggest that isotopic fractionation related to volatilisation is small.

Adsorbed and dissolved Se species

Experiments have found Se(IV) adsorbed onto hydrous ferric oxides to be slightly enriched in the lighter isotope (0.80‰) relative to the growth solution (Johnson *et al.* 1999). This result suggests sorption of oxyanions induces little isotopic fractionation which is not surprising because the central atom in the oxyanion complex is bonded to the same number of oxygen atoms in the adsorbed as in the dissolved species (Johnson & Bullen 2004).

2.4.3. Recent applications of Se isotopes

The number of studies which involve the measurement of Se isotopes is still small. The types of samples which have been measured for Se isotopes include meteorites, igneous rocks, wetland sediments, hydrothermal sulphides, and marine sediments. The range of these analyses depends on the type of sample but overall, Se isotope values range between -8‰ and +5‰ (Fig 2.10). There has also been a lot of analysis of standard reference materials (Layton-Matthews *et al.* 2006; Rouxel *et al.* 2002).



Figure 2.10: Summary of selected literature data for Se isotopes, reported to NIST 3149. Data from (Rouxel *et al.* 2002; Rouxel *et al.* 2004b), (Johnson *et al.* 1999), (Hagiwara, 2000), and (Johnson, 2004). From (Carignan & Wen 2007).

^{82/76}Se values of CDT and three other iron meteorites were determined by Rouxel *et al.* (2002). CDT had the highest ratio (+0.22 ‰ relative to NIST 3149) and the other meteorites ranged from -0.2‰ to -0.6‰, relative to CDT. Four basaltic reference materials, two glassy MORBs and one peridotite were also within 0.2‰ of CDT. According to Rouxel *et al.* (2002), these values suggest the Earth's mantle is close in isotopic composition to CDT, and CDT is a reasonable proxy for the bulk composition of the Earth. Two hydrothermally altered basalts from the mid-Atlantic Ridge have ^{82/76}Se values enriched in the lighter isotope by ~1.7‰ while ^{82/76}Se values for sulphide minerals were enriched in the lighter isotopes, ranging from CDT values to -5.1‰ and averaging -1.3‰. These values suggest partial reduction of oxidised Se along the flow path of fluids through the crust (Rouxel *et al.* 2002).

Wetlands are the most heavily studied environment for Se isotopes with the most notable being the San Joaquin Valley, California (Presser et al. 1994). Herbel et al. (2002) found little isotopic contrast existed between oxidised waters containing 320 nmol L^{-1} Se(VI) entering the system and the reduced Se forms present in the sediments. The small isotopic difference suggested that dissimilatory reduction is not the dominant accumulation mechanism. If it were, it would be expected that the accumulated Se(0) is enriched in the lighter isotope. Instead, incorporation of Se into macrophyte and algae tissues, followed by decay and conversion of its Se to Se(0) is more consistent with the data. A more recent study of Se isotopes took place at Sweitzer Lake, located south of Delta, Colorado, USA (Clark & Johnson 2008). The aim was to quantify the removal of Se(VI) from surface water bodies when the removal is driven by reactions occurring in pore waters of underlying sediments. As Se(VI) is removed the isotope fractionation caused by reactions within the pore waters will be expressed in the surface waters. The measured isotope ratios in the surface waters should change as a function of the quantity of the pollutant removed. Using laboratory experiments, isotope fractionation factors (ϵ) for Se(VI) reduction in wetland sediments, were determined. In all experiments Se(VI) became progressively enriched in heavier isotopes as reduction took place and a range of ε values for the different sediment conditions were calculated from $0.60 \pm 0.15\%$ to 1.83 \pm 0.21‰. Two different ϵ values were determined – an effective ($\epsilon_{eff})$ and an intrinsic (ε_{int}) fractionation factor. Interestingly in the experiments, ε_{eff} was roughly half that of ε_{int} . This suggests that when authigenic reduction takes place in sediments, with the Se source in the overlying water, the fractionation observed in the sediments is only half that of the initial fractionation from microbial reduction. Additionally, the fractionation factor for the Sweitzer Lake mixed slurry ($\varepsilon = 1.83\%$) is half that observed in an earlier study with a similar mixed slurry collected from a similar wetland ($\varepsilon =$

2.33‰; (Ellis *et al.* 2003). This aptly demonstrates the problem of applying fractionation factors determined under one set of conditions to sites that initially appear similar, but cause a different degree of fractionation (Clark & Johnson 2008). The concept of effective fractionation factors could also be used for laboratory experiments designed to measure isotope fractionation factors that will be applied to field settings (Clark & Johnson 2008).

Our knowledge of the Se isotopic composition of seawater is limited due to the very small concentrations of Se in seawater. However, as Se oxyanions in seawater are scavenged in marine ferromanganese concretions (Takematsu *et al.* 1990), it has been suggested that the Se isotopic composition of Mn nodules might approximate the Se isotopic composition of seawater (Rouxel *et al.* 2002). One such modern Pacific Ocean Mn nodule (USGS reference material NOD-P-1) was measured to have a Se isotopic composition of $\delta^{82/76}$ Se_{NIST 3149} = 0.04‰ (Rouxel *et al.* 2002), which is similar to the bulk Earth ($\delta^{82/76}$ Se_{NIST 3149} = -0.04 ± 0.38‰ (Carignan & Wen 2007). The lack of fractionation between seawater Se oxyanions and organic material (section 2.4.2) suggests that the Se isotopic composition of organic material might also approximate the Se seawater isotopic composition.

Finally, a survey of Se isotope variations in marine sediments and sedimentary rocks of varying ages was carried out by Hagiwara (2000) (Table 2.9). Interestingly, there is no strong enrichment in lighter isotopes within unweathered shale samples and the three Black Sea sediments. In comparison, δ^{34} S values in Phanerozoic shales are strongly enriched in lighter isotopes relative to CDT because of the kinetic isotope effect associated with sulphate reduction (Canfield, 2001); the three Black Sea sediments (Table 2.9) have δ^{34} S values between -37 and -38‰ relative to CDT. This lack of enrichment in lighter isotopes for Se confirms that the biogeochemical cycling

of Se differs from that of S. In many cases, near-surface alteration has altered Se isotope ratios – samples from the Phosphoria formation (Idaho, USA) were probably altered by deep groundwater or hydrothermal fluids which lead to high Se concentrations (Hagiwara, 2000). Some of the other samples were from outcrops where redistribution of Se might have taken place during weathering (Hagiwara, 2000).

		[Se] mg	
Material Age and type	Location	kg ⁻¹	^{80/76} Se (‰) SRM 3149 ^a
Holocene sediment-core	Mid Atlantic	0.88	-0.95
	Black Sea-anoxic	1.88	-0.43
		2.69	0.00
		1.97	-0.37
Eocene Shale-outcrop	Mancos Fm., Colorado, USA	0.57	-0.42
		0.86	-1.05
Cretaceous shale - outcrop	Niobara Fm., Kansas, USA	102	3.04
Cretaceous chalk - outcrop		4.17	0.97
Cretaceous shale-outcrop	Pierre Fm., Wyoming, USA	21.9	0.34
Pennsylvanian shale-outcrop	Pottsville Fm., Pennsylvania, USA	4.03	1.94
Pennsylvanian shale-core	Hermosa Fm., Colorado, USA	13.1	-1.11
Devonian shale-core	New Albany Fm., Illinois, USA	4.85	0.08
		2.29	0.35
Permian shale-altered	Phosphoria Fm., Idaho, USA	249	-1.24
		5380	-4.80
		1070	-2.45
		242	0.44
		91	-0.96

Table 2.9: $\delta^{82/76}$ Se values of marine sediments and rocks (Hagiwara, 2000)

^aCorrected to SRM 3149 from original data measured vs. MH 495

Selenium isotope ratios have more recently been measured in the Yutangba Se deposit, Hubi Province, China (Wen *et al.* 2007). The Yutangba Se deposit is the only sedimentary-type Se deposit in the world and consists of nine orebodies which are distributed along a lithological interface between carbonaceous chert and carbonaceous shale of the Lower Permian Maokou formation. The average Se concentration is 0.13 wt.% and $\delta^{82/76}$ Se_{NIST} values vary from -12.77‰ to +4.93‰. This is the largest Se isotopic variation found so far in natural terrestrial samples (compare to fig 2.7). The variations in Se isotope ratios along with other geochemical evidence (C/N ratio) suggests the large enrichments and variations in isotope ratios are a result of repeated Se(IV) to Se(VI) to Se (0) transformations. The discovery of these large Se isotope fractionations in natural samples indicates the potential of Se isotopes as a new geochemical redox tracer (Wen *et al.* 2007).

2.5. Hypothesis

The redox controlled geochemistry and isotope system of selenium make it an ideal candidate for a new ocean oxygenation palaeoredox proxy. A summary of the key features of each is below:

Selenium geochemistry

- Se(IV) and (VI) are the dominant form in seawater, and upon reduction, Se (0) and Se(-II) in inorganic sulphides/ selenides may be formed.
- Se strongly bio-concentrates in living matter where the soluble oxyanions, (IV)/
 (VI) are converted into organic selenium compounds.
- Se shows bio-intermediate behaviour where it is almost totally removed from the ocean surface by marine production.

- Se(IV) is drawn down to the sediment-water interface by attaching to Fe/Mn oxy-hydroxides and there is a diagenetic and authigenic flux into the sediments.
- There is a large volatile flux from the atmosphere to the ocean surface mixed layer, and with a residence time of ~ 24 years with respect to this atmospheric flux, the ocean surface layer becomes well mixed on geological timescales.

Selenium isotope system

- Most reduction reactions, either chemical or biological, cause a significant isotope fractionation with the product enriched in the lighter isotopes.
- Assimilation, oxidation, and adsorption reactions are thought to induce negligible isotopic fractionation.
- Where authigenic reduction of Se oxyanions has taken place in the post-oxic region of the sediments, the overall isotope ratio of the sediment will be enriched in the lighter isotopes.
- Reduction of dissolved Se oxyanions in the oceans produces reduced Se enriched in the lighter isotopes relative to the parent seawater.

Therefore our main hypothesis is **selenium isotope variations in seawater, preserved through the sedimentary record, reflect changes in ocean oxygenation, on a global scale, through geological time.** The theoretical background behind this hypothesis comprises of three parts which will be tested in this thesis:

 Mechanisms of Se cycling in oxic and anoxic seawater will be different. Under oxic seawater conditions, organic selenides undergo oxidative regeneration to Se(IV)/ Se(VI). Also, addition of authigenic Se to sediments may occur via reduction of dissolved Se(IV) or Se(VI) in the post-oxic sediments. In contrast, under anoxic seawater conditions the vertical downward flux of organic selenide is dominant and undergoes very little regeneration.

- 2. The overall isotope fractionation will vary between those sediments deposited under oxic and anoxic seawater conditions. Within the oxic sediments, bacterial and/or abiotic reduction will cause a significant negative fractionation between the seawater Se(VI)/ Se(IV) and authigenic Se (0). In contrast, the isotope fractionation between seawater and organic matter is small.
- Airborne transport of the volatilised Se within the atmosphere does not cause an additional fractionation and because of the large atmospheric flux of Se, Se isotope values of ocean surface waters will be well-mixed on geological time scales.

Chapter 3: Analytical Methods and Instrumentation

3.1. Introduction

As described in chapter 2, Se concentrations do not reach more than ppm levels in most modern sediment and rocks. In most circumstances it is therefore not normally possible to use standard multi-element extraction techniques and instrumentation protocols. In order to measure Se concentrations accurately and precisely in geological samples specialised extraction protocols (see 3.5 and 3.6), a sample introduction mechanism (3.7), and instrumentation have been developed (3.8 and 3.9). The aims of this chapter are to: describe the methods used in this thesis for extracting total Se from sediments; outline the methods used to purify, concentrate, and extract the Se for isotope analysis; explain the instrumentation used to analyse for Se including specialised sample introduction systems; and define the precision and accuracy of these analytical techniques. This chapter will also outline the techniques (LECO C-S and XRF) used to provide multi-element geochemical data on the Bermuda Rise samples.

3.2. Sample preparation

Samples from the Cariaco Basin (ODP Leg 165) were already crushed and powdered when received, so no further physical preparation was required. Samples from the Bermuda Rise (ODP Leg 172) were obtained and the following preparation procedures were carried out. Samples were removed from their containers and dried in an oven at 40°C for 2-3 days. The samples were gently ground by hand using a ceramic pestle and mortar and then placed in the oven at 40°C for a further two days to completely dry. Total received weights were recorded and ranged between 13.7 and

29.5 g. Colour estimates (hue, value, and chroma) of the samples were measured with Munsell soil colour charts using loose material (Munsell Color Company Inc. 1975).

3.3. LECO CS230 Carbon/ Sulphur Determination

3.3.1. Sample preparation

The powdered sample (~0.2 g) was weighed into a ceramic crucible and one level LECO 773-579 metal scoop of iron and tungsten/tin chip accelerants were added in order to facilitate burning. One sample (1063A-6H-4-145-147) was measured initially using 0.2 g of sample but the measured S concentration exceeded the upper limit of detection; therefore a sample size of 0.025 g was used. Between three and eight replicates of each sample were analysed, the exact number was dependent on the relative precision of the analyses at the time of measuring.

3.3.2. Instrumental methodology

Total C and S contents were obtained by induction furnace combustion of the sediment followed by infra-red (IR) absorption on the released CO_2 and SO_2 gases. Once the sample crucible was loaded onto the machine, the system was purged with O_2 to drive off residual atmospheric gases. The O_2 then continued to stream throughout the combustion process. Power was applied until the accelerants were molten, with carbon given off as CO_2 & CO and sulphur given off as SO_2 . A dust filter prevents silicates (a potential infra-red wavelength overlap) from entering the infra-red cells. The combustion gases were then passed through a drying tube of magnesium perchlorate and then onto the SO_2 infra-red cell. After the SO_2 absorbance was determined, the gases passed through a platinised silica gel catalyst to convert any CO to CO_2 and SO_2 to SO_3 . The SO_3 is then removed from the system by a cellulose filter. The CO_2 content was then determined in the CO_2 infra-red cell and the gases were vented from the system. The infra-red absorption cells use a nichrome wire as the IR source, heated to

approximately 850°C. The infra-red energy was chopped at a rate of ~87.5 Hz and filtered to achieve a monochromatic infra-red wavelength corresponding to the energy of the CO_2/SO_2 adsorption wavelengths respectively. The IR cell output was then converted from an analogue to a digital signal, and time vs. intensity peak areas integrated. These values were corrected for sample weight, blank value and calibration factors to give a total carbon/sulphur result.

Lower and upper limits of detection for a sample size of ~ 0.2 g are between 35 ppm and 12 wt. % for carbon and between 23 ppm and 20 wt. % for sulphur. However if the sample size is varied this range can possibly be extended. The method accuracy was determined by measuring reference material BAS ECRM 877-1 (a furnace dust) at regular intervals. The certified value for carbon is 0.83 wt. % and for sulphur is 0.18 wt. %. The average measured carbon content for this reference material was 0.86 ± 0.04 wt. % (2 σ ; n=36) and the average measured sulphur content was 0.204 ± 0.02 wt % (2 σ ; n=36). These results yield average RSD's of 4.4% and 8.6% respectively. A measure of the precision for the Bermuda Rise samples was obtained by duplicating measurements on seven samples on a separate day and three further samples were re-analysed later the same day. Each duplicate was analysed between two and four times. The samples chosen span the approximate range of total C and S contents in the Bermuda Rise samples. The analytical precision for C content on original and duplicate sample preparations is 1.6% and 0.9%; the analytical precision for S content on original and duplicate sample preparations is 26.3% and 14.4% (Table 3.1). The estimated method precisions for C contents and S contents are between 0.00-7.52% and 0.16-64.7% respectively. Samples 10H-3-122-124, 10H-4-44-46, and 10H-5-11-13 were analysed later on 25/01/2008 to monitor instrumental drift; this was minimal for carbon with the original and duplicate mean concentrations within 1σ . For sulphur concentrations, instrumental drift was greater with the difference in the duplicate concentrations for all samples, except 10H-5-11-13, greater than 1σ (Table 3.1).

			Car	bon (wt	. %)		Sulphur (wt. %)				
^a Date	^b Sample ID	^c Orig	$1\sigma_{n-1}$	^c Dup	1σ _{n-1}	^d RSD	^c Orig	1σ _{n-1}	^c Dup	1σ _{n-1}	^d RSD
26/11/07	2H-6-95-97	2.46	0.11	2.60	0.02	3.78	0.16	0.01	0.12	0.01	17.7
	4H-3-122-124	4.60	0.08	5.12	0.03	7.52	0.01	0.01	0.03	0.01	64.7
	6H-1-37-39	1.87	0.01	2.06	0.01	6.63	0.10	0.04	0.13	0.02	15.2
16/01/09	6H-2-35-37	1.79	0.01	1.94	0.01	5.66	0.10	0.02	0.10	0.00	6.66
10/01/00	6H-4-145-147	1.58	0.04	1.63	0.06	1.87	11.08	0.74	11.10	1.27	0.16
	8H-2-65-67	5.54	0.05	6.10	0.02	6.81	0.58	0.13	0.88	0.23	28.9
	8H-6-70-72	6.65	0.03	7.34	0.06	7.00	0.01	0.00	0.01	0.00	23.9
	10H-3-122-124	1.40	0.02	1.38	0.01	1.07	0.16	0.04	0.33	0.02	48.7
25/01/08	10H-4-44-46	0.97	0.01	0.97	0.01	0.07	0.05	0.02	0.10	0.00	54.0
	10H-5-11-13	1.23	0.02	1.23	0.01	0.00	0.40	0.09	0.48	0.05	11.7

Table 3.1: Precision measurements on samples from the Bermuda Rise

^aInitial date of measurement. All samples were re-analysed on 25/01/2008

^bAll samples were drilled as part of ODP Leg 172, site 1063, hole A, and are part of a larger sample set which is discussed in detail in chapter 7

^cOrig = original measurement; Dup = duplicate measurement

^dMethod precision = standard deviation of two duplicate concentrations/mean concentration per sample

3.4. X-Ray Fluorescence Spectroscopy (XRF)

3.4.1. Sample preparation

Two preparation techniques were carried out:

Powder pellets for trace element analysis

Approximately 10 g of sample was weighed and placed in a 32 mm diameter die press, the surface smoothed, and the top of the die and plunger were replaced. No binding agent was required for the samples from the Bermuda Rise due to their high clay content and the constituent water included in the clays. The die was then placed in the hydraulic press, set on a 50 ton ram and pressed to a maximum of 10 tons per square inch. Once this pressure was reached the sample was allowed to come to equilibrium with the applied force for a minute. The pressure on the die was then released, the die removed, inverted, and the pellet pushed out of the barrel of the die and allowed to dry for a minimum of 3-4 hours. All the equipment was thoroughly cleaned between samples with damp tissue and then dried with dry tissue to avoid contamination.

Fusion beads for determination of major element concentrations

Approximately 4-5 g of sample were put into a 10 mL glass vial, dried overnight in a drying oven at 110°C to remove low-temperature absorbed volatiles, and then stored in a desiccator. The weight loss on ignition (LOI) was then determined in fused Al₂O₃ (ALSINT) ceramic crucibles. The weight of the crucible (W1) and the weight of the crucible plus sample before (W2), and after ignition (W3), were recorded in order to determine the weight loss. The ignition used a muffle furnace at 950°C and the sample was heated for 1-1.5 hours. After ignition the samples were allowed to cool to room temperature in a dessicator before reweighing. The ignited powders were then stored in a dessicator prior to preparing fusion beads. The percentage weight loss (LOI) was determined following the formula:

$$LOI = 100*(W2-W3)/(W2-W1)$$

Before making fusion beads a flux weight loss determination was made. Approximately 3 g of cool, dried flux was accurately weighed into a Pt/5 % Au crucible and placed on a gas burner for 5 minutes. The crucible was then placed in a desiccator and allowed to cool to room temperature. When cooled the crucible and flux were reweighed and the weight loss determined. The acceptable range of weight loss was 0.1-0.3 weight %. For the Bermuda Rise samples two types of flux were used. For samples with a LOI of <12%, a eutectic mixture of 80% lithium metaborate (LiBO₂) and 20% lithium tetraborate (Li₂B₄O₇) was used. Carbonate-rich samples, identified by LOI values >12% will not produce a stable glass with this mixture. However, lithium tetraborate is capable of producing stable glasses by itself, so for carbonate samples the flux used was pure lithium tetraborate.

Samples were then prepared as follows: 3 g plus the previously determined weight loss of dried flux (LiBO₂ + Li₂B₄O₇) was accurately weighed into a Pt/Au crucible and then 0.6 g of the ignited sample was weighed on top of the flux, resulting in a sample to flux ratio of 1:5. For samples which were prepared using the lithium tetraborate only flux, 0.6 g of the dried powder was used rather than the ignited powder. The crucible and its contents were then mixed together and placed on the Spartan gas burner. During the fusion process, the liquid was agitated in order to remove particles of powder stuck to the crucible sides and to remove bubbles from the liquid. To facilitate good mixing, the crucible was kept warm by swirling over a Meker gas burner. When the liquid was satisfactorily homogenised and there were no particles left on the side or base of the crucible, the fusion was brought back up to temperature using the Spartan gas burner. The contents of the Pt/ Au crucible were then poured into a pre-heated casting dish (heated to operational temperature), and the resulting disc was left to cool for 3-4 minutes until it is able to separate from the casting dish.

3.4.2. Instrumental methodology

The XRF laboratory currently operates a PANalytical Axios Advanced X-Ray Fluoresence spectrometer. The instrument uses a 4 kW rhodium anode end window super sharp ceramic technology X-Ray tube. The spectrometer is controlled via a PC running Microsoft Windows XP software. Control and processing software used is the PANalytical SuperQ system with IQ+, WROXI and ProTrace extensions.

Major element analysis was performed on fused beads to eliminate mineralogical effects and reduce inter-element effects. All major elements were analysed using the default PANalytical SuperQ conditions. Instrumental conditions

were selected to avoid any significant line overlaps within the usual compositional range of most geological materials. Selected suitable drift monitoring samples were analysed during and at the end of the analytical run. Calibrations were made by analysing numerous reference materials (Table 3.2a) under identical conditions and regressing the measured count ratios against the recommended concentrations, principally from values published on the GeoREM reference site, using the Philips based fundamental parameters correction technique. For samples which used a mixture of lithium metaborate and lithium tetraborate flux and ignited powder, the concentrations of the major elements must be corrected for the LOI. In contrast, samples which used a lithium tetraborate flux only the LOI value is added to the total major element composition.

All trace elements analyses were performed on pressed powder pellets under optimised analytical conditions which balance stability and sensitivity. These corresponded in almost all cases to the default parameters within the PANalytical ProTrace software. Suitable drift monitoring samples were also analysed at the start and during the analytical run. For most trace elements a high and low angle background determination was performed with a weighted average value corrected for spectral curvature subtracted from the gross peak intensity. For trace elements with analysed characteristic X-rays higher in energy (i.e. shorter wavelength) than the Fe-K absorption edge, mass absorption effects were corrected by ratioing to the Rh-K α Compton peak following the method originally proposed by (Reynolds 1967). For elements with analysed characteristic X-ray energies between the Fe-K and Ca-K absorption edges, the correction technique proposed by Nesbitt *et al.* (1976) was utilised. For trace elements with analysed characteristic X-rays of lower energies than the Ca-K absorption edge, no corrections for variation in mass absorption were made. Calibrations for trace

elements were prepared from the same group of reference materials used for major element calibration plus in some cases artificial calibration spikes to give better coverage of the full concentration range found with geological materials (Table 3.2b).

The overall accuracy measured by the recovery for the major elements for all standards was 9.16% excluding the P₂O₅ data. Each major element is accurate within 1 standard deviation with SiO₂ being the most accurately measured major element and P₂O₅ being the least accurate major element analysed (Table 3.2a). SCO-1 (Cody Shale, Wyoming, USA) is a similar composition standard to the Bermuda Rise sediments, with a maximum C_{org} concentration of 0.3 wt.% and a certified Se concentration of 0.89 ppm, which had an accuracy of 1.08 ± 0.05 ($1\sigma_{n-1}$).

The overall average accuracy for the trace elements is $1.03 \pm 0.31 (1\sigma_{n-1})$ (Table 3.2b). Average recoveries for Ag, Cd, Sb, and Sn are not included in the overall average because the concentrations of these elements in the Bermuda Rise samples are below the limits of detection. The NIST and JSd standards are soil and stream sediment samples respectively and so are a similar sample type to those from the Bermuda Rise. Average recoveries for the NIST and JSd standards are $1.00 \pm 0.21 (1\sigma n-1)$ and $0.98 \pm 0.23 (1\sigma n-1)$ respectively. These six standards span a range of Se concentrations between 0.1 ppm–19.2 ppm; they therefore cover the entire range of Se concentrations measured in the Bermuda Rise samples (see Chapter 7).

Provenance	CRM	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5
	JB-1A	1.02	1.02	1.01	1.02	0.97	1.00	1.03	1.00	0.91	0.96
	JB-2	1.00	1.00	1.01	1.01	1.00	1.01	1.00	1.02	0.99	0.94
	JB-3	1.00	1.00	1.01	1.01	0.99	0.97	1.00	1.00	0.93	0.99
	JA-2	1.02	1.04	1.03	1.03	1.00	0.95	1.01	1.04	1.07	1.30
Geological	JA-3	1.00	0.99	1.01	1.02	1.03	1.00	1.01	1.02	1.00	0.92
Society of Japan	JG-2	1.00	0.98	0.80	0.99	1.06	1.00	0.95	1.02	1.00	4.00
Jupun	JR-1	1.01	1.04	1.00	1.00	1.04	1.00	1.21	1.01	1.00	0.86
	JR-2	1.01	0.91	1.00	1.00	1.04	0.93	1.01	1.02	0.99	0.83
	JP-1	1.04	1.33	0.97	1.04	1.06	1.04	1.04		1.33	2.50
	JG-3	1.00	1.00	1.00	1.01	1.01	1.01	1.02	1.02	1.01	1.01
	AGV-1	1.02	1.04	1.01	1.03	1.09	0.98	1.02	1.02	1.03	1.01
	BIR-1	0.99	1.01	1.00	1.02	0.93	0.95	1.00	1.01	1.53	1.10
	G-2	1.01	1.03	1.00	1.02	1.10	1.01	0.99	1.00	1.01	0.94
United	BCR-1	1.01	1.03	0.99	1.01	1.03	1.02	1.02	1.04	1.05	1.01
States Geological	GSP-1	1.01	1.05	1.00	1.02	1.08	1.03	0.97	1.00	1.02	0.98
Survey	RGM-1	1.00	1.02	1.01	1.03	1.14	0.99	1.03	0.99	0.91	0.92
	SCO-1	1.09	1.02	1.07	1.10	1.08	1.10	1.06	1.17	1.09	1.00
	SDC-1	1.01	1.03	1.01	1.13	1.06	1.04	1.02	1.04	1.04	0.91
	STM-1	1.01	0.95	1.01	1.03	1.05	0.79	1.09	1.01	1.02	1.01
	GA	1.01	0.96	1.02	0.99	0.96	0.97	1.01	1.00	1.03	0.98
CRPG ^D	AL-1	1.00	0.67	0.99	0.96	1.00		0.99	1.01	0.93	1.03
	AN-G	1.00	1.05	1.01	1.01	0.98	0.81	1.02	0.99	1.25	1.50
ANRT ^b	DR-N	1.00	1.00	1.00	1.03	1.01	0.95	1.01	1.00	0.99	0.92
	DT-N	0.99	1.03	1.00	0.92	0.25		0.78	1.03	0.99	0.88
SABS ^c	NIM-G	1.01	1.06	1.01	0.98	0.86	0.45	1.02	1.00	1.00	0.70
	BCS375	1.01	1.02	1.01	1.04	1.00	0.72	0.95	0.98	0.90	
Bureau of	BCS376	1.02		1.03	0.95	1.00		0.98	0.97	0.96	
analysed	BCS353	1.00	0.99	0.99	0.99	1.02	1.00	0.99	0.98	1.12	1.01
samples	BCS354	0.99	0.88	0.99	0.99	0.92	1.25	1.00	1.07	1.02	1.03
	BCS372/1	1.00	0.97	0.99	1.00	1.06	1.04	1.01	0.90	1.02	1.10
CANMET ^u	MRG-1	1.04	1.02	1.04	1.02	0.95	1.04	1.03	1.03	0.87	0.80
University	Blank										
of Leicester	SiO ₂	1.01									
	Al_2O_3			1.00							
	Average	1.01	1.00	1.00	1.01	0.99	0.97	1.01	1.01	1.03	1.14
	1σ _{n-1}	0.02	0.10	0.04	0.04	0.15	0.14	0.06	0.04	0.13	0.63
	n	- 32	30	32	31	31	28	31	30	31	29

Table 3.2a: List of reference materials run once during the analytical run and the recoveries for major element analysis by XRF^a

^aThe values in these tables are a ratio of the measured value relative to the certified value. Therefore a value of 1 means the same measured and certified concentration were measured; a value less than 1 means the measured concentration was less than the certified concentration; a value greater than 1 means a the measured concentrations was greater than the certified concentration; ^bCRPG and ANRT = Centre de Recherches Pétrographiques et Géochimiques; ^cSABS = South African Bureau of Standards; ^dCANMET =Canada Centre for Mineral and Energy Technology

		Soils		Strea	m sedi	ment	Ba	salt	Gabbro	Granite			
	NIST 2709	NIST 2710	NIST 2711	JSd-1	JSd-2	JSd-3	BIR-1	BE-N	MRG-1	G-2	Mo=100	Mo=90	Average
Ag		0.98	0.96	58.44	1.50	1.34							12.65
As	0.95	0.98	0.85	0.01	1.05	1.04		2.85					1.10
Ba	0.93	1.17	0.95	0.96	0.97	0.97	0.64	1.16	0.60	0.93			0.93
Cd	3.02	0.92	0.95	7.86	1.12	3.20							2.84
Ce	0.93	1.57	0.98	0.87	0.92	0.96	1.21	1.14	1.59	0.97			1.11
Co	0.88	1.05	0.99	0.86	0.96	1.06	1.01	1.02	1.03	1.53			1.04
Cr	0.82	0.83	0.81	1.09	1.03	0.88	0.96	0.95	1.08				0.94
Cu	0.71	1.02	0.81	1.32	0.86	0.85		0.92	0.98	1.58			1.01
Ga	1.04	1.09	0.96	0.95	0.96	1.03	0.94	0.99	1.06	0.95			1.00
La	1.04	1.12	0.98	0.96	1.22	1.21		1.01		1.06			1.07
Mn	1.00	1.09	0.98	0.74	0.76	0.69	0.72		0.74				0.84
Mo	0.98	0.75	1.36	1.99	1.06			1.10	2.33		1.02	1.10	1.30
Nb				1.01	0.89	0.98		1.04	1.02	0.93			0.98
Nd	0.84	1.58	0.88	0.92	1.21	1.21		1.08	1.27	0.89			1.10
Ni	0.85	0.85	0.81	1.01	1.06	0.91	1.00	1.02	1.02				0.95
Pb	1.05	1.00	0.98	1.16	1.04	1.04	1.88	1.29	0.87	1.14			1.15
Rb	0.96	1.08	1.03	0.99	1.05	0.97		1.11	1.29	0.97			1.05
Sb	0.86	0.98	1.03		0.97	0.29	2.54	3.44	0.37				1.31
Sc	0.92	1.30	1.10	0.89	1.19	0.92	0.89	1.13	1.03	0.98			1.04
Se	0.58	·	1.34	0.15	0.99	1.23							1.03
Sn		0.57	0.95	0.46	1.19	1.07				4.00			0.85
Sr	0.97	1.00	0.98	1.00	1.01	1.01	0.99	1.00	1.01	1.00			1.00
Th	0.88	0.76	0.93	1.11	1.10	0.91		1.17	0.88	1.03			0.97
U	0.98	0.84	0.53	0.98	0.17	0.71	0.00	3.39	1.05	1.00			1.09
V	0.96	1.19	0.96	0.97	1.10	0.99	0.98	1.03	1.07	1.02			1.03
W	0.05	1.12	1.00	0.02	0.04	0.90	0.00	1.17		0.54			1.06
Y	0.93	1.54	1.33	0.93	0.96	0.93	0.88	0.93	0.75	0.76			0.99
Zn	0.89	1.58	0.95	0.97	1.00	0.96	0.96	0.99	1.11	0.96			1.04
Zr	0.89		1.16	0.98	1.04	1.01	1.48	1.03	1.01	0.98			1.06

Table 3.2b: List of reference materials and recoveries for trace element analysis by XRF^{a,b,c}

^aSee table 3.2a

^bBlank values indicate no certified value is available

^c*Italicised* values are not included in the accuracy and precision calculations for each standard because their concentrations in the Bermuda Rise sediments are below the limits of detection (Appendix 3).

Overall precision on the sample set was obtained by processing duplicate samples and comparing their measured major and trace element (Table 3.3) concentrations with their original concentrations. The precision on samples at 72.32 and 75.52 mbsf was very good with both measuring almost identical major element concentrations for both the original and duplicate fusion beads ($1\sigma = 1.2\%$ and 0.2% respectively). Two shallower samples (34.23 and 38.65 mbsf) were also duplicated but the standard deviation for both samples is very large ($1\sigma = 40.7\%$ and 29.7% respectively), possibly because these two fusion beads were processed using 0.3 g of sample due to limited sample quantities. The precision of the trace element data is 4.5%, 4.3%, and 8.5% for the samples 38.65, 72.32, and 75.52 mbsf respectively. The trace elements with the worst precision (>10%) were As, Mo, and U due to their low concentrations in the samples.

	72.3 m	bsf (9H-1	-52-54)	75.52 m			
Element	Orig	Dup	RSD	Orig	Dup	RSD	^b Average
SiO ₂	48.6	48.7	0.2	47.6	47.6	0.1	0.1
TiO ₂	0.7	0.8	1.2	0.8	0.8	0.4	0.8
Al ₂ O ₃	15.1	15.1	0.0	16.4	16.5	0.4	0.2
Fe ₂ O ₃	6.5	6.6	0.7	6.8	6.9	0.1	0.4
MnO	0.2	0.2	1.8	0.2	0.2	0.0	0.9
MgO	3.0	3.1	0.8	3.7	3.7	0.1	0.4
CaO	8.0	8.0	0.5	7.3	7.3	0.1	0.3
Na ₂ O	2.1	2.1	0.1	2.0	2.0	0.4	0.3
K ₂ O	3.2	3.2	0.9	3.7	3.7	0.1	0.5
P_2O_5	0.1	0.1	0.5	0.2	0.2	0.4	0.4
SO_3	0.4	0.3	7.3	0.1	0.1	0.5	3.9
LOI	11.6	11.6	0.0	11.1	11.1	0.0	0.0
^c Average			1.2			0.2	

Table 3.3: Estimate of precision for the major and trace elements.

	38.65 m	bsf (5H-4	-35-37)	72.32 m	bsf (9H-1	-52-54)	75.52 mbsf (9H-3-72-74)			
	Orig	Dup	RSD	Orig	Dup	RSD	Orig	Dup	RSD	Average
Ag	<2.5	<2.6		<2.6	<2.6		<2.5	<2.6		
As	<5	8.3		5.8	7.3	17.0	7.3	<5.1		17.0
Ba	371.9	384.2	2.3	357.5	352.2	1.1	393.3	321.2	14.3	5.9
Cd	<2.7	<2.8		<2.7	<2.8		<2.7	<2.8		
Ce	68.9	67.6	1.4	64.6	57.5	8.2	74.7	65.3	9.5	6.4
Со	15.8	15.5	1.7	16.4	18.8	9.5	20.1	19.2	3.1	4.8
Cr	72.0	73.3	1.3	70.1	70.7	0.6	83.6	74.0	8.6	3.5
Cu	21.5	20.5	3.2	25.3	29.1	9.9	25.2	23.5	5.0	6.0
Ga	19.9	18.8	4.2	18.5	18.7	0.7	19.6	18.4	4.6	3.2
La	39.8	35.3	8.4	31.2	32.7	3.4	41.0	38.4	4.8	5.5
Мо	1.5	1.8	12.3	1.7	1.5	6.1	1.1	1.3	12.1	10.2
Nb	13.8	14.1	1.5	12.9	12.9	0.0	13.4	12.7	4.2	1.9
Nd	32.7	30.5	4.8	28.1	27.7	1.2	33.8	26.7	16.5	7.5
Ni	45.3	43.8	2.3	41.6	41.0	1.1	53.7	47.5	8.6	4.0
Pb	22.6	25.9	9.5	21.5	23.1	5.1	25.0	24.8	0.5	50
Rb	129.6	132.2	1.4	116.4	118.6	1.3	130.2	128.1	1.1	1.3
Sb	<3.1	<3.2		<3.2	<3.2		<3.1	<3.2		
Sc	13.1	13.2	0.3	13.1	12.0	6.3	15.4	11.8	18.7	8.4
Se	<1.1	<1.1		<1.1	<1.1		<1.1	<1.1		
Sn	<2	<2		<2	<2		<2	<2		
Sr	222.3	225.2	0.9	301.6	305.3	0.9	251.8	249.1	0.8	0.9
Th	12.4	12.8	2.3	11.3	12.3	6.2	13.3	12.6	3.9	4.1
U	1.4	2.2	31.5	2.4	2.8	13.4	3.2	1.8	41.7	28.8
V	90.9	92.2	1.0	94.4	93.8	0.5	106.7	92.1	10.4	4.0
W	<2.3	<2.3		<2.4	<2.3		<2.3	3.5		
Y	25.5	26.2	1.9	24.9	25.2	0.9	25.2	24.4	2.3	1.7
Zn	84.2	85.3	0.9	84.5	83.7	0.6	86.6	79.3	6.2	2.6
Zr	129.3	130.6	0.7	136.8	138.9	1.1	127.7	126.4	0.7	0.8
Average			4.5			4.3			8.5	

^aRSD value is one standard deviation of the two concentrations per element/ mean concentration per element; ^bAverage RSD value for each element; ^cAverage RSD value for each sample

3.5. Total Se extraction protocols

3.5.1. Parr[®] total HNO₃ digestion

Total Se in Cariaco Basin sediments was extracted using Parr[®] acid digestion bombs. Approximately 0.5 g of sediment was weighed out and pre-digested on a 90°C hotplate for 3 hours using 3 mL analytical grade concentrated HNO₃ in capped 15 mL Savillex[®] PFA vials. Samples were then transferred to PTFE Parr[®] bomb liners with a 0.5 mL concentrated HNO₃ rinse of the Savillex[®] PFA vials to ensure complete transfer. The Parr[®] acid digestion bombs, with the Parr[®] bomb liner and pre-digested sample inside, were assembled following the manufacturer's instructions and placed in an oven overnight (~10 hours) at 165°C. Once cool, samples were transferred back to 15 mL Savillex[®] PFA vials, evaporated to incipient dryness at ~80°C, and then re-dissolved in 5 mL 4 M HCl. Vials were tightly closed and placed in an ultrasonic bath for 15 minutes to dissolve and release as much Se as possible from any remaining solids. The vials were then heated at 100° C for one hour to ensure all Se is Se(IV) (Cabon & Erler 1998; Herbel et al. 2000). Samples were then transferred to centrifuge tubes and centrifuged for 15 minutes to separate the solids. The supernatant was then transferred to a borosilicate tube and capped. A further 5 mL 4 M HCl was added to the pellet, resuspended, and centrifuged as before and the supernatant added to the borosilicate tube. The final volume was made up to 20 or 25 mL using 4M HCl.

3.5.2. Pilot study – A Comparison of Acid Digestion Methods for the Determination of Selenium in Sediments by Hydride-Generation Atomic Fluorescence Spectrometry

The measurement of total Se concentrations for samples from Bermuda Rise was undertaken in collaboration with the British Geological Survey (BGS), Keyworth, Nottingham. Initially as part of this collaboration, this pilot study was devised to compare a HNO_3 - $HCIO_4$ acid digest based on the method of Cutter (1985), a

microwave-assisted digestion using concentrated HNO₃ acid developed at the University of Leicester, and a non-microwave-assisted *aqua regia* digestion based on US EPA method 3051(a) and routinely used in BGS Laboratories. The aim of this study was to select one of these three digestion methods to extract the total Se from samples from the Bermuda Rise. The procedure selected had to be practical, able to deliver near complete yields, and produce repeatable and accurate measurements. The samples chosen to test the three methods consisted of selected reference materials (Table 3.4) and four deep-ocean sediments from our complete set of samples from the Bermuda Rise.

Table 3.4: Provenance and selenium values for the certified reference materials used in this pilot study.

CRM	TH-2	MESS-3	405	2709	GBW07404
Supplier	NWRI ^a	NRCC ^b	IAEA ^c	NIST ^d	NRCCRM ^e
Provenance	Great Lakes Basin, USA	Beaufort Sea	Tagus estuary, Portugal	San Joaquin Valley, California	Yishan, Guangxi, China
Sediment type	Ocean sediment	Ocean sediment	Intertidal mudflats	Agricultural soil	Limy-yellow soil
Certified [Se] mg kg ^{-1(f)}	$\begin{array}{c} 0.825 \pm 0.167; \\ (0.53^{g}); (0.20^{h}) \end{array}$	0.72 ± 0.05	0.44 ± 0.12	1.57 ± 0.08	0.64 ± 0.18

^aNational Water Research Institute; ^bNational Research Council of Canada; ^cInternational Atomic Energy Agency; ^dNational Institute of Standards and Technology; ^eNational Research Centre for Certified Reference Materials; ^fWhole rock analyses; ^gRecoverable (or "environmentally available") Se extracted using strong acid digestion without HF;^hLeachable (or bioavailable) Se extracted using a cold acid leach procedure.

Average precision of duplicate measurements on individual sample solutions was 3.0% (n = 9), 3.2% (n = 9), and 2.2% (n = 12) for the HNO₃-HClO₄, HNO₃microwave and *aqua regia* digestions respectively. The individual measured Se concentrations of all five reference materials for the three digestion methods were within error of the certified Se values with the exception of the HNO₃-HClO₄ digestions of NIST 2709 and HNO₃-microwave digestions on MESS-3. Overall the HNO₃microwave digestion produced the closest recoveries to the certified value while the HNO₃-HClO₄ and *aqua regia* digestions averaged lower recoveries than the certified value. However, all three methods were accurate within error. TH-2 also reports a recoverable Se concentration of 0.53 mg kg⁻¹ and a leachable Se concentration of 0.20 mg kg⁻¹ (Table 3.4). As the measured Se concentrations for all three digestion methods were within error of the certified total Se concentrations, it can be assumed that both the hydrogenous and detrital Se fractions are being extracted efficiently by these methods. For extracting Se from the Bermuda Rise sediments, the HNO₃-microwave digestions produced on average 12% higher yields for the four sediments when compared to the HNO₃-HClO₄ digestion and 8% higher compared to the *aqua regia* digestion.

The HNO₃-microwave procedure was the most efficient method of extracting Se from the CRMs analysed and produced significantly higher yields on our selection of samples from Bermuda Rise. As this is a closed vessel digestion, higher temperatures are reached, resulting in a more aggressive digest, and therefore a more complete reaction can occur. Fewer evaporation steps in the sample preparation procedure also decreases the chance of losing volatile Se species. This method also has advantages in terms of sample throughput and ease of use compared to the other methods assessed. Thus, of the three protocols examined, the HNO₃-microwave digestion was proposed as the most suitable method for extracting Se from the samples of the Bermuda Rise.

3.5.3. Microwave-assisted HNO₃ digestion

Approximately 400 mg of sediment was accurately weighed into a teflon-PFA microwave vessel and 10 mL analytical grade concentrated HNO_3 (70%) was added. The acid-sediment mix was left in a fume hood to allow any initial reaction to take place. The samples then underwent a three-stage heating protocol in the microwave

digestion unit (CEM MarsXpressTM): the first involves a 10 minute ramp and 20 minute hold at 90°C; the second a 5 minute ramp and 1 minute hold at 100°C; and the third a 5 minute ramp and 30 minute hold at 150°C. Once cool, the contents were transferred into a 15 mL Savillex[®] PFA vial and evaporated in an aluminium block on a hotplate at 120°C, to incipient dryness. The residue was then re-suspended in 4 M HCl and heated under reflux conditions at 100°C for 1 hour to convert Se(VI) to Se(IV). The sample was centrifuged and the supernatant decanted into a volumetric flask. Three 10 mL 4M HCl washes of the sediment residue were added to the volumetric flask and the supernatant is made up to 50 mL using 4M HCl. The supernatant was then transferred to a HNO₃-treated borosilicate glass tube capped with a teflon-lined lid for storage.

No direct comparison of the HNO₃-microwave and HNO₃ ParrBomb extraction methods was carried out. However the extraction efficiency of both these methods were compared to the HNO₃-HClO₄ extraction method. As previously described the HNO₃-microwave digestion gave ~12% higher yields compared to the HNO₃-HClO₄ digestion in samples from the Bermuda Rise. The HNO₃ ParrBomb digestion gave between 12–20% higher yields compared to the HNO₃-HClO₄ digestion for samples from the Oxford Clay (unpublished results).

3.6. Se isotope preparation protocols

3.6.1. Making Thiol-cotton fibre (TCF)

As a technique for pre-enrichment and separation for trace element analysis, modified "home-made" thiol cotton fibre (TCF) has many excellent properties such as simple preparation, low price, strong hydrophilicity, large number of adsorbable elements, good selective capabilities, multi-enrichment and easy desorption compared to many thiol chelating adsorption resins (Yu *et al.* 2002). The thiol group (-HS) has a very strong affinity for Se(IV), and cotton which is impregnated with thioglycollic acid quantitatively adsorbs selenium from water (Yu *et al.* 1983). This method for making thiol-impregnated cotton is modified from Yu *et al.* (1983).

20 mL thioglycollic acid, 14 mL of acetic anyhydride, 6.4 mL glacial acetic acid and 0.064 mL concentrated sulphuric acid (all Fisher Scientific ACS grade reagents) were mixed together in a wide-mouth bottle. This mixture becomes hot, due to an exothermic reaction, so the contents were cooled to room temperature. Once cool, approximately 6 g of medical grade hydrophile cotton, were weighed and submerged completely into the liquid. Because esterification is an exothermic reaction, the bottle was placed in fridge to cool for at least 45 minutes. After it had cooled, the cotton was allowed to come back up to room temperature. The closed bottle was then placed in an oven at 40° C (the oven must remain between 35-45°C to ensure the TCF is effective) for 4 days, agitated twice daily. Once removed from the oven and allowed to cool, the solution was suctioned off and the TCF repeatedly washed with MQ water until the water becomes clear. The filter and reservoir were checked for a neutral pH and washing continued if not neutral. The TCF was then removed and placed on aluminium foil and covered with filter paper and placed in an oven at 35° C for ~ 2 days until dry. The final TCF was kept at a low temperature and in a sealed container protected from direct sunlight. The TCF prepared using the above method should have a thiol content of 0.7-1% (Yu et al. 2001).

3.6.2. Chemical separation of Se using TCF

The chemical separation of Se using TCF followed the method of Rouxel *et al.* (2002) with minor modifications needed to decrease the abundance of interfering dissolved organic molecules in the final solution. The advantages of using this chemical separation method before analysis by HG-MC-ICP-MS are: (1) removal of matrix-interfering elements during hydride generation such as transitional metals is possible;

(2) a separation of Se from other hydride-forming elements, which cause isobaric interferences during mass spectrometry, such as Sb, As, and Ge is achieved (Rouxel *et al.* 2002).

For isotope analysis 100 ng Se in 4M HCl, which has been pre-heated to convert all Se to Se(IV), was required. Prior to TCF processing, the double isotope spike solution (77 Se + 74 Se; section 3.9.2) is added. The amount added is chosen so as to obtain a 2:1 ratio of ⁷⁷Se:⁷⁸Se. If total Se concentrations were low, the amount was reduced to a minimum of 20 ng ⁷⁸Se. The TCF (0.145 \pm 0.005 g) was inserted into a Bio-Rad polypropylene chromatography column (2 mL bed volume; 10 mL reservoir column) and saturated with 3 mL H₂O. The TCF was then conditioned with 1 mL 6 M HCl and 1 mL 0.8 M HCl. Sample solutions were then diluted to a concentration of 0.8 M HCl and passed through the column to bind Se to the thiol groups. The TCF was then washed with 2 mL 6 M HCl, followed by 3 mL H₂O until the liquid is pH 7 to elute Sb and residual matrix. Next, the TCF was suctioned dry to remove as much liquid as possible. The TCF was then transferred to 15 mL polypropylene centrifuge tubes. To release the adsorbed Se, 1 mL of a 5:2:3 mixture of HNO₃:30% H₂O₂:H₂O was added, and the tube was heated in a boiling water bath for 20 minutes. The solution was allowed to cool, 3.5 mL H₂O was added, and the solution was separated from the TCF via centrifuging. Solutions were then transferred to 15 mL PFA vials, 1 mL concentrated HNO₃ was added, and the solutions evaporated to incipient dryness. To break down remaining organic molecules, a 0.1 mL of mixture of a 1:2 HNO₃:30% H₂O₂ solution was added and then evaporated to incipient dryness and repeated three further times. Samples were then dissolved in 5 mL 5 M HCl, heated at 100°C for 60 minutes, and stored in borosilicate tubes for analysis.

3.7. Hydride Generation (HG)

Metalloids such as Se have low ionisation potentials when introduced into an ICP system as a liquid (Thompson & Walsh 1983). For both Se concentration and Se isotope analysis, Se in the sample solutions was converted to H₂Se and injected into the ICP system in the gas phase, in a technique known as Hydride Generation (HG). This method increases the sensitivity by delivering nearly 100% of the Se to the plasma and decreasing the load of H₂O and other matrix components in the plasma. The advantages of a HG sample injection system are 4-fold:

- 1. 100% efficiency in transport
- 2. No blockage problems
- Separation from non-hydride matrix components, reducing the limits of interferences
- 4. Analyte pre-concentration (HG system has a large sample flow rate)

In order to generate Se hydride, a strong reducing agent, normally sodium borohydride (NaBH₄) is used, which reduces Se(IV) to H₂Se. It is important to note that this method is selective for Se(IV) only; Se(VI) is un-reactive. To separate the gaseous H₂Se product from the liquid a Gas-Liquid Separator (GLS) was used, in which an Ar carrier gas passes through the solution as fine bubbles. This ensures efficient mixing of the acid-sample solution and uniform mixing of the H₂Se with the Ar carrier gas.

Interferences affecting the HG process can result in poor recoveries. Large amounts of oxidising acids such as HNO₃ must be removed prior to reaction with the NaBH₄. These acids could preferentially react with the NaBH₄ and decrease the effectiveness of Se reduction. One proposed mechanism is that some of the nitric acid is reduced to nitrite, which then reacts to oxidise the H₂Se before it is released (Cutter 1983). Transition metal ions present in the reaction matrix, e.g. Cu, Ni, and Co, can

interfere with the production of H_2Se by generating Me(0) and metal boride and also can cause catalytic decomposition of the NaBH₄ itself (Thompson & Walsh 1983; D'Ulivo *et al.* 1991; Bax *et al.* 1988). These interference effects can bias results toward lower values, but the interferences are all corrected for by our standard addition protocol.

3.8. Atomic Fluorescence Spectroscopy for Se concentration measurement

3.8.1. Background

Fluorescence spectroscopy is a type of electromagnetic spectroscopy which analyses the fluorescence from a sample. Molecules have various electronic states which correspond to specific energy levels. Molecules have a ground electronic state and various excited electronic states of higher energy. In fluorescence spectroscopy, atoms absorb a photon and are excited from their ground state to one of the various higher energy electronic states. Collisions with other atoms cause the excited atoms to lose energy until it reaches the lowest of the excited energy electronic states. The atom then drops down further to one of the energy levels of the ground electronic state, emitting a photon (Fig 3.1).



Figure 3.1: Jablonski energy diagram illustrating the various energy levels involved in the absorption and fluorescence of light from an atom

Spectro-fluorometers use diffraction grating monochromators to isolate the incoming light from the fluorescent light. Collimated light illuminates the diffraction grating and exits with a different angle depending on the wavelength. The monochromator is then adjusted to select which wavelengths to allow through. A flame is used to solvate and atomise the sample and then a light, at a particular wavelength, shines into the flame and excites the analyte atoms in the flame. A proportion of the incoming light is absorbed by the sample causing the molecules in the sample to fluoresce at certain Se-specific wavelengths. This fluorescent light then passes through a second filter or monochromator that selects for a particular Se-specific wavelength and reaches the detector. The detector is placed at 90° to the incoming light beam to decrease the risk of incoming light reaching the detector. The intensity of this fluoresceing light is used to quantify the amount of analyte element in the sample.
3.8.2. Instrumental methodology

Selenium concentrations were measured on a P S Analytical (PSA) Excalibur™ hydride-generation atomic fluorescence spectrometer (HG-AFS) at the British Geological Survey, Keyworth, UK. Sample solutions were introduced using a PSA 20. 400 auto-sampler. The hydride-generation (HG) system comprises a pair of two-channel peristaltic pumps connected to a four-way switch valve which controls mixing of HCl carrier acid (9 mL min⁻¹), sample solution (9 mL min⁻¹) and the NaBH₄ reducing agent (4.5 mL min⁻¹) before they enter the GLS. As described (section 3.7) HG is effective when solutions contain only Se(IV); if there is a delay between sample preparation and analysis, changes in the speciation of Se may occur et al. 1997). Solutions were therefore refluxed in 50 mL pyrex boiling tubes fitted with air condensers, in an aluminium block for 30 minutes at 140°C immediately prior to analysis. On mixing with the sample solution, the NaBH₄ reduces any Se(IV) present to selenium hydride (H₂Se). The gaseous H₂Se was separated in the GLS, transferred using a flow of argon (2.5 L min⁻¹) through the Perma Pure[™] continuous moisture removal system, and atomised using a hydrogen diffusion flame fed by excess H₂ generated by the reaction of HCl with NaBH₄. The GLS was constructed from glass and was designed with low foaming characteristics to provide minimal carryover from previous samples.

The PSA Millennium Software[™], running under MS Windows[™], was used for system control and data acquisition. Se was measured at a wavelength of 196 nm. A typical analysis sequence takes 85 seconds per sample, during which the height of the flat-topped peak is measured over 30 seconds.

3.8.3. Precision and accuracy for Se concentration measurements

At the beginning of each analytical run, an eight-point calibration was carried out in the concentration range of 0-5 μ g L⁻¹ Se. All calibrations were linear with a least

squares $r^2 > 0.99$. The instrumental detection limit was 0.015 ng g⁻¹ based on 3σ of the intensity of the HCl carrier acid run several times throughout the analysis. Five process blank samples were run in triplicate to establish a limit of detection for the HNO₃microwave digestion of 15 ng g⁻¹. This was calculated using 3σ of repeated measurements of the processed blanks. Repeat measurements were made of at least two standard solutions (0.2, 0.5, 1 and 2 μ g L⁻¹ Se) every five unknown samples to enable a drift correction to be applied to the data. The average and standard deviation of the percentage recovery of the standards bracketing the five unknown solutions is calculated. If the difference of the average percentage recovery subtracted from 100 was greater than the standard deviation, then a correction factor equal to the remaining difference was applied to those five unknown solutions. During analysis of samples digested by the HNO₃-microwave method, instrumental drift was minimal. Only a small number of samples were drift corrected with factors between -6.63% and +5.97%. The average RSD of the repeated Se standard solutions was 3%. These figures are comparable to recently reported values using similar instrumentation (Zhang et al. 2007). Correction for interference effects involved the method of standard addition. A 0.2 mL 100 μ g L⁻¹ Se(IV) spike solution was added to 20 mL sample solution and analysed immediately after the non-spiked sample solution. The appropriate correction was then applied to the unspiked sample Se concentration based on the spike recovery. The average spike recovery for the HNO₃-microwave digestion was $101.67 \pm 2.81\%$.

Over half of the individual sample solutions were measured in either duplicate or triplicate at an analytical precision of 3.9%. Four samples were re-digested in triplicate and six samples in duplicate in order to obtain an estimate of the method precision. The highest average Se concentrations of the four triplicate digest samples are 0.401 and 0.729 ppm and these have RSD values of 2.7 and 1.9 % respectively. The

lowest average Se concentrations of the four triplicate digest samples are 0.158 and 0.260 ppm and these have RSD values of 10.7 and 8.7 % respectively. The precision of the duplicated digest samples ranged between 2 and 30 %. Six digests of a reference material, MESS-3, were measured for Se concentrations to test the accuracy of the AFS and the HNO₃-microwave extraction protocol. The certified Se value of MESS-3 is 0.72 \pm 0.05 ppm; our average measured Se concentration of MESS-3 was 0.716 \pm 0.046 ppm.

3.9. HG-MC-ICP-MS for Se concentration and Se isotope measurement

3.9.1. Background

All multi-collector-inductively coupled plasma mass spectrometers (MC-ICP-MS) consist of three main regions: ion source, ion optics (ion acceleration, ion beam focusing, isotope mass separation), and ion collection. Ions are produced by thermal processes in the source region. The sample is injected into the source region either as a nebulised liquid aerosol or in a gaseous stream that passes through high temperature plasma (~10,000°C) at atmospheric pressure. At this temperature the atoms of most sample materials are efficiently ionised (Bullen & Eisenhauer 2009). However this is not the case for Se which has a low ionisation potential as a solvent (Thompson & Walsh 1983).

The ions produced in the source region then enter the optics region where they are accelerated through a large potential (upto 10 kV) and focused electronically to create a discrete ion beam. Over the distance of this optics region, the ions are transferred to a series of chambers where pressure is successively decreased from atmospheric pressure to ~10⁻⁸ torr, via efficient mechanical and electrical pumps. The accelerated and focussed ion beam then passes through a slit into the flight tube; the

width of this slit determines the ability of the mass spectrometer to separate the analyte ions from isobaric interferences – the thinner it is the greater the resolving power (Bullen & Eisenhauer 2009). The ion beam then passes through an electrostatic sector, from which ions with differing energies have slightly differing paths that allow them to all focus into the detectors. Without this device, focus would be poor because ions are ejected from the plasma with varying energies and follow varying paths through the magnetic sector analyzer (Bullen & Eisenhauer 2009). The magnetic sector subjects the ions to a strong electromagnetic field, which disperses the different isotopes of the element into diverging trajectories. Within this magnetic field, ion flight paths are bent, parallel to the long axis of the flight tube, depending on the ratio of ion mass to charge: light ions are bent more and heavy ions are bent less (Fig 3.2) (Bullen & Eisenhauer 2009).

Various ion collectors are then configured to perfectly intersect the resulting flight paths of the individual isotope ion beams for the element, e.g. ⁷⁴Se, ⁷⁶Se, ⁷⁸Se, ⁸²Se. This can either be achieved through moving the individual collectors or by adjusting the trajectories of the ion beams themselves by further electronic focussing (Bullen & Eisenhauer 2009). Collectors are either Faraday cups, which trap the ions and result in a measurable total ion current on the surface, or ion counters which record individual ion collisions with the counter surface. The signals from either collector are then converted into signals that can be interpreted by computer software as relative isotope abundances for that element (Bullen & Eisenhauer 2009).



Figure 3.2: Generalised schematic of the important aspects of MC-ICP-MS used for determination of metal stable isotope compositions (Bullen & Eisenhauer 2009)

The Nu Plasma HR at University of Illinois, Urbana-Champaign uses the above described double-focussing (electrostatic analyzer and magnetic- sector analyzer) technology to separate the masses, and dual electrostatic lenses to focus the various isotopic ion beams into a detection array consisting of 12 Faraday collectors and 3 Ion counters.

3.9.2. Instrumental methodology

Isotope ratios for samples from the Cariaco Basin and the Bermuda Rise were measured on the Nu Instruments Nu Plasma high-resolution (HR) MC-ICP-MS located at the University of Illinois at Urbana-Champaign (Table 3.5). The method for isotope ratio measurement follows those of Rouxel *et al.* (2002, 2004) and Carignan & Wen (2007), with one major difference: these studies determined instrumental mass bias using sample-standard bracketing. In the present study, following on from Clark & Johnson (2008), selenium isotope ratio measurements employed a double spike approach (Johnson *et al.* 1999) where a spike of known isotope composition is added to the sample. During mass spectrometry, the instrument has a strong but nearly constant bias in favour of heavier isotopes relative to lighter ones (mass bias). The measured ratio of the spiked isotopes in the mixture is highly sensitive to this mass bias. The mass bias is monitored and corrected for via an iterative data reduction algorithm (Johnson *et al.* 1999). Because the double spike is added as early as possible during sample preparations and it is added in the same valence state as the analyzed Se, this method also corrects for isotopic fractionation that may occur during sample preparations when full recovery is not achieved. A double spike solution enriched in ⁷⁴Se and ⁷⁷Se was used for all Se isotope measurements. This double spike enables determination of ⁸²Se/⁷⁸Se and ⁸²Se/⁷⁶Se ratios in the sample.

Parameters	Nu Plasma HR
RF Power	1300 W
Plasma gas	13 L min ⁻¹
Carrier gas 1	1.15 L min ⁻¹
Carrier gas 2	0.20 L min ⁻¹
Measurement time	10 sec.
Number measurements	30-50
Flow rate, sample	0.75 ml min ⁻¹
Flow rate, reducing agent	0.75 ml min ⁻¹
Reducing agent	0.20 % (w/v) NaBH ₄ in 0.075 M NaOH
Sample acidity (HCl)	2.0 M HCl
Measured isotope ratio	⁸² Se/ ⁷⁶ Se and ⁸² Se/ ⁷⁸ Se
Sample concentration	2-10 ppb
Ratios/block	10
Blocks per analysis	3-5
On-peak zeros	Yes

Table 3.5: MC-ICP-MS settings for Nu Plasma HR MC-ICP-MS

MC-ICP-MS analysis of Se involves corrections for numerous interfering species (Table 3.6). The Ar-based plasma generates polyatomic ions, Kr is a ubiquitous trace gas in compressed Ar and is also in the atmosphere and so diffuses into sample solutions. Traces of Ge, Br, and As also occur in prepared samples. Many of these interferences are eliminated or reduced by measuring signal intensities on blank solutions and subtracting them from the measured intensities.

74	76	77	78	80	82
⁷⁴ Ge	⁴⁰ Ar ³⁶ Ar	⁴⁰ Ar ³⁷ Cl	⁴⁰ Ar ³⁸ Ar	⁴⁰ Ar ⁴⁰ Ar	⁸² Kr
⁵⁸ NiO	³⁸ Ar ³⁸ Ar	⁷⁶ SeH	⁷⁸ Kr	⁸⁰ Kr	⁸¹ BrH
	⁷⁶ Ge	⁶¹ NiO	⁷⁷ SeH	⁷⁹ BrH	
	⁷⁵ AsH		⁶² NiO		
	⁶⁰ NiO				

Table 3.6: Possible interferences for Se isotopes

For the Nu Plasma instrument, the ⁴⁰Ar⁴⁰Ar ion produces a very strong interference signal which is approximately the same size as the measured ⁸⁰Se signal. Smaller ⁴⁰Ar³⁸Ar and ⁴⁰Ar³⁶Ar ion beams interfere with measurements of ⁷⁸Se and ⁷⁶Se. Most of these interferences are removed by subtracting on-peak zeros. However, the ArAr⁺ intensity drifts significantly over a period of minutes, so on-peak zero measurements are inadequate for precise measurements. In order to monitor and remove drifts in ArAr⁺ which are not removed by the on-peak zeros, the beam intensity at mass 80 is monitored; subtracting the calculated ⁸⁰Se intensity provides an estimate for the residual ⁴⁰Ar⁴⁰Ar⁺ intensity. Residual ³⁶Ar⁴⁰Ar⁺ and ³⁸Ar⁴⁰Ar⁺ intensities are calculated using natural Ar isotope abundances and the mass bias determined via the double spike technique.

Two isotopes of Ge; ⁷⁴Ge and ⁷⁶Ge (35.9% and 7.4% abundance respectively), have severe interferences with Se isotope measurements (Table 3.6) with a majority of the Ge coming from the quartz-distilled HCl. A Ge correction is used which involves measuring the ⁷³Ge signal in each sample using an ion counter. Calculation of the ⁷⁴Ge and ⁷⁶Ge intensities assumes their abundances relative to ⁷³Ge reflect natural abundances, and takes into account the mass bias determined by the Se double spike isotope procedure.

There are three isotopes of Kr which interfere with Se measurements: ⁷⁸Kr, ⁸⁰Kr, and ⁸²Kr (0.35%, 2.28%, and 11.58% of total Kr respectively) (Table 3.6). These Kr interferences are effectively removed by measuring and subtracting the on-peak zeros,

provided ⁸⁴Kr is monitored to ensure the Ar supply is not particularly Kr-contaminated. In similar fashion, the ⁴⁰Ar³⁷Cl at mass 77 (Table 3.6) can also be removed using the on-peak zeros provided the HCl concentration in the samples matches within 5 % the HCl concentration of the blank acid used to measure the on-peak zeros.

Hydride interferences from ⁷⁵AsH⁺, ⁷⁶SeH⁺, ⁷⁷SeH⁺, ⁷⁹BrH⁺, and ⁸¹BrH⁺ at masses 76, 77, 78, 80, and 81 are small and are corrected for by measuring As, Se, and Br intensities and calculating the concentrations of their respective hydrides based on measured AsH⁺/As⁺, SeH⁺/Se⁺, and BrH⁺/Br⁺ ratios. An NiO⁺ interference on masses 74, 76, 77, 78, and 80 could arise from the Ni sample and skinner cones. However NiO⁺ beam intensities are very small and the on-peak zero subtraction appears to remove any interference effectively.

Selenium enters the plasma of the MC-ICP-MS via a continuous flow HG system similar to that used by Rouxel *et al.* (2002) but with minor differences: a mixing coil is not used, the GLS is at room temperature instead of being cooled at 4°C, and an in-line PTFE filter keep moisture from the HG from entering the plasma. At the start of each day, a 0.2 ppb Ge solution was used to measure the ion counter efficiency relative to Faraday cups. A Se acquisition programme is run with the signals recorded in the nine Faraday detectors which are tuned to all masses from 74 through 82. A Ge correction programme is then run and the ⁷³Ge value for each sample noted. After applying the relevant corrections, various raw Se isotope ratios were processed to determine the mass bias and the $\delta^{82/76}$ Se value of the sample, with the double spike mathematically subtracted. These calculations are achieved via an iterative data reduction algorithm as described in Johnson *et al.* (1999).

Se concentrations on samples from the Cariaco Basin are also measured on the Nu Plasma HR-MC-ICP-MS at the University of Illinois. All samples are diluted to

~1ppb concentration and acidified to 2M HCl to match the carrier acid used in the hydride generation. Before analysis all samples were pre-heated to 100°C in a hot block for 1 hour to ensure all Se is as Se (IV). Samples are then delivered into the plasma via the HG system using the same operating conditions as for Se isotope measurements. ⁷⁸Se intensity was used to determine concentration; ³⁸Ar⁴⁰Ar interference was removed via subtraction of on-peak zeroes. In order to correct for sample matrix effects, the method of standard addition was used. A known concentration Se(IV) spike solution was added to the sample solution and analysed immediately after the non-spiked sample solution. The appropriate correction was then applied to the unspiked sample Se (IV) standard solution was run after every spiked sample. Assuming the drift was linear the appropriate correction was applied to the sample solutions.

3.9.3. Precision and accuracy for Se concentration and Se isotope measurements

Se concentrations of samples from the Cariaco Basin were analysed over numerous days. Quality control for Se concentration measurements using the Nu Plasma consist of repeated standard sample solutions and duplicate measurements on single sample solutions. The instrumental detection limit was 0.003 ng g⁻¹ based on 3σ of the intensity of the 2M HCl blank run several times throughout the analysis. A linear drift correction was applied between repeated measurements of a 1 ppb standard solutions; the drift applied varied between 0.42% and 3.0% depending on the day of analysis. The average spike recoveries, from our standard addition protocol, varied between 88.91 ± 2.60 (2σ) and 102.65 ± 4.84 (2σ); the range probably a result of changing instrumental conditions and the varied sample matrices in the Cariaco Basin sediments. Method accuracy was determined by comparing measured Se concentrations against certified Se concentrations of NIST 1646a (Estuarine sediment) and NIST 2709

(Soil from San Joaquin Valley, California). Both were digested using the HNO3 ParrBomb method and analysed by HG-MC-ICPMS. NIST 1646a [Se_(cert) = 0.193 \pm 0.028 ug g⁻¹] was measured at 0.180 \pm 0.001 ug g⁻¹ which is a 93% recovery and is within error of the certified value. NIST 2709 [Se_(cert) = 1.57 \pm 0.08 ug g⁻¹] was measured at 1.663 \pm 0.015 ug g⁻¹ which is a 106% recovery but is also within error of the certified value. The analytical precision is 9.76% based on 31 duplicate Se concentration measurements. Based on the root mean square (RMS) difference of the 31 duplicate sample measurements, the uncertainty in the Se concentration values is \pm 0.39 ppm (1 σ).

Se isotope ratios of standards and samples are presented as $\delta^{82/76}$ Se relative to SRM 3149 standard. Quality control data includes replicate sample results and standard measurements for both Cariaco Basin and Bermuda Rise sediments. SRM 3149 standard solutions were processed through the Se purification step and resulted in a mean and standard deviation of $\delta^{82/76}$ Se = 0.03 ± 0.05 ‰ (n=6). An unprocessed SRM 3149 standard solution was also measured at regular intervals which allowed the drift in the standard to be monitored during the analytical runs. Based on the root mean square (RMS) difference of 27 replicate sample preparations, the uncertainty in the $\delta^{82/76}$ Se of the Cariaco Basin sample values is ± 0.24‰ (2 σ). Based on the RMS difference of 11 replicate sample preparations and duplicate measurements, the uncertainty in the $\delta^{82/76}$ Se of the Bermuda Rise samples values is ± 0.26‰ (2 σ). A further check of the quality of the Se isotope ratios reported in this thesis is a check on the theoretical relationship between $\delta^{82/76}$ Se and $\delta^{82/78}$ Se (Figs 3.3 and 3.4). For both the Cariaco Basin and Bermuda Rise samples, almost all analyses conform to the expected relationship.



Figure 3.3: $\delta^{82/78}$ Se vs. $\delta^{82/76}$ Se for samples from the Cariaco Basin. Grey line represents the expected relationship (0.66) between these two ratios. Error bars represent ±0.1‰.



Figure 3.4: $\delta^{82/78}$ Se vs. $\delta^{82/76}$ Se for samples from the Bermuda Rise. Grey line represents the expected relationship (0.66) between these two ratios. Error bars represent ±0.1‰.

Chapter 4: Global climate and the Cariaco Basin over the last 500 ka

The aims of this chapter are to:

- Describe global and regional climatic events that occurred during the last 500 ka
- Introduce the Cariaco Basin, describe the variations in the sedimentary sources, changes in the local hydrography on seasonal and glacial-interglacial scales, and the tectonic influence on the Cariaco Basin.
- Assess whether the Cariaco Basin is connected to the global ocean system.

The chapter concentrates on the last 500 ka (late Pleistocene–Holocene) because this is the time period that is covered by our samples, from the Cariaco Basin and Bermuda Rise, used in this thesis. There is a focus on the Cariaco Basin because of the necessity to understand the complex oceanographic conditions, which characterise the basin, before discussing and making conclusions on the selenium data presented in the following chapters.

4.1. Global and regional climate events of the last 500 ka

4.1.1. Introduction

Onset of major glaciations in the northern hemisphere began around 2.7 Ma and was probably induced by climate cooling during the late Pliocene (Bintanja & Van De Wal 2008). The waxing and waning of these glaciations are linked to variations in the Earth's orbital parameters (Bintanja & Van De Wal 2008). These interglacial-glacial climate oscillations have been recurring at ~100 ka periodicity for the last 900 ka. However this was not always the case; at 2.7 Ma the interglacial-glacial cycles were at a more frequent

periodicity of 41 ka. Bintanja *et al.* (2008) suggest the change from 41 to 100 ka periodicities is due to the behaviour of the Northern Hemisphere (NH) ice sheets. The boundaries between major glacials and interglacials are inferred from abrupt changes in marine δ^{18} O records of benthic foraminifera (Fig. 4.1A) and ice core records of changes in the concentration of greenhouse gases such as CO₂ and CH₄, and variations in the dust concentration (Fig. 4.1B).



Figure 4.1: (A) Global δ^{18} O curve for the last 500 ka from the LR04 stacked δ^{18} O curve based on benthic foraminifera from 57 ocean sediment cores (Lisiecki & Raymo 2005) and glacial terminations (I-V) (Lisiecki & Raymo 2005); (B) Vostok ice core CH₄, CO₂, dust data for the last 450 ka (Petit *et al.* 1999). Glacial stages (2, 4, 6, 8, 10, and 12) are shaded and their boundaries based on ages from (Bassinot *et al.* 1994).

To aid in communication, it is common to refer to individual interglacials and glacials by a Marine Isotope Stage (MIS) number; the current interglacial (the Holocene) is MIS 1 and the last glacial maximum at ~15 ka is MIS 2 (Fig 4.2).



Figure 4.2: (Top) Geological timescale for the current period of glaciations in Earth's history; Intensification of ice-sheets in the northern hemisphere (NH) was at 2.7 Ma (Bintanja & Van De Wal 2008); (Bottom) Last 500 ka relating the interglacial (red/ odd numbers) and glacial (blue/ even) periods to their age (ka) (Bassinot *et al.* 1994).

Using an oxygen isotope record of the past million years from 57 globally distributed sites, (Bintanja *et al.* 2005) modelled atmospheric temperature and global sea level over the last 500 ka. The mean air temperature over the last 500 ka was 9.4° C below present levels with an extreme of 17° C below present day levels. During glacial extremes, the sea level was 125 ± 12 m below present (Fig 4.3).



Figure 4.3: δ^{18} O LR04 stacked record with present day value of 3.22‰ subtracted (top), reconstructed surface air temperature (middle) and reconstructed sea level over the last 500 ka (bottom) (modified from (Bintanja & Van De Wal 2008).

Within the larger glacial-interglacial oscillations, climate instability on shorter timescales such as a few thousand years appears to be the norm. Proxy records of the past 2.7 Ma show the Earth's climate has varied significantly on timescales as short as a few thousand years (Raymo *et al.* 1998; Oppo *et al.* 1998).

4.1.2. 500-130 ka

Five major glaciations took place on Earth during the past 500 ka. Rapid transitions from cold to warm climate conditions, known as "terminations" occurred approximately every 100 ka (Fig 4.1). The cause of these terminations is thought to be a change in the seasonal distribution of solar insolation. (Schulz & Zeebe 2006) present a mathematical analysis of variations in midsummer insolation in both hemispheres at 65° latitude. They conclude that prior to each termination the insolation in both hemispheres increases, with a

Southern Hemisphere (SH) lead. Röthlisberger *et al.* (2008) suggest a relationship between the SH glacial terminations and Antarctic surface temperature, sea ice extent around Antarctica, and South American climate. Using duration and amplitude changes in δD from the EPICA Dome C ice core over glacial-interglacial transitions, the rate of change is similar across all terminations, implying once a termination has been triggered, the climate system will progress at its own pace (Röthlisberger *et al.* 2008).

The fine structure of the past four interglacials has revealed significant climate differences between cycles (Winograd *et al.* 1997). The Lake Baikal biogenic silica record divides MIS 5, 7, and 9 into five substages and MIS 11 into three substages (Fig 4.4). The warm periods are inferred from higher proportions of biogenic silica and the cooler stadials by lower biogenic silica values.



Figure 4.4: Lake Baikal biogenic Si record of the last four interglacial stages [from Prokopenko *et al.* (2001)].

Prokopenko *et al.* (2001) attribute changes to low biogenic silica content during stadials 5d and 7d (Fig 4.4) to abrupt regional glaciations in Siberia, controlled by strong insolation minima. A more gradual decrease in biogenic silica during stadial 9d (Fig 4.4) is coincident with a moderate insolation forcing. Lake Baikal also records millennial scale events found in North Atlantic and European records. For example, the drop in biogenic silica (Fig 4.4) during sub-stage 5e represents the mid-Eemian cool event (Karabanov *et al.* 2000). Between 103-100 ka (5c) the pronounced cooling represents the short-lived Montaigu cooling event observed in European pollen records (Reille *et al.* 1992). Initial warmings at the 9d/9c and 5d/5c transition, marked by highs in the Lake Baikal record, are followed by pronounced coolings. During 5c, the cooling is short-term, whereas during 9c is longer.

MIS 11 (423-362 ka) is split into 3 substages (Fig 4.4) in both marine and continental records. It is an unusually long interglacial (Howard 1997) with studies estimating a duration of ~30 ka in contrast to an average of 22 ka for the recent interglacials (Winograd *et al.* 1997; Poore & Dowsett 2001). The first 12 ka have been proposed as analogous to the Holocene due to similarities in amplitudes of orbital forcing (Dickson *et al.* 2009). A number of interesting features occurred in the second half of MIS 11. Minimum values were reached in the LR04 stacked δ^{18} O record (Fig 4.1), maximum SST (Sea Surface Temperature) values were reached in the subpolar North Atlantic Ocean, and a large reduction in the size of the Greenland Ice sheet is suggested by a high abundance of thermophilous pollen [Dickson *et al.* (2009) and refs. therein]. Poore & Dowsett (2001) used microfossil and isotopic data from the Cariaco Basin to suggest global sea level was 10-20 m higher than present day due to absence or a total reduction of the West Antarctic and Greenland ice sheets during MIS 11. These northern hemisphere climate signals are also observed in climate proxies such as dust and alternating loess/soil found in sequences from the western North Pacific Ocean and China respectively (Fig 4.5). Layers of silty loess (Kukla *et al.* 1988) and increased dust (Clemens & Prell 1990) indicate glacial periods, providing evidence of dry and windy conditions. In contrast, interglacials are shown by clay-rich soils and decreased dust concentrations. Both records show variations on the 100 ka frequency, the same tempo of ice sheet fluctuations in the Atlantic (Kukla *et al.* 1988; Hovan *et al.* 1991).



Figure 4.5: Alternating layers of windblown loess and soils in Southeast Asia (left) and variations in dust from Western Pacific (right) show changes that closely match δ 180 (ice volume) changes. [Adapted from Kukla *et al.* (1988) and Hovan *et al.* (1991)].

In a lake core from the eastern Andes in Colombia, cold periods are characterised by increases in grass pollen and warm periods by increases in tree pollen (Hooghiemstra *et al.* 1993) at the same 100 ka frequency of the North Atlantic ice cores (Fig 4.6).



Figure 4.6: Lake core from eastern Andes of Columbia showing major shifts between forest and grassland pollen that match 100 ka glacial-interglacial ice volume changes in northern hemisphere [Adapted from Hooghiemstra *et al.* (1993)].

4.1.3. The last 130 ka

The most recent climate oscillation spanning the last 130 ka has been studied intensively and numerous continental, marine and ice core records exist. The last 130 ka oscillation began with MIS 5e followed by the last glacial period (MIS 4-2) and the present Holocene interglacial (stage 1) beginning at ~14.5 ka (Fig 4.7).



Figure 4.7: δ^{18} O LR04 record for the last 130 ka showing interglacial-glacial boundaries (Lisiecki & Raymo 2005).

MIS 5e (~130-120 ka) is broadly seen as the closest counterpart in the geological past to our current interglacial with similar sea surface temperatures and slightly higher sea levels (Adams *et al.* 1999). The start of the last interglacial varies between 130 and 140 ka, depending on the climate record utlised, with a warming phase of uncertain duration taking the Earth out of an extreme glacial phase (Adams *et al.* 1999). It is proposed the warming at the beginning of this period occurred in two major steps (Seidenkrantz *et al.* 1996; Seidenkrantz *et al.* 1995), similar to the last deglaciation. A range of dates for the start of MIS 5e, from terrestrial and marine sites, suggest warm conditions were attained at different times at various locations throughout the world [Adams *et al.* (1999) and refs. therein]. Kukla *et al.* (1997) use the La Grande Pile pollen record to suggest the warming started at ~130 ka but ended much later than the ice core records suggest, and that the duration of on-land interglacials are longer than the period of lower ice volume recorded in δ^{18} O of ice cores.

Evidence suggesting large-scale climate instabilities during MIS 5e is of great interest. The GRIP ice core (Dansgaard *et al.* 1993) shows MIS 5e was punctuated by short-lived cold events lasting a few thousand years; the magnitude of cooling was similar to the difference between glacial and interglacial conditions and the shift between these warm and cold periods extremely rapid, possibly occurring over a few decades or less (Fig 4.8).



Figure 4.8: GRIP δ^{18} O record showing MIS 5e (130-110 ka) and climate instabilities during this period (Dansgaard *et al.* 1993). Black arrow represents approximate location of cold, dry event at ~122 ka (Adams *et al.* 1999).

Combined sources of evidence suggest a widespread cold and dry event occurred at about 122 ka (Fig 4.8) which was characterised by a change in North Atlantic circulation, a several degree decline in Nordic and Atlantic SST's, and an opening up of the west European forests to a mixture of steppe and trees (Adams *et al.* 1999). Previous interglacials, e.g. MIS 7, 9, 11, also show large and relatively sudden cool phases (Fig 4.4) (Winograd *et al.* 1997). Between 115 and 14 ka, there are numerous interstadials recognised in the Greenland ice-core known as Dansgaard-Oeschger (D-O) events (Dansgaard *et al.* 1993). Ice-core and ocean data suggest D-O cycles typically show an immediate increase in temperature followed by a gradual, stepwise decline, through a series of smaller cooling events (Rasmussen *et al.* 1997) (Fig 4.9). The duration of these warm phases ranged from a few decades to a few thousand years (Mayewski *et al.* 1997). These short-lived warm phases are also recognised in the eastern Pacific and central China (Behl & Kennett 1996), western Siberia, and the Arabian Sea (Schulz *et al.* 1998).



Figure 4.9: GRIP δ^{18} O record (Dansgaard *et al.* 1993). D-O events are numbered and Heinrich events are indicated by arrows. D-O events taken from (Bond *et al.* 1993) and dates of Heinrich events from (Hemming 2004).

Between 80 and 20 ka, the shifts in ocean-atmosphere temperature are bundled into cooling cycles each lasting 10-15 ka. Each cycle is ended by an enormous discharge of icebergs into the North Atlantic, known as a Heinrich event (Bond *et al.* 1993) (Fig 4.9). Heinrich events are extreme, short-lived cold events (Heinrich 1988) which were first

recognised as periods with intense ice-rafting in the North Atlantic. These events occur against the general glacial climate background and represent the climatic effects of massive surges of icebergs into the North Atlantic. Heinrich events only appear to occur when there is an ice sheet on the North American continent that is big enough to dramatically collapse. They are also times of sea surface cooling, reduced fluxes of foraminifera, and exceptionally large discharges of icebergs from the Laurentide ice sheet that left obvious layers of detrital carbonate in deep sea sediment (Bond *et al.* 1993; Heinrich 1988). Heinrich events show themselves in the Greenland ice cores as an additional 3-6°C drop in temperature from the already cold glacial climate (Bond *et al.* 1993). The cause of these events is either internal ice-sheet dynamics or external climate changes linked with orbital parameters, e.g. precession, obliquity, eccentricity.

Between 85 and 48 ka, carbonate mud and clay was deposited in Lake Petén Itzá, Guatemala, suggesting that Central American conditions were relatively moist during MIS 5a, MIS 4, and the early part of MIS 3 (Hodell *et al.* 2008) (Fig 4.7). A gypsum layer occurs at 48 ka and may have been deposited at the same time as H5 (Fig 4.9). The onset of gypsum precipitation at 48 ka signifies a hydrologic regime shift in lowland Central America toward wet-dry cycles beginning in the latter part of MIS 3. Hodell *et al.* (2008) suggest this change may have been related to a more dynamic Laurentide ice sheet with increased meltwater input to both the North Atlantic and Gulf of Mexico.

Between 48 and 23 ka, rapid climate changes during late MIS 3 are marked by millennial-scale oscillations in gypsum and clay deposition. This signifies the Central American climate changed to wetter conditions during the warm interstadials from the glacial dryer conditions, mimicking the temperature pattern from Greenland ice cores, i.e. D-O events. The results for MIS 3 from Petén Itzá support the hypothesis of northerly shifts

of the Intertropical Convergence Zone (ITCZ) associated with interstadials, and southerly shifts of the ITCZ during stadials, especially during Heinrich Events (Hodell *et al.* 2008).

4.1.4. Last Glacial Maximum (LGM) interval 23-14.6 ka

The last 25 ka have been extensively studied through ice cores, marine sediments, and continental records. As a result, records have been split into distinct time periods by their climate differences (Fig 4.10).



Figure 4.10: 5 point moving average of δ 180 values from the GRIP ice core (Dansgaard *et al.* 1993) illustrating key climate events over the last deglaciation. BA = Bǿlling-Allerǿd; YD = Younger Dryas; PB = Preboreal.

The LGM refers to the most recent time of maximum ice extent peaking approximately at 20 ka. Ice sheets covered Iceland and all but the most southern part of the UK as well as northern Europe to Svalbard. In North America the ice covered all of Canada and reached as far south as the Ohio and Missouri rivers and as far east as New York City. In the southern hemisphere the Patagonian ice sheet covered most of Chile and western Argentina to 41°N. Sea Surface Temperature (SST) reconstructions show a 2.5-3°C cooling of the glacial tropics relative to present day (Lea *et al.* 2003). The CLIMAP (Climate: Long range Investigation, Mapping and Prediction) project was undertaken in the 1970s and 1980s to produce a map of the climate conditions during the last glacial maximum (Fig 4.11).



Figure 4.11: CLIMAP project results illustrating climate conditions during last glacial maximum. Figure contains an outline of the continents after a 130 m sea level reduction, the positions of continental ice sheets and winter sea ice, and the change in ocean sea surface temperatures (CLIMAP 1981). Image created by Robert A. Rohde / Global Warming Art (http://www.globalwarmingart.com/wiki/Image:CLIMAP_jpg)

Ice-core records spanning the last 25 ka from the tropical Andes of South America show cooler conditions at higher elevations than found today, although the magnitude of cooling does depend on the particular proxy (i.e. pollen, ice cores). Insoluble dust and anion concentrations in the ice cores reveal that LGM hydrological conditions in the tropics (9°S) were much drier than today, whereas at 18°S, LGM conditions were much wetter. This probably reflects the migration of the tropical Hadley Cell in response to a different meridional temperature gradient. Low nitrate concentrations in LGM ice from the Andes suggest that the Amazon Basin forest cover may have been much less extensive (Thompson *et al.* 2000) (Fig 4.12).



Figure 4.12: Inferred changes in major vegetation types in South America from the LGM to the present. Shown are selected geomorphological features along with the location of the ice cores used in Thompson *et al.* (2000). Modified from (Clapperton 1993).

The LGM is bounded by Heinrich Events 2 and 1 (Fig 4.10) and the mean position of the Inter Tropical Convergence Zone (ITCZ) was further north between 23 and 18 ka than it was during the Heinrich events (Hodell *et al.* 2008). The period between 18 and 14.4 ka is the start of the last deglaciation yet is associated with cooling observed in Greenland ice (Dansgaard *et al.* 1993) and in sea surface temperature records from the subtropical North Atlantic (Bard *et al.* 2000). These events are associated with a regional shift in Central America from relatively moist to dry conditions at approximately 18 ka coinciding with Heinrich Event 1 (Hodell *et al.* 2008).

4.1.5. Bólling-Alleród (BA) interval 14.6-13 ka

Wetter conditions, indicated by a change to clay deposition in Lake Petén Itzá (Hodell *et al.* 2008), an increase in Caribbean temperatures and a decrease in surface salinity (Lea *et al.* 2003) mark the beginning of the BA interval. Sedimentological data from the Cariaco Basin also record an increase in precipitation associated with the northward migration of the ITCZ (Peterson *et al.* 2000). This warming event marked the

termination of the last glacial period; δ^{18} O values in ice cores show a significant increase (Fig 4.14). A rapid sea level rise of ~20 m in 500 years was caused by Meltwater pulse 1A (MWP 1a) at 13.8 ka BP, sourced from the Laurentide ice sheet (Adams *et al.* 1999). However, recent evidence suggests that melting of the Antarctic ice sheet is needed to reconcile the warming temperatures that are observed during this period (Weaver *et al.* 2003). Hodell *et al.* (2008) suggest the presence of gypsum layers in lowland Central America during MWP 1a indicate drying there.

4.1.6. Younger Dryas (YD) 13-11 ka

The Younger Dryas was a strong cooling event appearing in many records at approximately 11 to 13 ka. For example a dramatic depletion in the GRIP ice δ^{18} O record (Fig 4.10). The Younger Dryas has similarities to Heinrich events and is sometimes referred to as H0 (Fig 4.9). In Lake Petén Itzá, clay deposition ceased and gypsum deposition resumed at 12.8 ka indicating a return to dry conditions (Hodell *et al.* 2008).

A southward shift of the ITCZ during the YD is supported by regional records (Lea *et al.* 2003):

- 1. Lake Titicaca experienced maximum lake levels
- 2. Reduction in meridional SST gradients in the eastern equatorial Pacific
- 3. Modelling studies that suggest melt water input to the North Atlantic and associated thermohaline circulation collapse would be accompanied by a southward ITCZ shift and cooling and drying of the Venezuelan coast.

Cariaco Basin sediments show enrichments in δ^{13} C of C₃₀ and C₃₂ n-alkanoic acids implying dryer conditions and arid grassland dominating the South American vegetation during the YD. At the YD-PB transition, δ^{13} C values depleted rapidly implying a shift from

arid grassland to wet, humid forest. However these changes in tropical vegetation lagged climate shifts in the tropics by several decades (Hughen *et al.* 2004).

4.1.7. Holocene 11 ka - present

A number of rapid, widespread climate changes are recorded in the palaeoclimate record (see Fig 4.10) at the start of the Holocene. In the north Atlantic region, these changes have the same 1500 year periodicity as found for previous glacial periods (Bond *et al.* 1997). At their coldest, sea surface temperatures were 2°C cooler than at the warmest part (Adams *et al.* 1999). A decrease in ¹⁸O/¹⁶O ratios on ostracod shells from the ocean-connected, silled, Lake Miragoane in Haiti, confirms the global change to higher sea levels and regionally, to more humid conditions. The increase in lake levels is attributed to increased precipitation as well as to a rising sea level (Hodell *et al.* 1991).

A sudden cooling event at 8.2 ka brought widespread cooling lasting ~200 years before a return to warm and moister conditions (Adams *et al.* 1999). Records in north Africa and southern Asia at this time show markedly more arid conditions due to a summer monsoon failure (Sirocko *et al.* 1993). Cold and arid conditions also hit northernmost South America, eastern North America and parts of northwest Europe (Alley *et al.* 1997). Drier conditions in central South America existed towards the late Holocene, shown by increased δ^{18} O from Lake Miragoane, indicating higher evaporation. These conditions allowed dry forest communities at Lake Miragoane to become established (Hodell *et al.* 1991).

More recently, the Little Ice Age began in late Medieval times and ended about AD 1650. It may have been the most rapid and largest change in polar circulation during the Holocene according to chemical indicators of wind-blown sea salt in GISP 2 ice core (O'Brien *et al.* 1995).

4.2. Synthesis of history of the Cariaco Basin

4.2.1. Location and Geological setting

The Cariaco Basin is an east-west trending pull-apart basin on the northern continental shelf of Venezuela. The basin covers an area of 17, 760 km² at sea level (Schubert 1982) making it the 2nd largest anoxic marine body in the world behind the Black Sea. The approximate volume of the basin below 180 m is 5.2 x 10¹² m³ (Taylor *et al.* 2001). The basin is formed by right-lateral strike slip between two plates along the Morón-Sebastian-El-Pilar fault system (Fig 4.13), with slip rates of 12–50 mm yr⁻¹, causing a 25-100 km total offset since the basin initiation at 2 Ma (Schubert 1982).



Figure 4.13: Structural interpretation map of the Cariaco Basin which is outlined by the 200 m contour. Indicated are the El Pilar Fault Zone (EPFZ) and Morón Fault Zone (MFZ). A = Araya Peninsula; M = Margarita Island; T = Tortuga (modified after (Schubert 1982).

The Cariaco Basin consists of two sub-basins with maximum water depths of 1400 m separated by a central saddle with a depth of 900 m (Fig 4.14). The northern side of the Cariaco Basin is separated from the open Caribbean Sea by the shallow (<100 m deep) Tortuga Bank. This is bisected by two deep-water channels; the Centinela in the west (146 m) and Tortuga in the north-east (120 m) (Clayton *et al.* 1999). The shallow sill and two channels are key to controlling the sedimentation and hydrography within the basin. To the

south the basin is bounded by the Unare platform which slopes gently northward from the Venezuelan coast. To the east, the basin is bounded by several basement highs including Margarita Island and the Araya Peninsula while to the west is the eastern end of the Coastal Range of the Caribbean Mountains and central Venezuelan borderland (Schubert 1982).

The regional geology of the area around the Unare platform and Cariaco Basin, consists of greenschist facies Mesozoic rocks (gneiss, schist, phyllite, amphibolite, and acid intrusive protoliths) which crop out on Margarita Island; late Tertiary and Pleistocene sediments on Tortuga Island; Cretaceous sandstone and limestone along the southeastern part of Unare bay; and late Tertiary to Holocene sediments in the coastal plains (Schubert 1982). The average sediment thickness in the basin is >1 km with much of the recent sedimentation being fault controlled (Peterson *et al.* 2000).



Figure 4.14: Internal bathymetry of Cariaco Basin showing ODP site 1002 (from (Clayton *et al.* 1999). Arrows indicate location of deep water channels (Centinela - west; Tortuga - north) across Tortuga Bank. Inset map shows the location of the Cariaco Basin on the northern continental margin of Venezuela, South America.

4.2.2. Sources of sediment to the Cariaco Basin

The Cariaco Basin currently lies down-current of two major South American river systems, the Amazon and Orinoco (Fig 4.15). The transport of this fine-grained material to the Cariaco Basin depends on the effect of ocean circulation and sea level on the entrance of coastal currents into the shallow-silled basin, and upon the strength of the Guiana current (Peterson & Haug 2006). Other minor sediment sources include the Lesser Antilles Volcanic Arc and eolian Saharan dust (Clayton *et al.* 1999). Four rivers drain directly into the Cariaco basin, the rivers Neveri, Unare, Tuy and Manzanares (Clayton *et al.* 1999; Peterson & Haug 2006). With the exception of the Manzanares River, which enters the basin at its eastern end where the Unare Platform is at its smallest, the mouths of the other three rivers are currently 50 km or more away from the basin and discharge directly onto the Unare Platform (Fig 4.15).



Figure 4.15: Drawing of Amazon and Orinoco river catchments in South America, and location of four rivers draining into the Cariaco Basin. T = Tuy; U = Unare; N = Neveri; M = Manzanares.

The most important factor in determining the composition of Amazon sediments is relief (Gibbs 1967). In mountainous regions, physical weathering dominates and the clay mineral composition reflects this, in that kaolinite, smectite, and illite are present in similar concentrations (Clayton *et al.* 1999). At the mouth of the Amazon, the clay mineral concentrations are 27 % smectite, 28 % illite, and 36 % kaolinite; 1400 m to the northwest, near the Orinoco delta, the concentrations are 40 % smectite, 18 % illite, and 32 % kaolinite (Gibbs 1977). Physical weathering is more active in the Andes during wetter climatic phases, increasing the contribution of illite and chlorite relative to smectite and kaolinite; during drier periods, the abundance of lowland-derived smectite and kaolinite increases (Debrabant *et al.* 1998). The rate of supply of Amazon mud to the Caribbean during glacial periods has not been quantified but is considered to decrease while still remaining volumetrically significant (Bowles & Fleischer 1985).

Clay minerals of the Orinoco river system are different from those of the Orinoco delta mud; the delta samples have a greater abundance of expandable minerals and the kaolinite: illite ratio is higher (Eisma *et al.* 1978). The river mud composition varies seasonally with illite being much higher during the wet season (Pujos *et al.* 1997). Smectite values obtained for delta samples are similar to those obtained from off the Amazon mouth and this is explained by mixing of Orinoco and Amazon sediments. It is estimated that 80 % of the $< 2 \mu m$ fraction in the Orinoco delta is of Amazon origin (Eisma *et al.* 1978). Parra *et al.* (1997), using isotope evidence, suggest during dry glacial conditions there is a relative increase in the contribution of clay minerals to the Orinoco River from older upland granitic batholiths of the Guiana Shield.

From the Lesser Antilles Volcanic Arc, ~400 km northeast of the Cariaco Basin, high kaolinite concentrations are found in regions of high rainfall, and high smectite

concentrations in the dry regions. In addition the alteration of marine volcanic ash derived from these islands would contribute additional smectite (Beaven & Dumbleton 1966). Higher contribution from a Saharan eolian source might be expected to lead to an increase in kaolinite (Johnson 1979) but kaolinite abundances show no relationship with δ^{18} O values of the Cariaco Basin (Clayton *et al.* 1999). Data from local rivers flowing into the Cariaco Basin is sparse. Clayton *et al.* (1999) report abundant illite-smectite with minor illite and kaolinite; they suggest the abundance of expandable clays being brought into lagoons by local rivers is higher than in Amazon/ Orinoco derived material.

Clayton *et al.* (1999) identified two major sources of the sediment within the Cariaco Basin using differences in clay mineralogy.

- Locally-derived river material which is illite-smectite rich and illite poor. A discharge-load figure for the river Tuy is 12 x 10⁶ tons yr⁻¹ while the Neveri, Unare and Manzanares discharge-load figures are 0.51 x 10⁶ tons yr⁻¹ combined (Milliman & Syvitski 1992).
- Amazon/ Orinoco river system material which is illite-rich and illite-smectite poor. Average annual discharges are 175,000 m³ s⁻¹ (Gibbs 1967) and 17,123 m³ s⁻¹ (Nieto *et al.* 2008) respectively.

The relative contribution of each source to Cariaco sediment is dependent on sea level (Fig 4.16). In high sea level periods (interglacial), the local sediment contribution is trapped on the Unare Platform and the dominant source, by volume, comes from the mixed Amazon/Orinoco source. However, during periods of lower sea level (glacial) the opposite occurs; the basin becomes isolated from the open Caribbean Sea and the width of the Unare Platform will decrease to a few km, allowing sediment from the local rivers to become volumetrically significant. At lower sea levels, the virtual isolation of the Cariaco Basin due to the low-lying sills would increase transport distance of the mixed Amazon/Orinoco sediment to the Cariaco Basin, resulting in a decrease of significance for this sediment source. If sea level was 120 m lower than present day the material could only enter the basin through the Centinela channel. Raising sea level by only 20 m from this lowstand would allow material to enter in both sides of the basin (Clayton *et al.* 1999) (Fig 4.16).



Figure 4.16: Sediment transport pathways (modified after Clayton et al. 1999). Closed and open arrows indicate relatively important and less important transport directions respectively. (a) Interglacial = high sea level; (b) Glacial = low sea level. CB = Cariaco basin.

4.2.3. Cariaco Basin hydrography

The location of the Cariaco Basin means its climate is heavily influenced by the ITCZ. The ITCZ is the region near the equator where the northern and southern trade winds meet (Fig 4.17). Buoyant air movement upward and away from the tropics due to thermal expansion (Hadley cell) reduces the weight of the column of overlying air and produces low surface pressures; water vapour carried by the trade winds contributes to the rising air motion and abundant rainfall along the ITCZ. Seasonal shifts of the Sun between hemispheres affect the location of the ITCZ. It moves northward during the northern hemisphere's summer (June to September) and southward during the southern hemisphere's summer (December to March).



Fig 4.17: Location of ITCZ at the Equator in a region where the northeast and southeast trade winds meet, in an area of low pressure due to upward moving air.

Ocean circulation in the tropical North Atlantic is controlled by seasonal and interannual variations in the trade winds and the position of the ITCZ. These two factors control the amount of upwelling that is generated along the South American coastline. Surface circulation is dominated by the general east-west flow of the Caribbean current which carries equatorial Atlantic water into the Gulf of Mexico and ultimately to the North Atlantic.

Recent studies have demonstrated that the sills at the northern and western edge of the Cariaco Basin exert a key control on the hydrography of the basin (Clayton *et al.* 1999; Peterson *et al.* 2000; Haug *et al.* 1998). Surface water in the basin is generated from upwelled, nutrient-rich, sub-thermocline water which enters over the sill from the Caribbean, whilst the sill restricts horizontal exchange at depth (Haug *et al.* 1998). Migration of the ITCZ gives rise to a two-season cycle which is manifested in the sediments from the Cariaco Basin. Winter and Summer seasons have the following respective oceanographic and atmospheric parameters (Figures 4.18 and 4.19):
Northern Hemisphere Winter

- ITCZ is over or to the south of Equator.
- Strong easterly trade winds (>7 m s⁻¹) result in Ekman drift-induced upwelling of cool nutrient rich waters across the basin (Astor *et al.* 2003).
- Vertical advection is at its strongest raising isotherms by as much as 175 m and average sea surface temperatures (SSTs) drop to 22°.
- Gross production rates within the basin (2–7 g C m⁻² day⁻¹) are 20 times higher than in the open Caribbean (Muller-Karger *et al.* 2001).
- Southward motion of ITCZ triggers the dry season.
- Resultant decrease in local river runoff



Figure 4.18: (Left) Location of ITCZ during winter season (Haug *et al.* 2003). (Right) Atmospheric/ oceanic parameters operating across the Cariaco Basin during winter (Adapted from Haug *et al.* 1998). Mixed layer = the homogenous upper layer of ocean surface water (5-200 m) caused by wind stress. Thermocline = thermally stratified layer of surface water that separates the upper, warmer, less dense zone from the lower, colder, denser zone.

Summer

- ITCZ shifts to the north of the equator, between $6-10^{\circ}$ N.
- Trade winds are weaker (< 6 m s⁻¹) over the Cariaco Basin and coastal upwelling is weakened or largely shut off (Astor *et al.* 2003).
- Sea surface temperatures over the Cariaco Basin warm to 27-28°C.
- Low production rates (< 1 g C m⁻² d⁻¹) (Muller-Karger *et al.* 2001).
- Northward motion of ITCZ triggers the rainy season north of 5°N.
- Local river runoff increases.



Figure 4.19: (a) Location of ITCZ during summer season (Haug *et al.* 2003). (b) Atmospheric/ oceanic parameters operating across the Cariaco Basin during summer (Adapted from Haug *et al.* 1998).

The seasonal change also gives rise to a seasonal cycle in local biota. During the summer-fall rainy season when coastal upwelling is reduced or absent, the stability of the water column is high and level of primary productivity is low. Blue green algae and

dinoflagellates dominate the phytoplankton with diatoms of only minor importance (Peterson *et al.* 1991). Conditions of minimum standing stock over the basin are found to coincide with a more diverse faunal assemblage dominated by *Globigerinoides ruber* and an absence of *Globigerina bulloides* (Peterson *et al.* 1991). During January and February, the portion of the upwelling season when vertical advection is strongest, the initial bloom of diatoms over the Cariaco Basin is closely followed by a nearly monospecific bloom of *G. bulloides*. Maximum foraminifera standing stock in the surface waters are observed at this time (Peterson *et al.* 1991).

4.2.4. Sedimentary record of the Cariaco Basin

The upper Quaternary succession at Site 1002 (Fig 4.14) is generally dominated by terrigenous sediment components with variable biogenic contributions of nannofossils, diatoms, foraminifers (both planktonic and benthic), and pteropods. As there are no bulk changes in major sediment composition the sediments of site 1002 are considered to form one lithologic unit. The succession is sub-divided into eight sub-units based on a repetition of three major lithologies (Fig 4.20). The entire unit is described as olive-grey to greenish-grey nannofossil silty clays with minor, but stratigraphically significant, intervals rich in clays, diatoms, and foraminifers. Small contributions come from sponge spicules, quartz, mica, fish debris, ostracods, molluscan debris, amorphous organic matter and framboidal pyrite (Sigurdsson *et al.* 1997).



Figure 4.20: Stratigraphic column for ODP hole 1002C showing the distribution of laminated intervals (black) and defined lithologic units (1A-1H) (adapted from Clayton *et al.* 1999).

Much of the core is laminated (Fig 4.20) including present day sedimentation. The laminations, where well-developed (e.g. sub-unit 1A), are millimetre to sub-millimetre in thickness and consist of light and dark sediment couplets (Table 4.1). ²¹⁰Pb analyses of the paired couplets confirm their interpretation as annual varves (Hughen *et al.* 1996), reflecting the seasonal alternation between river runoff and upwelling (Haug *et al.* 2001). The couplets are preserved because of the low oxygen environment they were deposited under.

	Winter (Dry)	Summer (Wet)
Colour	Light coloured	Dark colouring
Composition	Diatom and nanofossil rich; high accumulation of opaline and CaCO ₃ tests	Siliciclastic and clay rich material dominates
Dominant source	Biological production	River-run off

Table 4.1: Composition of Cariaco Basin seasonal couplets

4.2.5. Basin processes on interglacial-glacial timescales

Peterson *et al.* (2000) suggest that the long term ventilation history of the Cariaco Basin can be inferred from the variable distribution of laminated and bioturbated intervals in the basin's sedimentary record. The most recent switch from bioturbated (sub unit IB) to laminated sediments (sub unit IA) is correlated with the last glacial-interglacial transition at 14.5 ka by Sigurdsson *et al.* (1997). However, the longer record of anoxia, as indicated by the presence of laminated sediments, is not simply related to glacial-interglacial cycles. Much of the glacial MIS 3-4 is characterised by intervals of laminated sediments, while interglacials MIS 5, 7, and 9 show a clear record of bioturbation. In general, laminated sediments make up much of site 1002 before MIS 9 but are less commonly distributed during MIS 6-9 (Peterson *et al.* 2000). Laminations are generally found at periods of maximum interglacial conditions following a deglaciation.

The laminations deposited currently, and in the recent geological past, are a result of the water column in the basin being anoxic. At present, the transition to anoxic water occurs at 300 m below current sea level. Anoxia develops when the rate of oxygen

consumption exceeds rate of oxygen supply. The presence or absence of anoxic conditions in the marine environment involves complex interactions and balances between biological, chemical, and physical-transport processes (Peterson *et al.* 2000).

When global sea levels are high enough for the thermocline to be above the sill, nutrient-rich water from below the mixed layer of the Caribbean enters the basin (Fig 4.21). Deep circulation in the basin is weak as a result of a strong pycnocline and limited horizontal exchange of deep waters due to the sill. If trade winds are strong enough to cause upwelling, surface productivity is stimulated. The high productivity and increased supply of organic detritus creates an oxygen demand that overwhelms the capacity of the internal basin circulation to ventilate the deep basin. An additional factor controlling the basin circulation is the variation in rainfall associated with the movement of the ITCZ. Increased rainfall will create a lower density surface layer on top of the denser, deep waters, which will enhance the anoxia within the basin.

In contrast, when global sea levels are low, the thermocline is close to or below the sill and only nutrient-depleted water from the Caribbean mixed layer enters the basin (Fig 4.21). Therefore, regardless of the strength of the trade winds and the resultant upwelling across the basin, the surface productivity will be low. This low surface productivity combined with a decreased supply of organic detritus creates less oxygen demand, and the deep basin is able to maintain an oxic water column.



Figure 4.21: Effect of fluctuating sea levels on nutrient cycling, productivity, and oxygen concentrations in the Cariaco Basin (Modified from Haug *et al.* 1998). Diagram is vertically exaggerated relative to the horizontal. Wind direction is represented by crosses in circles.

Studies using Ti and Fe abundances have used changes in Cariaco Basin sediments to suggest the ITCZ has moved its mean position over longer than seasonal timescales. Fe and Ti are used as a simple chemical proxy for the input of land-derived materials and changes in the hydrological cycle (Peterson *et al.* 2006). Higher values reflect increased rainfall, river discharge, and terrigenous sediment delivery to the basin. According to Haug *et al.* (2001), high Ti and Fe values in the early Holocene suggest a more northerly mean position of the ITCZ and its high rainfall belt, relative to the later Holocene. Drier conditions during later Holocene suggest a southward migration of the ITCZ (Haug *et al.* 2001). Peterson & Haug (2006) studied percentage Ti and Fe variations during MIS 3 (26-40 ka) (Fig 4.22). During periods of cooler SSTs, on timescales of the Younger Dryas to

the cold periods of the last glacial, there is a decreased detrital delivery from local rivers suggesting a mean southward shift in the ITCZ position. During interstadials, periods of deglacial warmth, and the Holocene, a mean northward shift of the ITCZ and its associated convective rainfall belt are inferred from the increase in detrital delivery. This pattern mimics the movement of the modern seasonal cycle (Fig 4.18 and 4.19). However, when the Holocene and MIS 3 Ti (%) values are compared, glacial (Ti range = 0.5-0.7 %) Ti input to the Cariaco Basin is at least double that of the Holocene (Ti range = 0.1-0.3 %). The difference is due to lower sea levels during the last glacial (see section 4.2.3).



Figure 4.22: Ti concentrations (%) in Cariaco Basin deposited in ODP Hole 1002C during MIS 3 compared to measured δ^{18} O from ice of the Greenland GISP II ice core (Stuiver & Grootes 2000). Laminated intervals reflect deposition under anoxic conditions. Interstadials (numbered) in the GISP II record are marked by higher Ti concentrations, with the exception of interstadial 6, indicating greater rainfall and higher terrigenous input to the Cariaco Basin (from Peterson *et al.* 2006).

4.2.6. The tectonic influence on Cariaco Basin deposition

Schubert & Valastro (1976) suggest continuous uplift of the Caribbean and Central American region has occurred during the Quaternary. Clayton *et al.* (1999) also suggested uplift, in conjunction with the strike-slip motion, has occurred through progressive movement along the Morón fault zone (Fig 4.13). Using ²³⁰Th/²³⁸U dating and heights of wave-cut notches above current sea level on La Orchilla Island (Fig 4.23) there has been approximately 33 m of uplift over the last 2.5 Ma which is consistent with other estimates across the region (Schubert & Valastro 1976).



Figure 4.23: Location of La Orchilla Island relative to Cariaco Basin (Schubert & Valastro 1976).

The effect of this tectonic uplift is illustrated by modelling variations in water column height above the sill over the past 500 ka. A clear interglacial-glacial cycle is observed in the variation of water column depths above the sill. Interglacial water column depths have stayed relatively constant at ~150 m with MIS 9 and 11 having slightly higher sea levels than present day. In contrast, glacial water column heights appear to have decreased with time and the LGM (~20 ka) is the most extreme sea level low stand (~130 m below present sea level) of the last 500 ka (Waelbroeck *et al.* 2002) (Fig 4.24)



Figure 4.24: Modelled variation of water column depth above the sill in the Cariaco Basin without tectonic uplift (line) and including for tectonic uplift (fill). Water column depths were calculated every 10 ka using: RSL–146 m. [Current water depth to deepest sill is 146 m (Peterson *et al.* 2000)]. Relative Sea Level (RSL) values taken from Waelbroeck *et al.* (2001). RSL was calculated by applying a transfer function to benthic δ^{18} O values from Pacific and North Atlantic ocean cores and using sea level data from corals and other evidence (see Waelbroeck *et al.* (2001) for full details). Shaded/ numbered regions are glacial periods. Rate of tectonic uplift was calculated using two heights of wave-cut notches at 3 and 33 m with Th/U ages of 131 and 2500 ka (Schubert & Valestro 1976). Amount of uplift was then added to the RSL estimate.

As tectonic uplift of the region took place, the depth of the sill relative to the sea surface during each glacial decreased, resulting in the LGM having the smallest water column. This variation in water column height has important consequences for basin productivity and water column processes. The height of the water column over the sill controls nutrient availability, whether the water column becomes anoxic or oxic, and the overall connectivity of the basin to the global ocean (see section 4.2.5). The connectivity of the Cariaco Basin to the global ocean will be considered in the following section as this is crucial to our hypothesis of establishing if the selenium isotope ratios measured in the Cariaco Basin represent a global signal.

4.3. Cariaco Basin as part of the global ocean system

With any new palaeoredox proxy the ability of that new proxy to show global variations is very valuable. Molybdenum isotopes provide information about changes in oxygenation and metal cycling in ancient oceans on a global scale (Anbar & Rouxel 2007). This study aims to realise the potential of selenium isotopes to act as a global palaeoredox proxy. In order to begin this process, the ability of the Cariaco Basin to record global signals must be assessed. To accomplish this, the Cariaco Basin δ^{18} O record will be compared to two global stacked δ^{18} O records, currently used in the literature.

4.3.1. SPECMAP δ180 record

SPECMAP (Imbrie 1984) is a composite proxy record spanning the last 750 ka covering 5 North Atlantic sites. The sites were chosen from open-ocean sites in low- and mid-latitudes that accumulated relatively rapidly and at depths unaffected by dissolution. The study was limited to mixed layer foraminifera with four cores based on *Globigerinoides sacculifer*, and one using *Globigerina bulloides*. Each of the five cores were normalised to have zero mean and the same standard deviation, superimposed, sampled, and averaged at intervals of 1 ka, and then smoothed with a 9-point Gaussian filter. (Imbrie *et al.* 1984) (Fig 4.25).



Figure 4.25: Comparison of the SPECMAP δ^{18} O curve of Imbrie *et al.* (1984) and the Cariaco Basin δ^{18} O curve of Peterson *et al.* (2000). Shaded and numbered regions represent glacial intervals.

The Cariaco Basin δ^{18} O curve closely follows the global SPECMAP curve but with a smaller amplitude, likely the result of muted temperature variations around the equator. SPECMAP δ^{18} O values are a function of three processes: (1) global ice volume changes (estimated at between 0.9 – 1.2‰); (2) temperature; (3) salinity (Fig 4.26). The glacialinterglacial amplitude of δ^{18} O in the Cariaco Basin is approximately 2.2‰. After accounting for the global ice volume, the remaining ~ 1‰ is either attributed to temperature or salinity effects. Alkenone temperature estimates (Herbert & Schuffert 2000) (Fig 4.34) show little change in temperature within the Cariaco Basin. Therefore, the 1‰ remainder in the δ^{18} O signal either equates to an approximate 2‰ increase in salinity, using standard salinity δ^{18} O correlations (Craig & Gordon, 1965), or to a reduction of local surface run-off (Peterson *et al.* 2000) (Figure 4.26).



Figure 4.26: Factors contributing to SPECMAP, Cariaco Basin and LR04 δ^{18} O records. The overall glacial-interglacial amplitude of the Cariaco Basin record is 2.2‰. Of this, 1.2‰ is attributed to meltwater addition during deglaciation (Fairbanks 1989). The remaining 1‰ is due to changes in salinity. LR04 glacial-interglacial amplitude is ~2‰; however, the stack cannot accurately address the relative contributions of individual components. SPECMAP is controlled by temperature changes whereas the control of the Cariaco Basin record is salinity.

Higher salinities during sea level lowstands is also shown by the dominance of the salinity-tolerant foraminifera species *G. ruber* in Cariaco Basin sediments during the last glacial (Peterson *et al.* 1991). Higher salinities during glacials could result from:

- 1. Physical isolation of the Cariaco Basin from open ocean water
- Regional reductions in rainfall as ITCZ failed to advance as far north as it does today
- Decreased freshwater input into the Cariaco Basin from local tributaries and major South American river systems, e.g. Amazon and Orinoco (Herbert & Schuffert 2000)

4.3.2. LR04 δ^{18} O record (Lisiecki & Raymo 2005)

(Lisiecki & Raymo 2005) produced a detailed 5.3 Ma record of δ^{18} O from 57 globally distributed sites, known as the "LR04" stack (Figure 4.27). The sites are well distributed in latitude, longitude, and depth, predominantly in the Atlantic and Pacific oceans with two sites in the Indian ocean. Most of the δ^{18} O measurements in these records are from benthic foraminifera species *Uvigerina peregrina* or *Cibicidoides wuellerstorfi*.

Seven high-resolution δ^{18} O records spanning different time periods of the last 5.3 Ma were spliced together. Each δ^{18} O record is first aligned to these targets in the depth domain to create 7 short stacks which are then spliced together to form a transitional stack spanning the last 5.3 Ma. The transitional stack's time domain is divided into small, equally spaced intervals (ranging from 1-5 ka) and an average is taken of all the δ^{18} O measurements lying within each interval (number of data points per interval ranged from 15.5-30.6) (Lisiecki & Raymo 2005). Therefore each point in the final LR04 stacked record is an average of all the δ^{18} O data which fell within each particular time interval. No adjustments were made to the variance and mean of the records, except to make species offset corrections, the isotope curves were not adjusted based on their bottom water temperatures because the temperature differences between the sites may have changed dramatically over the last 5.3 Ma, and the records were not weighted based on their spatial distribution (Lisiecki & Raymo 2005).

The LR04 stack reconstructs the average δ^{18} O signal of each marine isotope stage and substage within the Pliocene and Pleistocene. The LR04 δ^{18} O record for the last 500 ka is shown in figure 4.30. The maximum δ^{18} O value of the stack is 5.08 ± 0.11‰ at 433 ka (MIS 12) (Fig 4.27) while the minimum is 2.65 ± 0.15‰ at 5.135 Ma.



Figure 4.27: Comparison of "LR04" stacked δ^{18} O record (Lisiecki & Raymo 2005) against Cariaco Basin δ^{18} O (Peterson *et al.* 2000). Numbered shaded areas represent glacial intervals.

Comparing the LR04 stack to Cariaco Basin δ^{18} O records (Fig. 4.27) and the SPECMAP δ^{18} O record (Fig. 4.25) the amplitude of the glacial-interglacial differences is larger for these latter records due to the analysis of planktonic rather than benthic foraminifera. The LR04 and SPECMAP stacks are quite similar back to 625 ka, with the planktonic SPECMAP stack having more variance in the eccentricity and precession bands and less in obliquity (Lisiecki & Raymo 2005). Lisiecki & Raymo (2005) argue that benthic δ^{18} O records produce a better stack than planktonic records because the deep ocean is more uniform in temperature and salinity than surface water. However, the Cariaco Basin does not include a temperature component in its δ^{18} O record (Fig 4.26), implying any deviations between its record and the LR04 record are salinity controlled.

4.3.3. Deviations of Cariaco Basin $\delta^{18}O$ record from SPECMAP $\delta^{18}O$ record

Although the SPECMAP and Cariaco Basin δ^{18} O records are closely matched, there are two interesting time periods where there is a significant deviation of the Cariaco Basin record from the global record. The first of these occurs during the most recent glacial-interglacial transition, MIS 2-1, at approximately 14.5 ka (Fig 4.28).



Figure 4.28: MIS 2-1 boundary in SPECMAP. Core V30-40 (Imbrie *et al.* 1984) and Cariaco Basin (Peterson *et al.* 2000) δ^{18} O records. MIS 2 is indicated by the shaded area. YD = Younger Dryas.

The SPECMAP and V30-40 (only core with appropriate resolution) records show a more gradual change in δ^{18} O during the deglaciation compared to the sudden change recorded in the Cariaco Basin curve. The ~1‰ shift to lighter δ^{18} O values in the Cariaco Basin record occurs at ~11.5 ka. However, the abrupt sedimentological change from bioturbated to laminated sediments within the basin, indicating a change from oxic to anoxic water column conditions, occurs at 14.5 ka, 3,000 years earlier. Mo/Al data (Lyons *et al.* 2003) confirm the change in water column conditions at 14.5 ka. Therefore conflicting evidence regarding the timing of the MIS 2-1 boundary exists. A decrease in the δ^{18} O does occur at 13.9 ka soon after the transition, and might be a residual effect of MWP

1a, a possible cause of the large sea level rise associated with this boundary. The lack of a MWP 1a signal in the SPECMAP record is probably a result of the smoothing and averaging techniques undertaken to produce the record. An increase in δ^{18} O coinciding with the Younger Dryas stadial then extends from 13 ka to 11.5 ka. The Younger Dryas is a period of increased upwelling intensity within the basin (Lin *et al.* 1997) confirmed by the merging of δ^{18} O values analysed on both deep and shallow-dwelling foraminifera (Figure 4.29). This merging of δ^{18} O signals suggests mixing of deep and shallow water masses reducing the overall SST, and increasing the δ^{18} O.



Figure 4.29: δ^{18} O for three foraminifera species (Lin *et al.* 1997): (a) shallow dwelling *Globigerina bulloides, Globigerinoides ruber* (white), and the sub-thermocline dwelling *Neoglobigerina dutertrei.* Global ice volume curve from Fairbanks (1989). Shaded areas represent Younger Dryas stadial (11-10 ¹⁴C ka) and MIS 2 (28-12.6 ¹⁴C ka). Last glacialinterglacial transition is at 12.6 14C ka. Samples are a composite of cores PL07-39PC and PL07-43PC from the Cariaco Basin.

The second difference between δ^{18} O of SPECMAP and the δ^{18} O of the Cariaco Basin exists at ~120 ka (Figure 4.30).



Figure 4.30: SPECMAP (Imbrie *et al.* 1984), Cariaco Basin (Peterson *et al.* 2000), V22-174, and V30-40 δ^{18} O records for the 100-200 ka. V22-174 was an Atlantic ocean core used in making the SPECMAP record of Imbrie *et al.* (1984).

SPECMAP shows a decrease in δ^{18} O caused by decreasing global ice volume and warming surface temperatures. In contrast, the Cariaco basin record shows an initial decrease in δ^{18} O values, similar to SPECMAP, followed by an increase in δ^{18} O within the warm interval. Production of a heavier δ^{18} O signal requires a decrease in temperature or increase in salinity. Local cooling cannot be discounted but an increase in salinity due to higher aridity offers a better explanation. Al/Ti data (Yarincik *et al.* 2000), a proxy for aridity, show an increase in the aridity at this time.

Despite these deviations, the Cariaco Basin δ^{18} O record over the last 500 ka displays a similar profile to the SPECMAP (Fig 4.28) and LR04 (Fig 4.30) δ^{18} O records. These similarities therefore illustrate that the Cariaco Basin is well-connected with the global ocean throughout the last 500 ka. In future comparisons within this thesis, the SPECMAP δ^{18} O record will be used as the global record because the foraminifera used to make the record are planktonic, the same as the Cariaco Basin record.

Chapter 5: Geochemistry of the Cariaco Basin

5.1. Introduction

The aims of this chapter are to:

- Describe the chemical characteristics of the water column within the Cariaco Basin
- Review the existing geochemical data for sediments in the Cariaco Basin and the information gained about past oceanographic and climatic conditions of the basin.

Understanding the present geochemical behaviour of the Cariaco Basin provides a context for interpretation of past geochemistry and its controlling factors via various proxies. Current measurements of global climate, geochemical analyses of the water column and of the sediments all provide a basis for understanding the present basin oceanography. To identify and understand the processes that have taken place in the past, there is only indirect information from climate proxies and direct analysis of the sediments available. Therefore a good understanding of the present water column is necessary to produce an accurate geochemical model for the past Cariaco Basin (Fig 5.1).



Figure 5.1: Information available for identifying current processes occurring within the Cariaco Basin water column (left) and information available to identify past processes (right). Solid arrows represent flows of information from each reservoir to the other reservoirs. Dashed arrow symbolises information on current water column processes which can be used to suggest similar processes occurring in the past.

5.2. Chemical parameters of Cariaco Basin water column

5.2.1. Data source

The data used here to describe the chemistry of the Cariaco Basin water column were collected as part of the cooperative US-Venezuelan Carbon Retention in a Colored Ocean (CARIACO) programme. This programme consists of monthly Joint Global Ocean Flux Study-style productivity cruises and seasonal process cruises, continuous meteorological and remote sensing, and sediment flux measurements from an array of moored sediment traps. The CARIACO time-series station is located in the eastern subbasin in nearly 1400 m of water (10.5°N, 64.66°W). All results presented in the first part of this chapter are from this single site. The data are available at

http://www.imars.usf.edu/CAR/index.html.

5.2.2. Oxygen, salinity, temperature

Changes in redox conditions within a marine setting can be traced by understanding changes in the relative distributions of oxidising agents across a depositional gradient (Tribovillard *et al.* 2006). A redox grading has been developed which describes oxygen conditions at the sediment-water interface (Tyson & Pearson 1991). Oxic regions typically have greater than 2 mL O_2/L H₂O while suboxic regions are characterised by between 2–0.2 mL O_2/L H₂O. When O_2 levels decrease to less than 0.2 mL O_2/L H₂O but there is no free H₂S in the water column, the waters are termed anoxic. Euxinic conditions exist only when free H₂S is present in the water column and is usually restricted to semi-enclosed basins like the Black Sea and the Cariaco Basin (Tribovillard *et al.* 2006).

Euxinic water column conditions currently exist in the Cariaco Basin below ~300 m where dissolved H₂S concentrations steadily increase from zero to 30 μ g-at L⁻¹ just above the sediment-water interface (Fig 5.2A). The zone where O₂ decreases to zero and H₂S increases is known as the redox transition zone (RTZ), the thickness of which has fluctuated between 50-200 m (1982-1997) (Scranton *et al.* 2001).

The dissolved oxygen maximum and minimum values are the same all year round (Fig 5.2B). The only difference between the two seasons is the speed at which oxygen decreases in the upper 100 m of the water column. Between June-October (summer) oxygen decreases at a constant gradient; however, between December-May (winter) dissolved oxygen concentration decreases at a steeper gradient due to the large characteristic seasonal phytoplankton bloom (see chapter 4.2).



Figure 5.2: (A) Dissolved O₂ and H₂S profiles in the Cariaco Basin (measured 16th January, 1970) (Richards 1975). (B) Dissolved O₂ profile measured in 2007 on cruises 130-140 to Sta. CARIACO. This data are the most recent dissolved oxygen concentrations from the CARIACO site. No data were taken for January and November. Data are available from http://www.imars.usf.edu/CAR/index.html.

Salinity and temperature within the Cariaco Basin water column are nearly constant below 200 m (Fig 5.3A and B). In the upper 200 m of the water column, temperature increases towards the surface but the gradient depends on the season (Fig 5.3B) with lower sea surface temperatures observed during the winter (December-May). Seasonal differences in salinity also exist within the upper 200 m: between December and May, salinity increases slightly below the water surface before decreasing gradually to constant deeper values; between June and October, salinity increases to a peak at ~100 m before decreasing to constant deeper values. The salinity of the entire Cariaco Basin water column is within the range of average Atlantic Ocean salinities (33-37 psu) (Chester 2000).



Figure 5.3: 2007 (A) Salinity and (B) Temperature profiles from Sta. CARIACO. This is the most recent available salinity and temperature data from CARIACO. No data was taken for January and November. Data are available from <u>http://www.imars.usf.edu/CAR/index.html</u>.

The surface temperature difference is a result of the increased upwelling which mixes cold, deep, water with the warm, surface, water (see chapter 4.2) during the winter season (December-May). The lower salinity values between June-November, compared to between December-May, are surprising given the surface temperatures are ~3°C higher than between December and May. Between June and November, there is increased surface run-off from local rivers, which dilutes the surface waters. In contrast, increased upwelling between December-May brings denser, deep water to the surface.

5.2.3. Carbon

Annual primary production is estimated at between 540-600 g C m⁻² yr⁻¹ depending on the strength of short-lived upwelling events. This is significantly higher than reported from outside of the Cariaco Basin (200-400 g C m⁻² yr⁻¹) (Muller-Karger

et al. 2001). Monthly primary production, when integrated over the top 100 m of the water column, changes substantially with the seasons. High primary productivity is concurrent with the upwelling season (December-May) while lower productivity is associated with the rainy season (June-November) (Table 5.1). However, a secondary annual summer upwelling event has been identified during June-July for the period 2004-2006 when average annual production was lower at ~440 g C m⁻² yr⁻¹. Its occurrence has been linked to the seasonal increases in the cyclonic curl of the wind in the southern Caribbean and a concurrent increased frequency of anticyclonic eddies in the Venezuelan Basin (Rueda *et al. in prep*).

Table 5.1: 2004 seasonal average integrated primary production (0-100 m) and organic C fluxes in the Cariaco Basin water column. Data are from http://www.imars.usf.edu/CAR/index.html.

		December-May	June-November
Integrated primary production (0-100 m) (g C m ⁻³ day ⁻¹)		0.41	0.21
	225 m	0.09 ^a	0.06
Organia C Elux $(a C m^{-2} d^{-1})$	410 m	0.09	0.04
Organic C Flux (g C m d)	810 m	0.06^{b}	0.04
	1210 m	0.05	0.02

^aNo data is available for April 2004

^bNo data is available for the period between January-April 2004

Most of the particulate organic carbon produced in the upper 100 m of the water column is re-mineralised in the oxygen rich surface waters. However, a fraction does remain un-grazed and sinks through the water column, generating a flux of particles between the surface and the deep basin (Fig 5.4). It is this flux of decomposing sinking material, combined with restricted lateral movement of water due to the sills and the slow turnover of basin waters, which makes the Cariaco Basin permanently anoxic below ~250 m.



Figure 5.4: 2004 seasonal differences in particulate organic carbon (POC) concentration profiles measured at Sta. CARIACO. Data are from http://www.imars.usf.edu/CAR/index.html.

The vertical flux of organic carbon measured with the sediment traps follows a regular pattern of lower values during the rainy summer season (June-November) and higher values during the dry winter season (December-May) (Table 5.1; Fig 5.5). The magnitude of this flux tends to decrease with increasing water depth. Thunell *et al.* (2000) measured carbon fluxes at 275 m to be on average 5.6% of the integrated primary production and this flux decreases to ~5% at 455 m. However, between February-April when surface production is at its highest, the carbon flux can be essentially the same at both 275 and 455 m (between 6-7%) and in 25% of trap observations, the organic carbon flux to the 455 m trap exceeded that delivered to the 275 m trap (Thunell *et al.* 2000). The average carbon flux decreases to ~2.8% at 930 m, and to ~1. % at 1225 m (Thunell *et al.* 2000). The sediment trap and primary productivity observations suggest that between 10-11 g C m⁻² yr⁻¹ are delivered to the bottom sediment with a burial efficiency¹ of 40-60 % (Thunell *et al.* 2000).

¹ Proportion of carbon which reaches the seafloor that is subsequently incorporated into the sediment

Anoxic basins are considered to be sites of enhanced carbon preservation (Demaison & Moore 1980). However, the observed Cariaco Basin organic carbon fluxes are in excellent agreement with predicted fluxes determined using the (Pace *et al.* 1987) model which was developed using observations from an open, oxygenated ocean environment. The similarities with the results from the Pace *et al.* (1987) model suggest that organic matter degradation in the anoxic Cariaco Basin is as efficient as that occurring in well-oxygenated waters. The relatively high organic C burial rate and water column degradation within the Cariaco Basin suggests that anoxia alone is not the primary mechanism for accumulation of organic carbon-rich sediments in the ocean (Thunell *et al.* 2000).



Figure 5.5: 2004 integrated primary production (0-100m) and organic carbon fluxes at four depths through the water column from Sta. CARIACO. Missing bars represent no available data. Data is from <u>http://www.imars.usf.edu/CAR/index.html</u>.

The water column of the Cariaco Basin supports a highly stratified microbial assemblage of prokaryotes, protozoa, and viruses, all with maximum abundances in the top 50 m of the water column (Taylor et al. 2006). These abundances then decrease to \sim 20% of the surface values by 100 m and remain relatively constant through the remainder of the water column (Fig 5.6A). Interestingly, there is no significant difference in bacterial abundances between the two seasons. Heterotrophic production is high (>5.5 μ g C L⁻¹ d⁻¹) in the upper 100 m of the water column and then decreases quickly to $<0.1 \ \mu g \ C \ L^{-1} \ d^{-1}$ by 330 m (Fig 5.6B). Within the RTZ heterotrophic activity is greater than that which can be sustained by sinking organic matter from the mixed layer alone. Therefore another organic matter source is required; high rates of dark dissolved organic carbon assimilation by chemoautotrophic bacteria have been measured between 275-400 m, equivalent to 10-333% of estimated primary production (Taylor et al. 2001) (Fig 5.6B). According to Taylor et al. (2001), these high rates of dark dissolved organic carbon assimilation suggest the existence of a secondary microbial food web in the RTZ. This is fuelled by chemoautotrophic production and can potentially supply a second source of labile, chemically unique, biogenic debris to the sediments of the Cariaco Basin (Taylor et al. 2001).



Figure 5.6: (A) Summary of total prokaryotic abundances (bacteria and archaea). Samples were collected monthly during 2004; (B) Summary of heterotrophic prokaryotic productivity collected on 18^{th} May 2004 (for detailed methodologies see Taylor et al. 2001, 2006). Grey box and dashed line show current RTZ and O₂-H₂S interface positions. Data are from <u>http://www.imars.usf.edu/CAR/index.html</u>

5.2.4. Nutrient and trace metal profiles

Since the anoxic-oxic interface in the water column is a region of vigorous carbon cycling, this section focuses on the effect this carbon cycling has on the nutrient and trace metal profiles (Figs 5.7 and 5.8). Fixed nitrogen, mostly as NO₃⁻, is very low in the near surface waters and then increases steadily to a maximum value of 12 μ M at 200 m due to nitrification. Other important species of fixed nitrogen (NH₄⁺ and NO₂⁻) are at relatively constant concentrations of < 1.0 μ M at surface waters (Fig 5.7). Between 200-300 m, all three forms of fixed nitrogen quickly decrease to zero due to anammox² reactions taking place in the water column by some variant of the following reaction (Piper & Calvert 2009):

² Abbreviation of **An**aerobic **Amm**onium **Ox**idation, a stage in the nitrogen cycle where nitrite and ammonium are converted to dinitrogen gas.

$$3.33NH_4^+ + 2NO_2^- + 0.66HCO_3^- + 0.33CaCO_3 = 2.66N_2 + CH_2O + 0.33Ca^{2+} + 6H_2O^{-1}$$

Below 300 m, NO₃⁻ and NO₂⁻ concentrations are at zero while ammonium concentrations gradually increase reaching a maximum of ~25 μ M in the deep waters (Fig 5.7). The distributions of NH₄⁺, NO₂⁻, and NO₃⁻ suggest that dissimilatory nitrogen cycling is consistently operative in the upper layer of the water column and might account for some of the observed chemoautotrophy. The nitrogen speciation suggests that nitrifying bacteria are active between 25-75 m. The shallow NO₂⁻peak may be indicative of NH₄⁺ oxidation, while in situ oxidation of NO₂⁻ contributes to NO₃⁻ accumulation in water between 25-200 m, and phytoplankton assimilation accounts for total depletion in shallower waters (Taylor *et al.* 2001).



Figure 5.7: 2004 monthly dissolved nutrient profiles measured at Sta. CARIACO. Monthly values are averaged into six month periods. Erroneous April measurements are not included. Dashed line indicates current position of O_2 - H_2S interface. Shaded region indicates RTZ. Data are from http://www.imars.usf.edu/CAR/index.html



Figure 5.8: Depth profiles of selected trace elements in the Cariaco Basin. Colour coding represents water column oxygen conditions: blue (oxic), yellow (sub-oxic), and green (anoxic). Compiling previous data - see Piper & Calvert (2009) for sources. Plot taken from Piper & Calvert (2009).

Phosphate and silicic acid have low concentrations at the surface and then gradually increase with depth to maxima of 5 and 95 μ M respectively (Fig 5.7). Phytoplankton utilise nutrients such as phosphate and silicate in the euphotic zone because as they grow they extract these trace elements from the water, thus leading to their depletion in these surface waters. As the organisms die and sink, they undergo oxidative decay, during which there is regeneration of the nutrients and the trace elements go back into solution (Chester 2000).

The dissolved Fe and Mn profiles feature low surface concentrations which then increase rapidly over the O_2 -H₂S interface to maxima at ~400 m and ~500 m respectively, before decreasing slightly with depth but still maintaining greater concentrations than surface levels (Fig 5.8A). Particulate Fe also has low surface concentrations, but at and below the O_2 -H₂S interface the concentration slowly increases with depth to a maximum of 25 nmol L^{-1} (Fig 5.8A). Particulate Mn concentrations are at zero for the upper 200 m and then rapidly increase to a maximum of 34 nmol L^{-1} at the O₂-H₂S interface and then returns to almost zero by 400 m where it remains at those levels through the lower water column (Fig 5.8B). Dissolved Mo and V both have similar patterns to each other above the O₂-H₂S interface where the concentrations are relatively constant until the interface. Dissolved Cd is slightly different to Mo and V due to its affinity for organic matter - it is depleted at the surface and increases in concentration towards the O₂-H₂S interface. Below the interface, the concentrations of all three metals drop quickly and remain constant throughout the water column. This is in contrast to Ni where concentrations are between 2-3 nmol L^{-1} throughout the entire water column, regardless of the changing conditions (Fig 5.8B and C).

Taylor *et al.* (2001) suggest that the Mn and Fe distributions are consistent with the hypothesis that these metals serve as "redox shuttles", where the dissolved reduced

metals (Mn^{2+} and Fe^{2+}) diffuse up to oxic waters and rapidly oxidise abiotically, forming colloids and particulates (MnO_2 and $Fe(OH)_3$). Newly-formed particulates sink back to the RTZ and are biologically reduced through dissimilatory respiration by bacteria, then diffuse back up to the interface for re-oxidation. This mechanism allows for deeper and faster penetration of oxidant into the RTZ and repetitive cycling of the same redox pairs (Taylor *et al.* 2001). The maxima in the dissolved Mn and Fe profiles at ~300 m coincides with the O₂-H₂S transition and is present because of the reductive dissolution of metal oxides sinking into the anoxic water (Jacobs *et al.* 1987) where Fe³⁺ and Mn⁴⁺ are reduced to Fe²⁺ and Mn²⁺ respectively. The particulate Fe distribution near the surface is complicated by a high lithogenous contribution.

The Ni profile in the Cariaco Basin indicates no response to the onset of anoxia within the water column (Fig 5.8B). Depletion of this trace nutrient in the photic zone, but is not observed because only 10 % of the Ni available to phytoplankton is utilised. The uniform concentration of Ni in the bottom water of the basin also illustrates that there is little input of Ni into the sediment from the water column (Piper & Calvert 2009). In contrast, the Cd profile reflects its uptake in the photic zone by phytoplankton (90% of available Cd is taken up by phytoplankton), remineralisation below the photic zone of the organic matter, and its additional removal from the bottom water as a hydrogenous fraction (Piper & Calvert 2009). Relatively higher Mo and V concentrations in the surface waters are because both metals are only weakly bio-reactive. The decreasing concentrations through the suboxic zone to mimima in the anoxic zone are because both metals are strongly redox reactive (Piper & Calvert 2009).

A surprising feature of the chemoautotrophic activity in the Cariaco Basin is that a significant proportion of dissolved carbon assimilation takes place in a dark, low O_2 environment (Fig 5.2 and 5.6), suggesting the bacterial populations use terminal

electron acceptors other than O_2 . The peak of chemoautotrophic production at ~300 m (Fig 5.6) coincides with the disappearance of NO_3^- (Fig 5.7) and particulate Mn and Fe, as well as enrichments of dissolved Mn and Fe (Fig 5.8). Taylor *et al.* (2001) conducted stimulation experiments, confirmed by Madrid (2000), which suggested that chemoautotrophic communities are dominated by bacteria capable of oxidising thiosulphate, sulphide, and capable of facultative respiration of Fe, Mn and NO_3^- (dentrifiers). Heterotrophs which require organic matter for growth but also assimilate CO_2 at the expense of $S_2O_3^{2-}$ may play a role in energy flow and S-cycling, and facultative anaerobes capable of reducing sulphite, thiosulphate, and tetrathionite to sulphide using low-molecular weight fatty acids may also be present (Taylor *et al.* 2001). Assimilation of Se as a nutrient will occur in this zone of production just like within the zone of photosynthetic production near the water surface.

The data presented illustrate that a simple one-dimensional vertical model of carbon flux with depth, in which export production purely from the photic zone is progressively decomposed and becomes increasingly energy depleted and is capable of supporting diminishing biomasses (e.g. Pace *et al.* 1987) is not applicable to the Cariaco Basin. Instead, the Cariaco Basin water column supports a secondary bacterial chemoautotrophic production within the RTZ which contributes significantly to overall biological productivity and controls elemental cycling across the oxic-anoxic interface.

5.3. Chemical oceanography of the sediments within the Cariaco Basin

5.3.1. Theory of sedimentary chemical proxies

To identify the processes which took place in the Cariaco Basin over the last 500 ka, trace elements are used as proxies for reconstructing the palaeoredox conditions. Trace elements in seawater exist in either a soluble form or adsorbed onto particles. Removal from the water to sediment is split into biotic and abiotic processes. Biotic processes encompass the uptake of trace elements that serve as micro-nutrients for plankton. Abiotic uptake processes are relatively limited in oxic conditions but in suboxic environments some enrichment may occur through diffusion of trace elements from the water column across the sediment-water interface, or through remobilisation and repartitioning along redox gradients within the sediments (Tribovillard et al. 2006). Abiotic processes are particularly efficient under reducing conditions such as adsorption of metals onto organic or mineral substrates, formation of organometallic complexes, and precipitation of (iron)sulphides and/or insoluble oxyhydroxides (Tribovillard et al. 2006). Trace elements are also efficiently concentrated through redox cycling of Fe and Mn. Under reducing conditions the following abiotic processes are particularly efficient: (1) adsorption of metallic ions or ionic species onto organic or mineral substrates; (2) formation of organo-metallic complexes; (3) precipitation of (iron) sulphides and insoluble oxy-hydroxides (Tribovillard et al. 2006).

Concentrations of redox-active elements in marine sediments are controlled by the following (Yarincik *et al.* 2000b):

- 1. Variations in the oxygenation of the water column
- 2. Oxygenation of the bottom water, including the top 1-2 cm of the sediment
- 3. Concentration of the given elements in biogenic sources

4. Portion of the detrital inventory that is refractory

Certain trace metals such as Ag, Cd, Cr, Cu, Mo, Ni, U, and V are all removed from seawater under suboxic and/or anoxic bottom water conditions. These fall into two categories:

- Metals that are readily fixed in solid phases under sub-oxic conditions, e.g. Cr, Re, U and V without the requirement for the presence of dissolved sulphide.
- Metals that are fixed under highly reducing conditions, e.g. Ag, Cr, Cd, Mo, Ni, Zn.

This behavioural difference can be used to distinguish between sub-oxic and anoxic sedimentary environments (Calvert & Pedersen 2007). A sub-oxic environment will see an enrichment of type 1 relative to type 2, and therefore a higher ratio. An anoxic environment will see a lower ratio as both groups of metals are precipitating out of the water column. A typical ratio used to distinguish between these two environments is Re/Mo. Re is not associated with the authigenic oxide phases but is strongly removed under sub-oxic conditions. Mo is adsorbed onto Mn-oxyhydroxides under oxic conditions and is removed to anoxic sediments at high dissolved HS⁻ levels.

5.3.2. The recent glacial-interglacial transition

Various geochemical tracers (Table 5.2) have been measured on Cariaco Basin samples across the most recent glacial-interglacial boundary. Trace element profiles are normalised to Al, to remove any effects of dilution by planktonic carbonate and silica components, so the metals can be studied relative to the terrigenous inventory (Yarincik *et al.* 2000b). Multiple redox-sensitive elements, including metals that respond differently to the redox state of the system, enable researchers to isolate the effects of bottom water oxygenation; other proxies reveal changes in source material, physical and
chemical weathering rates, relative basin isolation and processes of pyrite formation occurring within the basin (Fig 5.10).

Total Al values range between 3.78-11.1 wt %, total Fe values are in the range of 1.91-5.18 wt %, and pyrite S values range between 0.06 - 3.24 wt % (Fig 5.9, 5.10). The lower 4 m of the core 1002A/B are characterised by continuous decreasing Al concentrations upwards across the transition from 11.1 to 3.8 wt %. Upwards from ~ 4.3 m the Al concentration remains relatively constant with an average of 6.1 ± 0.33 (RSD = 5%) (Fig 5.9). Over the laminated interval average total Fe is 2.99 ± 0.56 (RSD = 19%) while over the bioturbated unit average total Fe is 4.49 ± 0.57 wt % (RSD = 13%). The concentration decrease in the lower 4 m of the core is shown in both Fe and Al profiles, at a relatively constant Fe/Al ratio of 0.50 ± 0.03 (1 σ). This is likely to reflect either a decrease in the detrital (riverine) input of both metals or increased dilution by non-detrital (biogenic components) (Fig 5.9). The upper 7.3 m has a relatively constant pyrite S values averaging 2.16 ± 0.40 (RSD = 18%) with a sharp decrease occurring below 7.3 m, the limit of sulphide diffusion (see below) (Fig 5.10). This is a post-depositional feature caused by downward diffusion of sulphide from the reducing sediments into the underlying oxic sediments (Lyons *et al.* 2003).



Figure 5.9: Total Fe and Al concentrations across the last glacial-interglacial transition from core 1002A/B. Data are from Lyons *et al.* (2003). Between 8.0–6.5 mbsf the sediment is bioturbated, between 6.5–4.2 mbsf the sediment is distinctly laminated, and between 4.2–0 mbsf the sediment is laminated.

Figure 5.10 (next page): Downcore profiles for a number of geochemical proxies across the recent glacial - interglacial boundary from various cores in the Cariaco Basin. The glacial-interglacial boundary is at 650 cmbsf (14.5 ka) and is indicated by the solid black line. Younger Dryas stadial indicated by the dashed box between 420-550 cmbsf. Mn/Al, Fe/Al, Mo/Al, V/Al, and TOC from (Yarincik *et al.* 2000b). Al/Ti, K/Al and terrigenous (%) are from hole 1002C from (Yarincik *et al.* 2000a). δ^{18} O (‰) are measured on *G. ruber* (white morphotype) of hole 1002C (Peterson *et al.* 2000). ^{187/188}Os are from hole 1002C (Oxburgh *et al.* 2007). δ^{34} S_(pyrite), S_{pyrite}, and laminated intervals are from hole 1002A measured by Lyons *et al.* (2003).



Table 5.2: Description of the geochemical tracers used in figure 5.10 measured across the
last glacial-interglacial transition within the Cariaco Basin.

Proxy	Explanation
Fe/Al and	Fe and Mn are more soluble in their reduced states and therefore their
Mn/Al	concentrations in bulk sediment should be lower during periods of water column
	anoxia. However, formation of syngenetic and diagenetic phases such as pyrite
	complicates this interpretation (Yarincik et al. 2000b).
Mo/Al and	The solubility of Mo and V decreases in the reduced state. As a result, both are
V/Al	enriched in sediments that are deposited during periods of anoxia and depleted
	during periods of bottom water oxygenation (Yarincik et al. 2000b).
Al/Ti	Used to understand variations in wind-blown and hemipelagic sources of
	deposition. Al/Ti variations are caused by concentration changes of rutile (TiO ₂)
	and the seasonal shifting of the ITCZ which changes the trade wind strength
	(Balsam <i>et al.</i> 1995).
K/Al	Proxy for the illite/ kaolinite ratio which identifies the source of weathered
	matter being deposited. Illite is a weathering product in temperate/ arid climates
	where physical weathering dominates; kaolinite is a product of chemical
	weathering in tropical, humid climates (Yarincik et al. 2000a).
%	Terrigenous matter, an indicator of continentally-derived material, was
terrigenous	calculated using a Ti-based normative calculation of (Murray & Leinen 1996):
	% terrigenou s = $\frac{i_{sample}}{100}$
^{187/188} Os	Provide information on the history of chemical weathering intensity in the
	Cariaco Basin. There is a large contrast in the isotopic composition between Os
	derived from continental weathering ($^{18//188}$ Os ~1.5) and that from seafloor
	alteration of peridotites (~0.12-0.13) and dissolution of micrometeoritic dust
	(~ 0.12) . Assuming the latter two remain constant, then the ratios in the
	sediments will reflect changes in the global continental weathering flux
	(Oxburgh <i>et al</i> . 2007).
S _(pyrite) and	Identify the mechanisms of pyrite formation and provide a measure of basin
$\delta^{34}S_{(pyrite)}$	isolation respectively (Lyons <i>et al.</i> 2003). $S_{(pyrite)}$ data represents total reduced
	inorganic sulphur (TRIS) which includes pyrite S, acid-volatile S, and elemental
	S). However, TRIS was assumed to represent almost entirely pyrite S (Lyons <i>et</i>
- 15	<i>al.</i> 2003).
δ ¹⁵ N	Illustrates the importance of N_2 fixation and, indirectly, denitrification through
	its effect on the nitrate budget as described in Haug <i>et al.</i> (1998). The $\delta^{13}N$ of
	newly fixed nitrogen is ~ 0‰, close to the isotopic composition of N_2 in air
	(Haug <i>et al.</i> 1998).
TOC and	Both proxies represent changes in productivity derived from active upwelling of
CaCO ₃	nutrient-rich waters, controlled by sea level fluctuations on glacial-interglacial
	timescales (Peterson et al. 2000).

At 650 cmbsf, the character of the sediments changes from bioturbated to distinctly laminated and there are changes in the geochemical proxies (Fig 5.10). Mo/Al and V/Al ratios increase abruptly across the glacial-interglacial boundary. During the glacial period, the Mo/Al and V/Al ratios are low, as are the TOC values; however, the two profiles are not highly correlated. During the interglacial period, higher element/Al ratios track TOC with a very strong positive correlation. Mn/Al and Fe/Al ratios are slightly elevated in the bioturbated sediments compared to the laminated sediments. Al/Ti, K/Al, and ^{187/188}Os ratios all increase across the boundary while % terrigenous sediment content decreases at the same point. Finally, S_(py) values show an abrupt increase at ~730 cm and the $\delta^{34}S_{(py)}$ ratios before this point fluctuate between -20 and +16‰. Between 730-650 cm, a fall from 3 wt% to 2 wt% in S_(py) values occurs while $\delta^{34}S_{(py)}$ ratios decrease from ~-10‰ to ~-32‰. At 650 cm and above, both S_(py) and $\delta^{34}S_{(py)}$ remain relatively constant at ~2 wt% and -32‰ respectively.

The bioturbated-laminated boundary reflects increased nutrient fluxes and increased productivity upwards, which creates a larger oxygen demand within the water column (Yarincik *et al.* 2000b). The change from bioturbated to laminated sediments occurred because the water column changed from oxic to anoxic, as shown by the trace elements proxies. Mn is more labile than Fe during anoxic conditions and is dissolved from the bottom sediment. It diffuses into the overlying anoxic water column, leaving the sediment depleted. Fe behaves in a similar manner but is not as sensitive because of the strong tendency for it to be retained as FeS₂ and its greater detrital inventory. Because of a higher seawater concentration and its higher sensitivity, Mo records stronger enrichments than V during anoxic conditions and is therefore more useful for bottom water oxygenation studies (Piper 1994). The Fe and Mn profiles are not linked simply to depositional redox in the overlying water column or to organic matter

availability (Lyons & Berner 1992). Comparatively, Mo and V enrichments are intimately coupled to organic matter availability, especially in the presence of high HS⁻ concentrations found in an anoxic water column (Yarincik *et al.* 2000b).

The rise in sea level associated with the worldwide deglaciation at this time is confirmed by the $\delta^{34}S_{(py)}$ trend. Below 730 cm, the positive $\delta^{34}S$ values are a result of sulphate reduction occurring within a restricted pore-water reservoir and indicate the Cariaco Basin became isolated (Lyons et al. 2003; Werne et al. 2003). The periodic negative δ^{34} S excursions reflect "open system" behaviour in terms of balance between sulphate consumption and availability/ replenishment and indicate the basin underwent brief periods of increased connectivity with the open ocean (Lyons et al. 2003). Pyrite formation is C_{org} -limited as indicated by the low S_{py} concentrations (Lyons *et al.* 2003). A "sulphide-diffusion" zone (730-650 cm) was created because of the abrupt juxtaposition of sediments with very different chemical properties. Excess HS⁻ diffused out of the water column and Corg-rich sediments into the underlying oxic layer and reacted with Fe (III) oxide phases, forming diagenetic pyrite. The upwards decreasing $\delta^{34}S_{py}$ indicates a diffusion gradient existed at this time; light $\delta^{34}S$ from anoxic water column mixed with heavy δ^{34} S from the restricted basin. At the redox boundary (650 cm), the $\delta^{34}S_{(py)}$ values are at a steady value of -32‰, the composition of the modern day Cariaco Basin water column. The steady state values continue up core and indicate SO_4^{2-} is continuously replenished as a result of the higher sea levels and syngenetic³ pyrite formation is dominating (Lyons et al. 2003).

The material reaching the bottom of the Cariaco Basin is dominated by lithogenic material but is also rich in opal, carbonate and organic material (Thunell *et al.* 2000). Changes in the source of the Cariaco Basin sediments are illustrated by Al/Ti, %

³ A primary sedimentary feature formed contemporaneously with sediment deposition

terrigenous matter, and K/Al profile changes. The Al/Ti of the Cariaco Basin sediments illustrates a Ti-rich signature compared to average upper crustal values (Taylor & McLennan 1985) throughout this time interval (Fig 5.10). Sediments are further enriched during the glacial period because of an increased contribution of Ti-rich northern Saharan African dust (Ganor 1991). More Ti-rich aeolian material is created due to grain size fractionation which reflects wind strength changes and flux changes associated with variations in aridity and source area. Increased influence from local rivers during the last glacial is shown by higher % terrigenous content and a decrease in the K/Al ratio (local material is kaolinite-rich) (Yarincik et al. 2000a). Hemipelagic input from local Venezuelan rivers is more significant in the Cariaco Basin during glacials, since it is the only source region with a direct pathway into the basin during times of increased basin isolation caused by lowered sea levels. In contrast, during the interglacial, less eolian material is transported across the Atlantic, and the Al/Ti ratio is less affected by the Ti-rich Saharan inputs (Yarincik et al. 2000a). An increase in the K/Al ratio represents a relative reduction in local river inputs due to the opening of the two channels which allows sediment from other source regions to enter the basin.

Less radiogenic ^{187/188}Os values are observed during glacials (Fig 5.10) and are interpreted as representing a decrease in either the flux or the ^{187/188}Os ratio of Os derived from the more radiogenic continental source (Oxburgh *et al.* 2007). This is in contrast to the K/Al and % terrigenous matter profiles. However, the ^{187/188}Os profile is advocated, by the authors, as representing a global signal due to the similarity of the Os signal to the LR04 stacked δ^{18} O curve and global climate variations (Oxburgh *et al.* 2007). Therefore, the difference might be due to the scale they represent with the K/Al and % terrigenous profiles a locally-derived signal. The global nature of the Os signal is represented by the effect of temperature and aridity on it (Oxburgh *et al.* 2007). Lower

temperatures exist when large ice sheets are present. Their presence would decrease the surface area of continental crust available for weathering and expose only less radiogenic continental material. As the ice sheets wane, more radiogenic high-shield rocks (Peucker-Ehrenbrink 1996) are exposed and eroded providing an easily leachable source of radiogenic Os to the oceans, driving the ^{187/188}Os ratio to higher values during the interglacial. Aridity is another parameter and this is supported by a suggested correlation (Oxburgh *et al.* 2007) between the Os isotope data and the dust concentration of Antarctic ice (Petit *et al.* 1999). There is a strong relationship between water flux and weathering yield (Berner & Berner 1996) and thus reduced chemical weathering during arid periods leads to reduced continental weathering rates and reduced fluxes of radiogenic Os to the oceans Oxburgh *et al.* (2007).

A second feature of a majority of the proxies is observed between 420-550 cm (Fig 5.10). This depth corresponds to the Younger Dryas stadial (Lyons *et al.* 2003); proxies indicate it is a period of lower temperatures until 450 cm (δ^{18} O), stronger trade winds bringing an increase in the rutile flux from the Saharan-region (Al/Ti), and a lower redox potential but not as low as that of full glacial periods (Mo/Al and V/Al). The C_{org} values drop within this interval which is contradictory to the conclusions reached with other proxies- that the Younger Dryas was in fact a time of increased productivity (Werne *et al.* 2000; Lyons *et al.* 2003). However, when dilution effects caused by terrestrial inputs and biogenic materials (Werne *et al.* 2003) are accounted for and an accumulation rate, is higher during the Younger Dryas than the rest of the Holocene (Werne *et al.* 2000). If the redox potential of the water column has decreased, then the drop in C_{org} could also a result of increased re-mineralisation. The K/Al and % terrigenous contents do not return to glacial levels during the Younger Dryas and

actually reach their maximum and minimum levels respectively. This is because a drop in sea level did not occur during the Younger Dryas, so the size of the local riverine input relative to other sediment sources remained low.

5.3.3. Interglacial-glacial variations between 100-500 ka

The second set of samples used in this study cover the period of 100-500 ka, which spans the last 4 glacial-interglacial cycles (MIS 5-12). Similar geochemical proxies to those previously described have been measured and described to interpret the history of the Cariaco Basin (Table 5.2). The long term ventilation history can be inferred from the variable distribution of laminated and bioturbated intervals (Fig. 5.11).

Figure 5.11 (next page): Geochemical proxies from the Cariaco Basin over the period 100-500 ka from core 1002C. Fe/Al, Mn/Al, Mo/Al, and V/Al ratios (Yarincik *et al.* 2000b); Al/Ti, K/Al, and % terrigenous matter (Yarincik *et al.* 2000a); δ^{18} O, % TOC and % CaCO₃ of Peterson *et al.* (2000); Laminations taken from Sigurdsson *et al.* (1997). Shaded areas represent glacial intervals 6, 8, 10, and 12 downcore. Non-shaded intervals represent interaglacial intervals 5, 7, 9, and 11 downcore.





Values for Mn/Al in the Cariaco Basin range from 0.0023 to 0.0115,

significantly less than that of PAAS (Post Archean Average Shale) (~0.0085) (Taylor & McLennan 1985) while values for Fe/Al are in the range of 0.37 to 0.68, generally greater than PAAS (~0.43) (Taylor & McLennan 1985). Sedimentary Mn/Al and Fe/Al proxies are both comparatively higher during glacial periods. Values for Mo/Al range from below the detection limit (0.0003) to 0.0026, while V/Al values range from 0.0015 to 0.0037 and both data sets are generally greater than their respective PAAS values (Taylor & McLennan 1985) (Fig 5.11).

Yarincik *et al.* (2000b) undertook cross-spectral analyses of metal/Al ratios against the δ^{18} O record. Strong relationships exist between δ^{18} O and the Mo/Al and Mn/Al records at the 100 and 41 kyr Milankovitch frequencies. Both Fe/Al and V/Al show weaker relationships with δ^{18} O; the retention of reactive Fe as iron sulphide under anoxic conditions (Yarincik *et al.* 2000b) and higher concentrations of refractory Fe (Yarincik *et al.* 2000b) and V (Emerson & Huested 1991) in terrigenous matter are suggested as likely causes. At higher frequencies (41 kyr, 23 kyr, and 19 kyr), the relationships between redox metal/Al ratios and δ^{18} O are less clear; an exception is Mo/Al exhibiting a strong coherence at the 23 kyr frequency (Yarincik *et al.* 2000b). Spectral similarities between the δ^{18} O and TOC records (Fig 5.11) show TOC is coherent with negative δ^{18} O at 100 and 41 kyr frequencies; therefore, TOC does increase during interglacial periods and is dominantly controlled by sea level changes (Yarincik *et al.* 2000b).

Yarincik *et al.* (2000b) conclude these strong relationships at the lower frequencies indicate oxygenation state of the Cariaco Basin is varying in concert with the global climate state; in contrast, the lack of relationships at the higher frequencies indicate that other processes are operating to regulate the distribution of redox-sensitive

metals. Possible processes might include provenance changes, which would affect Fe and V records especially, or local diagenetic redistribution of trace elements, which would be more important over short stratigraphic distances which are statistically sampled by the higher frequency cross-spectral analysis (Yarincik *et al.* 2000b).

Al/Ti and K/Al ratios range from 17.5-23.5 and 0.16-0.26 respectively (Fig 5.11). Both proxies show a strong relationship at low Milankovitch frequencies with the δ^{18} O record, being significantly higher during interglacial periods and lower during glacials. K/Al also shows a strong relationship with CaCO₃ compared to Al/Ti. Peterson *et al.* (1991) suggest CaCO₃ production is controlled by variations in nutrient supply, which is regulated by sea level changes. Production is minimised during lowstands owing to advection of nutrient-poor waters into the Cariaco Basin. It is therefore likely that K/Al variations are also responding to sea level change.

Other factors affected by sea level change are nutrient supply, N/P balances, and the importance of N_2 -fixation to the nitrogen cycle in the Cariaco Basin (Fig 5.12).



Figure 5.12: δ^{18} O *G. ruber*, δ^{15} N and % TOC (from Haug *et al*. 1998) of core 1002C in the Cariaco Basin for the last 600 ka. Interglacial stages are numbered.

TOC and δ^{15} N records show a strong relationship with the *G. ruber* δ^{18} O record. Interglacial periods are characterised by low δ^{15} N; values vary between 2 and 3.2‰ compared to heavier values in the range of 5-6‰ which typify glacial periods. Interglacial TOC contents range from 3 wt.% during MIS 5, 7, 9, and 13 to 5 wt.% in stages 1 and 11. Glacial TOC contents are as low as 0.1-1 wt.%. Correlations between the δ^{18} O and TOC records confirm that the variation in sea level combined with the specific topography of the Cariaco Basin alters export productivity in the area.

The parallel bulk sediment δ^{15} N variations suggest coincident changes in the nutrient cycling of the Cariaco Basin and indicate large glacial-interglacial variations in N₂ fixation with higher rates during interglacials. (Haug *et al.* 1998) suggest N₂ fixation responds to glacial-interglacial changes in the [NO₃]/[PO₄] ratio of nutrient supply to Cariaco surface waters driven by changes in the dentrification rate. During periods of anoxia, denitrification takes place removing nitrate from thermocline depths resulting in a deficit of nitrate relative to phosphate. This deficit encourages N₂ fixing cyanobacteria to consume the excess available phosphate; N₂ fixation leads to the low δ^{15} N values in sinking organic matter observed during interglacial periods. When surface productivity is lower, e.g. lower sea levels, the water column remains oxic and denitrification does not take place. This does not create a nitrate deficit and the N:P ratio remains close to the Redfield ratio of 16:1. N₂ fixation is discouraged and the sinking organic matter has a δ^{15} N close to the source material of ~5‰.

Relatively constant alkenone $(U^{k'}_{37})$ temperature reconstructions over the last 160 ka are a result of the basin bathymetry, latitudinal position, and global sea level changes (Herbert & Schuffert 2000). The mean palaeotemperature estimate for the entire alkenone record is 24.8°C, ranging from a high of 27.3°C during MIS 5e to lows of between 21-22°C during brief intervals across the MIS 2-1 transition and during MIS

3-5. MIS 3, 4 and substages 5a-c contain high frequency swings in estimate temperatures with some estimates greater than modern values juxtaposed with intervals as cold as 21°C. The LGM and MIS 6 show very little cooling from Holocene and MIS 5e respectively (Herbert & Schuffert 2000) (Fig 5.13).



Figure 5.13: Alkenone unsaturation estimates of SST for the lat 160 ka (Herbert & Schuffert 2000). Numbered and shaded regions correspond to glacial intervals

During glacial intervals, sea level is reduced and the Cariaco Basin becomes relatively isolated from the open ocean due to the sills on the north and west sides of the basin. Lateral movement of water is restricted and only waters from the warmer mixedlayer can be imported. With a relatively high insolation at its latitude of 10°N, and few mechanisms to reduce its SST, the Cariaco Basin may have been buffered to glacialinterglacial temperature variations. During interglacials when sea levels were generally higher, (e.g. MIS 3-5C), and when sea level increased quickly, [e.g. the glacialinterglacial transition at ~130 ka (MIS 6-5) and at ~15 ka (MIS 2-1)], SST's are lower than modern day. A deeper water column over the sills will have existed at this time and increased the basin's connection with the open ocean. Colder water would then enter the basin lowering the SST compared to modern day temperatures (Herbert & Schuffert 2000).

Chapter 6: Se in the Cariaco Basin (ODP Leg 165)

6.1. Introduction

This chapter reports Se concentrations and $\delta^{82/76}$ Se ratios on sediments from the Cariaco Basin across the last glacial-interglacial boundary and through four previous glacial-interglacial cycles (MIS 5-12). These new Se measurements will be interpreted in the context of existing data previously described in Chapters 4 and 5. The chapter will conclude with a discussion concerning the hypothesis of whether Se can be used as a palaeoredox proxy and the extent to which the signal recorded is global in scale.

6.2. Sample information

The samples are from Ocean Drilling Programme (ODP) core 1002, drilled as part of Leg 165; a site adjacent to Deep Sea Drilling Programme (DSDP) Site 147 (Fig 4.14). Site 1002 is located on the western edge of the central saddle in the Cariaco Basin. The site is positioned on a flat, well-stratified sediment package at a water depth of 893 m (Sigurdsson *et al.* 1997). A total of five holes (A-E) were drilled, two of which were dedicated mudline cores taken for geochemical studies (A and B), and three more taken for high-resolution palaeoclimatic reconstructions (C-E) (Sigurdsson *et al.* 1997).

6.2.1. Depth-age relationship for site 1002

The depth-age model was constructed by Peterson *et al.* (2000) who compared site 1002 and SPECMAP δ^{18} O records in the orbital bands of precession and obliquity; both records are well matched at these scales. Biostratigraphic datums were also used to constrain the δ^{18} O stratigraphy [Table 2 in (Peterson *et al.* 2000)]. This age model

indicates a basal age of Site 1002 of ~580 ka yielding an average sedimentation rate over the last 500 ka of 280 m Ma^{-1} (Fig 6.1) (Peterson *et al.* 2000).



Figure 6.1: Age-depth relationship for Hole 1002C derived from the correlation of its δ 18O record to the SPECMAP stack (Peterson *et al.* 2000).

The locations of the five holes drilled as part of site 1002 are close enough to each other to not significantly vary the depths at which unit boundaries occur. For example, the boundary between unit IB and IA, corresponding to the last glacialinterglacial transition, is at 6.5 mbsf in hole A and 6.43 mbsf in hole C. This ~1% difference is equivalent to ~120 years which is not deemed large enough to be corrected for when applying the depth-age relationship for hole C to samples from hole A.

6.2.2. Sample locations for the last 18 ka

The cores were collected by advanced hydraulic piston coring (APC) with recovered lengths of 9.77 and 6.24 m for holes 1002A and 1002B respectively. This resulted in the redox transition at ~14.5 ka being successfully retrieved in core 1002A (Sigurdsson *et al.* 1997). In contrast, the mudline was recovered in core 1002B but the core was of insufficient length to penetrate the redox transition. Geochemical records of the two cores were spliced together using magnetic susceptibility records (Lyons *et al.* 2003).

The laminated sediments of the upper 6.5 m belong to subunit IA while the bioturbated sediments below 6.5 m belong to subunit IB (Fig 4.20). This abrupt change of sediment has been dated at 12.6^{14} C ka BP using conventional radiocarbon techniques on bulk carbonate (Peterson *et al.* 1991). Lin *et al.* (1997) confirmed the change from bioturbated to laminated sediments at between 12.6 and 12.75¹⁴C ka using accelerator mass spectrometry on mono-specific samples of *Globigerina bulloides*. In both studies ages were reservoir corrected by subtracting 420 years from each measured date. (Lyons *et al.* 2003) estimate the age of this boundary at ~14.5 calendar ka BP.

A high resolution set of 27 samples were obtained from holes 1002A and B, which have been studied previously (Lyons *et al.* 2003; Werne *et al.* 2003), to encompass the last glacial-interglacial transition in the Cariaco Basin (Table 6.1; Fig 6.2). Each sample is a depth interval of 5 cm which yields a temporal sampling resolution of 60 to 120 years.

Sample ID ¹	mbsf ²	Age $(ka)^3$	Colour ⁴	Redox state	Unit ⁴	MIS ⁵
B-1-15-20	0.175	0.38				
B-1-75-80	0.775	1.72				
B-2-5-10	1.575	3.59				
B-2-80-85	2.325	5.39				
B-3-40-45	3.425	8.04				
B-3-80-85	3.825	8.98				
B-3-120-125	4.225	9.91				
B-4-40-50	4.925	11.46				
B-4-60-65	5.125	11.89	Dark aliva grav	Anovio	TA	1
B-4-80-85	5.325	12.30	Dark onve grey	Alloxic	IA	1
B-4-100-105	5.525	12.71				
B-4-120-125	5.725	13.11				
B-4-140-145	5.925	13.49				
A-4-50-55	6.025	13.68				
A-4-70-75	6.225	14.04				
A-4-80-85	6.325	14.22				
A-4-85-90	6.375	14.31				
A-4-90-95	6.425	14.40				
A-4-110-115	6.625	14.74				
A-4-125-130	6.775	14.98				
A-4-140-145	6.925	15.22	Light grey to light greenish grey			
A-5-10-15	7.125	15.52				
A-5-25-30	7.275	15.74		Oxic	IB	2
A-5-35-40	7.375	15.87				
A-5-55-60	7.575	16.14	Yellowish brown to light reddish			
A-5-65-70	7.675	16.26	brown			
A-5-75-80	7.775	16.38				

Table 6.1: Details for the 27 samples obtained from holes 1002 A and B (Leg 165) for the last glacial-interglacial transition.

¹Sample identification using standard ODP notation of Hole-Section-Top-Bottom. Each hole is split into sections of 1.5 m in length. For example sample B-4-100-105 is from hole B, section 4 which starts at a depth of 4.5 m, and is taken at 100-105 cm along section 4 which equals a depth of 5.50-5.55 m. Core 1002A over-penetrated by ~0.7 m below the seafloor which resulted in depths of core A being greater than expected when using this notation. ²Depths are the mid-point of each 5 cm interval.

³No published ages exist for these samples. The ages are calculated at mid-point depth using a third order polynomial best-fit through the age-depth data from Peterson *et al.* (2000). ⁴Taken from lithological descriptions of Sigurdsson *et al.* (1997) and figure 4.20. ⁵Marine Isotope Stage.



Figure 6.2: Location of 27 sediment samples from site 1002, holes A and B (filled circles). The last glacial-interglacial transition is at 6.5 mbsf where the sediment changes from bioturbated to laminated. Black circles are at mid-depth and grey boxes indicate the depth range of each sample.

Because of the change in global climate which characterises this period (see section 4.4), and the accompanying clear change in redox conditions, sampling was particularly intensive (~1 sample every 10 cm) across the glacial-interglacial boundary. The zone between 6.5 and 7.3 m within the bioturbated sediment is a zone where downward diffusion of sulphide altered the composition of the underlying, initially oxic sediments (Lyons *et al.* 2003).

6.2.3. Sample locations for four glacial-interglacial cycles (MIS 5-12)

The cores were collected by APC with recovered lengths of 185.5 m and 120.4 m for holes 1002C and 1002D respectively. Much of core 9h from hole C was disturbed during core recovery. To avoid including samples from this disturbed interval (~76 to

84.4 mbsf), samples were instead taken from hole 1002D and spliced into the sequence from hole 1002C (Peterson *et al.* 2000). A low resolution set of 16 samples spanning 100-500 ka from holes C and D were obtained to investigate the effect of alternating glacial-interglacial conditions on the behaviour of Se in the Cariaco Basin (Table 6.2; Fig 6.3). Sub-samples of 2 cm were used; this yields a temporal sampling resolution between 24 and 168 years.

Table 6.2: Details for the 16 samples obtained for the four glacial-interglacial cycles (MIS 5-12)

Sample ID ¹	mbsf ²	Age $(ka)^3$	Colour ⁴	Unit ⁴	MIS
C-5h-3-113-115	41.03	106.01	Oliva grav to light aliva grav	IC	
C-5h-4-113-115	42.60	112.26		IC.	5
C-5h-6-113-115	45.60	124.24	olive grey	ID	
C-6h-2-56-58	47.23	133.54			
C-6h-3-101-103	49.18	141.23			6
C-6h-5-55-57	51.72	151.30			
C-8h-5-17-19	70.62	193.37	(deal) are easily areas	IE	7
D-9h-5-12-14	77.00	229.04	(dark) greenish gray	IE	/
D-10h-3-117-119	83.94	267.26			0
C-10h-2-24-26	85.45	276.66			0
C-11h-2-93-95	95.06	330.22			9
C-11h-6-96-98	101.45	339.95	Light bluish grey and pale brown interbedded layers	IG	10
C-12h-3-124-126	107.29	358.60			10
C-13h-4-28-30	117.29	403.54			11
C-14h-2-35-37	123.35	437.90	Olive green to olive grey in colour	IH	10
C-14h-4-126-128	127.26	463.25			12

¹Sample identification using standard ODP notation of Hole-Core-Section-Top-Bottom. Each core is split into sections of 1.5 m in length. For example sample C-5h-3-113-115 is from hole C, core 5h which according to core logs (Sigurdsson *et al.* 1997) represents 36.9-46.4 m, section 3 of core 5h which starts at 39.9 m, and is taken at 113-115 cm along section 3 which equals a depth of 41.03-41.05 m.

²Depths are the top of each sample.

³Values taken from (Yarincik *et al.* 2000a).

⁴Taken from lithological descriptions of Sigurdsson *et al.* (1997) and figure 4.20



Figure 6.3: Location of samples from site 1002 holes C and D, through four recent glacialinterglacial cycles (MIS 5-12). The distribution of laminated intervals and MIS is illustrated. Glacial periods are shaded and indicated by even numbers. Crosses are at top depth of each sample interval.

6.3. Se concentrations in the Cariaco Basin

6.3.1. The last glacial-interglacial transition

Se concentrations over the last glacial-interglacial transition range from a minimum 0.51 ppm at 15.74 ka to a maximum 11.30 ppm at 8.04 ka (Table 6.3). In the bioturbated unit (16.38-14.74 ka), Se concentrations range from 0.51 to 6.67 ppm, averaging 0.83 ± 0.43 ppm (Table 6.4; Fig 6.4a) excluding the anomalously high Se concentration of 6.67 ppm at 15.22 ka. In contrast, Se concentrations in the laminated unit (14.40-0.38 ka) range from 1.06 to 11.3 ppm and are mostly higher than Se concentrations within the bioturbated unit (Table 6.4; Fig 6.4a). Within the laminated unit, there is an anomalously high Se concentration of 11.3 ppm at 8.04 ka and the Younger Dryas is represented by anomalously low Se concentrations of 2.86 and 1.06 ppm at 11.89 and 12.71 ka respectively (Table 6.3; Fig 6.4a).

Sample ID	Age (ka)	Depth (m)	Se (ppm)	$\delta^{82/76}$ Se (‰)	$\pm 2 se \delta^{82/76} se (\%)$
B1-15-20	0.38	0.175	6.64	0.19	0.05
B1-75-80	1.72	0.775	7.68	0.10	0.08
B2-5-10	3.59	1.575	4.83	0.35	0.07
B2-80-85	5.39	2.325	5.77	0.30	0.11
B3-40-45	8.04	3.425	11.3	0.17	0.07
B3-80-85	8.98	3.825	7.15	0.13	0.16
B3-120-125	9.91	4.225	7.43	-0.39	0.10
B4-40-50	11.46	4.925	3.79	0.56	0.07
B4-60-65	11.89	5.125	2.86	0.77	0.07
B4-80-85	12.30	5.325	4.21	-0.25	0.06
B4-100-105	12.71	5.525	1.06	-0.43	0.08
B4-120-125	13.11	5.725	6.16	-0.32	0.07
B4-140-145	13.49	5.925	8.70	-0.20	0.06
A-4-50-55	13.68	6.025	6.95	0.04	0.06
A-4-70-75	14.04	6.225	4.88	-0.10	0.06
A-4-80-85	14.22	6.325	6.87	-0.45	0.04
A-4-85-90	14.31	6.375	7.80	0.36	0.05
A-4-90-95	14.40	6.425	5.91	0.24	0.08
A-4-110-115	14.74	6.625	1.40	0.24	0.07
A-4-125-130	14.98	6.775	1.61	-0.59	0.07
A-4-140-150	15.22	6.925	6.67	-0.36	0.04
A-5-10-15	15.52	7.125	0.53	0.22	0.09
A-5-25-30	15.74	7.275	0.51	-1.05	0.18
A-5-35-40	15.87	7.375	0.78	-0.82	0.05
A-5-55-60	16.14	7.575	0.71	-0.21	0.04
A-5-65-70	16.26	7.675	0.53	-1.06	0.03
A-5-75-80	16.38	7.775	0.58	0.23	0.15

Table 6.3: Se concentrations (ppm) and $\delta^{82/76}$ Se across the last glacial-interglacial transition, where the change from bioturbated to laminated sediment occurs (dotted line).

Table 6.4: Statistical data for Se concentrations in the laminated and bioturbated units.

	Laminated	Bioturbated ¹
Mean Se concentration (ppm)	6.11	0.83
1σ _{n-1}	2.32	0.43
Maximum Se concentration (ppm)	11.3	6.67
Minimum Se concentration (ppm)	1.06	0.51

¹Excluding the anomalously high concentration of 6.67 at 15.22 ka

Normalising the Se concentrations to Al removes dilution effects from biogenic silica and $CaCO_3$ (Yarincik *et al.* 2000a) and allows enrichment factors to be calculated by comparing Se/Al ratios with those of other suitable reservoirs. It is not possible to calculate Se/Al ratios and Se enrichments for all the samples listed in table 6.3 because secondary Al data (Lyons *et al.* 2003) were used, and Al concentrations were not

measured in all the samples in that study. Using an average continental crust Se/Al ratio of 0.01 ppm/wt % metal oxide (Gao *et al.* 2004), the Se enrichment factors across the entire last glacial-interglacial transition vary from 5 to 131 (Fig 6.4b). Immediately below the glacial-interglacial boundary, Se is enriched 18 x relative to continental crust. In older samples, Se is less enriched relative to continental crust with values between 5 and 7. The exception is the large Se enrichment at 15.22 ka which corresponds to the anomalously large Se concentration of this age. Within the laminated interval all samples are enriched relative to the continental crust, with the enrichment factors varying between 22 x and 171 x (Fig 6.4b). The low enrichment at 12.71 ka coincides with the start of the Younger Dryas. The Se/Al ratios closely mimic the profile for Se concentrations (Fig 6.4a) because the Al concentrations within the laminated interval are relatively constant (Fig 6.5) and the fluctuating Se concentration is the dominant control over the Se/Al ratios.

The variability in the Se enrichments within the laminated unit possibly implies the processes causing the enrichments have themselves been changeable, over a time period when the Cariaco Basin is thought to have remained constantly anoxic. Se enrichments occur in marine sediments through three processes - adsorption to Fe and Mn particulates, bound in sulphides, and incorporation within organic matter (see chapter 2). If Se was dominantly adsorbed to particulates within the water column, this might be demonstrated by a relationship with Fe (Fig 6.4 c). In contrast, if Se was dominantly incorporated into sulphides, this might be illustrated by a relationship with S (Fig 6.4 d). Finally, if Se was dominantly incorporated into organic matter, this might be shown by a relationship with organic C (Fig 6.4 e).



Figure 6.4: Behaviour of Se over the last glacial-interglacial transition (14.5 ka) (a) Se and Organic C concentrations, (b) Se/Al ratio (top) and Se enrichment factor (Gao *et al.* 2004) (bottom), (c) Se/Fe ratio, (d) Se:S ratio, (e) Se/ org C ratio. Total Al, total Fe, organic C, and total S values are from (Lyons *et al.* 2003).

The Se/Fe and Se/S profiles (Fig 6.4c and d) are similar to the Se concentration and Se/Al profiles (Fig 6.4a and b) because Fe and S concentrations are relatively constant (Fig 6.5), with the exception of low S concentrations in the oldest sediments. Within the laminated interval, the Se/Fe and Se/S profiles have maximum values at ~8 and 13.5 ka; minimum values within the laminated unit occur at 12.71 ka. Within the bioturbated zone the Se/Fe and Se/S profiles decrease to their lowest values with the exception of the anomalous sample at 15.22 ka. The limit of sulphide diffusion coincides with the large increase in the Se/S ratio at 15.87 ka. Samples from older strata have Se/S ratios greater than those within the sulphide diffusion zone, and similar to those of the laminated sediments.

In contrast, the total Se/C_{org} profile (Fig 6.4e) is not similar to the Se concentration profile (Fig 6.4a). Relatively constant Se/C_{org} ratios (mean ~2.2 x 10^{-5}) characterise the laminated unit. The bioturbated unit has higher ratios (mean ~3.6 x 10^{-5}) that are somewhat more variable (Fig 6.4e). Two anomalous Se/C_{org} ratios are present - one anomalously low ratio in the laminated unit at 12.71 ka and one anomalously high ratio in the bioturbated unit at 15.22 ka.



Figure 6.5: Total Al, Fe and pyrite S concentrations (wt %) across the last glacial-interglacial transition (data from (Lyons *et al.* 2003). Dashed line represents limit of sulphide diffusion zone.

Further insight into the dominant process causing Se enrichment in the Cariaco Basin sediments can be achieved by investigating the interrelations between the four individual components. Cross plots (Fig. 6.6) and ternary composition diagrams (Fig. 6.7) illustrate the relationships between total Se-C_{org}-Fe-S in the Cariaco Basin across the last glacial-interglacial transition. Absolute concentrations are illustrated in the cross-plots while the ternary diagrams emphasise the relative concentrations and ratios so that the relationships among the three variables are independent of dilution effects by biogenic silica and CaCO₃ (Dean & Arthur 1989).



Figure 6.6: Cross plot relationships between total Se-Fe-S-Organic C. Laminated (interglacial) samples are represented by filled circles and bioturbated (glacial) samples are represented by open squares. S, Fe and organic C data from (Lyons *et al.* 2003) and Se concentrations measured as part of this study. The shaded areas indicate approximately where the majority of samples are distributed. Circles highlight anomalous samples which are referred to in the text.



Figure 6.7: Ternary diagrams (A-C) illustrating relationships between Fe-C_{org}-S-total Se. Laminated (interglacial) samples are represented by filled circles and bioturbated (glacial) samples are represented by open squares. S, Fe and organic C data from (Lyons *et al.* 2003) and Se concentrations measured as part of this study. Axis ticks represent 10% intervals.

A strong positive correlation exists between total Fe and total S at a gradient of 0.51 for samples within both the laminated and bioturbated units (Fig 6.6). The exception to this is the sample at 15.87 ka which is S-depleted relative to the other samples within the bioturbated unit - this sample is below the sulphide-diffusion zone and is typical of Cariaco Basin sediments deposited under oxic conditions prior to the sulphide overprint. The second strong positive correlation is between organic C and Se where two distinct correlations exist between the samples in the laminated and bioturbated units (Fig 6.6). Two exceptions are at 12.71 and 15.22 ka, which have anomalous high and low Se concentrations, respectively, relative to adjacent samples (Table 6.3). The strong correlations between Fe-S and C_{org} -Se are confirmed on ternary diagrams (Fig 6.7).

In contrast, no correlations exist between Fe-Se, S-Se, and C_{org} -S (Fig 6.6). S and Fe concentrations within the laminated unit for all three graphs occur within a very narrow range and the distribution of the samples is controlled by the samples' Se and organic C contents. Within samples from the bioturbated unit, two distinct groups are observed. The first group is those within the sulphide diffusion zone which are characterised by high S and Fe contents and low organic C content. Deeper samples not affected by sulphide diffusion are circled in Fig 6.6 and are characterised by low S and high Fe contents and low organic C contents for these samples are low, with the exception of the sample at 15.22 ka.

The Fe-S data show a positive correlation with a gradient of ~0.51 (Fig 6.6). In the Fe-S-C_{org} ternary plot, data cluster close to a constant S/Fe line; this suggests the sedimentary sequence is iron-limited (Dean & Arthur 1989). The gradient does not match that expected based on the stochiometric ratio of pyrite line (S = 1.15 Fe) (Fig 6.6); this suggests ~56 % of the Fe in the sediment is not reactive. (Lyons *et al.* 2003)

suggest that the primary sulphur species in the Cariaco Basin sediments is pyrite. The distinct clusters of samples along this constant S/Fe line (Fig 6.7A and B) reflect a combination of the amount of Fe and C_{org} in the samples which are affected by changes in productivity and oxygen availability. The bioturbated samples from immediately below the laminated-bioturbated boundary plot close to the S-Fe axis (Fig 6.7A and B). The occurrence of large amounts of pyrite in organic C-poor sediments suggests that sulphide diffused into the organic C-poor sediment from more organic C-rich anoxic sediments above (Dean & Arthur 1989). The sample at 15.87 ka is just below this sulphide diffusion zone and represents the typical Fe-S-C_{org} values of oxic sediments that have not been overprinted by sulphide. The location of this sample close to the Fe-C_{org} axis (Fig 6.7A) suggests the organic matter is un-reactive (Dean & Arthur 1989). This is expected, as under oxic water column conditions the organic material is being re-mineralised as it falls through the water column and the remaining organic material reaching the sediment would be depleted in reactive components.

The Fe-S-Se ternary diagram (Fig 6.7B) illustrates that with a fixed Fe-S ratio the Se concentrations vary and are not affected by the apparent iron-limitation in the system. The S-C_{org}-Se diagram (Fig 6.7C) illustrates the strong correlation of Se with organic C and the distinct trend lines for samples in the laminated and bioturbated units. Samples from the laminated unit cluster strongly with Se-S ratios of about 2×10^{-4} , but likely reflects the fixed Fe (and thus, pyrite) content of these samples and not any mechanistic connection between Se and S. Within the bioturbated unit, Se and S vary more and are clearly independent of each other. Samples which do not plot on the constant Se-C_{org} lines, such as the anomalously high Se concentration at 15.22 ka and the anomalously low Se concentration at 12.71 ka, suggest other processes are enriching and depleting the Se relative to the amount of organic C present in the sediment.

The age profiles of the Se/Fe, Se/S and total Se:C_{org} ratios, cross plots and ternary diagrams of the Fe-C_{org}-S-total Se system provide a means of identifying the major process that are causing Se enrichment within the sediment. If Se is adsorbing to Fe and Mn particulates within the water column, then a strong correlation between Fe and Se might be expected. However, according to the Se-Fe cross-plot (Fig 6.6), Se-S-Fe ternary diagram (Fig 6.7), and similarities between the Se/Fe profile and the Se/Al profile (Fig 6.4), no correlation exists between Se and Fe. The relatively constant Fe profile across the last glacial-interglacial transition (Fig 6.5) suggests the fluctuations exhibited in the Se/Fe ratio are caused by variations in the Se concentrations, and this is confirmed by the Fe-Se cross-plot. Therefore, adsorption is not a major pathway for Se to the sediment.

If Se is incorporated into sulphides then a strong correlation between Se and S is also expected. However, the relatively constant S values accompanying the large change in Se concentration across the glacial-interglacial transition (Fig 6.5), the lack of a constant Se/S ratio on the Se-S cross-plot (Fig 6.6), and the similarity of the Se/S profile to the Se/Al profile (Fig 6.4), all suggest a lack of strong mechanistic connection between Se and S. Therefore, Se bound in pyrite and/or other sulphides is not an important pathway into the sediment. However diagenesis might have subsequently redistributed the Se and it now might be found in pyrite and other sulphide structures. The similarities in the geochemistry of Se and S (see chapter 2) might lead researchers to believe that both elements would behave in a similar fashion within a certain environment. However, our data for the last glacial-interglacial transition suggest that Se and S are geochemically de-coupled from each other within the Cariaco Basin sediments.

If Se is delivered to sediment predominantly via its incorporation into organic matter, then a strong correlation between total Se and organic C is expected. The C_{org} -Se cross-plot (Fig 6.6), the Se-S- C_{org} ternary diagram (Fig 6.7), and the constant Se: C_{org} profile across the last glacial-interglacial transition (Fig 6.4) all show a strong correlation between Se and organic C. This suggests Se bound to organic matter is the dominant pathway of Se delivery into the Cariaco Basin sediment. The Se: C_{org} values in both the laminated and bioturbated units are mostly larger than those measured for cultured phytoplankton, plankton/ bacteria uptake ratios, riverine sediments, and deep Pacific sediments. However, the Se: C_{org} ratios are similar to previously reported values in anoxic shales and Mediterranean sapropels (Fig 6.8).

Higher Se/C_{org} ratios in the Cariaco Basin samples compared to phytoplankton is might be because of the different loss rates of metals from dying cells during their descent through the water column. (Fisher & Wente 1993) determined that Se is lost more rapidly than particulate organic C in plankton such as diatoms, dinoflagellates, and coccolithophores. This has the effect of decreasing the Se/C_{org} ratio over time. However, in the Cariaco Basin, there is a zone of secondary production which is likely to raise the Se:C_{org} ratio back to similar values to that of the original primary production. As the organic matter is re-mineralised again, Se ions are then re-released but due to the anoxic conditions the Se ions are either precipitated or bound to particulates and organic material while the organic C is lost. This has the effect of increasing the overall Se:C_{org} ratio to greater values than those found in phytoplankton.

The exception to the elevated Se: C_{org} ratio in the laminated unit is the anomalously low ratio of 3.1 x 10⁻⁶ mol mol⁻¹ at 12.71 ka. This ratio is similar to the plankton uptake and cultured phytoplankton Se: C_{org} ratios from the literature (Fig 6.8). One mechanism which can change the Se: C_{org} ratio is re-mineralisation of the Se out of

the organic material and back into the water column by an influx of O₂-rich water into the basin (Cutter & Bruland 1984). One possible driver of such an influx might be increased upwelling, as indicated by the merging of δ^{18} O ratios from different depthdwelling foraminifera at this time (see section 4.3.3).

The larger average Se: C_{org} ratio in the bioturbated unit might be a result of an additional source of Se into the sediment. The strong Se: C_{org} correlation in samples from the bioturbated unit lies on a different line from that of samples within the laminated unit and the trend line has a positive Se axis intercept (Fig 6.6). This trend line is shifted towards the Se apex on the Se-S- C_{org} ternary diagram (Fig 6.7) suggesting a supplementary source of Se present in these samples. These features suggest an authigenic Se fraction exists within the sediment. There are two alternative mechanisms of authigenic Se accumulation:



Figure 6.8: Comparison of Se:C_{org} molar ratios of sediments from the Cariaco Basin with previously reported literature Se:C_{org} ratios. X-axis is on a logarithmic scale. ¹(Sherrard *et al.* 2004); ²(Baines & Fisher 2001); ³(Doblin *et al.* 2006); ⁴(Cutter & Bruland 1984); ⁵(S.L.Meseck 2002); ⁶(van der Weijden 1993); ⁷(Nijenhuis *et al.* 1999); ⁸(Yao *et al.* 2002); ⁹(Kulp & Pratt 2004); ¹⁰(Gavshin & Zakharov 1996); ¹¹(Hatch & Leventhal 1992).

1. Adsorption onto Fe and Mn oxy-hydroxides

2. Reduction of soluble oxyanions from seawater to form elemental Se or selenide minerals at the post-oxic boundary below the sediment-water interface

Determining the relative sizes of these fluxes is complicated here; the apparent diffusion of sulfide downward across the laminated-bioturbated boundary (Lyons *et al.* 2003) could be accompanied by Se redistribution. Samples aged between 14.5-15.7 ka, the S concentration profile for the bioturbated unit shows similar values to those in the laminated unit (Fig 6.5). However, this is not the case for Se concentrations where values drop suddenly across the laminated-bioturbated transition (Fig 6.4a). The large Se concentration at 15.2 ka might correspond to the limit of Se diffusion within the sediment, slightly shallower in the core than the limit of S diffusion. Se is a heavier atom than S and will diffuse through the sediment slower and over the same time cover a shorter distance. The diffusion of sulphide might also have created a secondary redox front which caused Se to precipitate at that point.

The significant difference in Se: C_{org} ratios between the laminated and bioturbated unit is a result of different mechanisms operating to deposit Se with sediment and to draw dissolved Se down into the sediments. Within the laminated unit, a strong correlation with organic C and similar Se: C_{org} values to those previously reported is strong evidence for organic matter to be the principal mechanism. In contrast, the higher Se: C_{org} ratios in the bioturbated unit suggest an additional mechanism of authigenic enrichment of Se is occurring.

6.3.2. Cycling of Se in the Cariaco Basin during glacial and interglacial periods

The different processes involved in transporting Se from the surface to the sediment during the laminated and bioturbated interval are illustrated in figures 6.9 and 6.10, respectively. Pace *et al.* (1987) use a one-dimensional vertical carbon flux with depth where export production from the photic zone is progressively decomposed and becomes increasingly energy depleted and, hence, capable of supporting diminishing biomasses of heterotrophs (Taylor *et al.* 2001). Our model incorporates the redox behaviour of Se, a two stage primary and secondary vertical carbon flux, sedimentary Se concentrations, the geochemical characteristics of the water column and sediments (see chapter 5), and the hydrographic and oceanographic parameters of the Cariaco Basin (see chapter 4).

During periods of higher sea levels, e.g. interglacials, upwelling in the open Caribbean causes nutrient-rich waters from below the mixed layer to travel over the sill and stimulate a large amount of primary productivity (Fig 6.9).


Figure 6.9: Se cycling within the Cariaco Basin at periods of high sea level. Arrow colours represent various transport pathways for Se within the water column: green/yellow = organic; brown = particulate; blue = diffusion. Arrow thicknesses represent estimated importance of the individual fluxes. RTZ = Redox Transition Zone. Dashed lines at 100 and 300 m represent the base of the photic zone and the O_2 -H₂S interface respectively. Note the change in vertical scale.

Se (VI) and (IV) oxyanions are either adsorbed or incorporated into the organic matter in the mixed layer. Within the upper 100 m, ~90 % of the organic matter is remineralised (Thunell et al. 2000) and the Se oxyanions are re-released (Fisher & Wente 1993). The released Se oxyanions are then either recycled into the primary productivity or move down through the water column by diffusion or attached to particulates such as clays. The remaining organic matter and contained Se falls through the water column and is sufficient to create an oxygen demand which causes the water column to turn anoxic below 300 m. At the redox transition zone (RTZ) of the Cariaco Basin (~ 240-450 m), some Se (IV) is re-assimilated into new secondary bacterial organic matter, part of an active secondary microbial food web supported by the juxtaposition of dissolved oxygen and reduced S species. This secondary production is a potential source of labile, chemically unique, sedimenting biogenic debris to the basin floor (Taylor et al. 2001). Under the anoxic water column, re-mineralisation of the organic matter does still occur but to a lesser extent. Se released from the organic matter will quickly be reduced to Se (0) and possibly to HSe⁻, depending on the redox conditions at the time, thus remaining with the particulate fraction. Currently, $\sim 2\%$ of the original primary production reaches the sediment-water interface and $\sim 60\%$ of that is then incorporated into the sediment. The anoxic water column means bioturbation does not occur and the sediments remain laminated. Thus significant enrichments of Se occur under an anoxic water column with the dominant transport process being Se bound to organic material.

In contrast, during periods of low sea level, e.g. glacials, the water spilling over the sill is nutrient-depleted regardless of the strength of upwelling, and primary productivity is much lower (Fig 6.10).



Figure 6.10: Se cycling within the Cariaco Basin at periods of low sea level. Arrow colours represent various transport pathways for Se within the water column: green/yellow = organic; brown = particulate; blue = diffusion. Arrow thicknesses represent estimated importance of the individual fluxes. Dashed line at 100 m represents the base of the photic zone. Note the change in vertical scale. Note Se oxyanion reduction in sediments actually occurs very close to the sediment-water interface (Clark & Johnson 2008) and the distance on the diagram has been exaggerated to ensure clarity.

As with Se cycling under an anoxic water column, Se (VI) and (IV) oxyanions are either adsorbed or assimilated into the organic matter in the mixed layer. Using a model of decomposition of organic matter under an oxic water column (Pace et al. 1987) ~90 % of the organic matter is re-mineralised and the Se oxyanions are rereleased (Thunell et al. 2000). The released Se oxyanions are then either recycled into the primary productivity or move down through the water column by diffusion or attached to particulates such as clays. In contrast to the anoxic water column, the organic flux and hence organic Se flux is not large enough to create anoxic conditions in the deeper levels of the basin. The Se oxyanions are transported to the sediment through three pathways: 1) bound in organics, 2) diffusion across the sediment-water interface as oxyanions or 3) adsorbtion onto particulates. Breakdown of organic matter which does reach the sediment takes place, creating reducing conditions below the sea floor which transforms any Se oxyanions to the reduced Se (0) or Se (-II) species (Thomson et al. 2001). Se concentrations are lower compared to those occurring under anoxic conditions due to the initial lower primary productivity. Organically-bound Se is still an important transport pathway to the sediment but it is much smaller in magnitude and as a result, the other pathways are more significant.

The change in the Se: C_{org} ratio is the same within the top 100 m as for the previous diagram. However, below the photic zone no recycling of Se occurs and the Se: C_{org} ratio remains constant down to the sediment-water interface (SWI). A sub-oxic zone occurs within the sediments just below the SWI and at this point, Se oxyanions will be reduced to insoluble forms. The sediment Se: C_{org} ratio will increase rapidly, as the Se is precipitated and C_{org} is consumed by microbial processes.

6.3.3. Conclusion

Within the Cariaco Basin, higher Se concentrations are found in sediments which are deposited under an anoxic water column whereas lower sedimentary Se concentrations are found in sediments deposited under an oxic water column. This is partly because the cycling of Se within the water column and the transport pathways of Se to the sediment both depends on the oxygen content of the water column. However, the initial primary production rate in the surface waters, a result of fluctuating sea levels, is the dominant controlling factor - the oxygen demand caused by the decaying organic material actually creates the anoxic conditions. Also, the geochemical behaviour of Se differs greatly from that of S within Cariaco Basin sediments, with Se concentrations not being controlled by pyrite concentrations. Finally, the apparent relationship of Se concentrations with redox conditions within the Cariaco Basin water column suggests that Se concentrations can be used as a possible palaeoredox indicator.

6.4. Se concentrations in the Cariaco Basin over four glacialinterglacial cycles (MIS 5-12)

These samples span four glacial-interglacial cycles (MIS 5-12) and were obtained to: (1) investigate the behaviour of Se over a long time scale; (2) assess if the model proposed of Se cycling for the most recent glacial and interglacial (Figs 6.9 and 6.10) applies to previous glacial and interglacial periods. The scale of sampling is much larger compared to the last glacial-interglacial transition and so only general conclusions about the behaviour of Se in interglacial and glacial periods will be made. Fluctuations in the oxygen content of the Cariaco Basin have been inferred from cycles of laminated and non-laminated intervals [see chapter 4; (Peterson *et al.* 2000)]. However, unlike the last glacial-interglacial transition, there is no clear association of laminated intervals with interglacial periods and non-laminated intervals with glacial

periods (Fig 6.11).

6.4.1. Variation in Se concentrations

Se concentrations range from a minimum of 0.54 ppm at 340 ka to a maximum of 4.74 ppm at 330 ka, averaging 2.36 ppm over the entire section (Table 6.5).

Table 6.5: Se concentrations and $\delta^{82/76}Se$ over four glacial-interglacial cycles.

Sample ID	Depth (m)	Age (ka)	MIS	Se (ppm)	$\delta^{82/76}$ Se (‰)	$\pm 2 se \delta^{82/76} se (\%)$
C-5-3-113-115	41.03	106.01	5	3.03	0.50	0.03
C-5-4-113-115	42.60	112.26		3.64	0.27	0.09
C-5-6-113-115	45.60	124.24		2.53	-0.24	0.06
C-6-2-56-58	47.23	133.54	6	1.96	0.08	0.07
C-6-3-101-103	49.18	141.23		1.20	-0.11	0.06
C-6-5-55-57	51.72	151.30		0.60	-0.81	0.11
C-8-5-17-19	70.62	193.37	7	4.03	0.31	0.11
D-9-5-12-14	77.00	229.04		2.03	-0.01	0.02
D-10-3-117-119	83.94	267.26	8	0.93	-0.27	0.02
C-10-2-24-26	85.45	276.66		2.58	0.40	0.05
C-11-2-93-95	95.06	330.22	9	4.74	-0.28	0.04
C-11-6-96-98	101.45	339.95	10	0.54	-0.94	0.03
C-12-3-124-126	107.41	358.60		1.48	0.45	0.06
C-13-4-28-30	117.29	403.54	11	4.25	-0.21	0.07
C-14-2-35-37	123.35	437.90	12	2.67	0.33	0.05
C-14-4-126-128	127.26	463.25		1.60	-0.12	0.02

^aGrayed samples represent those deposited under or near to laminated intervals. Black samples are deposited in non-laminated intervals

^bDotted lines represent MIS boundaries (Bassinot *et al.* 1994)

Se concentrations during glacial periods (MIS 12, 10, 8, and 6) range from 0.54 to 2.67 ppm, averaging 1.51 ± 0.78 ppm (Table 6.6; Fig 6.11a). In contrast, Se concentrations in the interglacial periods (MIS 11, 9, 7, and 5) range from 2.03 to 4.74 ppm, averaging 3.46 ± 0.98 ppm (Table 6.6; Fig 6.11a). Glacial Se concentrations reach the same minima but cover a larger range and on average are greater compared to the most recent glacial. The opposite is the case for the interglacial Se concentrations where the range is much smaller and the average is much lower compared to the most recent interglacial. There is also an overlap of the minima in the interglacial periods and the

maxima in the glacial periods (Table 6.6), a feature not observed in the last glacialinterglacial after removing the two anomalies (Table 6.4).

	Interglacial	Glacial
Mean Se concentration (ppm)	3.46	1.51
1σ _{n-1}	0.98	0.78
Maximum Se concentration (ppm)	4.74	2.67
Minimum Se concentration (ppm)	2.03	0.54

Table 6.6: Statistical data for Se concentrations in the interglacial and glacial periods

With no clear association of the laminated and non-laminated sediments with interglacial and glacial periods respectively, the samples fall into one of the possible four depositional categories: (1) interglacial–laminated; (2) interglacial–non-laminated; (3) glacial–laminated; (4) glacial–non-laminated (Table 6.7).

Table 6.7: Summary of Se concentrations according to climate state and presence of laminations

The average Se concentrations for the two end-member environments of interglacial–laminated and glacial–non-laminated are different from each other, similar to the results from the recent glacial-interglacial transition. No difference exists between the laminated and non-laminated sediments in glacial periods and a small difference exists between the laminated and non-laminated sediments in interglacial periods (Table 6.7). Therefore interglacial environments contain higher Se concentrations than the glacial environments but the presence of laminations is not a pre-requisite for higher Se concentrations.



Figure 6.11: Behaviour of Se over four glacial-interglacial cycles (a) Se and Organic C concentrations, (b) Se/Al ratio (top) and Se enrichment factor using average continental crust Se/Al ratio of 0.01 ppm/wt % metal oxide (Gao *et al.* 1999) (bottom), (c) Se/Fe_(norm to Al) ratio, (d) total Se/organic C ratio. Total Al, Fe, and organic C values are from (Lyons *et al.* 2003). Shaded and even numbered areas represent glacial periods.

Se enrichment factors for the four glacial-interglacial cycles range from 5.4 to 76.5 (Fig 6.11b). Se enrichment factors average 52.4 and 19.2 in the interglacial and glacial periods respectively, a smaller range than that of the last glacial-interglacial transition. The minimum glacial Se enrichments are similar to those in the recent glacial while the maximum Se enrichments in the interglacial periods are significantly smaller than those in the recent interglacial. Both the Se/Al and Se enrichment profiles are identical to the Se concentration profile as Al concentrations are relatively constant over the entire period (Fig 6.12).



Figure 6.12: Total Fe and Al concentrations (wt %) for four glacial-interglacial cycles (Yarincik *et al.* 2000a). Shaded and even numbered areas represent glacial periods.

The Se enrichments are a result of three possible processes - adsorption to particulates, bound to sulphides, and incorporation within organic matter. As discussed in section 6.3.1 if Se was being transported to the sediment by any one of these three pathways we would expect a relationship to exist between Fe, S, and organic C respectively. Due to no available S data, only the importance of the adsorption to particulates and incorporation in organic matter transport pathways can be evaluated.

The Se/Fe profile (Fig 6.11c) is similar to the Se concentration and Se/Al profile (Fig 6.11a and b) because the Fe concentrations are relatively constant (Fig 6.12). The maximum and minimum ratios are at 330 and 339 ka respectively, the same as the Se concentration and Se/Al profiles. Continuing the same pattern previously described for Se concentrations the Se/Fe ratio for the four glacial-interglacial cycles have a smaller range and the interglacial maximum is lower when compared to the Se/Fe ratio of samples of the last glacial-interglacial transition. Assuming the strong Fe-S relationship observed for the last glacial-interglacial transition applies farther back in time and pyrite is still the dominant S phase, if S data was available for these four glacial-interglacial cycles, the Se/S ratio would also follow a similar profile to that of the Se concentrations, Se/Al, and Se/Fe profiles.

In contrast, the total Se:C_{org} profile (Fig 6.11d) is not similar to the Se concentration and Se/Fe profile. The average molar Se:C_{org} ratio is 2.33 x 10⁻⁵ which is similar to that of the laminated sediments of the last glacial-interglacial transition (Fig 6.4e). The interglacial periods are characterised by an average total Se:C_{org} ratio of 2.42 x 10⁻⁵ \pm 3.63 x 10⁻⁶ (1 σ_{n-1}) which is slightly higher than the glacial periods which have an average total Se:C_{org} ratio of 2.26 x 10⁻⁵ \pm 6.86 x 10⁻⁶ (1 σ_{n-1}) although the averages overlap within one standard deviation. The maximum total Se:C_{org} of 3.60 x 10⁻⁵ is found in MIS 6 at 151 ka and the minimum total Se:C_{org} value of 1.31 x 10⁻⁵ is found on the border of MIS 10/9 at 340 ka (Fig 6.11d). Following the pattern observed in all the other data for MIS 5-12 the range of Se:C_{org} ratios are much smaller (1.31 to 3.60 x 10⁻⁵) than that of the last glacial-interglacial transition (3.1 x 10⁻⁶ to 1.8 x 10⁻⁴). The Se:C_{org}

ratios are mostly similar to those of MIS 1, but there are a couple of samples from the glacial intervals that, like MIS 2, have higher ratios.

6.4.2. Relationships between Se-Fe-Organic C

As with the geochemical data from the last glacial-interglacial transition, further insight into which enrichment processes are operating in the Cariaco Basin over the four glacial-interglacial cycles can be achieved by analysing the relationships between total Se, Fe and organic C (Figs 6.13, 6.14).

Positive correlations are observed between total Se and organic C for both the interglacial and glacial periods (Fig 6.13a). The relatively constant total Se: C_{org} ratio for both the interglacial and glacial periods are confirmed on the ternary diagram (Fig 6.13b). The difference between the older interglacial and glacial periods is small - both lines of best fit cross the y-axis at very similar values, the gradients are close to each other, and there is also considerable overlap between samples from interglacial and glacial-interglacial transition (Fig 6.13a) where the lines of best fit are at different gradients, they cross different axes, and there is a clear distinction between samples from the interglacial (laminated) and glacial (bioturbated) units (Fig 6.6). Interestingly both glacial trend lines are on a similar gradient to each other while the interglacial trend lines are significantly different (Fig 6.13a). In contrast, no correlation is observed between total Se and Fe. The Fe values are within 3-5 wt % which is a wider range than the last glacial-interglacial transition (Fig 6.14).



Figure 6.13: Cross-plot (a) and ternary diagram (b) illustrating the relationship between Organic C and total Se. The MIS 1-2 lines in (a) are formed using the equations in figure 6.6. Organic C data are from (Yarincik *et al.* 2000b) and total Se concentrations are measured as part of this study.



Figure 6.14: Cross-plot illustrating the relationship between Se-Fe. Total Fe data are from (Yarincik *et al.* 2000a) and total Se concentrations are measured as part of this study. The shaded area indicates where the majority of the samples are distributed.

The age profiles, cross-plots and ternary diagrams of the total Se-Fe-organic C system provide a tool for identifying the dominant processes causing Se enrichments within the sediments. Following the same arguments applied to data from the last glacial-interglacial transition (see section 6.3.1), the strong correlation between total Se and organic C (Figs 6.11, 6.13) suggests Se bound to organic matter is the dominant pathway for Se into the Cariaco Basin sediment in all samples. With no correlation existing between Se and Fe (Fig 6.14), adsorption is not an important pathway for Se into the sediment.

In general, the data from the samples spanning the last glacial-interglacial transition and the data from the samples covering four glacial-interglacial cycles (MIS

5-12) lead to similar conclusions including: (1) the dominant transport pathway for Se to the sediments is bound to organic matter; (2) interglacials are characterised by higher Se concentrations; (3) Se enrichments relative to average continental levels occur in all samples from the Cariaco Basin. However significant differences in the ranges and maximum of the same datasets are observed between the older interglacial and the most recent interglacial data.

6.4.3. A refined model of Se cycling within the Cariaco Basin

Differences in the behaviour of redox metals such as Mo and V over varying timescales has been suggested previously for the Cariaco Basin (Yarincik *et al.* 2000a). The difference between the Se concentrations and related data, such as Al/Ti, K/Al, and δ^{18} O, in the interglacial and glacial periods over the four climate cycles is not as large as that of the last glacial-interglacial transition. The minimum Se concentrations observed in the glacial periods are similar to those of the minimums in the bioturbated unit of the recent glacial period. However, the maximum Se concentration values in the interglacial periods are significantly less than the maximums in the recent interglacial. This lesser distinction between interglacial and glacial-interglacial cycles (Fig 6.15), which have been previously described (see section 5.3.3.). Two clusters of samples occur at the extremes representing glacial and interglacial conditions. However, there are a significant number of samples which lie between the two extremes (Fig 6.15) which suggests our two models outlined in the previous section for the cycling of Se within the Cariaco Basin (Figs 6.9, 6.10) is not complete.



Figure 6.15: Relationships of Se with δ^{18} O (A), Al/Ti (B), and K/Al (C) for MIS 5-12. Interglacial samples are symbolised by diamonds and glacial samples by squares. Circled data are anomalous. Solid lines represent best fit lines through the entire data while dashed line represents best fit line through non-circled data. Shaded boxes indicate area where both interglacial and glacial samples are found along the trend lines. δ^{18} O from (Peterson *et al.* 2000); Al/Ti and K/Al from (Yarincik *et al.* 2000a).

Currently, the model consists of two-end members for Se cycling in the Cariaco Basin - one end member has high sea levels resulting in an anoxic water column (Fig 6.9) and the other end member has low sea levels resulting in an oxic water column (Fig 6.10). Both the geochemistry outlined previously and the distribution of laminations over the four glacial-interglacial cycles (MIS 5-12) indicates this needs refinement. Older interglacial and glacial periods include intervals of both laminated and nonlaminated sediment suggesting an individual interglacial or glacial period has undergone a cycling of anoxic and oxic water column conditions respectively. Therefore, the model needs to include two possible intermediate states - one which allows a glacial Cariaco Basin, which is normally oxic, to become anoxic and produce laminations and the other which allows an interglacial Cariaco Basin, which is normally anoxic, to become oxic and produce non-laminated sediments.

The primary difference between the two end-member situations is the water column depth to the sill which controls the quantity of nutrient-rich water entering the basin and therefore surface primary productivity. Sea level variations within individual interglacial and glacial periods and a progressive uplift of the northern part of the Cariaco Basin, including the sills, over the last 2 Ma have been well documented (Schubert 1982; Clayton *et al.* 1999). During earlier glacial periods, e.g. MIS 12, 10, 8, the global sea levels were lower than present interglacial (Fig 4.24) but the uplift of the sills was less. This would create a large enough water depth to sill which just allows nutrient-rich waters to flow into the basin, creating conditions for anoxia and laminated sediments to develop. However any small decrease in the water depth to sill will result in a return to oxic water column conditions and non-laminated sediments being deposited (Fig 6.16B). However, as uplift of the sills continued and global sea levels during more recent glacial fell (Fig 4.24), the water depth to sill decreased, resulting in

only nutrient-poor surface waters flowing over the sill into the basin. The surface primary productivity would not be great enough to create an oxygen demand, the water column would remain oxic, and sediment laminae would not form (Fig 6.16A). This was the situation during the most recent glacial (MIS 2).

In contrast, during earlier interglacial periods, e.g. MIS 11, 9, global sea levels were higher or similar to present day interglacial (Fig 4.24) but the uplift of the sills would have been less. This would create a condition where the water depth to sill was too great and both nutrient-rich waters and deep oxygenated water from the Caribbean would enter over the sill. The primary productivity would create the necessary oxygen demand to turn the water column anoxic but this would be balanced against the input of oxygenated water, resulting in a transient anoxic/oxic water column within the Cariaco Basin shown by alternate periods of laminated and non-laminated sediments (Fig 6.16D). With continued tectonic uplift and present day sea levels during the recent interglacial, the water depth to sill is deep enough to allow nutrient-rich water over the sill and into the basin but not deep enough to allow deeper oxygenated water in to the basin. The ensuing high surface primary productivity creates an oxygen demand and the result is an anoxic water column and laminated sediments being deposited. This is the condition which the Cariaco Basin is currently experiencing (Fig 6.16C).

6.4.4. Conclusion

A simple two end-member model for Se cycling within the Cariaco Basin is sufficient for the recent glacial-interglacial transition where permanent oxic and anoxic water columns characterise the glacial and interglacial periods respectively. However, previous glacial and interglacial periods are characterised by repeating laminated and non-laminated intervals representing short-lived anoxic and oxic water columns. Therefore, two intermediate stages are described to explain the alternating laminated

and non-laminated intervals within older glacial and interglacial periods. The Se cycles previously illustrated (Figs 6.9, 6.10) are still appropriate for the changing oxygen contents of the water column of the four glacial-interglacial cycles. The Se data measured in samples from these four glacial-interglacial cycles also indicates that the establishment of oxic conditions during interglacial periods does not change the characteristic geochemistry of the basin and the establishment of anoxic conditions during glacial periods does not result in higher Se concentrations in deposited sediments.



Figure 6.16: Possible conditions of the Cariaco Basin. (A) Shallow water depth to sill does not allow nutrients to enter the basin, maintaining an oxic water column; (B) A deep water depth to sill just allows nutrients into the basin, creating anoxic conditions, but a small change of the depth to sill will cause oxic conditions to return; (C) A deeper water depth to sill allows nutrients into the basin but not deep oxygen-rich water from the Caribbean creating an anoxic water column; (D) Greater water depth to sill allows both nutrients and deep oxygen-rich water into the basin creating a transient anoxic/oxic water column. "s/l" is sea level and "pz" is photic zone. Not drawn to vertical scale.

6.5. $\delta^{82/76}$ Se values over last glacial-interglacial transition

6.5.1. Introduction

In the previous section, using Se concentrations and other geochemical data, a model was developed to contrast the cycling of Se within the Cariaco Basin under a sub-chemocline anoxic water column with a wholly oxic water column. This section describes $\delta^{82/76}$ Se values measured on the same samples and interprets them in terms of this model. The aim is to identify the controlling factors on the $\delta^{82/76}$ Se values and, if possible, link these ratios to the Se cycling model.

6.5.2. Variation in $\delta^{82/76}$ Se values

The $\delta^{82/76}$ Se values spanning the last glacial-interglacial transition range from a minimum of -1.06‰ to a maximum of 0.77‰ (Table 6.3; Fig 6.17B). This range is notably narrow in light of the known potential for fractionation of several per mil in response to Se oxyanion reduction (Johnson & Bullen 2004) and references therein].



Figure 6.17: (A) Se concentrations and (B) $\delta^{82/76}$ Se values (relative to NIST 3149) for last glacial-interglacial transition in the Cariaco Basin. Limit of sulphide diffusion is indicated by the dashed line and boxed area represents the Younger Dryas stadial (Lyons *et al.* 2003). Shading is as figure 6.4 and unit descriptions are as figure 6.2. Error bars represent 2 standard error.

There is considerable scatter among the samples, with the ranges of the laminated and bioturbated units' $\delta^{82/76}$ Se overlapping considerably. Within the bioturbated unit (16.38-14.74 ka), $\delta^{82/76}$ Se values range from -1.06 to 0.24‰ (Tables 6.3; 6.8) with an average of -0.38 ± 0.54‰ (1 σ_{n-1}). In contrast, $\delta^{82/76}$ Se values within the laminated unit (14.40-0.38 ka) are generally higher, ranging from -0.45 to 0.77‰ (Table 6.3; 6.8) averaging 0.06 ± 0.35‰ (1 σ_{n-1}). There is a 1.2‰ increase in $\delta^{82/76}$ Se values during the Younger Dryas reaching +0.77‰, the highest value of the entire data set, at 11.89 ka.

 $\begin{tabular}{|c|c|c|c|c|c|} \hline Laminated & Bioturbated \\ \hline Mean \, \delta^{82/76} Se \, (\roldsymbol{\%0}) & 0.06 & -0.38 \\ \hline 1 \sigma_{n-1} & 0.35 & 0.54 \\ \hline Maximum \, \delta^{82/76} Se \, (\roldsymbol{\%0}) & 0.77 & 0.24 \\ \hline Minimum \, \delta^{82/76} Se \, (\roldsymbol{\%0}) & -0.45 & -1.06 \\ \hline \end{tabular}$

Table 6.8: Statistical data for $\delta^{82/76}Se$ in the laminated and bioturbated units

Two features are apparent in the δ^{8276} Se versus time relationship: (1) there is a general increase in δ^{8276} Se values (the mean rate derived from linear regression is 0.042‰ per thousand years); (2) the samples are remarkably invariant after 9.5 ka (almost identical within analytical uncertainty), whereas pre 9.5 ka, there are larger fluctuations in δ^{8276} Se which occur over varying timescales (Fig 6.18). δ^{8276} Se values within the bioturbated unit have large changes over a short period of time, e.g. the largest shift in δ^{8276} Se from -1.06‰ (16.38 ka) to 0.23‰ (16.26 ka) takes place over 120 years (0.0108‰ year⁻¹). Between 14.5-11 ka smaller magnitude shifts in the δ^{8276} Se values take place within the laminated unit and at a slower rate. For example, the shift from -0.25‰ (12.30 ka) to 0.77‰ (11.89 ka) takes place over 410 years (0.0005‰ year⁻¹). For the last 11 ka, the δ^{8276} Se values varied at a very low rate (< 0.0006‰ year⁻¹) (Fig 6.18).



Figure 6.18: Absolute rate of change of $\delta^{82/76}$ Se values for samples spanning the last glacialinterglacial transition. Points represent age mid-point between each sample and the error bars are the upper and lower age limits.

The $\delta^{82/76}$ Se values from the Cariaco Basin exhibit similar variability and are close to $\delta^{82/76}$ Se values measured on anoxic Holocene sediments from the Black Sea, and average marine and continental sediments (Table 6.9). The processes which are operating within the Cariaco Basin to control Se isotopes are probably similar in these other locations.

Material Age and Type	Location	δ ^{80/76} Se (‰)	$\delta^{82/76}$ Se (‰)*
¹ Holocene sediment-core	Black Sea-anoxic	-0.43	-0.65
	"	0.00	0.00
	"	-0.37	-0.56
² Marine and Continental			
Sediments			0.39 ± 1.11

¹(Hagiwara 2000) reported $\delta^{80/76}$ Se values relative to MH495 (Johnson *et al.* 1999; Johnson *et al.* 2000)

²(Carignan & Wen 2007)

*Converted from ^{80/76}Se using the relation: $\epsilon_{80/76} = \frac{2}{3} \epsilon_{82/76}$.

Lower Se concentrations tend to correspond with negative $\delta^{82/76}$ Se values while higher average Se concentrations are associated with relatively heavier $\delta^{82/76}$ Se values with some exceptions (Fig 6.19). This relationship is made clearer on a 1/Se vs. $\delta^{82/76}$ Se plot where a negative correlation exists between 1/Se and $\delta^{82/76}$ Se values of samples from the bioturbated unit and one outlier from the laminated unit. The remaining samples from the laminated unit form a group at the high $\delta^{82/76}$ Se value extension of the trend (Fig 6.20). With the exception of the outliers within the Younger Dryas period, these samples from the laminated unit scatter within a one per mil range in $\delta^{82/76}$ Se values and within a narrow range of Se concentrations (Fig 6.20; tables 6.4, 6.8).



Figure 6.19: Se concentrations vs. $\delta^{82/76}$ Se values for samples from the last glacialinterglacial transition. Linear trend line is based on all samples. Circled samples are in or near the Younger Dryas period. Dashed line is the mixing hyperbola with equations based on (Faure 1986). Anoxic end-member = 10 ppm, 0.03 ‰; Oxic end-member = 0.5 ppm, -0.97 ‰.



Figure 6.20: 1/Se vs ^{82/76}Se values for the last glacial-interglacial transition. A linear trend line for all samples excluding those circled is shown with the two end members: oxic (1/Se = 2; $^{82/76}$ Se = -0.97 ‰) and anoxic (1/Se = 0.1; $^{82/76}$ Se = 0.03 ‰ – grey envelope) conditions. Ages correspond with those in figure 6.17. Younger Dryas samples shown in circle.

This correlation between 1/Se and $\delta^{82/76}$ Se values (Fig 6.20) could be interpreted as resulting from two-component mixing (Faure 1986) between an anoxic high $\delta^{82/76}$ Se end member and an oxic low $\delta^{82/76}$ Se end member. This is consistent with our model of Se cycling. The high $\delta^{82/76}$ Se end member exists because under anoxic conditions the dominant pathway for Se into the sediments is assimilation into organic material (Fig 6.9). Assimilation of Se (VI) and Se (IV) by algae induces a small negative Se isotope fractionation (-1.5 to -3.9‰) (Hagiwara 2000) and there is also a limited negative abiotic fractionation (-0.80‰) between adsorbed Se(IV) and dissolved Se(IV) (Johnson *et al.* 1999). Assuming this fractionation of between -1.5 and -3.9‰ applies to assimilatory uptake for all biomass, $\delta^{82/76}$ Se values for organically-bound Se will be at

least 1.5% lighter relative to the seawater $\delta^{82/76}$ Se value (Fig 6.21). The spread of $\delta^{82/76}$ Se values within this anoxic end-member suggests additional local processes are taking place within the basin. The low $\delta^{82/76}$ Se end member exists because Se oxyanions from the water column undergo bacterial or abiotic reduction of Se (IV) to Se (0) within the post-oxic sediment (Fig 6.10). Bacterial and abiotic reduction results in a significant negative isotope fractionation estimated at between -9 to -13‰ and -15 to -19‰ respectively (Johnson 2004) and refs therein]. Reservoir effects within the sediments are expected to diminish the impact of these relatively large fractionations (Clark & Johnson 2008) so the authigenic $\delta^{82/76}$ Se is likely a few per mil lighter relative to the seawater $\delta^{82/76}$ Se value. Therefore, if it is assumed the seawater $\delta^{82/76}$ Se value has remained constant over the last 16.5 ka, formation of the authigenic component would tend to drive whole-sediment $\delta^{82/76}$ Se values lower relative to the laminated sediments which are dominated by organically-bound Se (Fig 6.21).



Figure 6.21: Theoretical end-members which make up the Se isotope system in the Cariaco Basin over the last glacial-interglacial transition

Our model of Se cycling indicates that Se: Corg ratios can be used to determine the dominant transport pathway of Se into the sediments during deposition. Constant, relatively low, Se: C_{org} ratios with a mean of 2.08 x $10^{-5} \pm 3.91$ x 10^{-6} ($1\sigma_{n-1}$) have been measured over the recent 9 ka (Fig 6.22B) which suggests assimilation into organic material has been the dominant transport pathway of Se into the sediment during this period. The sedimentary $\delta^{82/76}$ Se values are also relatively constant with a mean of 0.2 ± 0.1% ($1\sigma_{n-1}$) (Fig 6.22A) and are interpreted as resulting from constant Cariaco surface water $\delta^{82/76}$ Se (~+1.3% assuming a small biological fractionation factor of -1.1%) over the recent 9 ka. Between 12.5-9.5 ka, the Se: Corg ratio is at a relatively constant value of 2.01 x $10^{-5} \pm 3.02$ x 10^{-6} but during this period (grey box - Figs 6.22A and B) $\delta^{82/76}$ Se values increase from -0.25‰ at 12.30 ka to +0.77‰ at 11.89 ka before returning to -0.39‰ at 9.91 ka. The constant Se: Corg ratio suggests there has been no change in the Se transport mechanism but the varying $\delta^{82/76}$ Se values might suggest other mechanisms have altered the $\delta^{82/76}$ Se values. One such mechanism might be a change in the $\delta^{82/76}$ Se ratio of the ocean reservoir from which the Se is being removed. If the fractionation factor remained constant at -1.55‰, then a change in the seawater $\delta^{82/76}$ Se value from +1.30 to +2.32‰ would need to occur to produce the observed shift in $\delta^{82/76}$ Se values between 12.30 and 11.89 ka. However, this hypothesis cannot be tested because estimates of past seawater Se isotope compositions do not exist. One study measured the Se isotope composition of a modern Pacific Ocean Mn nodule (USGS reference material NOD-P-1), thought to be a close approximation of the seawater isotope composition, at ~ $0.04_{\text{NIST 3149}}$ % (Rouxel *et al.* 2002). This suggests at the time the nodule was formed seawater was not highly fractionated relative to the bulk Earth $(\delta^{82/76}$ Se_{NIST 3149} = -0.04 ± 0.38‰ (Carignan & Wen 2007)). However, this nodule

sample is a bulk samples with a possible age range expanding back as much as 30 Ma (Ito *et al.* 1998) so this provides little constraint on actual recent values.

Local reservoir effects within the Cariaco Basin cannot account for the observed δ^{8276} Se shift between 12.30 and 11.89 ka. Assuming the Se buried in sediments is isotopically light relative to the surface water, Cariaco basin surface waters could become isotopically heavy in response to the removal of the light Se. This could occur if communication between the basin's surface waters and the open ocean were poor and the removal rate of Se was great enough to strongly deplete surface waters in Se. These conditions might have existed during the bioturbated interval (MIS 2), where there was a lower global sea level and relatively little communication between the basin and the open ocean. However, mean δ^{8276} Se values are actually lesser for sediments from that time period and thus local reservoir effects, which would produce a shift in the opposite direction, cannot be invoked as the dominant control on δ^{8276} Se. Therefore, if the shift in δ^{8276} Se values between 12.30 and 11.89 ka is a result of a change in the δ^{8276} Se ratio of the ocean reservoir, it was possibly caused by a change in the global ocean δ^{8276} Se value. The large atmospheric Se flux mixes the surface ocean waters on relatively small timescales, and any reservoir effects are cancelled out.

A second possible mechanism is a change in the Se isotope fractionation factor between Se dissolved in seawater and that assimilated into organic material. Experimentally-determined fractionation factors vary depending on the specific conditions of the experiment. If the suggested global seawater $\delta^{82/76}$ Se value of +1.3‰ remained constant over this period, a change in the fractionation factor (Δ) for the assimilation of Se into organic matter from -1.55‰ to -0.53‰ would need to occur to produce the observed shift in $\delta^{82/76}$ Se values between 12.30 and 11.89 ka. This period between 12.5-9.5 ka includes the Younger Dryas stadial (black box – Figs 6.22A and B)

and it is possible the cooling global climate caused a change in either the $\delta^{82/76}$ Se values of the ocean reservoirs or the fractionation factor for Se uptake by organic material.



Figure 6.22: $\delta^{82/76}$ Se (‰) (A) and Se:C_{org} (mol/mol) (B) values for the current interglacial (14.5 ka to present). The redox boundary is at 14.5 ka. Grey box is referred to in text. Black box indicates Younger Dryas stadial. Error bars represent 2 standard error.

Samples within the bioturbated unit have higher average Se: C_{org} ratios which suggest authigenic enrichment has added Se into the sediment (Fig 6.23). Higher Se: C_{org} ratios in samples at 16.26, 15.74 and 14.98 ka are accompanied by significant negative isotope shifts (blue shading - Fig 6.23) which fits with our model that authigenic reduction of Se results in a negative isotope fractionation (Fig 6.21). Higher Se: C_{org} ratios are also observed at 16.38, 16.14, and 15.52 ka but these samples are accompanied by heavier $\delta^{82/76}$ Se values (green shading – Fig 6.23). This could occur if the Cariaco Basin was poorly connected to the open ocean and a reservoir effect occurred, with the preferential removal of the light isotopes leaving the surface waters isotopically heavy. This is a possibility because during MIS 2 the Cariaco Basin was in its most isolated state of the last 500 ka with the water depth to sill only ~16 m

compared to 146 m at present (Fig 4.24). At 15.22 ka there is a 10-fold increase in the Se: C_{org} ratio suggesting a large authigenic component but no accompanying change in the $\delta^{82/76}$ Se value. This either reflects an enrichment of Se, relative to the organic C present in the sediment, or a depletion of organic C by processes, neither of which involves a significant isotopic fractionation. The sample at 14.74 ka has a similar Se: C_{org} ratio and $\delta^{82/76}$ Se value to that of the laminated unit (Fig 6.23), suggesting the dominant Se transport mechanism into the sediment, at this time, was assimilation into organic material. This is surprising as this sample was deposited under an oxic water column and therefore is expected to show an additional authigenic Se component. For the sample at 15.87, a similar Se: C_{org} ratio to the laminated unit suggests assimilation as the dominant transport mechanism but the samples has a relatively lighter $\delta^{82/76}$ Se ratio. Therefore this sample might reflect one of our two alternative mechanisms previously discussed – either a change in the $\delta^{82/76}$ Se value of the global ocean reservoir from which the Se is being removed or a change in the Se isotope fractionation factor between Se dissolved in seawater and that assimilated into organic material.



Figure 6.23: Se:C_{org} vs. $\delta^{82/76}$ Se (‰) for samples from the last glacial-interglacial transition within the Cariaco Basin. Glacial samples identified by age and in shaded areas are referred to in the text. Dashed line and grey box represents the average Se:C_{org} ratio and $1\sigma_{n-1}$ for samples within the laminated unit with the exception of the outlier at 12.71 ka.

6.6. $\delta^{82/76}$ Se values over four glacial-interglacial cycles (MIS 5-12)

6.6.1. Variation in $\delta^{82/76}$ Se values

 $\delta^{82/76}$ Se values for four glacial-interglacial cycles (MIS 5-12) show isotopic variations, outside of analytical error, in a saw-tooth pattern (Table 6.5; Fig 6.24A).



Figure 6.24: (A) $\delta^{82/76}$ Se ratios relative to NIST 3149 (this study) and (B) Se concentrations (this study), for four glacial-interglacial cycles (MIS 5-12). Glacial periods are shaded and numbered. Laminated intervals are shown. 2 σ error on ^{82/76}Se measurements indicated. Error bars represent 2 standard error.

The range of $\delta^{82/76}$ Se ratios (1.44 ‰) is from a minimum of -0.94 to a maximum of 0.50‰. This range is slightly smaller than that of the last glacial-interglacial transition (Table 6.8). $\delta^{82/76}$ Se values for the glacial periods range from -0.94 to 0.45‰ (Tables 6.5, 6.10) with a mean of -0.11 ± 0.50‰ (1 σ_{n-1}). $\delta^{82/76}$ Se values for the interglacial periods range from -0.28 to 0.50‰ (Tables 6.5, 6.10) averaging 0.05 ± 0.31‰ (1 σ_{n-1}). This average is very similar to the average of samples from the laminated unit of the last glacial-interglacial transition (Table 6.8). Taking into account the uncertainties on the $\delta^{82/76}$ Se measurements, the means for glacial and interglacial periods overlap (Fig 6.24A), and the samples from glacial periods almost cover the full range of $\delta^{82/76}$ Se values observed during these four glacial-interglacial cycles (Table 6.10).

	Interglacial	Glacial
Mean δ ^{82/76} Se (‰)	0.05	-0.11
1σ _{n-1}	0.31	0.50
Maximum δ ^{82/76} Se (‰)	0.50	0.45
Minimum δ ^{82/76} Se (‰)	-0.28	-0.94
$1\sigma_{n-1}$ Maximum $\delta^{82/76}$ Se (‰) Minimum $\delta^{82/76}$ Se (‰)	0.31 0.50 -0.28	0.50 0.45 -0.94

Table 6.10: Statistical data for $\delta^{82/76}$ Se for the interglacial and glacial periods

These samples can fall into four possible depositional categories since there is no clear association of the laminated and non-laminated sediments with interglacial and glacial periods respectively. In contrast to the Se concentration data for these samples (Table 6.7) the two end-member environments of interglacial–laminated and glacial– non-laminated do not differ from each other with respect to their $\delta^{82/76}$ Se values (Table 6.11).

Table 6.11: Summary of $\delta^{82/76}Se$ values according to climate state and presence of laminations

	Interglacial	Glacial
Mean $\delta^{82/76}$ Se in laminated sediment (‰)	-0.11	0.45
n	4	1
1σ _{n-1}	0.28	
Mean δ ^{82/76} Se in non-laminated sediment (‰)	0.25	-0.18
n	3	8
1σ _{n-1}	0.25	0.48

However there is a difference between the laminated and non-laminated sediments in both glacial and interglacial periods (Table 6.11). In laminated sediments, samples from interglacial periods are isotopically lighter than those from the glacial periods. In contrast, in the non-laminated sediments, samples from the interglacial periods are isotopically heavier than those from the glacial periods. Therefore the presence of laminations does appear to be a controlling factor on the $\delta^{82/76}$ Se values.

Comparison of $\delta^{82/76}$ Se with Se concentration suggests the relationship observed for the last glacial-interglacial transitions holds for previous cycles. Plotting 1/Se vs. $\delta^{82/76}$ Se clarifies this, producing a similar pattern to that of the samples from the last glacial-interglacial transition (Fig 6.25). The interglacial samples again form an elongated cluster at a high $\delta^{82/76}$ Se-high Se concentration end-member (albeit at slightly lower Se concentrations), whereas the glacial samples produce a strong negative correlation (R^2 = 0.89) towards a low $\delta^{82/76}$ Se-low Se concentration end-member. This suggests the two end-members outlined for the last glacial-interglacial transition (Fig 6.21) are applicable to the older samples. Similar distributions between these two sample sets (Fig 6.25) also suggest that there has been no change in the transport mechanisms of Se into the sediment over the last 500 ka. If this interpretation is correct, it would further suggest the seawater $\delta^{82/76}$ Se value and fractionation factors must have remained reasonably constant over this time period as well.



Figure 6.25: 1/Se vs. $\delta^{82/76}$ Se ratios for four glacial-interglacial cycles (MIS 5-12) within the Cariaco Basin. Linear trend line is shown for glacial samples only (R² = 0.89). Data for last glacial-interglacial transition displayed in grey symbols for comparison. Blue envelope illustrates the anoxic end member of samples from the four glacial-interglacial cycles.

Most of the glacial and interglacial samples show very little variation in their Se: C_{org} ratios (Fig 6.26). The low Se: C_{org} ratios suggest assimilation of Se into organic matter is the dominant pathway of Se into the sediment at the time of deposition of these samples; this is confirmed by the relatively heavy $\delta^{82/76}Se$ values. The one exception is a glacial sample (151 ka) that exhibits a higher Se: Corg ratio and low $\delta^{82/76}$ Se value indicative of a significant authigenic enrichment of Se. The glacial sample at 340 ka is anomalous: Its Se concentration and $\delta^{82/76}$ Se value are both low and cause it to plot close to glacial samples with high Se: C_{org} ratios (Fig 6.25), yet it has the lowest Se: Corg ratio of this dataset (Fig 6.26). Unless this ratio is an analytical artifact, it suggests an unusual post-depositional loss of Se, change in the Se assimilation process, or shift in both $\delta^{82/76}$ Se and concentration of the Cariaco surface waters. This sample is located near a glacial-interglacial transition and laminated sediments overlie it, so perhaps some redistribution of Se occurred. It is also possible that unusual conditions existed at that time which shifted either the assimilation conditions in Cariaco surface waters or perhaps in the ocean reservoir. Local reservoir effects can be ruled out due to this sample having a negative $\delta^{82/76}$ Se value; therefore a change in the $\delta^{82/76}$ Se value of the global ocean reservoir might have occurred at this time.



Figure 6.26: (A) $\delta^{82/76}$ Se and (B) Se:C_{org} values for the last four glacial-interglacial cycles. Glacial periods are numbered and shaded. Dashed line and green box represents the average Se:C_{org} ratio and $1\sigma_{n-1}$ for samples within the laminated unit (MIS 1) with the exception of the outlier at 12.71 ka. Error bars represent 2 standard error.

The $\delta^{82/76}$ Se values show there is no clear relationship with the global climate state at the time of sediment deposition (Fig 6.26). This is confirmed when the relationship between $\delta^{82/76}$ Se and δ^{18} O values is explored (Fig 6.27). As with the Se concentration data and other chemical proxies (Fig 6.15), a number of interglacial and glacial samples lie near the extremes expected in our simple model (Figs 6.9, 6.10). These are when glacial conditions correspond to oxic conditions in the Cariaco Basin (lighter $\delta^{82/76}$ Se and heavier δ^{18} O values) and when interglacial conditions correspond to anoxic conditions in the Cariaco Basin (heavier $\delta^{82/76}$ Se and lighter δ^{18} O values) (Fig 6.27). However, a significant number of samples (red box, figure 6.27) have δ^{18} O values which suggest they were deposited under a global glacial climate but have $\delta^{82/76}$ Se values which overlap with samples deposited under an interglacial global climate. These samples correspond to those which have Se: C_{org} ratios similar to the MIS 1 laminated

unit (Fig 6.26) suggesting the samples are dominated by organically-bound Se.

According to our simple model of Se cycling, when Se in organic material is the dominant transport mechanism to the sediment, the water column is anoxic due to the creation of an oxygen demand by the decomposition of organic material in the water column. Therefore these samples appear to have been deposited under conditions similar to those described and illustrated in Figure 6.16B; in which the water depth to sill was great enough to allow nutrient-rich waters into the basin creating periods of intermittent anoxia. The sediments are bioturbated but the main pathway of Se into the sediment is via organic matter and the authigenic component is relatively small. However, only a slight decrease in the water depth to sill or a subtle change in the wind and ocean currents would need to occur to return the basin to wholly oxic water column conditions. Therefore, the intermediate conditions as illustrated in figure 6.16, were a common occurrence and need to be considered when attempting to understand the variations in the $\delta^{82/76}$ Se values for these four glacial-interglacial cycles (MIS 5-12). The less negative δ^{18} O value for the interglacial sample from MIS 5 (circled – Fig. 6.27) is a result of an increase in salinity within the Cariaco Basin (section 4.3.3.) while the sample from MIS 7 (circled – Fig. 6.27) is a result of that isotope stage generally being cooler compared to MIS 5, 9, and 11 (Fig 4.27).


Figure 6.27: $\delta^{82/76}$ Se values against δ^{18} O ratios (Peterson *et al.* 2000) for samples from the last four glacial-interglacial cycles (MIS 5-12). Interglacial and glacial labels on vertical axis apply to δ^{18} O values only. Circled samples and blue envelope are referred to in the text.

Samples from the last glacial-interglacial transition show a similar relationship between $\delta^{82/76}$ Se and δ^{18} O values to samples from the four glacial-interglacial cycles (Fig 6.27). A number of MIS 1 samples lie in the heavier $\delta^{82/76}$ Se - lighter δ^{18} O values end-member for interglacial (anoxic) conditions and a few MIS 2 samples lie in the lighter $\delta^{82/76}$ Se - heavier δ^{18} O end values end-member for glacial (oxic) conditions. However, a number of MIS 1 and 2 samples lie in the heavy $\delta^{82/76}$ Se-heavy δ^{18} O region (red box-figure 6.26). The MIS 1 samples in this area are between 12.3-14.4 ka (blue envelope – Fig 6.27) and, because of increased upwelling in the Younger Dryas which caused a merging of deep and shallow-dwelling foraminifera, positive δ^{18} O values are recorded representing cooler SST's (see section 4.3.3). Samples from MIS 2 in this region have been previously identified as having anomalously heavy $\delta^{82/76}$ Se values (Fig 6.23).

6.6.2. Conclusion

 $\delta^{82/76}$ Se values measured in sediments from the Cariaco Basin have fluctuated over the last 500 ka. The pattern observed in the $\delta^{82/76}$ Se values is consistent with a model consisting of two simple end-members – an anoxic high $\delta^{82/76}$ Se end member and an oxic low $\delta^{82/76}$ Se end member. The two end members differ in the relative fluxes of Se via two distinct pathways for Se into the sediment, assimilation into organic matter and authigenic reduction of Se (IV) within the post-oxic sediment. The authigenic Se is expected to have negative $\delta^{82/76}$ Se values because of isotopic fractionation induced by reduction of Se oxyanions drawn from oxic bottom water. At times of low Se: Corg ratios and relatively high $\delta^{82/76}$ Se values, assimilation into organic matter was the dominant transport of Se into the sediments; at times when Se: Corg ratios were higher and $\delta^{82/76}$ Se values relatively lower, authigenic enrichment of Se had taken place. Constant low Se: C_{org} and heavy $\delta^{82/76}$ Se values over the recent 9 ka suggest the seawater $\delta^{82/76}$ Se value has remained constant. However, the data from the Cariaco Basin suggests this has not always been the case. During the last glacial-interglacial transition and MIS 10, changes in the Se: C_{org} ratios and $\delta^{82/76}$ Se values possibly indicate shifts in the global ocean $\delta^{82/76}$ Se value occurred.

The high $\delta^{82/76}$ Se values which relates to assimilation of Se into organic material as the dominant pathway of Se into the sediment may or may not relate to anoxia. These high $\delta^{82/76}$ Se values might relate to intermittent anoxia or even just high productivity. Therefore, the $\delta^{82/76}$ Se values are providing information on the dominant transport mechanisms of Se into the sediment but do not necessarily provide information on the oxygen content of the Cariaco Basin at time of deposition. In the Cariaco Basin over the last 500 ka, alternating bioturbated/laminated sediments and alternating oxic/ anoxic water column conditions do not correspond to glacial/ interglacial cycles.

Chapter 7: Selenium in the Bermuda Rise (ODP Leg 172)

7.1. Introduction

This chapter will describe and provide interpretations of Se concentrations and $\delta^{82/76}$ Se values of sediments from the northeast Bermuda Rise spanning the last 500 ka. These Se measurements will be interpreted in the context of new major and trace element geochemical data measured in this study. The aims of this chapter are:

- 1. Report on the behaviour of Se concentrations and $\delta^{82/76}$ Se values under an oxic water column in an open ocean environment.
- 2. Compare and contrast the $\delta^{82/76}$ Se values from the Bermuda Rise with those from the Cariaco Basin. Are there any significant changes in $\delta^{82/76}$ Se which are observed in both records? Are the $\delta^{82/76}$ Se values therefore a global signal?
- 3. Are the variations in $\delta^{82/76}$ Se a result of changing local water column conditions or a change in the global proportion of anoxic to oxic sedimentation?

This site was chosen for the following reasons:

- Bioturbation is prevalent in the core which implies the water column was oxic during sediment deposition.
- It is away from the continental shelf and so the dominant sediment should be pelagic.
- The sedimentation rate is 200 cm ka⁻¹ during the last 500 ka, comparable to the Cariaco Basin rate of 300-1000 cm ka⁻¹.

 The dominant lithology in the section these samples are taken from is clay, silt, and nanno-fossils with variable amounts of biogenic silica (15-30%), similar to the Cariaco Basin.

7.2. ODP Leg 172 – Northwest Atlantic Sediment Drifts

7.2.1. Introduction

The main focus of ODP Leg 172 was to recover a sequence of high depositionrate sediment cores from sediment drifts in the western North Atlantic that document rapid changes in climate and ocean circulation during the middle Pliocene to Pleistocene times. Supplementary aims for Leg 172 were: (1) using the drilled sediments to provide a high-resolution history of magnetic field behaviour and a history of biotic changes; (2) investigate the sedimentary microstructures which reflect the combination of both down-slope and along-slope processes; (3) investigate the sediments of the eastern US continental margin which are deposited at a very high rate and with a high organic carbon content for an open ocean environment (Average C content of Atlantic surficial pelagic sediments = 0.4%; (Berner 1982) which, results in biogenic methane production and clathrate formation (Keigwin *et al.* 1998).

This area of the western North Atlantic forms the western boundary for deepand surface-water circulation in the subtropical North Atlantic. Between the northward flowing surface waters of the Gulf Stream and the net southerly flow of intermediate and deep waters, most of the climatically important exchanges of heat, salt, and water with other ocean basins occur in the westernmost North Atlantic. At the deepest levels of the western North Atlantic, Antarctic Bottom Water (AABW) flows northward and blends with several other water masses in the deep re-circulating gyres to form the North Atlantic Deep Water (NADW) (Fig 7.1) (Keigwin *et al.* 1998).



Figure 7.1: Schematic of circulation patterns in the deep western North Atlantic. BBOR = Blake-Bahama Outer Ridge (BBOR); CS = Carolina Slope; NADW = North Atlantic Deep Water; AABW = Antarctic Bottom Water. Thick lines represent generalised flow directions of NADW and AABW, which contribute to the Deep Western Boundary Current. Thin lines represent streamlines of two re-circulating gyres and small numbers are approximate transport in Sverdrups (1 Sv = $10^6 \text{ m}^3\text{s}^{-1}$). Taken from (Keigwin *et al.* 1998).

Eleven sites were cored during Leg 172: seven on the Blake-Bahama Outer Ridge (BBOR), two on the Carolina Slope (CS), one on the Bermuda Rise (BR), and one on the Sohm Abyssal Plain (SAB). Drilling these cores provided a depth transect for documenting changes in the depth distribution of water masses. Sites 1061-1064 are located to record distinctive changes in the AABW/ Lower NADW front. (Figs 7.2, 7.3). This chapter will focus on sediments from Site 1063 on the Northeast Bermuda Rise.



Figure 7.2: Map of the western North Atlantic Ocean showing the location of Leg 172 sites on the Caroline Slope 9CS; Sites 1054 and 1055), the Blake-Bahama Outer Ridge (BBOR; Sites 1056-62), the northeast Bermuda Rise (Site 1063), and the Sohm Abyssal Plain (Site 1064). Taken from (Keigwin *et al.* 1998).



Figure 7.3: Temperature-salinity diagram for the western North Atlantic showing the positions of the various water masses and the Leg 172 sites presently associated with each of the water masses (Keigwin *et al.* 1998). Water depths are indicated every 500 m along the temperature/ salinity plot. Site 1063 is at 4584 m depth.

7.3. Site 1063 - Northeast Bermuda Rise (ODP Leg 172)

7.3.1. Introduction and Location

Site 1063 is located on the northeast Bermuda Rise, in the northern Sargasso Sea, at a water depth of 4584 m. This location is close to the interface between Antarctic Bottom Water and North Atlantic Deep Water, marked by bottom water temperatures of $\sim 2^{\circ}$ C. Four holes were cored, with total recovery between 95-102% (Table 7.1). The interval 0 - 201.4m below sea floor (mbsf) was triple cored with the advanced hydraulic piston corer (APC) and provides a complete composite sequence back to the early Pleistocene.

			Water		Interval	Core	
			depth	Number	cored	recovered	Recovery
Hole	Latitude	Longitude	(mbrf) ^a	of cores	(m)	(m)	(%)
1063A	33°41.2043'N	57°36.8979'W	4595.2	45	418.40	400.34	95.7
1063B	33°41.1885'N	57°36.8982'W	4594.7	38	351.60	341.95	97.3
1063C	33°41.1818'N	57°36.9028'W	4596.0	24	212.70	204.39	96.1
1063D	33°41.1717'N	57°36.9067'W	4596.2	19	173.10	176.54	102.0
		Site 1	126	1155.80	1123.22	97.2	

Table 7.1: Summary of Hole 1063 drilling results (Keigwin et al. 1998)

^ambrf = meters below rig floor

7.3.2. Sedimentary sequence

The sediment drift that comprises the northeast Bermuda Rise is one of the highest resolution archives of palaeoclimate and palaeocean information known from the open sea. The overlying deep water in the North Atlantic basin is the most turbid as a result of the advection of clays and silts by the deep Gulf Stream return flow (Keigwin *et al.*, 1998 and refs therein). The source of this sediment is probably eastern Canada although (Laine *et al.* 1994) document local erosion on the eastern scarp of the BR and re-deposition on its plateau. The sediments recovered at Site 1063 record the rapid

deposition of clays, silts, and nannofossils and document the dynamics of deep-ocean advection and redeposition.

Hole 1063A has one recognised stratigraphic unit characterised by 70-100% clays alternating with nannofossil-bearing intervals (commonly 15-30%, but occasionally exceeding 60%), biogenic silica and silt (Keigwin et al. 1998). There are three correlatable sub-units of Site 1063A which are distinguished by the occurrence of biogenic silica and red lutites (Fig 7.4). The dominant lithology of Subunit IA (0.0-170.8 mbsf) is medium light olive grey to greenish grey clay with varying proportions of silt and carbonate and siliceous-bearing nannofossils. This subunit is defined by the variable presence of a dark greyish brown to greenish grey clay with biogenic silica. Within these intervals, worm burrows filled with tests of silicoflagellates, radiolarians, and diatoms are quite common. Any lithological change is subtle with the sedimentological composition staying fairly constant with only minor shifts in the abundances of accessory lithologies. The only prominent exception to this is the relative abundance of biogenic carbonate and nannofossil-rich beds (>50%), which occur between 64-68 mbsf and 82-85 mbsf (Keigwin et al. 1998). A common feature of these intervals is a basal contact defined by a sequence of sharp diagenetic colour changes (moderate to dark greenish grey band with an overlying, thinner, faint purple band) and a gradational upper contact (Keigwin *et al.* 1998). Red to reddish brown lutite beds are also common in Subunit IA. These intervals consist of massive and structureless reddish brown clay and clay with silt and usually contain sharp to very sharp basal contacts. These beds are derived from the Permo-Carboniferous deposits of the Canadian Maritime provinces and are transported by glaciers to the Nova Scotian continental margin. A single lutite bed ranges from 20 to 75 cm thick but they are generally grouped together over several meters and alternate with beds containing similar

lithologies but without reddish brown colouration. Using biostratigraphic and magnetic susceptibility data, the occurrence of red lutites generally coincides with the termination of glacial periods. However, one small bed is known to correspond to the termination of MIS 5e (Adkins *et al.* 1997). Distinctive zones of black mottling, due to precipitation of hydrotroilite during early diagenesis, are also present. In the red lutite beds greenish grey bioturbation mottles with black iron sulphide centres are also common with their greenish grey colour attributed to chemical reduction of the sediment surrounding the organic-rich burrows (Keigwin *et al.* 1998). Below subunit IA, the sediments are dominated by clays with periodic carbonate intervals and few occurrences of red lutite beds (Fig 7.4). Moderate to intense bioturbation is common throughout the entire sediment record; it is most apparent at sharp lithologic and/ or colour transitions.



Figure 7.4: Generalised lithostratigraphy, biostratigraphy, and magnetostratigraphy of Site 1063 (Keigwin *et al.* 1998). PL = Top Pseudoemiliania lacunose (0.46 Ma); B/M = Bruhnes/Matuyama boundary (0.78 Ma).

7.3.3. Biostratigraphic and palaeomagnetic data

Calcareous nanno-fossils are the dominant microfossils and are generally well preserved, except for some intervals where they are dissolved. Eleven nanno-fossil biohorizons have been constrained for the past 3.3 million years. Foraminifera assemblages are generally dissolved but eight foraminifer biohorizons are identified despite poor preservation. Where diatoms are present, the sediment has an unusual association of high sonic velocity with low bulk density. It is thought this stems from a core structural framework provided by the diatoms and other siliceous microfossils. The diatoms appear to be most prevalent in cold climate episodes, possibly reflecting a combination of higher surface-water productivity and better preservation (Keigwin *et al.* 1998).

Palaeomagnetic results from Site 1063 provide a detailed magnetostratigraphy down to the Gauss Chron. In hole 1063A, the Bruhnes/ Matuyama reversal boundary (0.78 Ma) is located at 138.5 mbsf. The integrated biomagnetostratigraphy suggests a sedimentation rate of 200 m Ma⁻¹ from 0 to 0.5 Ma. The sedimentation rate then decreases in the older sediments reaching 75 m Ma⁻¹ during the Pliocene (>2.5 Ma) (Keigwin *et al.* 1998).

7.3.4. Interstitial water geochemistry

Within the sulphate reduction zone, rapid increases in alkalinity, ammonium, and phosphate occur downhole while a decrease in sulphate takes place within the top 20 m (Fig 7.5). At 38 mbsf, methane concentrations start to increase. Below the sulphate-methane interface, alkalinity and phosphate decrease while ammonium increases but at a lower gradient compared to the top 20 m. These rapid down-hole decreases in sulphate and increases in ammonium, alkalinity, and phosphate concentrations in the top 20 m are caused by the microbial decomposition of organic

matter in the sulphate reduction zone (Keigwin *et al.* 1998). Below 38 mbsf, the reduction in phosphate concentrations suggests a reduced rate of organic matter degradation and probable adsorption on carbonate minerals (Morse & Mackenzie 1990) while the increase in ammonium concentrations can be explained by either continued organic matter degradation or the release from clay mineral sites by potassium replacement (Mackin & Aller 1984).



Figure 7.5: Interstitial water concentration profiles of alkalinity, ammonium (NH₄), sulphate (SO₄), methane, and phosphate (PO₄) vs. depth (mbsf) from hole 1063A. Yellow zone indicates the sulphate reduction zone, green shading indicates the methanogenesis zone, and the dashed black line is the sulphate-methane boundary. Data from Keigwin *et al.*, (1998). The 110 mbsf is the maximum depth of samples measured as part of this thesis.

Rapid down-hole decreases in the concentrations of calcium and strontium occur in the sulphate reduction zone at site 1063; whereas in the methanogenesis zone, Ca and Sr concentrations increase. In contrast, Mg and K concentrations decrease at shallower gradients throughout the whole core (Fig 7.6). Fe and Mn concentrations are high near the sediment-water interface while within the methanogenesis zone, Mn concentrations are continuously <3 μ M and Fe concentrations decrease to <10 μ M. In contrast, silica concentrations are low near the sediment-water interface and then increase rapidly and remain relatively constant throughout the whole core (Fig 7.7).



Figure 7.6: Metal concentrations vs. depth for interstitial waters at site 1063A. See caption of figure 7.5 for shading details and for comment on depth scale. Data from (Keigwin *et al.* 1998).

The decrease in the Ca, Mg, and Sr profiles in the first 30 m suggests precipitation of carbonate minerals has taken place within the sediment (Keigwin *et al.*, 1998). The down-hole decrease in K is probably caused by adsorption of K ions on clay minerals (Çagatay *et al.* 2001). Within the methanogenesis zone, the down-hole increase in Sr concentrations is possibly due to release of strontium into pore waters by either re-crystallisation or dissolution of biogenic carbonates; the concomitant downcore increase in calcium and decrease in magnesium suggests dolomite formation (Keigwin *et al.* 1998). Because of their redox controlled behaviour Fe and Mn are mobilised in the sulphate reduction zone resulting in the high concentrations in the surface interstitial waters. Decreasing Fe concentrations within the sulphate reduction zone indicate the formation of authigenic iron sulphides which manifest themselves as black mottling in the sediments (see 7.3.2). The low concentrations of iron and manganese within the methanogenesis zone suggest their incorporation into carbonate minerals such as ankerite and siderite, confirmed by XRD analysis of bulk sediment samples (Keigwin *et al.* 1998). The relatively high levels of dissolved silica suggest dissolution of biogenic silica within the sediments (see 7.3.2.).

7.4. Sample Information

7.4.1. Depth-age relationship for site 1063

An age-depth model for Site 1063 was derived by tuning the carbonate record to the Milankovitch precession and obliquity cycles for the last 900 ka (Grützner *et al.* 2002) (Fig 7.7). Because of the direct tuning to obliquity and precession, the derived time scales are phase-locked (with zero time lag) with two target curves. However, there is a delay between orbital forcing and the response of the climate system (Imbrie & Imbrie 1980) which was estimated to be ~5 ka for the precessional band of δ^{18} O changes (Imbrie 1984). Only minor phase differences between carbonate content and oxygen isotopes existed confirming that carbonate content variations in the western North Atlantic are in phase with global ice volume changes (Grützner *et al.* 2002). With these results a phase lag of 5 ka between was subtracted from the tuned ages to obtain the final age model (Grützner *et al.* 2002). Multiple holes were drilled at site 1063 so that the continuity of recovery was confirmed by developing composite depth sections (depth in meters composite depth, mcd) and splice points to join the records of the multiple holes together.



Figure 7.7: Age-depth relationship for site 1063 derived from the correlation of calcium carbonate records to astronomical precession and obliquity cycles (Grützner *et al.* 2002). Depth is given in meters composite depth (mcd) (Keigwin *et al.* 1998).

7.4.2. Sample locations

A set of sixty sediment samples were obtained from ODP Leg 172, site 1063, hole A which was drilled at a water depth of 4583.5 m. The samples were requested on 17/07/2007 and received on 10/08/2007 under IODP request number 21326A. This hole was drilled for a total length of 418.4 mbsf which provided a complete composite sequence back to the lower Pliocene. Sub-samples of 2 cm were used; this yields a temporal sampling resolution between 27 and 263 years, although bioturbation would increase this range. The range of sedimentation rates for these samples is from 0.10 to 0.77 m ka⁻¹, averaging 0.27 m ka⁻¹. These samples from site 1063A span the last 500 ka which includes MIS 1-12 and allow a direct comparison to the samples from the Cariaco Basin (Table 7.2; fig 7.8).

	Depth	Depth	Age		
Sample ID ¹	(mbsf) ²	$(\mathbf{mcd})^3$	$(ka)^4$	Colour ⁵	MIS
1H-1-80-82	0.80	0.93	6.09	Brown	1
1H-3-97-99	3.97	4.61	12.71	Reddish brown	1
2H-2-28.30	6.22	7.16	17.28	Dark greyish brown	2
2H-4-59-61	9.21	10.41	22.00	Brown	2
2H-6-95-97	12.75	14.25	27.46	Greyish brown	
3H-1-77-79	15.57	17.26	33.13	Olive grey medium light olive grey	
3H-2-135-137	17.65	19.38	38.85	Olive grey	3
3H-4-100-102	20.30	22.08	46.14	Light olive grey	
3H-6-23-25	22.53	24.36	52.50	Greyish brown	
3H-7-46-48	24.26	26.12	59.49	Dark greyish brown	4
4H-2-133-135	27.13	29.46	73.75	Grey	4
4H-3-34-35	27.64	30.06	76.47	Medium light olive grey	†
4H-3-122-124	28.52	31.08	86.75	Medium light yellowish grey	_
4H-5-48-50	30.78	33.72	102.87	Medium light pinkish grey	5
4H-6-21-23	32.01	35.15	114.55	Medium light brownish grey	
5H-1-43-45	34.23	37.67	130.70	Dark grevish brown	
5H-2-138-140	36.68	40.14	140.00	Dark greyish brown	
5H-4-35-37	38.65	42.13	145.57	Dark grevish brown	
5H-5-106-108	40.86	44.36	150.23	Reddish brown	6
6H-1-37-39	43.67	47.23	156.24	Grevish brown light brownish grey	
6H-2-35-37	45.15	48.85	162.26	Light brownish grey greyish brown	
6H-4-23-25	48.03	52.02	176.96	Light olive grey greenish grey	
6H-4-145-147	49.25	53.36	185.87	Light olive grey greenish grey	
6H-5-115-117	50.45	54.68	198.12	Light olive grey greenish grey	
6H-6-97-99	51.77	56.13	210.24	Greyish brown light grey	
7H-1-113-115	53.93	58.38	227.06	Light olive grey	7
7H-2-18-20	54.48	58.92	230.59	Medium dark greenish grey	
7H-2-135-137	55.65	60.07	238.09	Light olive grey light reddish brown	
7H-3-54-56	56.34	60.76	242.65	Moderate greenish grey	
7H-4-120-122	58.50	62.89	256.91	Yellowish grey light pinkish red	+
7H-5-48-50	59.28	63.66	261.57	Light greenish grey	
7H-6-70-72	61.00	65.36	271.31	Medium light greyish green	
8H-1-80-82	63.10	67.46	280.95	Dark greenish grey	8
8H-2-65-67	64.45	68.84	286.87	Very light olive grey	
8H-3-7-9	65.37	69.78	293.58	Very light olive grey	
8H-4-13-15	66.93	71.38	305.11	Light reddish brown	†
8H-5-5-7	68.35	72.83	315.09	Light olive grey	
8H-5-135-137	69.65	74.16	324.08	Light olive grey	9
8H-6-70-72	70.50	75.03	329.45	Light olive grey	
9H-1-52-54	72.32	76.96	337.70	Reddish brown	
9H-2-15-17	73.45	78.26	342.17	Reddish brown light greenish grey	+
9H-3-30-32	75.10	80.16	347.72	Light olive grey pale red	
9H-3-72-74	75.52	80.64	349.19	Light olive grey pale red	10
9H-3-124-126	76.04	81.24	351.09	Light olive grey pale red	
9H-4-117-119	77.47	82.89	357.06	Greenish grey	
9H-5-40-42	78.20	83.73	360.66	Greenish grey olive grey	
9H-6-9-101	80.29	86.14	371.14	Greenish grey	11
10H-1-56-58	81.86	87.89	381.39	Medium light greenish grev	
					1

Table 7.2: Details of the 60 samples obtained from site 1063A for the last 500
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10H-2-40-42	83.20	89.31	397.20	Moderate olive grey	
10H-3-38-40	84.68	90.88	405.91	Light greenish grey	
10H-3-122-124	85.52	91.77	408.57	Dark greenish grey	
10H-4-44-46	86.24	92.53	410.84	Dark greenish grey	
10H-4-105-107	86.85	93.18	412.77	Dark greenish grey	
10H-5-11-13	87.41	93.77	414.54	Dark greenish grey	
10H-5-121-123	88.51	94.94	418.02	Dark greenish grey	
10H-6-18-20	88.98	95.43	419.50	Dark greenish grey	
11H-1-48-50	91.28	97.86	426.12	Greenish grey reddish brown	
11H-2-90-92	93.20	99.87	431.20	Greenish grey reddish brown	12
11H-3-45-47	94.25	100.97	435.98	Greenish grey reddish brown	12
11H-4-5-7	95.35	102.12	441.57	Light greenish grey	

¹Sample identification using standard ODP notation of Core-Section-Top (cm)-Bottom (cm). Each core is split into sections of 1.5 m in length. For example sample 1H-3-97-99 is from core 1H which, according to core logs (Keigwin *et al.*, 1998) represents 0-5.3 m, section 3 of core 1H which starts at 3 m, and is taken at 97-99 cm along section 3 which equals a depth of 3.97-3.99 m.

²Depths are top of each sample.

³To apply the age-depth model (Fig 7.7) to the samples from site 1063A a depth conversion was applied to convert from meters below sea floor (mbsf) to meters composite depth (mcd). Working from the top of the sedimentary sequence a constant was added to the top depth (mbsf) for each core to arrive at a composite depth (mcd) for the top of that core. For example, core 2H had a top depth of 5.3 mbsf and a bottom depth of 14.8 mbsf which corresponded to a top composite depth of 6.6 mcd and a bottom composite depth of 16.48 mcd (Table 12-Keigwin *et al.*, 1998). Using these constants, a factor was calculated which allowed a linear interpolation between mbsf depths of the core and the composite depths of the core.

⁴Using age-depth model developed by Grützner et al., (2002) using composite depths (Fig 7.9).

⁵On-board ship visual descriptions made with Munsell soil colour charts (Munsell Color Company Inc. 1975) (Taken from core logs, Keigwin et al., 1998).

Using the core descriptions a number of the samples obtained from site 1063A are from areas of the core which have evidence of black sulphide mottling (e.g. 5.3-10.3 mbsf), undefined burrows (e.g. 53.8-57.8 mbsf), and the presence of pyrite (e.g. ~87-89 mbsf) (Keigwin *et al.* 1998). There are also samples in the following depth intervals, 64-68 mbsf and 82-85 mbsf, which are characterised by high abundances of biogenic carbonate and nanno-fossil rich beds and light colour intensity (Table 7.2). In cores 3H to 9H and 11H for site 1063A, it is remarked that there are green and purple diagenetic

laminae throughout the core or in particular sections. This feature is accompanied by iron sulphide replacement of small burrows throughout core 3H (Keigwin *et al.*, 1998).



Figure 7.8: Location of samples from site 1063 spanning the most recent 500 ka (MIS 1-12). Glacial MISs are shaded and indicated by even numbers. Note MIS 3 is part of the glacial period which includes MISs 2 and 4. Crosses are at top depth of each sample interval.

7.5. Chemical oceanography of sediments from the Bermuda Rise

7.5.1. Carbon Geochemistry

TOC contents used in this thesis are estimated values (symbolised as TOC_(eq)),

based on total C contents measured at University of Leicester (see section 3.3.2).

CaCO₃ contents were first estimated by using the measured CaO values (see Appendix).

The estimated $CaCO_3$ values were then converted to total inorganic carbon values; TOC_(eq) content was then determined by the difference between the measured total carbon value and the estimated inorganic carbon value. These TOC_(eq) values are compared to measured CaCO₃ and TOC contents following standard ODP analytical methods (Keigwin *et al.*, 1998).

Both measured and estimated calcium carbonate values at Site 1063 range from 1.33 to 60.55 wt%. The CaCO₃ concentrations show cyclic variations and correlate with the global δ^{18} O SPECMAP curve, especially <200 ka when sample spacing is smaller (Fig 7.9A). CaCO₃ accumulation rates range between 0.33 and 14.17 g cm⁻² ka⁻¹ and average 3.05 g cm⁻² ka⁻¹ for the last 600 ka. High carbonate deposition tends to occur during interglacial periods (>7 g cm⁻² ka⁻¹) e.g. MIS 11 and 13, whereas the lowest carbonate values are generally seen during glacial intervals (Fig 7.9A). The exception to this is during the latter stages of MIS 11 (~397 ka) where CaCO₃ contents fall sharply. This feature is known as the "Mid-Bruhnes dissolution event" where both the Atlantic and Pacific oceans experienced severe dissolution of carbonates (Thunell et al. 2002). In contrast, the total organic carbon (TOC) concentrations show an anti-correlation with SPECMAP; higher TOC concentrations are more typical in glacial periods and lower TOC concentrations characterise interglacial periods (Fig 7.9B). However the relationship of TOC with SPECMAP is not as strong as the relationship between CaCO₃ and SPECMAP. The measured TOC values range from <0.05 to 1.06 wt%, and average 0.54 wt%. In contrast, the TOC_(eq) values are much more muted and only range between 0.32 and 0.84 wt%. Accumulation rates on measured TOC values range from <0.05 to $0.36 \text{ g cm}^{-2} \text{ ka}^{-1}$ and average $0.14 \text{ g cm}^{-2} \text{ ka}^{-1}$ for the last 600 ka; highest organic carbon accumulation rates occur in MIS 6 (>1.5 g cm⁻² ka⁻¹) and at the MIS 12/11 boundary (Keigwin et al. 1998). C/N ratios can be used as an indicator of the organic matter

provenance. Average C/N values of marine zooplankton and phytoplankton tend to lie between 5 and 8, whereas land plants typically have ratios of 20 to 200. C/N ratios are highly variable at site 1063A and range between 0.10 and 16, averaging 7.85 (Fig 7.9C). The average C/N values generally indicate the bulk of the organic matter is derived from marine phytoplankton but higher C/N ratios in the last 60 ka suggest periodic influxes of land-derived organic material, with a provenance of the Canadian Maritime provinces (Fig 7.9C) (Keigwin *et al.* 1998). However, due to the low concentrations measured, errors on the C/N values are large and care must be taken when interpreting.





Figure 7.9: (A) $CaCO_3$ contents, (B) TOC concentrations, (C) C/N ratios for the last 600 ka from site 1063A. Note the change of SPECMAP scale in B. Data from Keigwin *et al.*, (1998) and estimated $CaCO_3$ and TOC values are from this thesis (see Appendix). Shaded and even numbered areas represent glacial periods.

7.5.2. Trace element geochemistry

To help constrain and identify processes which have operated in the Bermuda Rise over the last 500 ka, multiple redox-sensitive elements, including metals that respond differently to a particular redox state of the system, provide information on bottom water oxygenation at the time of deposition. Other proxies reveal changes in source material, and information on the physical and chemical weathering rates occurring in the surrounding continental regions; and trace elements distributions can also illustrate changing levels of primary production. Trace element profiles are normalised to Al, to remove any effects of dilution by planktonic carbonate and silica components, so the metals can be studied relative to the terrigenous inventory (Yarincik *et al.* 2000). The following trace element data, Se concentration, and Se isotope values were measured as part of this thesis. For information on the methodologies, accuracy, and precision see chapter 3. A complete data table is available in the Appendix.

Total Al ranges from 3.3 to 9.3 wt. %, total Fe ranges from 2.3 to 14.1 wt.%, and total S ranges from 0.011 to 11.08 wt.% (Fig 7.10). Excluding the large Fe peak at ~185 ka, the Al and Fe values cover a similar range to the Al and Fe values from the Cariaco Basin (Fig 5.9). In contrast, with the exception of the large S peak at ~185 ka, the S contents of sediments from the Bermuda Rise are significantly lower than those of the Cariaco Basin. There is possible evidence in the Fe, and Al profiles of a distinction between interglacial and glacial periods with glacial periods having greater values than interglacial periods. Changes in concentration occur simultaneously in the Al and Fe profiles, at a relatively constant Fe/Al ratio of 0.62 ± 0.06 (1 σ). The constant Fe/Al is likely to reflect changes in the detrital input of both elements, possibly from rivers, or increased dilution of both elements by non-detrital (biogenic) components. The decrease in both Al and Fe values across the MIS 12-11 transition is the largest individual change of the last 500 ka with the exception of the increase occurring at 185 ka. This is possibly because the magnitude of the climate changes at the MIS 12-11 transition is the largest of the last 600 ka (Howard, 1997). The S profile does have a similar overall pattern to both the Fe and Al profiles – but there is no significant drop in S contents across the MIS 12-11 transition (Fig 7.10). Where the Fe and S profiles do agree is the large increase in abundance at ~185 ka. This corresponds with the transition from the interglacial MIS 7 to glacial MIS 6. The simultaneous increase in Fe and S suggests that precipitation of iron sulphide minerals has taken place and the MIS 7-6 transition is also a redox front. Core logs indicate the presence of pyrite at this depth but no accompanying colour change (Keigwin et al. 1998). If this is a redox front, it would be expected to also feature in the profiles of redox sensitive elements, such as Se, Mo, V, and U.



Figure 7.11: Total Fe, S, and Al concentrations of sediments from the Bermuda Rise over the last 500 ka. Shaded and numbered areas represent glacial periods. Data measured as part of this thesis.

Mn/Al at the Bermuda Rise range from 0.009 to 0.05 g/g and Fe/Al ranges from 0.54 to 0.79 g/g (Fig 7.12); both elements are enriched relative to PAAS (~0.0085 wt. % and ~0.43 respectively) (Taylor & McLennan 1985). Sedimentary Mo/Al values are relatively constant with values less than 0.62 ppm/wt.%, while V/Al values range between 3.11 and 19.79 ppm/wt.%; both of these elements are close to their respective PAAS values of 0.1 and 15 ppm/wt.% (Taylor, McLennan 1985) (Fig 7.12). All four redox proxies show no clear relationship with the glacial-interglacial stages; however, there are significant variations within individual interglacial and glacial stages.



Figure 7.12: Downcore profiles for a number of geochemical proxies from the Bermuda Rise for the last 500 ka. (Top) Redox sensitive metals (Mn/Al, Fe/Al, Mo/Al, and V/Al). (Bottom) Al/Ti, K/Al, and terrigenous content (Table 5.2). Downcore profiles from the Cariaco Basin are shown for comparison (see figure 5.11 and Appendix). Shaded and numbered areas represent glacial periods. Data collected as part of this thesis.

The four redox proxies from the Bermuda Rise are significantly different to the profiles from the Cariaco Basin. The Mn/Al and Fe/Al values are greater than those from the Cariaco Basin whereas the Mo/Al and V/Al values are less than those from the Cariaco Basin. These differences indicate oxygen-rich conditions existed at the time of deposition at the Bermuda Rise (Table 5.2). Even though both V/Al and Mo/Al values are low at the Bermuda Rise, there is an obvious difference in the behaviour between them under the oxic water column. Whereas Mo requires free H_2S/HS^- to transform from a conservative element to a particle-reactive element, in the marine environment the V (IV) species can be removed to the sediment by either surface adsorption processes or by the formation of organometallic ligands (Tribovillard et al. 2006). This enrichment of V, which is not accompanied by a similar enrichment in Mo, suggests a suboxic depositional environment without free H_2S existed within the sediments at time of deposition (Tribovillard et al. 2006). An increase in the Mo concentration to 0.62 ppm/wt.%, - six times enriched relative to PAAS - exists at the MIS 7-6 transition (~185 ka). This coincides with the increases in Fe and S at ~185 ka, which adds further evidence to suggest a more reducing depositional environment, existed at this time.

Al/Ti values for sediments from the Bermuda Rise range from 15.3 to 19.3 g g⁻¹, K/Al values range from 0.11 to 0.41 g g⁻¹, and the terrigenous contents of the Bermuda Rise sediments range from 29.1 to 75.4% (Fig 7.12). For all three proxies there is no significant difference between the average values for interglacial and glacial periods over the last 500 ka but there are significant variations within individual interglacial and glacial periods. Al/Ti values from the Bermuda Rise are lower than Al/Ti values at the same time in the Cariaco Basin, K/Al values from the Bermuda Rise are significantly higher than those from the Cariaco Basin, while terrigenous contents of both locations are similar (Fig 7.12). Large decreases in Al/Ti from the Bermuda Rise within

interglacial periods indicate increased aeolian inputs while increased values during glacial periods suggests a decrease in aeolian inputs thus negatively correlating with the Al/Ti data from the Cariaco Basin (Figs 7.12, 5.11). Within individual interglacial stages, for example MIS 11, 9, and 5, the same pattern in Al/Ti values is observed – a large decrease occurs just after the deglaciation followed by a gradual increase in Al/Ti values towards the next glaciation. The high K/Al values suggest physical weathering is more prevalent at the sediment source of eastern Canada.

The differences in the Al/Ti and K/Al values between the Cariaco Basin and the Bermuda Rise can be interpreted as a result of the different atmospheric circulation patterns at the two sites. The equatorial Cariaco Basin (10°N) is in the ITCZ with strong trade wind variations on a glacial-interglacial timescale; the subtropical Bermuda Rise (33°N) is currently located just north of a sinking component of a Hadley Cell (Fig. 4.17), where the sinking air is adiabatically warmed, becomes gradually drier, and able to hold more water vapour. This flow prevents condensation from occurring in the subtropics which makes these latitudes a zone of low average precipitation and high evaporation (Ruddiman 2001). The variations in the Al/Ti values and terrigenous content of sediments from the Bermuda Rise possibly suggest a change, over interglacial-glacial timescales, of the wind patterns and importance of continentallyderived material. The current dominant wind direction at 33°N is from the south-west to east over the North American continent. During interglacial periods, when ice cover on the North American continent is low, the proportion of aeolian material from North America increases (low Al/Ti values) relative to material derived from the continents (terrigenous content is lower); during glacial periods when North America is covered in an ice sheet, the proportion of aeolian material decreases (high Al/Ti values) relative to continentally-derived material (terrigenous content is higher).

Any change in productivity at the Bermuda Rise will be reflected in the profiles

of P, Ba, Cd, and Ni (Table 7.3, Fig 7.13). Despite the recycling of exported organic

matter that occurs within the water column, the amount of C being buried in the

sediment is proportional to the total surface water productivity (Tribovillard et al.,

2006).

Table 7.3: Description of the trace element geochemical proxies used to estimate productivity at the Bermuda Rise (Tribovillard *et al.*, 2006; Calvert and Pederson, 2007)

Element	Explanation
Phosphorus	P is a limiting macro-nutrient for algal growth and has a fundamental role in many
	metabolic processes. The main source of P is the phytoplankton necromass which reaches
	the sediment-water interface plus fish scales and bones. Organic P is easily remineralised
	and the degree to which it is retained in sediment depends on the reduction capacity of the
	depositional system.
	Live phytoplankton in surface waters incorporate Ba either actively (metabolic uptake) or
Dominum	passively (adsorption) and Ba released during phytoplankton decay may precipitate as
Darium	barite. Like P, Ba can migrate during early diagenesis and precipitate in sediments
	deposited in the absence of high productivity.
	Cu behaves only partly as a micronutrient and is also scavenged from solution in deep
Copper	water. The complexation of Cu with organic matter, as well as adsorption onto particulate
	Fe/Mn oxyhydroxides will accelerate scavenging and sediment enrichment.
	In oxic marine environments Ni is a micronutrient and is present as soluble Ni ²⁺ cations,
Niekol	NiCl ⁺ ions, soluble NiCO ₃ , or adsorbed onto humic and fulvic acids. Ni also complexes
NICKEI	with organic matter which accelerates scavenging in the water column and thus sediment
	enrichment.

The four productivity proxies (P, Ba, Cu, and Ni) average 316.9 ± 35.8 ppm, 48.1 ± 20.4 ppm/ wt.%, 5.72 ± 2.21 ppm/ wt.%, and 5.68 ± 1.58 ppm/ wt.% respectively. None of these proxies show any significant difference between average values for interglacial and glacial periods, suggesting productivity at the Bermuda Rise has remained approximately constant on glacial-interglacial timescales over the last 500 ka (Fig 7.13). This corresponds with measured TOC contents which also show small

variations between glacial and interglacial stages (Fig 7.13). Similar to the Al/Ti, K/Al, and terrigenous profiles, there are variations of these productivity proxies within individual interglacial and glacial periods. There is one anomalously high concentration in the P and Ni profiles at 185 ka which would tend to suggest productivity increased but there is no similar increase in the $TOC_{(eq)}$ value (Fig 7.13). Therefore there is another cause for these anomalously high P and Ni concentrations - they correspond with the highs in the Fe and S profiles (Fig 7.11). In low productivity portions of the oceans, it is considered that P enrichment can be effectuated through redox cyling of Fe, with P sorption onto Fe-oxyhydroxide coatings and Fe-P coprecipitation (Tribovillard et al., 2006). Under the sulphate reducing conditions which exist below 38 m, Ni can be incorporated as the insoluble NiS into pyrite (Morse & Luther III 1999). Another feature which is distinctive for all four productivity proxies are their overall differences in profile shape over the last 500 ka. P and Ni are relatively constant over the last 500 ka with only occasional deviations from the average concentrations. At the MIS 7-6 transition, there is a decrease in the average Ni/Al value from 6.11 ± 0.82 before this transition to 4.59 ± 1.04 after the transition. This might reflect a change in the productivity but a similar feature is not observed in the remaining proxies. The Ba/Al profile generally decreases from a maximum of 101.7 ppm/ wt/% at 405.9 ka to a minimum of 8.6 at 86.7 ka before increasing after the MIS 5-4 transition. The peak Ba/Al value at 405.9 ka correlates with high carbonate contents (see section 7.3.4). Finally, the Cu/Al profile has a possible cyclical component to it with maximum concentrations occurring at 324 ka, 210 ka, and 86 ka with corresponding minimum concentrations occurring at 238 ka, 145 ka, and 22 ka respectively.



Figure 7.13: Palaeoproductivity proxies from the Bermuda Rise for the last 500 ka. Shaded and numbered areas represent glacial periods. Data was measured for this thesis. TOC data is our estimated values (see 7.5.1)

7.6. Se concentrations from the Bermuda Rise over the last 500 ka

7.6.1. Glacial-interglacial variations in Se concentrations

Se concentrations in sediments from the northeast Bermuda Rise range from a minimum of 0.08 ppm to a maximum of 1.73 ppm for the last 500 ka, averaging 0.45 ± 0.27 ppm (Table 7.4).

	Depth	Age			δ ^{82/76} Se	± 2 se $\delta^{82/76}$ Se
Sample ID	(mcd)	(ka)	MIS	Se (ppm)	(‰)	(‰) ^a
1H-1-80-82	0.93	6.09	1	0.131	-0.36	0.16
1H-3-97-99	4.61	12.71	1	0.582	-0.23	0.07
2H-2-28.30	7.16	17.28		0.441	-0.02	0.04
2H-4-59-61	10.41	22.00	2	0.460	-0.17	0.06
2H-6-95-97	14.25	27.46		0.401	-0.19	0.09
3H-1-77-79	17.26	33.13		0.214	-0.50	0.08
3H-2-135-137	19.38	38.85	3	0.425	-0.30	0.05
3H-4-100-102	22.08	46.14		0.345	-0.18	0.10
3H-6-23-25	24.36	52.50		1.002	-0.08	0.05
3H-7-46-48	26.12	59.49		0.514	-0.05	0.07
4H-2-133-135	29.46	73.75	4	0.209	-0.13	0.06
4H-3-34-35	30.06	76.47		0.409	-0.35	0.04
4H-3-122-124	31.08	86.75	5	0.158	-0.06	0.09
4H-5-48-50	33.72	102.87	3	0.137	-0.33	0.10
4H-6-21-23	35.15	114.55		0.084		
5H-1-43-45	37.67	130.70		0.493	-0.11	0.08
5H-2-138-140	40.14	140.00		0.394	0.19	0.06
5H-4-35-37	42.13	145.57		0.210	0.05	0.04
5H-5-106-108	44.36	150.23	6	0.349	-0.40	0.02
6H-1-37-39	47.23	156.24		0.462	-0.29	0.07
6H-2-35-37	48.85	162.26		0.428	0.14	0.03
6H-4-23-25	52.02	176.96		0.374	-0.43	0.05
6H-4-145-147	53.36	185.87		1.730	-0.73	0.06
6H-5-115-117	54.68	198.12		0.618	-0.27	0.11
6H-6-97-99	56.13	210.24		0.260		
7H-1-113-115	58.38	227.06	7	0.589	-0.14	0.06
7H-2-18-20	58.92	230.59		0.453	0.09	0.06
7H-2-135-137	60.07	238.09		0.117		
7H-3-54-56	60.76	242.65		0.403	-0.30	0.01
7H-4-120-122	62.89	256.91		0.447	-0.37	0.08
7H-5-48-50	63.66	261.57		0.462	-0.12	0.04
7H-6-70-72	65.36	271.31	8	0.831	-0.44	0.06
8H-1-80-82	67.46	280.95	0	0.628	-0.17	0.05
8H-2-65-67	68.84	286.87		0.285	-0.30	0.17
8H-3-7-9	69.78	293.58		0.250	-0.16	0.18

Table 7.4: Se concentrations and $\delta^{82/76} Se$ values for the last 500 ka

8H-4-13-15	71.38	305.11		0.715	-0.03	0.08
8H-5-5-7	72.83	315.09		0.177	-0.79	0.17
8H-5-135-137	74.16	324.08	9	0.216	-0.44	0.04
8H-6-70-72	75.03	329.45		0.101		
9H-1-52-54	76.96	337.70		0.357	-0.25	0.04
9H-2-15-17	78.26	342.17		0.419	-0.23	0.05
9H-3-30-32	80.16	347.72		0.436	-0.22	0.08
9H-3-72-74	80.64	349.19	10	0.358	-0.17	0.08
9H-3-124-126	81.24	351.09		0.485	-0.35	0.05
9H-4-117-119	82.89	357.06		0.503	-0.20	0.08
9H-5-40-42	83.73	360.66		0.586	0.04	0.04
9H-6-9-101	86.14	371.14		0.774	-0.15	0.05
10H-1-56-58	87.89	381.39		0.180		
10H-2-40-42	89.31	397.20		0.141		
10H-3-38-40	90.88	405.91		0.109	-0.12	0.14
10H-3-122-124	91.77	408.57	11	0.935	-0.36	0.03
10H-4-44-46	92.53	410.84		0.579	0.11	0.08
10H-4-105-107	93.18	412.77		0.624	0.04	0.07
10H-5-11-13	93.77	414.54		0.779	0.03	0.01
10H-5-121-123	94.94	418.02		0.729	0.03	0.08
10H-6-18-20	95.43	419.50		0.544	-0.29	0.05
11H-1-48-50	97.86	426.12		0.472	-0.30	0.11
11H-2-90-92	99.87	431.20	10	0.515	-0.12	0.01
11H-3-45-47	100.97	435.98	12	0.770	-0.06	0.06
11H-4-5-7	102.12	441.57		0.458	-0.30	0.03

^aMissing $\delta^{82/76}$ Se data due to problems during sample analysis

There is no statistical difference between Se concentrations in interglacial and glacial periods (Table 7.5; Fig 7.14). Excluding the anomalously large Se concentration at 185 ka does not significantly alter the statistics for the interglacial periods. The large Se concentration at ~185 ka coincides with the large concentrations in the Fe, S, and Mo profiles (section 7.5). As with the other geochemical data there are significant variations in Se concentrations within individual interglacial and glacial periods. The Se concentration profile (Fig 7.14a) appears to show some similarities with the Al/Ti and P profiles (Figs 7.12, 7.13). The Se concentrations for both interglacial and glacial periods are similar to the minimum Se concentrations measured in the glacial periods in the Cariaco Basin; they are significantly less than those measured in the interglacial period in the Cariaco Basin.

	^a Interglacial	Glacial
Mean Se concentration (ppm)	0.46 (0.41)	0.45
n	29 (28)	31
$1\sigma_{n-1}$	0.35 (0.26)	0.17
Maximum Se concentration (ppm)	1.73 (0.94)	1.00
Minimum Se concentration (ppm)	0.08	0.21

Table 7.5: Statistical data for Se concentrations in interglacial and glacial periods

^aValues in italics represent statistical data excluding the large Se concentration at 185 ka

Using an average continental crust Se/Al value of 0.01 ppm/ wt.% (Gao *et al.* 1998)Se enrichment factors range between 1.76 and 13.17 with the anomalously large Se concentration at 185 ka having an enrichment factor of 29.55 (Fig 7.14). There is no significant difference in the enrichment factors between interglacial and glacial periods with averages and standard deviations of 6.40 ± 2.79 and 6.25 ± 2.05 respectively. These enrichment factors are much lower than those from the Cariaco Basin (Figs 6.4 and 6.11). The Se/Al and Se enrichment profiles are similar in shape to the Se concentration profile because of the relatively stability in the Al values over the last 500 ka (Fig 7.11).

7.6.2. Relationships between Se-Fe-S-Organic C

As previously described, Se enrichments are a result of three possible processes: adsorption to particulates, binding to sulphides, and incorporation into organic matter. In order to assess if Se is being transported into the sediments by any of these mechanisms it is expected that a relationship will exist between Fe, S and organic C respectively.



Figure 7.14: Se concentrations and their relationship with Al, Fe, S, and organic C in sediments from the Bermuda Rise for the last 500 ka. (a) Se and organic C concentrations; (b) Se/Al and Se enrichment factor; (c) Se/Fe_(norm to Al) ratio; (d) Se/S ratio; (e) total Se/ organic C ratio. Dashed black line and green box represents the average and 2σ of the laminated Se/organic C values from the Cariaco Basin, with the exception of the low Se/ organic C value at 12.71 ka (Fig 6.4). Shaded and numbered areas represent glacial periods. All data collected at University of Leicester.

The Se/Fe profile is similar to the Se/Al, Se enrichment, and Se concentration profiles (Fig 7.14) because of the relatively constant Fe values (Fig 7.11). Se/Fe ratios range from 0.026 to 0.217, averaging 0.098 \pm 0.041. The average Se/Fe value for interglacial periods is 0.091 \pm 0.048 compared to the average Se/Fe value for glacial periods of 0.104 \pm 0.033; both interglacial and glacial periods overlap within error of each other. The sample at 185 ka which, in the Se concentration, Se/Al, P, and Ni profiles is anomalously high compared to the rest of the profile, is "normal" in the Se/Fe profile (Fig 7.14). The Se/S profile does show some different characteristics compared with the Se/Al, Se/Fe, and Se concentration profiles. For example, the coincident decrease between 410 and 380 ka which is observed in the Se concentration, Se/Al, and Se/Fe profiles is not observed in the Se/S profile (Fig 7.14). Other large Se/S values at 329 ka, 293 ka, and 87 ka are not observed in the Se/Fe, Se/Al, and Se concentration profiles. Where the Se/S profile is similar with the Se/Fe, Se/Al, and Se concentration profile is there is no difference in the average Se/S ratio between interglacial (1.80 x 10⁻⁴ \pm 1.17 x 10⁻⁴) and glacial periods (1.41 x 10⁻⁴ \pm 8.37 x 10⁻⁵).

In similar fashion to the Se:C_{org} profiles from the Cariaco Basin, the Se:C_{org} profile from the Bermuda Rise is different from the Se/Al, Se/Fe, and Se/S profiles. The Se:C_{org} ratios range between 2.37 x 10⁻⁶ and 7.34 x 10⁻⁵, averaging 1.66 x 10⁻⁵ \pm 1.29 x 10⁻⁵ (Fig 7.14). There is no significant difference in the average Se:C_{org} ratios between the interglacial (1.67 x 10⁻⁵ \pm 1.25 x 10⁻⁵) and glacial periods (1.65 x 10⁻⁵ \pm 8.54 x 10⁻⁶). The Se:C_{org} profile does show similar characteristics to the Se concentration profile because of relatively constant organic C values. On average, there is considerable overlap between Se:C_{org} ratios from the Bermuda Rise and the average Se:C_{org} ratio from the laminated sediments of the Cariaco Basin (Fig 7.14). However there are samples from the Bermuda Rise with Se:C_{org} values which are significantly less than the

average laminated Se: C_{org} value from the Cariaco Basin and other samples which have significantly larger Se: C_{org} values than the samples from the bioturbated unit in the Cariaco Basin (Fig 6.4). There are five samples which have greater Se: C_{org} values than the average laminated Se: C_{org} value from the Cariaco Basin, 52 ka, 185 ka, 271 ka, 287 ka, and 381 ka.

There are no clear relationships between Se and Fe and Se and S in the Bermuda Rise. There is a weak relationship between Se and organic C in sediments from the Bermuda Rise with Se: C_{org} values similar to those from the Cariaco Basin. This suggests that, similar to the Cariaco Basin, incorporation of Se into organic material might be an important transport mechanism for Se into the sediments. However, none of the three transport mechanisms are dominating the transport of Se in the Bermuda Rise. Further insight into the dominant transport mechanisms operating within the Bermuda Rise can be gained from analysing the relationships between the four components. Cross-plots (Fig 7.15) and ternary composition diagrams (Fig 7.16) illustrate the relationships between Se-Fe-S-Organic C in the Bermuda Rise for the last 500 ka.

No strong correlations exist between Fe-Se-organic C-S (Fig 7.15). The Seorganic C cross-plot shows that the samples from the Bermuda Rise do not lie on either the trend lines for laminated and bioturbated samples from the Cariaco Basin. The Bermuda Rise samples have generally greater Se concentrations at similar organic C contents compared to samples from the bioturbated unit from the Cariaco Basin (Fig 7.15). In all the cross-plots the variation between samples is controlled by the Se and S concentrations rather than changes in Fe and organic C which have a narrow concentration range. The relationship between Fe and S in samples from the Bermuda Rise is even further from the pyrite line than samples from the Cariaco Basin (Fig 7.15).

The lack of strong correlations in the Fe-Se-organic C-S system is also illustrated on the ternary diagrams (Fig 7.16).

The Fe-S data do not show a strong correlation and in the Fe-S-Organic C ternary diagram (Fig 7.16A) the Bermuda Rise samples do not cluster around a constant S/Fe line in contrast to the Cariaco Basin. This suggests that these samples are not iron-limited. The greater S/Fe ratio of the sample at 185 ka suggests that less than 50% of the iron is reactive; the core logs show that iron sulphide minerals are present (Keigwin *et al.*, 1998). The majority of the Bermuda Rise samples cluster around the 100% Fe point and overlap with the sample from the Cariaco Basin which is just below the limit of sulphide diffusion. The same explanation for the location of the Bermuda Rise samples can be used for the location of the sample from the Cariaco Basin – these samples represent the typical Fe-S-Organic C values of oxic sediments that have not bee overprinted by sulphide diffusion (Fig 7.16A). The samples from the Bermuda Rise are also close to the Fe-organic C axis which suggests the organic matter is unreactive (Dean & Arthur 1989). This is expected under oxic water column conditions because the organic material is being regenerated as it falls through the water column and the remaining organic material in the sediment is depleted of its reactive components.

The Se-organic C-S ternary diagram shows the overlap between samples from the Bermuda Rise and samples from the Cariaco Basin (green area - Fig 7.16C). Generally, the Se: C_{org} values from the Bermuda Rise are close to the average laminated Se: C_{org} value from the Cariaco Basin. The five samples which have greater Se: C_{org} values than the laminated Se: C_{org} value of the Cariaco Basin have Se: C_{org} values similar to that of the bioturbated samples from the Cariaco Basin. The samples in the blue box (Fig 7.16C) plot significantly below the average laminated Se: C_{org} line which suggests that processes are depleting the Se relative to the amount of organic C in the sediment.



Figure 7.15: Cross-plot relationships between total Se-Fe-S-Organic C values from the Bermuda Rise. The shaded areas indicate where the majority of samples are distributed. The cross-plots do not include the anomalous sample at 185 ka because it exerts too much control over the trend line. Trend lines are calculated using all the data points except those circled. Relationships between Se and organic C in the Cariaco Basin for laminated sediments and bioturbated sediments are shown by the solid bold and dashed lines respectively. Bioturbated Se-organic C values from the Cariaco Basin are also shown (circles). All values were analysed as part of this study.




The age profiles of the Se/S, Se/Fe, and total Se: C_{org} , cross plots and ternary diagrams of the Fe-Se-Organic C-S system can all provide information on the major transport mechanisms operating in the Bermuda Rise. If Se is adsorbing to Fe and Mn particulates within the water column then a strong correlation is expected between Fe and Se. According to the Se-Fe cross-plot (Fig 7.15) and the Se-Fe ternary diagram (Fig 7.16) there is a weak relationship between Se and Fe. The relatively stable Fe concentrations (Fig 7.11) suggest that any fluctuations within the Se/Fe ratios are caused by variations in the Se concentrations. Therefore it is likely adsorption is a potential pathway of Se into the sediment but it is not a dominant pathway.

Despite being deposited under an oxic water column there is sedimentary core log evidence of the occurrence of black mottling and the presence of pyrite, and porewater sulphate profiles also suggest that sulphate reduction is taking place below the sediment-water interface (Fig 7.5). All of this evidence suggests that there has been sulphide formation at the Bermuda Rise. If Se is incorporated into sulphides then a strong relationship between Se and S is expected. However, relatively low and stable S values (Fig 7.11), combined with no correlation between Se and S on the cross-plot (Fig 7.15) and on the ternary diagram (Fig 7.16) suggests the lack of a strong mechanistic connection between Se and S. Therefore incorporation of Se into sulphides does not take place and is not a transport mechanism for Se. However, the coincident Se and S enrichments at 185 ka might suggest that incorporation of Se into sulphides occurred at this time.

If Se is delivered to the sediment predominantly via its incorporation into organic material then a strong relationship is expected between Se and organic C. The weak relationship between Se and organic C (Fig 7.15), small differences between the Se/organic C profile and the Se/Al profile, and the considerable overlap of the Se: C_{org}

values from the Bermuda Rise with Se:C_{org} values of the laminated sediments from the Cariaco Basin (Fig 7.16C) all show a correlation exists between Se and organic C. This suggests that the incorporation of Se into organic material is a transport mechanism for Se to the sediments. The range of Se:C_{org} values from the Bermuda Rise samples are similar to those of oxic Pliocene marls (Fig 6.8). However, there are a number of samples from the Bermuda Rise which lie outside this range. Samples with low Se:C_{org} values, such as those within MIS 11, 9, and 5, might be caused by the regeneration of Se out of the organic material back into the water column. The samples with higher than average Se:C_{org} values, e.g. MIS 8, are likely to be caused by an additional source of Se into the sediment.

The aim of this analysis of possible transport mechanisms of Se to the sediment is to identify the cause of the Se enrichments (Fig 7.14). Unlike in the sediments from the Cariaco Basin there does not appear to be one dominant transport mechanism of Se through the water column in the Bermuda Rise. Instead, it appears that transport of Se to sediments might be controlled by adsorption to Fe and Mn particulates and incorporation into organic matter.

7.6.3. Se cycling at the Bermuda Rise

The similarities of the Se/Al profile with the Se concentration profile appear to suggest that the variations in Se/Al profile are caused by variations in the Se concentrations. As there is no dominant transport mechanism of Se into the sediments, variations in Se concentrations might also be related to changes in the quantities of the Se sources. A positive correlation exists between Se concentrations and Al/Ti and terrigenous content (Fig 7.17A/B). However there is still no clear interglacial-glacial difference between Se concentrations and Al/Ti. A similar relationship between higher

Se concentrations and Al/Ti ratios is also observed in the Cariaco Basin where there is considerable overlap between interglacial and glacial periods. The similarities between the Se concentration profile, Al/Ti profile, and the P profile suggest a link between Se concentrations, productivity in the surface waters of the Bermuda Rise, and wind strength. A weak negative correlation exists between Se concentrations and K/Al values (Fig 7.17C) and with no clear relationship between interglacial and glacial periods. The opposite correlation is observed between Se concentrations and K/Al in sediments from the Cariaco Basin (Fig 6.15).

These relationships suggest that there are two end-members controlling the variations of Se concentrations at the Bermuda Rise. The first end-member is typical of climates which are common in glacial periods, which has higher Se concentrations, increased productivity, less-wind-blown material but more continentally-derived material, and possibly slightly more chemical weathering. The second end-member is more typical of climates which are common in interglacial periods, which has lower Se concentrations, decreased productivity, increased wind-blown material but less continentally-derived material, and slightly more physical weathering. However, the switching between these two end-members is not controlled by interglacial-glacial cycles.



Figure 7.17: Relationship between Se and Al/Ti, terrigenous contents, and K/Al. Interglacial samples are filled symbols and glacial samples are open symbols. Trend lines do not include the circled sample which is the anomalously high Se concentration at 185 ka.

7.6.4. Summary

The trace elements indicating redox conditions and productivity confirm that the water column at the Bermuda Rise has been nearly constantly oxygenated and experienced relatively constant productivity over the last 500 ka. In all the proxies examined, there is no clear difference between glacial and interglacial periods. The continuous oxic conditions have resulted in lower Se concentrations and unlike the Cariaco Basin, there is no one dominant mechanism for transporting Se from the water column to the sediments in the Bermuda Rise. Therefore the cycling of Se at the Bermuda Rise is possibly similar to that illustrated under low sea level and oxic water column conditions within the Cariaco Basin (Fig 6.10).

7.7. $\delta^{82/76}$ Se values from the Bermuda Rise over the last 500 ka

7.7.1. Glacial-interglacial variations in $\delta^{82/76}$ Se values

The $\delta^{82/76}$ Se values for the Bermuda Rise over the last 500 ka are between -0.79‰ and +0.63‰ (Table 7.4; Fig 7.18). This range of 1.42‰ is similar to the range observed for the last four glacial-interglacial cycles in the Cariaco Basin (Fig 6.24) but much less than that measured for the last glacial-interglacial transition (Fig 6.17) in the Cariaco Basin (Table 7.6). Average $\delta^{82/76}$ Se values for interglacial and glacial periods overlap within error (Table 7.6; fig 7.18). Within individual interglacial and glacial periods the range of $\delta^{82/76}$ Se values varies considerably; the larger ranges occur in the interglacial periods with smaller ranges typical of glacial periods (Table 7.7). The larger $1\sigma_{n-1}$ for interglacial samples, compared to the $1\sigma_{n-1}$ for the glacial samples, is due to the four outliers (Fig 7.19). The $\delta^{82/76}$ Se values of the remaining samples cover a very limited range (-0.6 to +0.2‰) with samples from both interglacial and glacial periods plotting in a similar area.



Figure 7.18: Se concentrations and $\delta^{82/76}$ Se values relative to SRM NIST 3149 from the Bermuda Rise over the last 500 ka. Error bars represent 2 standard error. Glacial periods and shaded and numbered. Average and standard deviation of $\delta^{82/76}$ Se values for each interglacial and glacial period is shown (red). Shaded region representing MIS 2-4 is split into individual averages (see table 7.4 for details).

Table 7.6: Statistical data for $\delta^{82/76}Se$ values for interglacial and glacial periods from the Bermuda Rise

	Interglacial	Glacial
Mean $\delta^{82/76}$ Se (‰)	-0.21	-0.19
n	23	31
1σn-1	0.24	0.16
Maximum $\delta^{82/76}$ Se (‰)	0.11	0.19
Minimum $\delta^{82/76}$ Se (‰)	-0.79	-0.50

MIS	Average $\delta^{82/76}$ Se (‰)	$1\sigma_{n-1}$	n
1	-0.29	0.09	2
2	-0.09	0.10	2
3	-0.25	0.16	5
4	-0.09	0.06	2
5	-0.25	0.16	3
6	-0.12	0.26	7
7	-0.27	0.30	5
8	-0.26	0.13	6
9	-0.38	0.32	4
10	-0.23	0.07	5
11	-0.07	0.16	9
12	-0.19	0.13	4

Table 7.7: Statistical data of $\delta^{82/76}$ Se value for individual interglacial and glacial periods from the Bermuda Rise

In the Cariaco Basin a relationship existed between Se concentrations and $\delta^{82/76}$ Se values (Fig 6.19); for samples from the Bermuda Rise there is no such clear relationship (Fig 7.19).



Figure 7.19: Se concentrations vs. $\delta^{82/76}$ Se values for samples from the Bermuda Rise. Samples enclosed in the box and circled are explained in the text.

Although no clear relationship between Se concentrations and $\delta^{82/76}$ Se values, there is a slightly clearer relationship between 1/Se and $\delta^{82/76}$ Se values (Fig 7.20). The main difference between the Bermuda Rise samples and the Cariaco Basin samples are the former are characterised by lower Se concentrations. Only one sample from the Bermuda Rise (185 ka, fig 7.20) appears to fit the two-component mixing illustrated by the bioturbated and glacial samples from the Cariaco Basin although other samples are close. An envelope can be fitted around ~90% of all the samples from the Bermuda Rise which highlights a negative correlation between 1/Se and $\delta^{82/76}$ Se values, similar to the Cariaco Basin. This negative correlation suggests the distribution of $\delta^{82/76}$ Se values within the Bermuda Rise can also be interpreted as reflecting two-component mixing (Fig 7.20) between a high Se concentration, high $\delta^{82/76}$ Se end member and a low Se concentration, low $\delta^{82/76}$ Se end member. This is consistent with our proposed model of Se cycling at the Cariaco Basin.

The high Se concentration and high $\delta^{82/76}$ Se end member is very near (~0.1‰) to the anoxic high $\delta^{82/76}$ Se end member from the Cariaco Basin. Being so close to the anoxic end member from the Cariaco Basin, the Bermuda Rise samples are therefore likely to be more organic-rich and have relatively higher Se:C_{org} ratios. However, the low Se concentration and low $\delta^{82/76}$ Se end member is not near the oxic low $\delta^{82/76}$ Se end member from the Cariaco Basin. The main difference between these two low $\delta^{82/76}$ Se end members is the much lower Se concentrations in samples from the Bermuda Rise. At the time the samples were deposited, the climate was in a state that was probably more common to the interglacial periods but not exclusively. The much smaller Se concentrations at the Bermuda Rise are probably a result of increased regeneration of Se from organic matter due to the deeper water column. The amount of organic matter reaching the sediment would also be a lot smaller. What organic matter does reach the

sediment will decompose further creating reducing conditions which allows reduction of Se oxyanions to occur, resulting in a negative isotope fractionation. With such low Se concentrations and taking into account mass balance effects, only a small amount of reduction is required to lower the overall $\delta^{82/76}$ Se value of the sample.



Figure 7.20: 1/Se vs. $\delta^{82/76}$ Se values for the last 500 ka from the Bermuda Rise. Shaded area represents ~90% of samples indicating a slight negative correlation between 1/Se and $\delta^{82/76}$ Se. Solid line represents the two-component mixing line for samples from the Cariaco Basin for the last glacial-interglacial transition.

From the 1/Se vs. $\delta^{82/76}$ Se graph (Fig 7.20), compared to $\delta^{82/76}$ Se values from the Cariaco Basin, there is no evidence to suggest that the same two-component mixing is controlling the variations in $\delta^{82/76}$ Se from the Bermuda Rise (Fig 6.21). This is not surprising as the two-component mixing in the Cariaco Basin is based on changing oxygen levels in the water column. The redox trace element chemistry has shown that

this is uncommon at the Bermuda Rise. Within the water column, Se is transported by incorporation into organic material and attaching to Fe and Mn particulates. Adsorption and assimilation of Se do not significantly fractionate Se isotopes and so $\delta^{82/76}$ Se values will be similar to that of the seawater $\delta^{82/76}$ Se value. Within the sediments, reduction of Se is likely to take place and the extent of the reduction will alter the overall $\delta^{82/76}$ Se values of the sediments.

The causes of the outlying $\delta^{82/76}$ Se values are likely to be unusual processes that existed at the time of deposition. The large negative $\delta^{82/76}$ Se value at 185 ka is characterised by a high Se concentration and large Se:C_{org} value (Fig 7.14; 7.21). The high Fe and S contents which are also present in this sample (Fig 7.11) are interpreted as indicating more reducing conditions at the time of deposition which allowed iron sulphide minerals to precipitate. Se oxyanions were reduced within the sediment which had a significant negative fractionation, causing the negative $\delta^{82/76}$ Se value measured in this sample. The other negative $\delta^{82/76}$ Se value at 315 ka from the Bermuda Rise has a Se:C_{org} value similar to that of typical bacterial uptake Se:C_{org} ratios (Fig 7.21). In the Cariaco Basin, a sample at 340 ka has a similarly low Se:C_{org} ratio and negative $\delta^{82/76}$ Se ratio (Fig 6.26). The possible explanation for the negative $\delta^{82/76}$ Se value in the Cariaco Basin was a change in the $\delta^{82/76}$ Se value of the global ocean reservoir. A similar explanation might apply for the sample at 315 ka.

There is a muted variation in the Se:C_{org} and $\delta^{82/76}$ Se values from the Bermuda Rise with the exception of the two outliers (Fig 7.21). This might be caused by the processes operating within the water column. As Se is regenerated with depth, the Se:C_{org} value is decreasing with little change in the $\delta^{82/76}$ Se value. If authigenic enrichment of Se is occurring within the sediment then the Se:C_{org} ratio will begin to

increase and the $\delta^{82/76}$ Se value will get lighter with the final $\delta^{82/76}$ Se value dependant on how much authigenic enrichment occurred.



Figure 7.21: Se:C_{org} vs. $\delta^{82/76}$ Se values for the Bermuda Rise. Dotted line and green box represent the average Se:C_{org} value and 2 σ for the laminated sediments from the Cariaco Basin.

7.7.2. Comparison of $\delta^{82/76}$ Se values from the Cariaco Basin with $\delta^{82/76}$ Se values from the Bermuda Rise

The Cariaco Basin is the second largest, modern anoxic basin in the world behind the Black Sea. Previous studies have already established that the Cariaco Basin has undergone changes in oxygen content over the last 500 ka (Yarincik *et al.* 2000; Peterson *et al.* 1991). Se concentration measurements suggest that the cycling of Se differs in the water column depending on oxygen concentrations. This change in Se cycling has affected the $\delta^{82/76}$ Se values which are preserved in the sediments of the basin. Therefore, the $\delta^{82/76}$ Se values from the Cariaco Basin appear to fluctuate with changes in local oxygen concentration. Therefore, it can be hypothesised that changes in $\delta^{82/76}$ Se within the Cariaco Basin will change the global $\delta^{82/76}$ Se value of the ocean. To test this hypothesis, $\delta^{82/76}$ Se values from the Bermuda Rise, an oxic, open ocean, site, have been measured. If similar changes of $\delta^{82/76}$ Se values occur in both sites at similar times, this might suggest that Se isotope ratios are reflecting changes in ocean oxygenation on a larger scale. The main problem of interpreting coincident changes in $\delta^{82/76}$ Se values from the Cariaco Basin and the Bermuda Rise is the scale at which changes in $\delta^{82/76}$ Se have been recorded. The Bermuda Rise record is sampled at a much higher frequency over the last 500 ka compared to the Cariaco Basin record while the opposite is true for the last glacial-interglacial transition. Therefore the comparison in this study will focus on overall changes in $\delta^{82/76}$ Se values between MIS 5-12 (~75 ka to 475 ka).

As previously described, both the Cariaco Basin and Bermuda Rise $\delta^{82/76}$ Se profiles have similar ranges to each other. Where they differ is the intensity of the changes in $\delta^{82/76}$ Se occurring over the last four glacial-interglacial cycles (Fig 7.22). In MIS 12 the Cariaco Basin $\delta^{82/76}$ Se value increases to 0.33‰ at ~437 ka and a corresponding increase occurs in the Bermuda Rise but only to -0.06 ‰ at ~435 ka. Over the MIS 12-11 transition, both records illustrate a more negative $\delta^{82/76}$ Se value between ~408 ka and 403 ka. At the MIS 11-10 boundary, both the Cariaco Basin and Bermuda Rise $\delta^{82/76}$ Se profiles have increased to 0.45‰ at 359 ka and 0.04‰ at 360 ka respectively. During MIS 10, the $\delta^{82/76}$ Se values of both records decrease with the Cariaco Basin profile decreasing approximately 3 orders of magnitude more than the Bermuda Rise. During MIS 9, the two profiles are not following each other as closely as they have been previously. At ~ 280 ka, during MIS 8, the two records converge again with the Cariaco Basin $\delta^{82/76}$ Se value decreasing from 0.40‰ at 276 ka to -0.27‰ at 267 ka and the Bermuda Rise $\delta^{82/76}$ Se value decreasing from -0.17‰ at 281 ka to -

0.44‰ at 271 ka. From ~265 ka, the Cariaco Basin $\delta^{82/76}$ Se record increases to a maximum of 0.31‰ at 193 ka. The Bermuda Rise $\delta^{82/76}$ Se record also increases over a similar length of time but reaches it maximum of 0.62‰ a little earlier at 210 ka. From the MIS 7-6 transition, the Cariaco Basin $\delta^{82/76}$ Se profile decreases to a $\delta^{82/76}$ Se value of -0.81‰ at ~150 ka. Over a similar period, the Bermuda Rise $\delta^{82/76}$ Se value has also decreased to -0.40‰; however the Bermuda Rise $\delta^{82/76}$ Se record has varied significantly with large $\delta^{82/76}$ Se shifts occurring which are not observed in the Cariaco Basin due to the low sampling frequency. However, from ~150 ka, both $\delta^{82/76}$ Se records increase at a similar gradient, until the MIS 6-5 transition, where both records decrease over the boundary, before finally both $\delta^{82/76}$ Se profiles increase rapidly in the early stages of MIS 5. Interestingly, between 150 ka and 100 ka, the Cariaco Basin $\delta^{82/76}$ Se profile is lagging behind the Bermuda Rise $\delta^{82/76}$ Se profile by between ~4 and 8 ka.

Despite the difference in sampling frequency, there is a remarkable similarity between the two $\delta^{82/76}$ Se records. With the exception of MIS 9, the overall $\delta^{82/76}$ Se variations in the Cariaco Basin are matched in the $\delta^{82/76}$ Se record from the Bermuda Rise. The smaller variations in the Bermuda Rise record are within analytical error of each other but the general trends are enough to suggest that there is a connection between the two $\delta^{82/76}$ Se profiles. The variations observed in the $\delta^{82/76}$ Se isotope ratios at the Bermuda Rise, are possibly a result of the changing oxygen concentrations within the Cariaco Basin. Therefore this comparison is suggesting that a change in the global ocean oxygenation is represented by a change in the $\delta^{82/76}$ Se value of the sediments which are deposited. The complexities of the Se isotope system and the significant differences in the behaviour of Se at both locations suggest that using Se isotopes is not easy but does provide some intrigue. This thesis does provide not a conclusive answer

to whether Se isotopes can be used as a palaeoredox proxy. As a first study, the results suggest that with more data, Se has the potential to be a new palaeoredox proxy.



Figure 7.22: Comparison of the $\delta^{82/76}$ Se profile from the Cariaco Basin with the $\delta^{82/76}$ Se profile from the Bermuda Rise over the last 500 ka.

8.1. Introduction

This thesis is the first investigation into temporal variations over the last 500 ka of Se isotope ratios within the marine environment. The primary aim was to introduce and evaluate the potential of Se isotope ratios to record changes in the oxygenation of the oceans. This was to be first tested by investigating total Se concentrations and whole rock Se isotope ratios of sediments from the Cariaco Basin, a location which has undergone repeated changes of oxygen concentration over the last 500 ka. A comparison with an open ocean location, which has not undergone large changes in oxygen content, would provide an answer to whether a relationship exists between the isotope ratios of the Cariaco Basin and the open ocean location. This chapter summarises the key findings of this study and answers the hypothesis which was formed in chapter 2 before some suggestions for further work are made.

8.2. Hypothesis

The hypothesis of this thesis was to determine if sedimentary Se isotope ratios reflect changes in ocean oxygenation on a global scale through geological time. Three statements were given in chapter 2 which outlined the theoretical background to the hypothesis. These are discussed with regard to the results from the Cariaco Basin and the Bermuda Rise.

8.2.1. Mechanisms of Se cycling in oxic and anoxic seawater are different

The Cariaco Basin was found to be a suitable study area for testing the use of Se isotopes as a new palaeoredox proxy. The vast amount of available literature allowed

for a detailed understanding of the processes which take place in or near the Cariaco Basin. These included the complex interactions between the shallow sills and the rising and falling of sea level on surface productivity, the shifting position of the ITCZ over seasonal and glacial-interglacial timescales, and the tectonic history of the basin. It was important that the connectivity of the Cariaco Basin to the open ocean was established if comparisons of Se isotope signals were to be made. Strong positive relationships exist between the Cariaco Basin δ^{18} O record and global δ^{18} O records such as SPECMAP and LR04. These similarities illustrated that the Cariaco Basin is well-connected with the global ocean throughout the last 500 ka.

Two modes of Se cycling were suggested – one for when the water column was anoxic below 300 m and the other for a completely oxic water column. At the surface of the water column Se(VI) and (IV) oxyanions are either adsorbed or incorporated into the organic matter in the mixed layer and then ~90% of the organic matter is remineralised and the Se oxyanions are re-released. The released Se oxyanions are then either recycled back into the primary productivity or move through the water column by diffusion or attached to particulates such as clays. When the downward flux of organic matter is large enough due to high surface productivity, an oxygen demand is created and anoxic conditions develop. Below the oxic-anoxic interface which is currently at ~300 m, Se (IV) is re-assimilated into new secondary bacterial organic matter. Under the anoxic water column, re-mineralisation of the organic matter does still occur but at a slower rate than in the oxic water at the surface. Currently, ~2 % of the original primary production reaches the sediment-water interface and ~60 % of this is then incorporated into the sediment. Thus significant enrichments of Se occur under an anoxic water column with the dominant transport process being Se bound to organic matterial.

When the organic flux is not large enough to create anoxic conditions in the deeper levels of the basin, the water column remains totally oxic. The re-mineralised Se is then transported to the sediment through three pathways: 1) bound with organics, 2) diffusion across the sediment-water interface as oxyanions or 3) adsorbed onto particulates. The breakdown of organic matter which reaches the sediment takes place, creating reducing conditions which transforms Se oxyanions to Se (0). Organically-bound Se is still an important transport pathway to the sediment but it is much smaller in magnitude and as a result, the other pathways are more significant.

It was surprising to find that even under anoxic conditions a large proportion of organic matter is recycled in the upper part of the water column. This has implications for the causes of anoxia at depth – the initial primary production rate in the surface waters, a result of fluctuating sea levels, is the dominant controlling factor - the oxygen demand caused by the decaying organic material actually creates the anoxic conditions. Finally, despite the similar Eh-pH diagrams and similar locations in the periodic table, the behaviour of Se differs greatly from that of S within the Cariaco Basin.

A simple two end-member model for Se cycling within the Cariaco Basin is sufficient for the recent glacial-interglacial transition where permanent oxic and anoxic water columns characterise the glacial and interglacial periods respectively. However, previous glacial and interglacial periods are characterised by repeating laminated and non-laminated intervals representing short-lived anoxic and oxic water columns. Therefore, two intermediate stages are required to explain the alternating laminated and non-laminated intervals within individual glacial and interglacial periods - one which allows a glacial Cariaco Basin, which is normally oxic, to become anoxic and the other which allows an interglacial Cariaco Basin, which is normally anoxic, to become oxic. These intermediate stages are a result of changing sea levels over glacial-interglacial

cycles and the continual tectonic uplift of the sills that has taken place over the last 2 Ma. These two components change the water depth to sill which controls the quantity of nutrient-rich water entering the basin which, in turn changes the surface primary productivity and the capacity of the water column to remain oxic or become anoxic. During previous glacial periods, e.g. MIS 12, the global sea levels were lower than present and the tectonic uplift of the sills was less resulting in a water depth to sill which just allows nutrient-rich waters to flow into the basin, creating conditions for anoxia and laminated sediments to develop. During earlier interglacial periods, e.g. MIS 11, the sea levels were higher or similar to present day but the uplift of the sills would have been less. This would create a water depth to sill which is large enough to allow both nutrient-rich and deep-oxygenated waters into the basin. The balance of high productivity and oxygen-rich waters would create a transient anoxic/oxic water column resulting in alternating laminated/ non-laminated sediments.

8.2.2. The overall isotope fractionation varies between sediments deposited under oxic and anoxic seawater conditions.

The pattern observed in the $\delta^{82/76}$ Se values is consistent with a model consisting of two simple end-members – an anoxic high $\delta^{82/76}$ Se end member and an oxic low $\delta^{82/76}$ Se end member. The two end members differ in the relative fluxes of Se via two distinct pathways for Se into the sediment, assimilation into organic matter and authigenic reduction of Se (IV) within the post-oxic sediment. The authigenic Se is expected to have negative $\delta^{82/76}$ Se values because of isotopic fractionation induced by reduction of Se oxyanions drawn from oxic bottom water. At times of low Se:C_{org} ratios and relatively high $\delta^{82/76}$ Se values, assimilation into organic matter was the dominant transport of Se into the sediments; at times when Se:C_{org} ratios were higher and $\delta^{82/76}$ Se values relatively lower, authigenic enrichment of Se had taken place. Overall the range

of isotope fractionation was surprisingly narrow considering the large experimentallydetermined fractionation factors for Se reduction. However, recent studies have shown that the fractionations observed in nature are expected to be only half those of the determined fractionation factors. It is too simplistic to discuss variations of Se concentrations and Se isotope ratios in terms of glacial-interglacial cycles. In the Cariaco Basin over the last 500 ka, alternating bioturbated/laminated sediments and alternating oxic/ anoxic water column conditions do not directly correspond to glacial/ interglacial cycles.

8.2.3. Se isotope values of ocean surface waters will be well-mixed on geological time scales

Sediment samples from the Bermuda Rise were geochemically characterised and unlike the Cariaco Basin, this location was oxic and had a relatively constant productivity over the last 500 ka. In all the geochemical proxies measured, there is no significant difference between interglacial and glacial periods. The continuous oxic conditions have resulted in lower Se concentrations and unlike the Cariaco Basin, there is no one dominant mechanism for transporting Se from the water column to the sediments in the Bermuda Rise. Therefore the cycling of Se at the Bermuda Rise is probably similar to that illustrated under low sea level and oxic water column conditions within the Cariaco Basin. Two Se isotope end-members have also been identified at the Bermuda Rise; one end member has low Se concentrations and low $\delta^{82/76}$ Se values while the other has high Se concentrations and higher $\delta^{82/76}$ Se values. There is no discernable difference between glacial and interglacial periods; the local climate at the time of deposition is likely to exert more control over the Se isotope ratios than the global climate state.

The importance of the atmospheric flux of Se on the global cycling of Se is illustrated. Large fluxes of volatile Se compounds are rapidly rained out with a mean residence time off ~20 days helping to mix Se at the land and ocean surface. With no measured appreciable isotope fractionation for the volatilisation of Se, the Se isotope ratio of the surface ocean waters will be well-mixed on geological timescales and reflect the different processes affecting Se isotope ratios occurring all over the world.

There is a similarity between the low sampling frequency Cariaco Basin $\delta^{82/76}$ Se profile and the high sampling frequency $\delta^{82/76}$ Se Bermuda Rise records. The changing oxygen conditions of the Cariaco Basin change the proportions of organic and authigenic Se in the sediments. When the Cariaco Basin is anoxic, it represents an order of magnitude larger sink of Se than when the water column is completely oxic. Because of the larger Se sink under anoxic conditions the Se isotope ratio of seawater will be affected more dramatically than when the water column is oxic. An increase in anoxic sedimentation will cause the seawater Se isotope ratio to increase. Due to the surface ocean waters being well mixed with respect to Se isotope ratios, this change in the seawater Se isotope ratio might be observed in the open ocean and be reflected in the Se isotope ratios of the open ocean sediments. Therefore, the variations observed in the $\delta^{82/76}$ Se isotope ratios at the Bermuda Rise, are possibly a result of the changing oxygen concentrations within the Cariaco Basin. The complexities of the Se isotope system and the significant differences in the behaviour of Se at both locations suggest that using Se isotopes is not straight forward. This thesis does provide not a conclusive answer to whether Se isotopes can be used as a palaeoredox proxy. However, as a first study, the results suggest Se has the potential to be a new palaeoredox proxy.

8.3. Further work

The following suggestions would develop this study and provide more evidence of the applicability of Se isotope ratios to act as a palaeoredox proxy.

- Increase the sampling frequency from the Cariaco Basin, especially over the last four glacial-interglacial cycles, and add extra samples which are from MIS 3 and 4. This would provide more information to compare with the Bermuda Rise Se samples.
- Carry out high frequency sampling across an older interglacial-glacial transition at the Cariaco Basin, e.g. MIS 12-11, to compare to the last glacial-interglacial transition. This would indicate if all glacial-interglacial transitions show such large changes in Se isotope ratios or is the current transition unique?
- Undertake quantitative sequential chemical extractions of Se from sediments, e.g. organic fraction, elemental Se fraction, and pyrite-Se fraction. This would allow a more precise comparison of the different transport mechanisms operating under anoxic and oxic water columns. Measure $\delta^{82/76}$ Se ratios on these sequential extractions to allow proportions of the two-end members to be calculated and compared over glacial-interglacial timescales.
- Carry out similar investigations to this study on other anoxic basins, e.g. Black Sea or Orca Basin, alternative open ocean locations, e.g. Pacific or Indian ocean, and extend the investigation back in geological time to periods of well-documented change in global ocean oxygen concentrations, e.g. Ocean Anoxic Events.

		[Se] conc	[Se] conc	[Se] conc		Total	Average		Total
Sample ID	Age	#1	#2	#3	Dilution	volume	[Se] conc	Weight	[Se] _(sedt)
	(ka)	(ppb)	(ppb)	(ppb)		(mL)	(ppb)	(g)	(ppm)
B1-15-20	0.38	1.081			100	25	1.081	0.4069	6.642
B1-75-80	1.72	0.640			50	25	0.640	0.1042	7.680
B2-5-10	3.59	2.206			20	25	2.206	0.2282	4.833
B2-80-85	5.39	0.964	0.936		50	25	0.950	0.206	5.766
B3-40-45	8.04	1.027			50	25	1.027	0.1136	11.304
B3-80-85	8.98	1.358			20	25	1.358	0.0950	7.150
B3-120-125	9.91	1.212	1.264		50	25	1.238	0.2083	7.431
B4-40-50	11.46	0.334	0.306		50	25	0.320	0.1056	3.792
B4-60-65	11.89	1.110			20	25	1.110	0.1941	2.860
B4-80-85	12.30	0.723			50	25	0.723	0.2145	4.211
B4-100-105	12.71	0.170			50	25	0.170	0.2003	1.064
B4-120-125	13.11	1.043			50	25	1.043	0.2118	6.157
B4-140-145	13.49	1.389			50	25	1.389	0.1995	8.705
A-4-50-55	13.68	1.366			100	25	1.366	0.4914	6.948
A-4-70-75	14.04	0.144	0.108	0.134	100	20	0.129	0.0527	4.883
4-80-85	14.22	0.548			50	25	0.548	0.0997	6.866
A-4-85-90	14.31	0.426	0.380		100	20	0.403	0.1034	7.800
A-4-90-95	14.40	0.824	0.688		100	20	0.756	0.2559	5.912
A-4-110-115	14.74	0.308	0.274		20	20	0.291	0.0832	1.398
4-125-130	14.98	0.268			50	25	0.268	0.2078	1.614
4-140-150	15.22	1.071			50	25	1.071	0.2007	6.670
A-5-10-15	15.52	0.755	0.653		10	20	0.704	0.2680	0.525
5-25-30	15.74	0.084			50	25	0.084	0.2061	0.507
5-35-40	15.87	0.123	0.131		50	25	0.127	0.2034	0.780
A-5-55-60	16.14	0.496	0.476		10	20	0.486	0.1373	0.708
5-65-70	16.26	0.087			50	25	0.087	0.2046	0.531
A-5-75-80	16.38	0.136	0.126		10	20	0.131	0.0450	0.582

O	•	[Se] conc	[Se] conc	[Se] conc	Dilation	Total	Average	Malak (Total
Sample ID	Age	#1	#2	#3	Dilution	volume	[Se] conc	weight	[Se] _(sedt)
	(ka)	(ppb)	(ppb)	(ppb)		(mL)	(ppb)	(g)	(ppm)
C-5-3-113-115	106.01	0.489			50	25	0.489	0.2019	3.028
C-5-4-113-115	112.26	1.292	1.023	1.076	50	20	1.131	0.3107	3.639
C-5-6-113-115	124.24	0.408			50	25	0.408	0.2020	2.526
C-6-2-56-58	133.54	0.314			50	25	0.314	0.2008	1.958
C-6-3-101-103	141.23	1.103	0.788	0.851	20	20	0.914	0.3052	1.198
C-6-5-55-57	151.30	0.097			50	25	0.097	0.2032	0.599
C-8-5-17-19	193.37	0.687	0.670		50	25	0.679	0.2106	4.027
D-9-5-12-14	229.04	1.828	1.586		20	20	1.707	0.3360	2.032
D-10-3-117-119	267.26	0.152			50	25	0.152	0.2043	0.928
C-10-2-24-26	276.66	0.872	0.765		50	20	0.819	0.3171	2.582
C-11-2-93-95	330.22	0.775	0.697		100	20	0.736	0.3104	4.745
C-11-6-96-98	339.95	0.088			50	25	0.088	0.2029	0.542
C-12-3-124-126	358.60	1.250	1.071		20	20	1.160	0.3133	1.481
C-13-4-28-30	403.54	1.483	1.139	1.246	50	20	1.289	0.3037	4.246
C-14-2-35-37	437.90	0.458	0.451		50	25	0.455	0.2130	2.668
C-14-4-126-128	463.25	1.423	1.094	1.166	20	20	1.228	0.3071	1.599

Sample ID	Age	s ^{82/76} So	s ^{82/78} So	s ^{82/76} Se	s ^{82/78} So	s ^{82/76} So	s ^{82/78} So	s ^{82/76} Se	s ^{82/78} Se	s ^{82/76} Se	s ^{82/78} So	Average	Average
Campie ID	Age	0 50	0 50	0 50	0 50	0 50	0 30	0 36	0 50	0 50	0 30	δ ^{82/76} Se	δ ^{82/78} Se
	(ka)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
B1-15-20	0.38	0.19 ± 0.05	0.17 ± 0.04									0.19 ± 0.05	0.17 ± 0.04
B1-75-80	1.72	0.10 ± 0.08	0.06 ± 0.06									0.10 ± 0.08	0.06 ± 0.06
B2-5-10	3.59	0.29 ± 0.06	0.23 ± 0.02	0.40 ± 0.07	0.37 ± 0.09							0.35 ± 0.07	0.30 ± 0.06
B2-80-85	5.39	0.32 ± 0.16	0.22 ± 0.06	0.27 ± 0.06	0.20 ± 0.06							0.30 ± 0.11	0.21 ± 0.06
B3-40-45	8.04	0.17 ± 0.07	0.04 ± 0.03									0.17 ± 0.07	0.04 ± 0.03
B3-80-85	8.98	0.13 ± 0.16	0.20 ± 0.07									0.13 ± 0.16	0.09 ± 0.07
B3-120-125	9.91	-0.39 ± 0.10	-0.26 ± 0.04									-0.39 ± 0.10	-0.26 ± 0.04
B4-40-50	11.46	0.56 ± 0.07	0.35 ± 0.04									0.56 ± 0.07	0.35 ± 0.04
B4-60-65	11.89	0.77 ± 0.07	0.59 ± 0.03									0.77 ± 0.07	0.59 ± 0.03
B4-80-85	12.30	-0.25 ± 0.06	-0.09 ± 0.05									-0.25 ± 0.06	-0.09 ± 0.05
B4-100-105	12.71	-0.43 ± 0.08	-0.27 ± 0.01									-0.43 ± 0.08	-0.27 ± 0.01
B4-120-125	13.11	-0.34 ± 0.12	-0.17 ± 0.06	-0.30 ± 0.02	-0.19 ± 0.05							-0.32 ± 0.07	-0.18 ± 0.06
B4-140-145	13.49	-0.12 ± 0.06	0.02 ± 0.06	-0.27	-0.16							-0.20 ± 0.06	-0.07 ± 0.06
A-4-50-55	13.68	0.04 ± 0.06	0.01 ± 0.05									0.04 ± 0.06	0.01 ± 0.05
A-4-70-75	14.04	-0.10 ± 0.06	-0.05 ± 0.04									-0.10 ± 0.06	-0.05 ± 0.04
4-80-85	14.22	-0.39 ± 0.03	-0.26 ± 0.04	-0.51 ± 0.04	-0.34 ± 0.02							-0.45 ± 0.04	-0.30 ± 0.03
A-4-85-90	14.31	0.43 ± 0.08	0.35 ±0.05	0.53 ± 0.05	0.47 ± 0.04	0.13 ± 0.02	0.11 ± 0.03					0.36 ± 0.05	0.31 ± 0.04
A-4-90-95	14.40	0.26 ± 0.05	0.17 ± 0.04	0.18 ± 0.00	0.13 ± 0.03	0.27 ± 0.19	0.14 ± 0.09					0.24 ± 0.08	0.15 ± 0.05
A-4-110-115	14.74	0.24 ± 0.07	0.26 ± 0.02									0.24 ± 0.07	0.16 ± 0.02
4-125-130	14.98	-0.60 ± 0.07	-0.30 ± 0.03	-0.59	-0.35							-0.59 ± 0.07	-0.33 ± 0.03
4-140-150	15.22	-0.28 ± 0.04	-0.15 ± 0.04	-0.45 ± 0.04	-0.25 ± 0.05							-0.36 ± 0.04	-0.20 ± 0.05
A-5-10-15	15.52	0.14 ± 0.08	0.32 ± 0.01	0.31 ± 0.10	0.35 ± 0.07							0.22 ± 0.09	0.15 ± 0.04
5-25-30	15.74	-1.05 ± 0.18	-0.64 ± 0.02									-1.05 ± 0.18	-0.64 ± 0.02
5-35-40	15.87	-0.82 ± 0.05	-0.48 ± 0.03									-0.82 ± 0.05	-0.48 ± 0.03
A-5-55-60	16.14	-0.30 ± 0.03	-0.10 ± 0.03	-0.13 ± 0.05	-0.02 ± 0.03							-0.21 ± 0.04	-0.06 ± 0.03
5-65-70	16.26	-1.06 ± 0.03	-0.61 ± 0.06									-1.06 ± 0.03	-0.61 ± 0.06
A-5-75-80	16.38	0.23 ± 0.15	0.40 ± 0.09									0.23 ± 0.15	0.15 ± 0.09

Sample ID	Age	δ ^{82/76} Se	δ ^{82/78} Se	δ ^{82/76} Se	$\delta^{82/78}\text{Se}$	$\delta^{82/76}$ Se	δ ^{82/78} Se	δ ^{82/76} Se	δ ^{82/78} Se	δ ^{82/76} Se	δ ^{82/78} Se	Average δ ^{82/76} Se	Average δ ^{82/78} Se
	(ka)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
C-5-3-113-115	106.01	0.47 ± 0.02	0.29 ± 0.02	0.52 ± 0.03	0.36 ± 0.03							0.50 ± 0.03	0.33 ± 0.03
C-5-4-113-115	112.26	0.32 ± 0.04	0.29 ± 0.03	0.22 ± 0.15	0.19 ± 0.08	0.20 ± 0.09	0.17 ± 0.02					0.27 ± 0.09	0.24 ± 0.04
C-5-6-113-115	124.24	-0.24 ± 0.06	-0.20 ± 0.02									-0.24 ± 0.06	-0.20 ± 0.02
C-6-2-56-58	133.54	0.08 ± 0.07	0.09 ± 0.01	0.09 ± 0.07	0.08 ± 0.03							0.08 ± 0.07	0.08 ± 0.02
C-6-3-101-103	141.23	-0.17 ± 0.03	-0.06 ± 0.02	-0.24 ± 0.06	-0.04 ± 0.07	-0.05 ± 0.08	-0.01 ± 0.08	0.04 ± 0.08	0.08 ± 0.08			-0.11 ± 0.06	-0.01 ± 0.06
C-6-5-55-57	151.30	-0.81 ± 0.11	-0.54 ± 0.03									-0.81 ± 0.11	-0.54 ± 0.03
C-8-5-17-19	193.37	0.31 ± 0.11	0.22 ± 0.06									0.31 ± 0.11	0.22 ± 0.06
D-9-5-12-14	229.04	-0.03 ± 0.02	0.11 ± 0.06	0.01 ± 0.01	0.09 ± 0.08							-0.01 ± 0.02	-0.01 ± 0.07
D-10-3-117-119	267.26	-0.31 ± 0.02	-0.10 ± 0.06	-0.23	-0.18							-0.27 ± 0.02	-0.14 ± 0.06
C-10-2-24-26	276.66	0.28 ± 0.06	0.32 ± 0.07	0.42 ± 0.05	0.31 ± 0.04	0.44 ± 0.06	0.36 ± 0.03	0.44 ± 0.08	0.23 ± 0.05	0.41 ± 0.02	0.26 ± 0.00	0.40 ± 0.05	0.30 ± 0.04
C-11-2-93-95	330.22	-0.28 ± 0.04	-0.08 ± 0.02									-0.28 ± 0.04	-0.18 ± 0.02
C-11-6-96-98	339.95	-0.94 ± 0.03	-0.60 ± 0.04									-0.94 ± 0.03	-0.60 ± 0.04
C-12-3-124-126	358.60	0.45 ± 0.06	0.25 ± 0.07									0.45 ± 0.06	0.25 ± 0.07
C-13-4-28-30	403.54	-0.30 ± 0.15	-0.20 ± 0.11	-0.22 ± 0.01	-0.12 ± 0.01	-0.12 ± 0.06	0.02 ± 0.01					-0.21 ± 0.07	-0.07 ± 0.04
C-14-2-35-37	437.90	0.33 ± 0.05	0.22 ± 0.04									0.33 ± 0.05	0.22 ± 0.44
C-14-4-126-128	463.25	-0.07 ± 0.01	0.04 ± 0.02	-0.11 ± 0.05	0.02 ± 0.05	-0.19 ± 0.00	-0.11 ± 0.02					-0.12 ± 0.02	-0.02 ± 0.03

Appendix 2:	Se concentration and	$\delta^{82/76}$ Se values for the Bermuda Rise

Sample ID	Depth	Depth	Age		Se run #1	Se run #2	Se run #3	
campie 12	(mbsf)	(mcd)	(ka)	Digest	(daa)	(daa)	(ppb)	Mean
1H-1-80-82	0.80	0.93	6.09	J.	142	120		131
1H-3-97-99	3.97	4.61	12.71		591	595	559	582
2H-2-28.30	6.22	7.16	17.28		455	427		441
2H-4-59-61	9.21	10.41	22.00		477	440	462	460
2H-6-95-97	12.75	14.25	27.46	А	407			407
				В	407	370		389
				С	432	383		407
3H-1-77-79	15.57	17.26	33.13		244	185		214
3H-2-135-137	17.65	19.38	38.85		423	426		425
3H-4-100-102	20.30	22.08	46.14		366	324		345
3H-6-23-25	22.53	24.36	52.50		1025	1025	955	1002
3H-7-46-48	24.26	26.12	59.49	А	491	493		492
				В	537			537
4H-2-133-135	27.13	29.46	73.75		229	198	200	209
4H-3-34-35	27.64	30.06	76.47		419	398		409
4H-3-122-124	28.52	31.08	86.75	А	143	139		141
				В	175			175
				С	169	150		159
4H-5-48-50	30.78	33.72	102.87		140	135		137
4H-6-21-23	32.01	35.15	114.55		86	84	82	84
5H-1-43-45	34.23	37.67	130.70		498	490	490	493
5H-2-138-140	36.68	40.14	140.00		403	385	394	394
5H-4-35-37	38.65	42.13	145.57		221	204	205	210
5H-5-106-108	40.86	44.36	150.23		364	346	338	349
6H-1-37-39	43.67	47.23	156.24		460	467	460	462
6H-2-35-37	45.15	48.85	162.26		438	423	424	428
6H-4-23-25	48.03	52.02	176.96		381	366	373	374
6H-4-145-147	49.25	53.36	185.87	Α	2002	2005	1788	1931
				В	1559	1525	1502	1529
6H-5-115-117	50.45	54.68	198.12		616	624	615	618
6H-6-97-99	51.77	56.13	210.24	A	254	251		253
				В	286			286
				С	266	231	231	243
7H-1-113-115	53.93	58.38	227.06		609	570		589
7H-2-18-20	54.48	58.92	230.59		473	441	445	453
7H-2-135-137	55.65	60.07	238.09		149	85		117
7H-3-54-56	56.34	60.76	242.65		421	386		403
7H-4-120-122	58.50	62.89	256.91		463	450	430	447
7H-5-48-50	59.28	63.66	261.57	А	468	434	455	452
				В	485	479	450	472
7H-6-70-72	61.00	65.36	271.31		853	814	825	831
8H-1-80-82	63.10	67.46	280.95		639	632	612	628
8H-2-65-67	64.45	68.84	286.87		292	278		285
8H-3-7-9	65.37	69.78	293.58		265	232	252	250
8H-4-13-15	66.93	71.38	305.11		715			715
8H-5-5-7	68.35	72.83	315.09		192	162		177
8H-5-135-137	69.65	74.16	324.08		216			216
8H-6-70-72	70.50	75.03	329.45	A	102	73		87
				В	123	105		114
9H-1-52-54	72.32	76.96	337.70		357			357
9H-2-15-17	73.45	78.26	342.17		444	394		419
9H-3-30-32	75.10	80.16	347.72		436			436
98-3-72-74	75.52	80.64	349.19		358	460	470	358
911-3-124-120	70.04	01.24	257.06	٨	522	403	470	400
90-4-117-119	11.41	02.09	337.00	A D	535	479	402	490 507
04 5 40 42	70 20	02 72	260.66	D	525	500	491	507
911-5-40-42	80.20	86.14	371 14		802	751	770	774
10H-1-56-58	81.86	87.89	381 30		180	751	110	180
10H-2-40-42	83.20	89.31	307.00		153	135	135	141
10H-3-38-40	84 68	90.88	405 91		115	102	100	109
10H-3-122-124	85 52	91 77	408 57		935	102		935
10H-4-44-46	86.24	92.53	410 84		592	578	568	579
10H-4-105-107	86.85	93.18	412.77		624	010	000	624
10H-5-11-13	87.41	93.77	414.54		779			779
10H-5-121-123	88.51	94.94	418.02	А	718			718
	20.01			в	768	721		745
				C	750	728	692	724
10H-6-18-20	88.98	95.43	419.50	-	544			544
11H-1-48-50	91.28	97.86	426.12		472			472
11H-2-90-92	93.20	99.87	431.20		527	527	490	515
11H-3-45-47	94.25	100.97	435.98		770			770
11H-4-5-7	95.35	102.12	441.57	А	474	449	428	450
				В	465			465

Sample ID	Depth	Depth	Age		lst	run	2nd	run	mea	an
	(mbsf)	(mcd)	(ka)	Digest	δ ^{82/76} (‰)	δ ^{82/78} (‰)	δ ^{82/76} (‰)	δ ^{82/78} (‰)	δ ^{82/76} (‰)	δ ^{82/78} (‰)
1H-1-80-82	0.80	0.93	6.09		-0.36 ± 0.16	-0.19 ± 0.07			-0.36 ± 0.16	-0.19 ± 0.07
1H-3-97-99	3.97	4.61	12.71		-0.23 ± 0.07	-0.15 ± 0.04			-0.23 ± 0.07	-0.15 ± 0.04
2H-2-28.30	6.22	7.16	17.28		-0.02 ± 0.04	0.01 ± 0.02			-0.02 ± 0.04	0.01 ± 0.02
2H-4-59-61	9.21	10.41	22.00		-0.17 ± 0.06	-0.09 ± 0.07			-0.17 ± 0.06	-0.09 ± 0.07
2H-6-95-97	12.75	14.25	27.46		-0.19 ± 0.09	-0.11 ± 0.04			-0.19 ± 0.09	-0.11 ± 0.04
3H-1-77-79	15.57	17.26	33.13		-0.50 ± 0.08	-0.29 ± 0.04			-0.50 ± 0.08	-0.29 ± 0.04
3H-2-135-137	17.65	19.38	38.85		-0.30 ± 0.05	-0.21 ± 0.02			-0.30 ± 0.05	-0.21 ± 0.02
3H-4-100-102	20.30	22.08	46.14		-0.18 ± 0.10	-0.12 ± 0.05			-0.18 ± 0.10	-0.12 ± 0.05
3H-6-23-25	22.53	24.36	52.50		-0.08 ± 0.05	-0.06 ± 0.04			-0.08 ± 0.05	-0.06 ± 0.04
3H-7-46-48	24.26	26.12	59.49	A	0.07 ± 0.02	0.05 ± 0.03			-0.05 ± 0.07	0.00 ± 0.05
				В	-0.17 ± 0.11	-0.06 ± 0.07				
4H-2-133-135	27.13	29.46	73.75		-0.13 ± 0.06	-0.06 ± 0.05			-0.13 ± 0.06	-0.06 ± 0.05
4H-3-34-35	27.64	30.06	76.47		-0.35 ± 0.04	-0.20 ± 0.06			-0.35 ± 0.04	-0.20 ± 0.06
4H-3-122-124	28.52	31.08	86.75		-0.06 ± 0.09	-0.06 ± 0.04			-0.06 ± 0.09	-0.06 ± 0.04
4H-5-48-50	30.78	33.72	102.87		-0.33 ± 0.10	-0.18 ± 0.06			-0.33 ± 0.10	-0.18 ± 0.06
4H-6-21-23	32.01	35.15	114.55		0.29 ± 0.11	0.41 ± 0.07			0.29 ± 0.11	0.41 ± 0.07
5H-1-43-45	34.23	37.67	130.70		-0.08 ± 0.05	-0.08 ± 0.05	-0.13 ± 0.10	-0.10 ± 0.07	-0.11 ± 0.08	-0.09 ± 0.06
5H-2-138-140	36.68	40.14	140.00		0.07 ± 0.08	0.07 ± 0.04	0.31 ± 0.04	0.14 ± 0.02	0.19 ± 0.06	0.10 ± 0.03
5H-4-35-37	38.65	42.13	145.57		0.05 ± 0.04	0.01 ± 0.03			0.05 ± 0.04	0.01 ± 0.03
5H-5-106-108	40.86	44.36	150.23		-0.40 ± 0.02	-0.25 ± 0.02			-0.40 ± 0.02	-0.25 ± 0.02
6H-1-37-39	43.67	47.23	156.24		-0.29 ± 0.07	-0.23 ± 0.04			-0.29 ± 0.07	-0.23 ± 0.04
6H-2-35-37	45.15	48.85	162.26		0.14 ± 0.03	0.09 ± 0.02			0.14 ± 0.03	0.09 ± 0.02
6H-4-23-25	48.03	52.02	176.96		-0.37 ± 0.07	-0.22 ± 0.05	-0.48 ± 0.03	-0.31 ± 0.02	-0.43 ± 0.05	-0.27 ± 0.04
6H-4-145-147	49.25	53.36	185.87	A	-0.63 ± 0.03	-0.42 ± 0.03	-0.74 ± 0.09	-0.48 ± 0.07	-0.73 ± 0.06	-0.47 ± 0.05
				В	-0.79 ± 0.05	-0.50 ± 0.04	-0.76	-0.50		
6H-5-115-117	50.45	54.68	198.12		-0.27 ± 0.11	-0.16 ± 0.06			-0.27 ± 0.11	-0.16 ± 0.06
6H-6-97-99	51.77	56.13	210.24		0.36 ± 0.20	0.41 ± 0.10			0.36 ± 0.20	0.41 ± 0.10
7H-1-113-115	53.93	58.38	227.06		-0.14 ± 0.06	-0.08 ± 0.04			-0.14 ± 0.06	-0.08 ± 0.04
7H-2-18-20	54.48	58.92	230.59		0.09 ± 0.06	0.07 ± 0.06			0.09 ± 0.06	0.07 ± 0.06
7H-2-135-137	55.65	60.07	238.09		-0.44 ± 0.06	-0.16 ± 0.01			-0.24 ± 0.06	-0.16 ± 0.01
7H-3-54-56	56.34	60.76	242.65		-0.30 ± 0.01	-0.23 ± 0.02			-0.30 ± 0.01	-0.23 ± 0.02
7H-4-120-122	58.50	62.89	256.91		-0.37 ± 0.08	-0.21 ± 0.04			-0.37 ± 0.08	-0.21 ± 0.04
7H-5-48-50	59.28	63.66	261.57	A	-0.08 ± 0.03	-0.08 ± 0.04			-0.12 ± 0.04	-0.05 ± 0.04
				В	-0.17 ± 0.05	-0.03 ± 0.04				
7H-6-70-72	61.00	65.36	271.31		-0.44 ± 0.06	-0.26 ± 0.05			-0.44 ± 0.06	-0.26 ± 0.05
8H-1-80-82	63.10	67.46	280.95		-0.17 ± 0.05	-0.10 ± 0.05			-0.17 ± 0.05	-0.10 ± 0.05
8H-2-65-67	64.45	68.84	286.87		-0.30 ± 0.17	-0.16 ± 0.06			-0.30 ± 0.17	-0.16 ± 0.06
8H-3-7-9	65.37	69.78	293.58		-0.16 ± 0.18	-0.09 ± 0.09			-0.16 ± 0.18	-0.09 ± 0.09
8H-4-13-15	66.93	/1.38	305.11		-0.03 ± 0.08	-0.01 ± 0.05			-0.03 ± 0.08	-0.01 ± 0.05
8H-5-5-7	68.35	72.83	315.09		-0.79 ± 0.17	-0.43 ± 0.06			-0.79 ± 0.17	-0.43 ± 0.06
8H-5-135-137	69.65	74.16	324.08		-0.44 ± 0.04	-0.31 ± 0.04			-0.44 ± 0.04	-0.31 ± 0.04
8H-6-70-72	70.50	75.03	329.45		0.00 + 0.00	0.00 + 0.04	0.45 + 0.04	0.40 + 0.00	0.05 + 0.04	0.47 . 0.04
9H-1-52-54	72.32	76.96	337.70		-0.36 ± 0.03	-0.22 ± 0.04	-0.15 ± 0.04	-0.12 ± 0.03	-0.25 ± 0.04	-0.17 ± 0.04
9H-2-15-17	73.45	78.26	342.17		-0.23 ± 0.05	-0.10 ± 0.01			-0.23 ± 0.05	-0.10 ± 0.01
9H-3-30-32	75.10	80.16	347.72		-0.22 ± 0.08	-0.10 ± 0.06			-0.22 ± 0.08	-0.10 ± 0.06
9H-3-72-74	75.52	80.64	349.19		-0.17 ± 0.06	-0.10 ± 0.07			-0.17 ± 0.08	-0.10 ± 0.07
9H-3-124-126	76.04	81.24	351.09	^	-0.35 ± 0.05	-0.21 ± 0.04			-0.35 ± 0.05	-0.21 ± 0.04
98-4-117-119	11.41	02.09	357.00	A	-0.13 ± 0.05	-0.08 ± 0.04	0.25 ± 0.12	0.15 + 0.04	-0.20 ± 0.08	-0.12 ± 0.04
04 5 40 42	79 20	02 72	260.66	D	-0.22 ± 0.03	-0.12 ± 0.04	-0.25 ± 0.12	-0.15 ± 0.04	0.04 + 0.04	0.04 + 0.02
0H_6_0_101	80.20	86.14	371 14		-0.15 + 0.05	-0.07 ± 0.02			-0.15 ± 0.05	0.04 ± 0.02
10H-1-56-58	81.86	87.89	381 30		-0.64 ± 0.03	-0.32 ± 0.06			-0.48 ± 0.03	-0.32 ± 0.06
10H-2-40-42	83.20	80.31	307.39		-0.04 ± 0.13	-0.32 ± 0.00			-0.40 ± 0.15	-0.32 ± 0.00
10H-3-38-40	84.68	90.88	405.91		-0 12 + 0 14	-0.03 + 0.09			-0.12 ± 0.14	-0.03 + 0.09
10H-3-122-124	85 52	91 77	408 57		-0.36 + 0.03	-0.20 + 0.03			-0.36 ± 0.03	-0.20 + 0.03
10H-4-44-46	86 24	92 53	410 84		0.15 + 0.07	0.09 + 0.04	0.06 + 0.09	0.02 + 0.03	0.11 + 0.08	0.06 + 0.03
10H-4-105-107	86 85	93 18	412 77		0.04 + 0.07	0.07 + 0.02			0.04 + 0.07	0.07 + 0.02
10H-5-11-13	87.41	93.77	414.54		0.03 ± 0.01	0.02 ± 0.03			0.03 ± 0.01	0.02 ± 0.02
10H-5-121-123	88 51	94 94	418 02		0.03 + 0.08	0.04 + 0.05			0.03 + 0.08	0.04 ± 0.05
10H-6-18-20	88.98	95.43	419.50		-0.29 ± 0.05	-0.17 ± 0.03			-0.29 ± 0.05	-0.17 ± 0.03
11H-1-48-50	91.28	97.86	426.12		-0.32 ± 0.08	-0.12 ± 0.02	-0.28 ± 0.14	-0.16 ± 0.06	-0.30 ± 0.11	-0.14 ± 0.04
11H-2-90-92	93.20	99.87	431.20		-0.12 ± 0.01	-0.03 ± 0.02			-0.12 ± 0.01	-0.03 ± 0.02
11H-3-45-47	94.25	100.97	435.98		-0.06 ± 0.06	-0.02 ± 0.05			-0.06 ± 0.06	-0.02 ± 0.05
11H-4-5-7	95.35	102.12	441.57	А	-0.23 ± 0.04	-0.11 ± 0.05			-0.30 ± 0.03	-0.15 ± 0.04
				В	-0.37 ± 0.02	-0.19 ± 0.03				

Sample ID	Depth	Depth	Age	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na₂O	K₂O	P ₂ O ₅	SO₃	LOI	Total
	(mbsf)	(mcd)	(ka)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
1H-1-80-82	0.80	0.93	6.09	34.27	0.56	10.12	5.17	0.251	2.26	21.09	2.30	2.356	0.146	0.17	21.73	100.44
1H-3-97-99	3.97	4.61	12.71	52.59	0.75	14.65	6.24	0.122	2.70	5.25	3.06	2.949	0.141	0.49	11.00	99.93
2H-2-28.30	6.22	7.16	17.28	53.26	0.81	16.04	6.83	0.109	2.83	3.97	2.65	3.449	0.157	0.13	9.57	99.80
2H-4-59-61	9.21	10.41	22.00	52.89	0.80	17.62	7.69	0.133	3.22	2.24	2.97	3.835	0.171	0.10	8.84	100.51
2H-6-95-97	12.75	14.25	27.46	47.55	0.69	13.43	5.81	0.157	3.11	8.92	2.58	3.287	0.145	0.26	13.15	99.08
3H-1-77-79	15.57	17.26	33.13	38.65	0.59	11.37	5.35	0.189	2.72	16.53	2.49	2.907	0.146	0.22	18.68	99.84
3H-2-135-137	17.65	19.38	38.85	46.04	0.67	12.94	6.34	0.172	3.04	10.00	3.05	3.214	0.147	0.38	14.12	100.10
3H-4-100-102	20.30	22.08	46.14	37.82	0.54	10.79	5.21	0.190	2.63	17.77	2.53	2.730	0.133	0.17	19.43	99.94
3H-6-23-25	22.53	24.36	52.50	52.16	0.66	14.38	6.61	0.185	2.99	5.33	3.54	3.480	0.135	0.27	11.00	100.74
3H-7-46-48	24.26	26.12	59.49	55.98	0.78	15.42	6.56	0.171	3.32	2.65	3.26	3.599	0.160	0.08	7.61	99.59
4H-2-133-135	27.13	29.46	73.75	36.80	0.54	10.12	4.71	0.236	2.47	19.76	2.60	2.488	0.132	0.12	20.31	100.28
4H-3-34-35	27.64	30.06	76.47	46.09	0.57	12.33	5.50	0.286	2.53	10.67	3.64	2.836	0.123	0.61	16.14	101.32
4H-3-122-124	28.52	31.08	86.75	34.42	0.52	9.61	5.02	0.211	2.39	22.16	2.31	2.398	0.131	0.09	22.20	101.46
4H-5-48-50	30.78	33.72	102.87	44.31	0.68	12.20	5.56	0.147	2.60	13.52	2.26	2.893	0.134	0.14	15.39	99.83
4H-6-21-23	32.01	35.15	114.55	31.05	0.50	9.00	4.60	0.197	2.17	24.73	2.22	2.274	0.129	0.08	24.08	101.03
5H-1-43-45	34.23	37.67	130.70	50.43	0.76	14.85	6.80	0.139	2.58	7.33	2.19	3.167	0.150	0.65	10.79	99.84
5H-2-138-140	36.68	40.14	140.00	52.18	0.82	17.01	7.61	0.122	3.08	3.72	2.26	3.928	0.162	0.04	8.55	99.49
5H-4-35-37	38.65	42.13	145.57	49.18	0.80	16.82	7.12	0.153	3.54	5.99	2.22	3.769	0.169	0.05	9.90	99.71
5H-5-106-108	40.86	44.36	150.23	46.06	0.65	13.21	5.86	0.356	2.54	10.80	2.48	3.203	0.129	0.33	14.97	100.58
6H-1-37-39	43.67	47.23	156.24	49.25	0.72	14.77	6.25	0.183	3.30	6.97	2.68	3.170	0.151	0.15	11.39	98.98
6H-2-35-37	45.15	48.85	162.26	51.16	0.73	14.80	6.30	0.156	3.48	6.81	2.71	3.283	0.164	0.15	10.04	99.80
6H-4-23-25	48.03	52.02	176.96	45.40	0.62	12.49	5.77	0.198	2.49	11.93	2.90	2.928	0.129	0.62	14.45	99.91
6H-4-145-147	49.25	53.36	185.87	39.68	0.52	11.07	20.23	0.193	2.62	6.54	2.70	2.609	0.218	0.25	12.71	99.34
6H-5-115-117	50.45	54.68	198.12	52.17	0.71	14.61	6.12	0.190	3.47	5.55	3.09	3.139	0.135	0.18	10.59	99.94
6H-6-97-99	51.77	56.13	210.24	44.68	0.69	13.28	6.24	0.176	3.33	11.47	2.58	3.080	0.145	0.14	14.67	100.47
7H-1-113-115	53.93	58.38	227.06	43.51	0.59	11.89	5.56	0.148	2.71	6.48	3.05	2.865	0.110	0.26	12.47	89.62
7H-2-18-20	54.48	58.92	230.59	47.56	0.66	12.96	5.85	0.204	3.06	10.41	2.89	3.087	0.136	0.28	12.96	100.06
7H-2-135-137	55.65	60.07	238.09	39.68	0.59	11.88	5.90	0.152	2.66	15.48	2.15	3.016	0.136	0.18	18.23	100.06
7H-3-54-56	56.34	60.76	242.65	47.91	0.71	13.91	6.61	0.176	3.19	8.84	2.43	3.403	0.146	0.24	12.44	100.01
7H-4-120-122	58.50	62.89	256.91	35.74	0.56	10.49	5.40	0.171	2.46	20.53	2.03	2.669	0.148	0.74	19.77	100.70
7H-5-48-50	59.28	63.66	261.57	40.97	0.60	11.61	5.89	0.167	2.58	15.47	2.32	2.862	0.134	0.32	17.29	100.21

Sample ID	Depth	Depth	Age	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na₂O	K ₂ O	P ₂ O ₅	SO ₃	LOI	Total
	(mbsf)	(mcd)	(ka)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
7H-6-70-72	61.00	65.36	271.31	54.85	0.73	15.50	7.27	0.197	3.39	2.28	2.93	3.701	0.132	0.24	8.25	99.47
8H-1-80-82	63.10	67.46	280.95	52.90	0.71	14.41	6.19	0.156	3.47	5.26	3.10	3.150	0.137	0.16	10.00	99.63
8H-2-65-67	64.45	68.84	286.87	30.41	0.46	8.48	5.09	0.180	2.15	25.39	1.98	2.062	0.122	1.32	22.80	100.44
8H-3-7-9	65.37	69.78	293.58	21.07	0.35	6.23	3.24	0.219	1.66	30.58	1.70	1.631	0.124	0.09	29.66	96.55
8H-4-13-15	66.93	71.38	305.11	51.69	0.71	14.12	6.13	0.154	3.18	5.94	2.68	3.107	0.127	0.25	10.71	98.80
8H-5-5-7	68.35	72.83	315.09	34.95	0.52	9.92	5.06	0.260	2.50	20.60	2.41	2.460	0.128	0.15	21.22	100.16
8H-5-135-137	69.65	74.16	324.08	43.49	0.65	12.39	5.75	0.146	2.59	13.38	2.27	2.821	0.132	0.05	16.23	99.91
8H-6-70-72	70.50	75.03	329.45	23.81	0.40	7.23	4.26	0.228	1.73	31.25	1.64	1.858	0.144	0.03	28.44	101.02
9H-1-52-54	72.32	76.96	337.70	48.60	0.74	15.07	6.50	0.203	3.04	7.96	2.08	3.230	0.143	0.35	11.57	99.48
9H-2-15-17	73.45	78.26	342.17	47.64	0.74	15.40	6.55	0.154	3.56	7.87	2.00	3.314	0.146	0.09	11.93	99.40
9H-3-30-32	75.10	80.16	347.72	40.65	0.62	11.89	5.44	0.169	2.64	15.95	1.97	2.964	0.139	0.24	17.41	100.06
9H-3-72-74	75.52	80.64	349.19	47.56	0.76	16.36	6.84	0.167	3.70	7.27	2.01	3.693	0.155	0.13	11.08	99.72
9H-3-124-126	76.04	81.24	351.09	50.07	0.70	15.20	6.47	0.198	3.31	6.71	2.47	3.420	0.137	0.17	11.12	99.96
9H-4-117-119	77.47	82.89	357.06	54.35	0.74	15.54	6.48	0.195	3.54	3.96	2.94	3.615	0.148	0.23	8.33	100.07
9H-5-40-42	78.20	83.73	360.66	53.91	0.73	15.47	6.71	0.189	3.41	3.82	2.99	3.503	0.147	0.05	8.53	99.46
9H-6-9-101	80.29	86.14	371.14	54.81	0.71	14.58	6.54	0.230	3.39	3.90	3.22	3.202	0.135	0.08	9.23	100.03
10H-1-56-58	81.86	87.89	381.39	26.57	0.41	7.49	3.88	0.205	1.85	29.35	1.87	1.928	0.122	0.10	26.89	100.68
10H-2-40-42	83.20	89.31	397.20	40.95	0.65	11.34	5.66	0.166	2.61	16.13	2.12	2.706	0.140	0.04	17.17	99.68
10H-3-38-40	84.68	90.88	405.91	25.99	0.43	7.36	3.90	0.154	1.70	30.03	1.65	1.877	0.166	0.05	27.18	100.49
10H-3-122-124	85.52	91.77	408.57	53.07	0.76	16.59	7.42	0.123	3.04	3.53	2.19	3.730	0.143	0.09	9.18	99.88
10H-4-44-46	86.24	92.53	410.84	54.45	0.82	17.28	8.41	0.104	3.11	1.71	2.18	3.954	0.155	0.06	7.67	99.90
10H-4-105-107	86.85	93.18	412.77	55.32	0.78	15.89	9.03	0.123	2.95	2.06	2.00	3.861	0.165	0.03	8.14	100.35
10H-5-11-13	87.41	93.77	414.54	54.47	0.80	16.17	8.40	0.121	3.01	2.62	2.10	3.686	0.154	0.11	8.38	100.02
10H-5-121-123	88.51	94.94	418.02	54.07	0.81	17.51	8.60	0.138	3.17	1.44	2.21	3.949	0.159	0.05	8.08	100.19
10H-6-18-20	88.98	95.43	419.50	55.19	0.83	17.02	7.56	0.141	3.18	2.18	2.26	3.837	0.153	0.08	7.71	100.15
11H-1-48-50	91.28	97.86	426.12	49.03	0.74	15.40	6.95	0.180	3.94	6.93	2.19	3.588	0.161	0.28	10.69	100.09
11H-2-90-92	93.20	99.87	431.20	50.32	0.72	14.76	6.06	0.165	3.27	7.45	2.43	3.172	0.145	0.11	11.34	99.93
11H-3-45-47	94.25	100.97	435.98	56.27	0.73	15.79	6.84	0.137	3.39	2.24	3.18	3.488	0.140	0.05	7.74	100.00
11H-4-5-7	95.35	102.12	441.57	52.43	0.69	14.95	6.22	0.263	3.39	5.67	3.16	3.286	0.151	0.13	9.66	100.00

Sample ID	Ag	As	Ва	Cd	Ce	Со	Cr	Cu	Ga	La	Мо	Nb	Nd	Ni	Pb	Rb
		(ppm)														
1H-1-80-82	<2.6	5.5	326.3	<2.8	51.8	19.2	56.4	49.1	13.6	31.9	1.6	9.1	23.3	38.4	14.5	79.9
1H-3-97-99	<2.5	10.6	414.4	<2.6	68.1	17.9	69.8	35.8	18.1	38.7	2.4	13.8	32.1	38.8	21.2	117.3
2H-2-28.30	<2.5	11.9	431.9	<2.6	76.3	19.7	82.1	31.4	19.5	38.8	1.7	15.2	36.1	39.8	23.7	125.1
2H-4-59-61	<2.4	7.5	459.6	<2.6	85.7	18.2	94.3	30.5	21.0	42.0	1.3	15.2	36.6	42.2	24.4	139.8
2H-6-95-97	<2.4	6.4	354.7	<2.6	58.4	15.2	62.6	29.6	15.5	31.3	1.3	11.4	25.8	37.9	19.0	108.1
3H-1-77-79	<2.6	<5.2	234.3	<2.7	46.5	14.5	49.4	26.8	12.9	26.2	1.2	8.9	23.2	30.5	17.2	91.5
3H-2-135-137	<2.5	7.1	389.8	<2.6	62.4	17.9	62.1	45.2	15.7	40.8	1.3	10.5	25.0	37.7	20.3	102.0
3H-4-100-102	<2.6	<5.2	103.3	<2.7	18.9	9.5	31.5	18.0	11.7	16.8	1.4	8.8	10.8	22.4	21.4	81.3
3H-6-23-25	<2.3	7.7	276.2	<2.5	33.1	14.6	39.0	44.0	14.3	25.0	1.1	10.3	16.5	34.4	21.9	102.9
3H-7-46-48	<2.4	5.5	436.2	<2.5	73.5	20.3	65.1	45.2	17.9	35.8	1.7	13.5	31.5	44.3	22.1	117.3
4H-2-133-135	<2.6	<5.2	207.0	<2.7	37.7	15.9	41.7	45.0	11.4	19.5	1.5	7.8	20.0	33.5	16.4	79.2
4H-3-34-35	<2.4	6.1	63.4	<2.5	12.9	12.7	23.9	42.2	8.9	16.3	1.3	8.7	8.9	24.4	25.3	75.1
4H-3-122-124	<2.6	<5.4	43.6	<2.8	9.9	14.3	20.1	54.5	8.2	12.9	1.2	7.4	9.2	22.8	19.6	67.5
4H-5-48-50	<2.5	<5.1	93.0	<2.7	20.2	9.8	30.7	13.8	10.9	16.3	1.4	9.7	12.4	21.9	20.6	84.4
4H-6-21-23	<2.6	<5.3	199.4	<2.8	33.7	13.3	40.8	27.8	10.6	24.7	1.2	7.4	17.6	23.2	17.2	70.8
5H-1-43-45	<2.5	12.2	269.8	<2.7	57.8	13.9	58.7	29.0	16.8	29.9	2.0	13.8	24.0	32.4	24.8	117.1
5H-2-138-140	<2.5	5.8	404.7	<2.7	70.3	19.1	80.9	25.4	19.6	34.5	1.3	14.6	30.6	42.2	25.0	139.1
5H-4-35-37	<2.5	<5	371.9	<2.7	68.9	15.8	72.0	21.5	19.9	39.8	1.5	13.8	32.7	45.3	22.6	129.6
5H-5-106-108	<2.5	<5	71.0	<2.6	13.8	11.4	30.2	25.5	11.5	15.7	1.4	10.1	6.9	24.4	21.9	90.6
6H-1-37-39	<2.5	6.9	65.9	<2.6	20.3	12.1	27.3	23.2	12.9	18.6	1.3	11.5	9.0	21.1	28.8	101.2
6H-2-35-37	<2.5	<5	112.9	<2.7	25.1	12.0	32.1	26.8	13.3	18.7	1.2	11.7	11.1	23.3	25.5	104.2
6H-4-23-25	<2.4	<4.9	145.5	<2.6	26.5	15.1	42.5	44.2	11.9	23.7	1.5	9.5	13.9	26.8	20.7	83.8
6H-4-145-147	<2.8	14.9	232.9	<3	39.4	25.5	96.0	42.4	15.2	20.3	3.6	8.7	13.6	81.6	20.9	95.2
6H-5-115-117	<2.4	7.7	457.8	<2.5	72.4	20.9	71.7	68.9	16.3	32.5	1.5	11.7	27.4	54.1	20.8	108.2
6H-6-97-99	<2.6	6.5	215.5	<2.7	38.2	21.5	47.4	85.2	14.3	22.6	1.7	10.2	16.3	42.8	21.6	96.6
7H-1-113-115	<2.3	<4.6	292.1	<2.4	50.7	17.1	58.6	56.3	15.8	31.0	1.5	10.9	20.7	40.8	20.7	98.1
7H-2-18-20	<2.4	<4.8	159.5	<2.6	34.0	18.3	39.0	52.5	12.8	20.8	1.8	10.4	16.4	36.7	23.4	90.0
7H-2-135-137	<2.6	<5.2	352.1	<2.7	66.3	13.8	61.9	25.0	14.7	36.5	1.1	10.1	31.6	33.5	20.2	97.5
7H-3-54-56	<2.5	7.5	324.7	<2.7	58.8	19.1	60.6	38.6	16.0	34.6	1.5	11.5	26.7	39.6	22.3	106.4
7H-4-120-122	<2.6	6.0	383.6	<2.8	55.0	15.0	56.0	29.4	13.1	36.7	1.6	8.6	24.2	33.0	14.3	86.0
7H-5-48-50	<2.6	<5.2	357.0	<2.7	58.5	17.1	58.5	41.8	15.1	34.6	1.6	10.1	25.0	37.9	16.3	91.3

Sample ID	Ag	As	Ва	Cd	Ce	Co	Cr	Cu	Ga	La	Мо	Nb	Nd	Ni	Pb	Rb
		(ppm)														
7H-6-70-72	<2.4	10.2	474.5	<2.5	83.0	26.7	73.5	52.8	18.1	34.4	2.8	13.0	35.2	65.4	20.1	120.7
8H-1-80-82	<2.4	8.6	452.9	<2.5	74.9	18.6	71.8	58.0	17.4	38.8	2.1	12.8	28.6	42.1	21.4	106.9
8H-2-65-67	<2.6	7.9	345.0	<2.8	51.4	14.4	49.9	37.7	10.9	28.2	1.8	7.3	24.4	28.5	15.0	68.8
8H-3-7-9	<2.7	<5.5	265.6	<2.9	43.0	11.2	37.8	30.7	9.4	18.9	1.5	5.4	22.1	18.9	9.8	55.5
8H-4-13-15	<2.4	<4.8	425.4	<2.6	66.5	18.7	72.5	59.3	17.2	41.7	1.9	12.4	29.0	45.5	22.0	109.2
8H-5-5-7	<2.6	<5.2	331.3	<2.8	56.6	12.8	48.4	22.4	12.9	27.0	1.6	8.2	25.5	30.0	14.4	79.1
8H-5-135-137	<2.5	<5	363.4	<2.7	62.3	19.9	60.0	69.5	15.4	30.3	1.5	10.6	28.7	43.9	19.3	92.3
8H-6-70-72	<2.8	<5.6	309.4	<2.9	47.9	11.4	40.9	20.1	10.4	23.0	1.3	6.2	21.3	22.6	10.7	61.7
9H-1-52-54	<2.6	5.8	357.5	<2.7	64.6	16.4	70.1	25.3	18.5	31.2	1.7	12.9	28.1	41.6	21.5	116.4
9H-2-15-17	<2.5	5.1	379.8	<2.7	69.5	22.7	81.2	26.8	18.7	33.0	1.5	12.9	31.3	54.5	22.9	122.3
9H-3-30-32	<2.5	<5.2	337.2	<2.7	56.1	14.8	60.5	32.1	15.8	37.1	1.1	9.7	25.9	35.8	16.6	96.4
9H-3-72-74	<2.5	7.3	393.3	<2.7	74.7	20.1	83.6	25.2	19.6	41.0	1.1	13.4	33.8	53.7	25.0	130.2
9H-3-124-126	<2.4	<4.9	399.7	<2.6	69.5	19.7	69.8	45.2	17.2	34.5	1.1	11.6	32.4	47.1	21.1	117.4
9H-4-117-119	<2.4	<4.8	469.3	<2.6	80.4	19.4	75.6	45.1	18.1	36.7	1.8	12.7	31.5	48.5	19.9	117.1
9H-5-40-42	<2.4	<4.8	478.5	<2.6	74.4	18.8	78.9	46.6	18.5	42.2	1.4	12.6	33.2	47.7	20.2	115.9
9H-6-9-101	<2.4	<4.7	417.5	<2.5	73.1	23.6	66.0	58.3	17.1	39.8	1.6	11.7	31.0	46.9	20.2	104.9
10H-1-56-58	<2.7	<5.5	313.1	<2.9	52.8	11.9	42.8	25.6	10.3	27.1	0.8	5.8	23.1	26.0	10.7	62.3
10H-2-40-42	<3.3	<6.6	517.2	<3.5	80.7	22.6	79.9	30.1	16.2	40.2	1.8	12.6	37.0	47.6	19.4	111.2
10H-3-38-40	<3.4	7.7	396.1	<3.6	63.2	14.9	53.2	28.1	11.7	36.6	1.1	8.2	27.0	26.9	13.2	75.9
10H-3-122-124	<3.1	6.4	476.6	<3.3	95.4	25.8	96.5	53.5	24.3	44.6	2.0	17.6	41.4	58.2	29.9	159.5
10H-4-44-46	<3.2	13.9	490.2	<3.4	95.6	23.8	108.0	40.1	25.4	53.3	1.6	18.7	41.9	52.9	32.8	168.6
10H-4-105-107	<3.3	9.6	465.9	<3.5	100.6	18.3	117.4	38.3	22.5	47.6	1.5	16.9	43.7	44.7	29.6	164.1
10H-5-11-13	<3.2	14.8	491.3	<3.4	101.2	23.9	107.4	40.7	24.8	42.3	2.0	17.6	43.3	52.6	30.5	158.5
10H-5-121-123	<3.2	11.4	521.6	<3.4	107.5	27.7	113.0	42.7	26.2	48.8	2.2	17.9	42.7	52.6	30.2	169.8
10H-6-18-20	<3.1	15.6	546.7	<3.3	107.1	24.7	109.5	39.0	24.7	47.1	1.7	18.5	42.8	56.0	29.5	166.8
11H-1-48-50	<3.2	7.2	522.2	<3.4	94.1	22.9	98.4	34.5	23.3	48.1	1.5	15.7	37.1	60.4	25.6	153.8
11H-2-90-92	<3.2	<6.3	118.6	<3.4	32.0	17.1	35.4	39.2	16.6	16.4	1.9	14.7	12.7	39.2	32.7	126.2
11H-3-45-47	<2.4	<4.7	155.2	<2.5	36.8	16.1	39.1	44.8	15.1	20.2	1.6	11.9	18.2	31.7	30.3	107.8
11H-4-5-7	<2.5	<4.9	476.9	<2.6	81.4	26.9	72.5	53.6	17.8	35.6	1.8	12.1	33.6	58.8	21.8	110.8

Sample ID	Sb	Sc	Se	Sn	Sr	Th	U	V	w	Y	Zn	Zr	Total C	CaCO ₃ (eq)	TIC(eq)	TOC(eq)
	(ppm)		(wt%)	(wt%)	(wt%)	(wt%)										
1H-1-80-82	<3.2	12.5	<1.2	<2	690.6	8.2	1.8	82.1	<2.4	17.2	64.1	100.8	5.36	37.65	4.52	0.84
1H-3-97-99	<3.1	14.2	<1.1	<1.9	232.2	10.5	2.3	103.1	<2.3	24.6	81.4	155.7	1.58	9.37	1.12	0.46
2H-2-28.30	<3.1	15.9	<1.1	2.1	191.7	12.2	1.9	109.2	<2.3	27.5	88.8	158.2	1.42	7.09	0.85	0.57
2H-4-59-61	<3.1	14.5	<1.1	3.1	150.6	14.6	2.1	122.5	<2.2	28.3	98.5	141.0	0.98	4.00	0.48	0.50
2H-6-95-97	<3.1	11.3	<1.1	<1.9	308.3	11.3	1.3	79.0	<2.2	22.5	72.8	133.6	2.49	15.94	1.91	0.58
3H-1-77-79	<3.2	10.1	<1.1	<2	540.8	8.4	2.2	60.2	<2.3	18.8	64.1	100.5	3.77	29.52	3.54	0.23
3H-2-135-137	<3.1	12.5	<1.1	<1.9	362.6	8.8	2.8	91.2	3.2	21.4	87.5	115.5	2.62	17.85	2.14	0.48
3H-4-100-102	<3.2	5.4	<1.1	<2	545.3	10.1	2.6	33.0	<2.3	16.3	92.1	92.7	4.24	31.73	3.81	0.43
3H-6-23-25	<2.9	6.4	<1	<1.8	226.0	9.7	2.4	53.7	<2.1	21.4	69.9	106.1	1.53	9.52	1.14	0.38
3H-7-46-48	<3	9.2	<1	<1.9	184.7	12.0	2.5	91.3	<2.2	24.1	90.5	141.9	0.93	4.73	0.57	0.36
4H-2-133-135	<3.2	7.5	<1.1	<2	626.9	8.9	1.6	55.2	<2.3	17.1	61.2	92.9	4.72	35.28	4.23	0.49
4H-3-34-35	<3	1.7	<1	<1.9	321.7	7.4	1.2	20.3	<2.1	17.0	47.3	92.8	2.82	19.05	2.29	0.53
4H-3-122-124	<3.3	4.2	<1.2	<2	612.9	7.2	2.0	22.0	<2.3	15.0	37.8	88.5	5.13	39.57	4.75	0.38
4H-5-48-50	<3.2	6.2	<1.1	<2	412.9	8.8	1.7	32.3	2.3	20.3	46.1	121.3	3.25	24.15	2.90	0.35
4H-6-21-23	<3.3	7.8	<1.2	<2.1	743.9	7.5	4.4	51.6	<2.3	16.2	55.3	84.0	5.66	44.15	5.30	0.36
5H-1-43-45	<3.1	9.6	<1.1	<2	291.0	13.3	3.7	81.5	<2.3	25.7	95.9	150.2	1.99	13.09	1.57	0.42
5H-2-138-140	<3.1	14.8	<1.1	<2	187.0	12.0	2.9	113.5	<2.3	28.0	96.8	147.3	1.20	6.64	0.80	0.40
5H-4-35-37	<3.1	13.1	<1.1	<2	222.3	12.4	1.4	90.9	<2.3	25.5	84.2	129.3	1.67	10.69	1.28	0.39
5H-5-106-108	<3.1	5.1	<1.1	<2	354.7	8.7	2.8	26.6	<2.1	21.4	50.1	111.6	2.85	19.28	2.31	0.54
6H-1-37-39	<3.1	2.2	<1.1	<1.9	250.6	11.1	1.7	27.1	<2.2	22.5	53.9	114.9	1.94	12.45	1.49	0.45
6H-2-35-37	<3.1	4.5	<1.1	<2	261.2	10.3	1.7	34.1	<2.2	23.6	62.5	121.6	1.83	12.17	1.46	0.37
6H-4-23-25	<3.1	4.9	<1.1	2.5	425.0	8.9	1.8	36.5	3.0	20.0	64.0	100.8	2.91	21.29	2.56	0.35
6H-4-145-147	<3.5	5.2	<1.3	<2.2	315.4	8.9	2.5	59.0	<2.7	17.5	81.2	91.3	1.76	11.68	1.40	0.36
6H-5-115-117	<3	12.2	<1	<1.9	237.3	10.5	2.4	103.2	<2.1	22.3	93.7	119.0	1.74	9.92	1.19	0.55
6H-6-97-99	<3.2	6.5	<1.1	<2	355.7	10.4	2.2	54.7	<2.3	19.5	75.4	105.2	2.91	20.48	2.46	0.45
7H-1-113-115	<2.9	8.0	<1	<1.8	270.2	10.9	1.6	79.0	<2.1	19.0	86.0	108.3	2.02	11.57	1.39	0.63
7H-2-18-20	<3	6.1	<1.1	<1.9	341.3	9.9	2.4	48.3	<2.1	19.8	69.2	109.7	2.49	18.58	2.23	0.26
7H-2-135-137	<3.2	14.8	<1.1	<2	523.0	10.2	2.5	81.3	<2.3	21.0	80.1	105.7	3.51	27.65	3.32	0.19
7H-3-54-56	<3.1	10.6	<1.1	<2	305.5	10.4	2.6	81.4	<2.3	21.5	77.0	121.7	2.37	15.79	1.90	0.47
7H-4-120-122	<3.2	12.2	<1.2	<2	650.8	8.6	2.6	76.8	<2.4	17.9	69.4	94.5	4.86	36.67	4.40	0.46
7H-5-48-50	<3.2	13.1	<1.1	<2	545.0	9.5	3.8	81.5	<2.3	20.0	72.6	105.2	3.82	27.62	3.31	0.51

Sample ID	Sb	Sc	Se	Sn	Sr	Th	U	V	w	Y	Zn	Zr	Total C	CaCO ₃ (eq)	TIC(eq)	TOC(eq)
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)		(wt%)	(wt%)	(wt%)	(wt%)
7H-6-70-72	<3	12.3	<1	<1.9	161.2	11.4	1.0	108.1	<2.2	23.8	101.1	127.4	0.91	4.07	0.49	0.42
8H-1-80-82	<3	11.7	<1	2.5	232.3	12.2	2.2	98.0	<2.2	22.1	98.7	126.1	1.62	9.39	1.13	0.50
8H-2-65-67	<3.3	12.9	<1.2	<2.1	841.7	9.1	5.4	69.9	<2.4	15.0	60.3	84.6	5.54	45.34	5.44	0.10
8H-3-7-9	<3.3	9.3	<1.2	<2.1	1034.7	7.1	3.6	56.5	<2.4	11.6	47.6	67.9	7.44	54.61	6.55	0.89
8H-4-13-15	<3	13.1	<1.1	<1.9	247.5	11.7	2.4	105.2	<2.2	23.3	99.4	133.0	1.87	10.60	1.27	0.60
8H-5-5-7	<3.2	14.1	<1.1	<2	695.3	9.5	1.6	70.7	<2.4	15.8	61.7	89.0	4.88	36.79	4.41	0.47
8H-5-135-137	<3.1	13.5	<1.1	<2	510.5	9.4	3.5	85.6	<2.3	22.4	76.5	119.6	3.33	23.89	2.87	0.46
8H-6-70-72	<3.4	9.5	<1.2	<2.1	1027.1	8.0	3.2	58.3	<2.5	12.8	47.8	71.8	7.05	55.80	6.70	0.35
9H-1-52-54	<3.2	13.1	<1.1	<2	301.6	11.3	2.4	94.4	<2.4	24.9	84.5	136.8	2.18	14.21	1.70	0.48
9H-2-15-17	<3.1	15.4	<1.1	<2	282.7	11.8	3.3	102.7	3.1	23.6	83.2	130.3	2.14	14.05	1.69	0.45
9H-3-30-32	<3.2	13.5	<1.1	<2	546.9	9.7	2.6	82.4	<2.3	21.1	69.0	117.0	4.00	28.47	3.42	0.58
9H-3-72-74	<3.1	15.4	<1.1	<2	251.8	13.3	3.2	106.7	<2.3	25.2	86.6	127.7	1.95	12.98	1.56	0.39
9H-3-124-126	<3	13.2	<1.1	<1.9	271.7	11.6	2.0	102.9	<2.3	23.6	82.8	124.3	1.91	11.98	1.44	0.47
9H-4-117-119	<3	13.0	<1.1	<1.9	220.1	10.6	1.6	102.4	<2.2	23.0	93.9	129.2	1.20	7.06	0.85	0.35
9H-5-40-42	<3	14.3	<1.1	<1.9	219.4	10.8	1.2	103.6	<2.2	23.0	94.0	124.7	1.26	6.82	0.82	0.44
9H-6-9-101	<3	11.8	<1	<1.9	213.1	9.9	1.9	95.3	<2.2	20.6	89.7	124.8	1.27	6.96	0.83	0.44
10H-1-56-58	<3.3	10.1	<1.2	<2.1	1001.2	6.4	3.6	64.7	<2.5	14.4	69.8	75.9	6.33	52.42	6.29	0.04
10H-2-40-42	<4.1	19.6	<1.4	<2.6	752.4	12.1	2.6	118.8	<3	23.7	93.3	147.9	3.84	28.79	3.46	0.38
10H-3-38-40	<4.2	15.0	<1.5	<2.6	1261.0	10.0	3.8	75.1	3.2	18.3	59.1	102.1	6.76	53.63	6.44	0.32
10H-3-122-124	<3.8	16.8	1.4	3.2	226.3	16.2	2.2	135.0	<2.8	32.4	132.2	169.9	1.40	6.31	0.76	0.64
10H-4-44-46	<3.9	15.4	1.7	<2.5	168.8	16.4	2.6	142.0	4.4	33.7	115.0	181.4	0.87	3.06	0.37	0.50
10H-4-105-107	<4	14.4	1.4	<2.5	174.1	15.0	2.8	148.2	<3	33.1	113.0	196.7	1.11	3.68	0.44	0.67
10H-5-11-13	<3.9	16.5	1.7	<2.5	201.0	14.6	3.3	145.0	<2.9	33.5	110.5	192.4	1.23	4.68	0.56	0.66
10H-5-121-123	<3.9	17.9	2.1	<2.5	163.8	15.9	3.6	152.1	3.9	33.3	120.1	171.5	1.03	2.58	0.31	0.72
10H-6-18-20	<3.9	14.6	<1.3	<2.4	187.9	15.2	2.6	142.9	<2.9	33.9	116.9	187.7	1.06	3.89	0.47	0.59
11H-1-48-50	<3.9	16.7	<1.4	<2.5	325.5	15.5	1.4	120.0	4.3	29.5	112.6	151.2	2.02	12.38	1.49	0.53
11H-2-90-92	<3.9	4.7	<1.4	<2.5	349.8	14.2	2.2	42.8	<2.8	26.8	78.5	144.7	2.20	13.31	1.60	0.61
11H-3-45-47	<3	4.8	<1	<1.9	183.4	11.9	1.6	48.5	<2.1	22.5	82.8	118.5	1.00	4.00	0.48	0.52
11H-4-5-7	<3.1	12.1	<1.1	<1.9	285.0	11.0	2.4	94.1	<2.2	21.4	92.1	112.9	1.75	10.12	1.21	0.54

Lyons et al. (2003) - Cariaco Basin last glacial-interglacial transition Peterson (2000) - Cariaco Basin Mo_(tot) Depth TIC Depth $\delta^{18}O$ Depth CaCO₃ $\delta^{34}S_{(pv)}$ Fe_(tot) Al_(tot) C_{org} (wt%) S_(py) (wt%) Fet/Alt DOP C_{org} (wt%) TIC (wt%) Mo/Al (wt%) (‰) (wt%) (wt%) (‰) (wt%) (mbsf) (ppm) (mbsf) (mbsf) 0.5 -1.39 0.00 3.84 5.56 1.93 0.75 0.16 25.41 4.35 3.05 3.78 5.68 1.87 -32.6 0.52 2.07 -1.28 0.56 27.83 4.30 3.34 0.05 0.10 3.71 6.08 1.66 -33.2 2.78 5.86 0.48 0.48 95 0.00163 2.25 -1.33 0.96 26.96 3.99 3.24 3.87 5.46 -31.9 2.73 0.44 0.53 80 -1.45 3.81 3.83 0.15 1.87 6.15 0.0013 3.17 1.36 31.94 0.20 3.86 5.58 1.98 -33.8 0.52 3.37 -1.37 1.66 28.12 3.23 3.37 0.25 3.85 5.85 1.81 -33.3 2.7 5.8 0.47 0.53 93 0.0016 3.75 -1.48 2.06 30.58 3.34 3.67 0.30 3.99 5.68 2.44 -32.7 2.82 5.58 0.5 0.57 112 0.00201 3.97 -1.54 2.46 29.57 3.06 3.55 0.35 3.92 5.22 2.06 -32.9 0.54 4.17 -1.43 2.86 28.63 3.32 3.44 0.40 4.03 5.49 1.84 -32.7 0.49 4.67 3.02 -1.17 3.16 25.15 3.16 0.45 3.78 5.5 1.78 2.89 6.03 0.48 0.53 4.87 -1.52 3.56 3.82 3.41 103 0.00171 28.45 0.55 4.27 5.42 2.14 -32.3 2.83 0.49 0.55 97 0.00167 5.07 -0.76 3.96 5.54 2.44 5.8 20.31 5.25 2.08 0.57 2.91 3.12 0.65 4 5.25 0.01 4.36 25.97 0.75 3.92 5.12 2.23 -32.9 0.55 5.47 -0.10 4.66 20.40 1.94 2.45 0.85 3.66 5.25 1.86 3.07 6.13 0.5 0.54 97 0.00158 5.67 0.39 5.06 2.10 3.17 26.43 0.95 4.17 4.81 2.45 -31.3 0.57 5.87 0.36 5.46 27.94 2.95 3.35 2.13 1.05 3.94 5.22 -31.7 0.57 6.07 -0.27 5.86 16.36 3.61 1.96 3.62 4.82 3.16 6.28 0.5 0.53 78 0.00124 6.37 0.43 23.35 2.80 1.15 2.09 6.16 4.66 1.25 4.2 4.64 2.2 -33.2 2.77 5.53 0.5 0.58 82 0.00148 6.57 0.50 6.56 20.12 0.65 2.41 1.35 3.85 4.23 2.4 0.58 6.75 0.12 6.96 5.96 0.31 0.72 1.45 4.34 4.21 2.21 -33.8 0.56 6.97 -0.03 7.36 4.10 0.10 0.49 3.86 2.33 3.15 0.06 7.66 7.82 0.32 1.55 4.17 6.16 0.51 0.57 47 0.00076 7.17 0.94 3.93 2.44 -32.8 0.58 1.70 4.33 7.37 0.09 1.85 3.55 4.66 2.24 0.56 7.67 -0.09 2.00 3.56 4.23 2.26 0.56 7.82 -0.32 40.13 15.96 1.13 1.92 2.15 3.77 4.13 2.2 3.13 6.38 0.49 0.56 79 0.00124 7.84 -0.44 40.50 18.21 0.93 2.19 2.30 3.64 4.32 2.08 -33.8 0.55 40.87 23.36 2.10 2.80 2.45 3.74 3.92 2.28 0.56 40.51 -1.42 41.22 24.88 2.64 2.99 2.60 3.83 3.85 2.41 3.24 6.4 0.51 0.57 81 0.00127 40.79 -0.42 41.59 28.43 1.88 3.41 2.75 3.69 4.37 2.31 -17.5 0.58 41.04 0.03 41.96 30.36 2.06 3.64 2.90 2.16 0.52 0.54 -0.28 42.34 2.52 3.94 3.61 4.07 3.37 6.56 95 0.00145 41.41 32.81 3.00 3.42 2.17 -30.5 0.55 41.86 -0.94 42.62 30.25 2.51 3.63 5.15 3.20 3.17 4.78 2.08 0.55 42.06 -1.80 42.99 26.49 2.73 3.18 3.40 2.96 6.21 2.07 3.4 6.61 0.51 0.55 163 0.00247 42.34 -1.36 43.36 22.67 3.49 2.72 3.60 3.17 5.72 2.11 0.55 42.62 -1.43 43.73 26.16 3.29 3.14 3.80 2.94 6.13 1.89 -27.8 3.1 5.94 0.52 0.56 187 0.00315 42.90 -1.74 44.01 18.34 3.09 2.20 0.53 1.87 4.00 3.03 5.09 1.58 43.18 -1.08 44.39 15.62 2.64 2.28 4.20 3.31 4.86 1.67 0.58 43.26 -1.24 44.76 18.96 1.71 4.40 3.94 2.89 1.97 0.51 0.56 0.00172 43.56 45.12 1.98 1.37 3.9 67 -1.16 16.51 1.68 4.45 3.91 2.74 1.46 -27.4 0.55 43.84 -0.94 45.40 12.05 1.63 1.45 4.50 3.52 2.85 1.32 -26.2 1.91 3.78 0.51 0.55 62 0.00164 44.12 -0.82 45.79 13.19 1.63 1.58 4.70 3.82 2.65 1.46 2.04 3.89 0.53 0.56 60 0.00154 44.66 -1.00 46.45 19.79 1.44 2.37 4.90 3.76 2.73 1.72 2.35 4.46 0.53 0.56 64 0.00144 45.05 -1.57 46.78 25.08 0.85 3.01 5.10 4.02 2.71 1.76 -28.2 2.56 5.01 0.51 0.53 65 0.0013 45.32 -0.88 47.06 15.89 1.91 1.11 5.30 3.59 3.2 1.74 2.83 5.54 0.51 0.52 103 0.00185 45.61 -1.86 47.42 19.56 1.97 2.35 5.21 1.64 2.62 2.69 5.50 3.08 4.85 0.54 0.58 154 0.00318 45.89 -1.16 47.78 22.38 1.32 5.70 2.19 3.7 2.36 3.24 6.05 0.00241 46.46 -0.10 48.05 2.30 0.54 0.64 146 19.13 1.13 5.90 2.63 5.51 2.15 -26.5 2.82 5.1 0.55 0.69 178 0.00349 46.80 0.04 48.41 21.30 1.10 2.56 6.00 2.53 4.35 2.09 -28.4 3.63 7.15 0.51 180 0.00252 47.07 1.08 48.76 20.43 0.50 2.45 6.10 1.05 2.29 2.51 -25.5 4.33 8.5 0.51 144 0.00169 47.31 0.79 49.40 23.45 0.33 2.81 6.15 1.04 5.72 1.76 -26.1 47.70 0.46 49.76 30.58 0.21 3.67

6.20	1.56	3.75	2.23	-27.4	3.5	6.85	0.51		162	0.00236	47.93	0.48	50.11	20.83	1.21	2.50
6.25	2.84	4.89	2.38	-28.3							48.65	0.38	50.48	10.35	1.23	1.24
6.35	2.21	4.3	2.46		3.9	7.65	0.51		172	0.00225	49.40	0.31	50.75	21.32	0.14	2.56
6.40	2.27	4.13	2.59								51.35	0.88	51.11	19.28	0.22	2.31
6.49	2.31	4.13	2.86	-27.9	3.93	7.42	0.53		162	0.00218	54.18	0.20	51.47	18.45	0.18	2.21
6.51	0.75	1.37	3.24	-28.7	4.87	9.55	0.51		76	0.0008	55.53	0.19	51.83	16.54	0.28	1.98
6.60	2.85	1.08	2.57	-30.5	3.65	7.66	0.48		8	0.0001	56.52	-0.29	52.14	12.84	1.42	1.54
6.65	3.05	0.81	2.56	-29.1							57.26	0.22	52.47	19.26	0.40	2.31
6.70	2.73	0.84	2.36	-27.4	3.7	8.27	0.45		3	0.00004	58.55	-0.30	52.86	16.04	1.41	1.92
6.75	2.6	0.81	2.41	-24.5							59.77	-0.28	53.22	16.29	0.37	1.95
6.80	3.42	0.82	2.55	-23							61.08	0.69	53.53	20.01	1.00	2.40
6.85	2.21	0.56	2.6	20	3.95	8.45	0.47		3	0.00004	62.37	-0.30	53.89	9.20	1.05	1.10
7.05	0.79	0.26	2 94	-12.2	0.00	0.10	0		•	0.0000	67.81	-0.47	54 25	21 11	1 18	2 53
7.00	0.00	0.20	2.01	-12.8	47	9 79	0.48		5	0.00005	69.13	-0.77	54 61	10.10	1.10	1 21
7.10	1 1	0.20	3.05	-13	4.7	0.10	0.40		0	0.00000	70.43	-1 11	54.87	7 9/	1.50	0.95
7.15	0.14	0.50	2.05	_8.8	4.0	0.70	0.5		3	0 00003	70.43	-0.77	55 21	8 73	0.78	1.05
7.20	0.14	0.13	2.5	-0.0	4.9	9.79 11 1	0.3		2	0.00003	71.70	-0.17	55.21	5.75	0.70	0.67
7.30	0.32	0.19	0.52	-7.0	4.02	11.1	0.43		3	0.00003	73.00	-0.19	55.55	5.55	0.96	0.07
7.40	0.5	0.55	0.12	-21.2	4.98	11.1	0.45		2	0.00002	74.30	-0.62	50.03	3.41	1.09	0.41
7.45	0.28	0.17	0.11	-13.4							75.64	-0.21	56.69	3.48	1.06	0.42
7.55	0.68	0.33	0.19								76.78	0.10	57.02	5.59	0.80	0.67
7.60	0.3	0.17	0.06	-23	5.18	10.9	0.48		2	0.00002	78.23	-0.62	57.36	7.15	0.85	0.86
7.70	0.2	0.16		16.7							81.13	0.48	57.71	7.80	1.35	0.94
7.75	0.59	0.23	0.18	3.9							82.58	0.29	57.90	8.66	0.65	1.04
7.80	1.05	0.33	0.29	19.1							83.96	0.69	58.28	5.59	1.31	0.67
7.85	1.77	0.59	0.48	-8.3	4.16	9.06	0.46		2	0.00002	85.05	-0.12	58.61	3.78	1.16	0.45
7.95	2.34	0.83	0.71	-21.6							85.71	-0.03	58.95	8.51	0.83	1.02
											87.01	-0.92	50 20	11.80	1 09	1 / 2
											01.01	0.02	00.20	11.00	1.00	1.72
Yarincik et a	ıl. 2000a a	nd 2000b -	Cariaco Ba	asin							88.33	-0.19	59.53	11.40	1.33	1.37
Yarincik et a	N. 2000a a	nd 2000b -	Cariaco Ba	asin Mo.oom	Vppm	Ti ppm	K wat %	Terrigeno			88.33	-0.19	59.53	11.40	1.33	1.37
Yarincik et a Depth	n l. 2000a a Al (wt%)	nd 2000b - Fe (ppm)	Cariaco Ba Mn ppm	asin Mo ppm	V ppm	Ti ppm	K wt %	Terrigeno us wt%			88.33 89.66	-0.19	59.53 59.87	11.40 3.92	1.33	0.47
Yarincik et a Depth 0.47	il. 2000a a Al (wt%) 5.52	nd 2000b - Fe (ppm) 27327	Cariaco Ba Mn ppm 159	asin Mo ppm 79.4	V ppm 195	Ti ppm 2472	K wt % 1.37	Terrigeno us wt% 48			88.33 89.66 91.00	-0.19 0.03 -0.83	59.53 59.87 60.19	11.40 3.92 5.62	1.33 1.09 1.08	0.47 0.67
Yarincik et a Depth 0.47 1.05	I I. 2000a a Al (wt%) 5.52 5.59	Fe (ppm) 27327 27234	Cariaco Ba Mn ppm 159 158	asin Mo ppm 79.4 80.7	V ppm 195 205	Ti ppm 2472 2503	K wt % 1.37 1.26	Terrigeno us wt% 48 49			88.33 89.66 91.00 92.24	-0.19 0.03 -0.83 -0.83	59.53 59.87 60.19 60.50	11.40 3.92 5.62 6.87	1.03 1.09 1.08 0.59	0.47 0.67 0.82
Yarincik et a Depth 0.47 1.05 1.96	Al (wt%) 5.52 5.59 5.73	re (ppm) 27327 27234 27795	Cariaco Ba Mn ppm 159 158 208	asin Mo ppm 79.4 80.7 38.7	V ppm 195 205 169	Ti ppm 2472 2503 2609	K wt % 1.37 1.26 1.25	Terrigeno us wt% 48 49 50			88.33 89.66 91.00 92.24 93.59	-0.19 0.03 -0.83 -0.83 -0.37	59.53 59.87 60.19 60.50 60.84	11.40 3.92 5.62 6.87 8.44	1.03 1.09 1.08 0.59 0.73	0.47 0.67 0.82 1.01
Yarincik et a Depth 0.47 1.05 1.96 2.55	Al (wt%) 5.52 5.59 5.73 6.34	Fe (ppm) 27327 27234 27795 30409	Cariaco Ba Mn ppm 159 158 208 216	asin Mo ppm 79.4 80.7 38.7 47.1	V ppm 195 205 169 168	Ti ppm 2472 2503 2609 2837	K wt % 1.37 1.26 1.25 1.39	Terrigeno us wt% 48 49 50 55			88.33 89.66 91.00 92.24 93.59 94.82	-0.19 0.03 -0.83 -0.83 -0.37 -1.48	59.53 59.87 60.19 60.50 60.84 61.14	11.40 3.92 5.62 6.87 8.44 6.02	1.33 1.09 1.08 0.59 0.73 1.33	1.42 1.37 0.47 0.67 0.82 1.01 0.72
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46	II. 2000a a Al (wt%) 5.52 5.59 5.73 6.34 6.43	Fe (ppm) 27327 27234 27795 30409 31872	Cariaco Ba Mn ppm 159 158 208 216 167	asin Mo ppm 79.4 80.7 38.7 47.1 80.7	V ppm 195 205 169 168 172	Ti ppm 2472 2503 2609 2837 2991	K wt % 1.37 1.26 1.25 1.39 1.57	Terrigeno us wt% 48 49 50 55 55 57			88.33 89.66 91.00 92.24 93.59 94.82 96.17	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16	59.53 59.87 60.19 60.50 60.84 61.14 61.51	11.40 3.92 5.62 6.87 8.44 6.02 11.84	1.33 1.09 1.08 0.59 0.73 1.33 1.74	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05	II. 2000a a AI (wt%) 5.52 5.59 5.73 6.34 6.43 5.04	Fe (ppm) 27327 27234 27795 30409 31872 24817	Cariaco Ba Mn ppm 159 158 208 216 167 135	Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0	V ppm 195 205 169 168 172 150	Ti ppm 2472 2503 2609 2837 2991 2525	K wt % 1.37 1.26 1.25 1.39 1.57 1.31	Terrigeno us wt% 48 49 50 55 57 46			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96	II. 2000a a AI (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57	red 2000b - Fe (ppm) 27327 27234 27795 30409 31872 24817 22745	Cariaco Ba Mn ppm 159 158 208 216 167 135 139	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4	V ppm 195 205 169 168 172 150 102	Ti ppm 2472 2503 2609 2837 2991 2525 2326	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2	Terrigeno us wt% 48 49 50 55 57 46 42			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76	II. 2000a a AI (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24	re (ppm) 27327 27234 27795 30409 31872 24817 24817 22745 26522	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1	V ppm 195 205 169 168 172 150 102 165	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31	Terrigeno us wt% 48 49 50 55 57 46 42 47			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98	re (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8	V ppm 195 205 169 168 172 150 102 165 194	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4	Terrigeno us wt% 48 49 50 55 57 46 42 47 62			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46 62.83	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54	re (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8	V ppm 195 205 169 168 172 150 102 165 194 117	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46 62.83 63.14	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57	re (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5	V ppm 195 205 169 168 172 150 102 165 194 117 204	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46 62.83 63.14 63.47	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10 13	nd 2000b - Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6	V ppm 195 205 169 168 172 150 102 165 194 117 204 217	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8	Terrigeno us wt% 48 49 50 55 55 57 46 42 47 62 68 90 99			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.46 62.83 63.14 63.47 63.80	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 5.82	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54	$\begin{array}{c} 1.42\\ 1.37\\ 0.47\\ 0.67\\ 0.82\\ 1.01\\ 0.72\\ 1.42\\ 1.34\\ 1.01\\ 2.12\\ 0.94\\ 1.11\\ 1.43\\ 0.70\end{array}$
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32	re (ppm) Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.4	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.83 63.14 63.47 63.80 64.14	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 9.21 11.88 5.82 7.61	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51	re (ppm) Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 32241 41272	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 67	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.4 1.4 1.4 1.4 1.4 1.4 1.4 1.4	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 99 67 69			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.64	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.23	59.53 59.87 60.19 60.50 60.84 61.14 61.51 62.14 62.46 62.83 63.14 63.47 63.80 64.14 64.39	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 5.82 7.61 7.04	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87 9 63	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35	re (ppm) Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241 41272 41006	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3636 3828 4044	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.44 1.4 1.4 1.4 1.4 1.4 1.39	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67 69 70			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.46 62.83 63.14 63.47 63.80 64.14 63.80 64.14	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 5.82 7.61 7.04 6.44	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60	$\begin{array}{c} 1.42\\ 1.37\\ 0.47\\ 0.67\\ 0.82\\ 1.01\\ 0.72\\ 1.42\\ 1.34\\ 1.01\\ 2.12\\ 0.94\\ 1.11\\ 1.43\\ 0.70\\ 0.91\\ 0.84\\ 0.77\end{array}$
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87 9.63	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35	re (ppm) 27327 27234 27795 30409 31872 24817 224817 22522 36226 35305 46299 50747 33241 41272 41006	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.44 1.4 1.39	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67 69 70			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 103.95	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75	59.53 59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.83 63.14 63.47 63.80 64.14 64.39 64.72 65.03	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 5.82 7.61 7.04 6.44 8.35	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84 0.77 1.00
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.67 6.66 7.06 7.57 8.13 8.87 9.63	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35	re (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241 41272 41006	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.44 1.4 1.39 1.72	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67 69 70			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 110.27	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75 -0.20	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46 62.83 63.14 63.47 63.80 64.14 64.39 64.72 65.03 66.97	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 11.85 7.84 9.21 11.88 5.82 7.61 7.04 6.44 8.35	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84 0.77 1.00 1.34
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87 9.63 40.08	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35 8.2 8.17	nd 2000b - Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241 41272 41006	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308 291	Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8 54.5 22.2	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044 3976 2846	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.44 1.4 1.39 1.72 1.72	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 99 67 69 70 74 72			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 110.27 111.55 112.51	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75 -0.20 -0.20 -0.21	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46 62.83 63.14 63.47 63.80 64.14 64.39 64.72 65.03 66.97 67.23	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 5.82 7.61 7.04 6.44 8.35 11.19 10.61	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20 1.23 1.23	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84 0.77 1.00 1.34 1.27
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87 9.63 40.08 41.03	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 6.98 7.54 9.57 10.13 7.52 7.51 7.35 8.2 8.17 7.04	nd 2000b - Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241 41272 41006 39938 41514 2355	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308 291 302 255	Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8 54.5 22.2 25 2	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162 178 174	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044 3976 3846 2195	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.4 1.6 1.78 1.8 1.44 1.4 1.4 1.4 1.4 1.6 1.78 1.44 1.4 1.4 1.4 1.57 1.57 1.31 1.4 1.6 1.75 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.31 1.57 1.57 1.31 1.57 1.57 1.31 1.57 1.57 1.31 1.57	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67 69 70 74 73 82			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 110.27 111.55 112.80	-0.19 0.03 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75 -0.20 -0.17 -0.27	59.53 59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.83 63.14 62.83 63.14 63.80 64.14 64.39 64.72 65.03 66.97 67.23 67.55	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 5.82 7.61 7.04 6.44 8.35 11.19 10.61 11.64	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20 1.23 1.22 0.81	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84 0.77 1.00 1.34 1.27 1.42
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87 9.63 40.08 41.03 41.62	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35 8.2 8.17 7.04 6.54	re (ppm) Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241 41272 41006 39938 41514 33355 22609	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308 291 302 250 220	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8 54.5 22.2 25.3 11 8	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162 178 174 168	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044 3976 3846 3195 2001	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.44 1.39 1.72 1.73 1.69 1.44	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67 69 70 74 73 69 70			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 110.27 111.55 112.80 113.55 114.65	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75 -0.20 -0.17 -0.27 -0.24	59.53 59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46 62.83 63.14 63.47 63.80 64.14 64.39 64.72 65.03 66.97 67.23 67.59	$\begin{array}{c} 3.92\\ 5.62\\ 6.87\\ 8.44\\ 6.02\\ 11.84\\ 11.15\\ 8.41\\ 17.65\\ 7.84\\ 9.21\\ 11.88\\ 5.82\\ 7.61\\ 7.04\\ 6.44\\ 8.35\\ 11.19\\ 10.61\\ 11.64\\ 1$	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20 1.23 1.22 0.81 1.06	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84 0.77 1.00 1.34 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.27 1.27 1.27 1.29 1.27 1.29 1.29 1.21 1.21 1.21 1.21 1.21 1.21 1.22 1.21 1.21 1.22 1.22 1.21 1.21 1.22 1.22 1.21 1.21 1.21 1.21 1.22 1.21 1.21 1.27 1.20 1.20 1.27 1.20
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87 9.63 40.08 41.03 41.62 42.6	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35 8.2 8.17 7.04 6.54	re (ppm) Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241 41272 41006 39938 41514 33355 32598 22594	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308 291 302 250 220 220	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8 54.5 22.2 25.3 11.8	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162 178 174 168 169	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044 3976 3846 3195 3045	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.4 1.4 1.4 1.39 1.72 1.73 1.69 1.41 1.41 1.42 1.41 1.44 1.44 1.39	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67 69 70 70 74 73 62 58			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 110.27 111.55 112.80 113.55 114.50	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75 -0.20 -0.17 -0.27 -0.91 1.04	59.53 59.53 59.87 60.19 60.50 60.84 61.14 61.51 62.14 62.46 62.83 63.14 63.47 63.80 64.14 64.39 64.72 65.03 66.97 67.23 67.59 67.92 67.92 67.92	$\begin{array}{c} 11.40\\ 11.40\\ 3.92\\ 5.62\\ 6.87\\ 8.44\\ 6.02\\ 11.84\\ 11.15\\ 8.41\\ 17.65\\ 7.84\\ 9.21\\ 11.88\\ 5.82\\ 7.61\\ 7.04\\ 6.44\\ 8.35\\ 11.19\\ 10.61\\ 11.64\\ 16.11\\ 12.72\end{array}$	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20 1.23 1.22 0.81 1.06 1.06	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84 0.77 1.00 1.34 1.27 1.40 1.93 2.72
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87 9.63 40.08 41.03 41.62 42.6 43.13	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35 8.2 8.17 7.04 6.54 6.54 6.55	re (ppm) Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241 41272 41006 39938 41514 33355 32598 33504 26422 30942 3094 3094 3095 3094 3095 3095 3095 3095 3095 3005 4005 3005 3005 3005 4005 3005 3005 4005 3005 3005 3005 4005 3005 4005 3005 4005 4005 4005 3005 4005 3005 4005 3005 4005 3005 4005 4005 3005 4005 3005 4005 3005 4005	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308 291 302 250 220 267	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8 54.5 22.2 25.3 11.8 22 25.3 11.8 22 25.3	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162 178 174 168 169 182	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044 3976 3846 3195 3001 3155	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.44 1.4 1.39 1.72 1.73 1.69 1.41 1.49 1.49 1.41	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67 69 90 99 67 70 74 73 62 58 62 58 61			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 110.27 111.55 112.80 113.55 114.50 115.99	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75 -0.20 -0.17 -0.27 -0.91 -1.04	59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.46 62.83 63.14 63.47 63.80 64.14 64.39 64.72 65.03 66.97 67.23 67.59 67.92 68.25	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 5.82 7.61 7.04 6.44 8.35 11.19 10.61 11.64 16.11 22.78	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20 1.23 1.22 0.81 1.06 1.84 2.22	$\begin{array}{c} 1.42\\ 1.37\\ 0.47\\ 0.67\\ 0.82\\ 1.01\\ 0.72\\ 1.42\\ 1.34\\ 1.01\\ 2.12\\ 0.94\\ 1.11\\ 1.43\\ 0.70\\ 0.91\\ 0.84\\ 0.77\\ 1.00\\ 1.34\\ 1.27\\ 1.40\\ 1.93\\ 2.73\\ 2.73\end{array}$
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.27 6.66 7.06 7.57 8.13 8.87 9.63 40.08 41.03 41.02 42.6 43.13 44.1	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35 8.2 8.17 7.04 6.54 6.85 6.5	re (ppm) 27327 27234 27795 30409 31872 24817 224817 22522 36226 35305 46299 50747 33241 41272 41006 39938 41514 33355 32598 33504 30481	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 443 324 308 291 302 250 220 267 243	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8 54.5 22.2 25.3 11.8 22 79.9	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162 178 174 168 169 182 201	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044 3976 3846 3195 3001 3155 2904	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.44 1.4 1.39 1.72 1.73 1.69 1.41 1.49 1.48	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 67 69 70 70 74 73 62 58 61 57			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 110.27 111.55 112.80 113.55 114.50 115.99 117.12	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75 -0.20 -0.17 -0.27 -0.91 -1.04 -1.46	59.53 59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46 62.83 63.14 63.47 63.80 64.14 64.39 64.72 65.03 66.97 67.23 67.23 67.29 67.25 68.54 62.55 68.54	11.40 3.92 5.62 6.87 8.44 6.02 11.84 11.15 8.41 17.65 7.84 9.21 11.88 5.82 7.61 7.04 6.44 8.35 11.19 10.61 11.64 16.11 22.78 23.37	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20 1.23 1.22 0.81 1.06 1.84 2.03	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84 0.77 1.00 1.34 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.00 1.34 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.27 1.40 1.53 2.73 2.80
Yarincik et a Depth 0.47 1.05 1.96 2.55 3.46 4.05 4.96 5.76 6.62 7.66 6.27 6.66 7.06 7.57 8.13 8.87 9.63 40.08 41.03 41.62 42.6 43.13 44.1	Al (wt%) 5.52 5.59 5.73 6.34 6.43 5.04 4.57 5.24 6.98 7.54 9.57 10.13 7.32 7.51 7.35 8.2 8.17 7.04 6.54 6.55 6.5 7.64	nd 2000b - Fe (ppm) 27327 27234 27795 30409 31872 24817 22745 26522 36226 35305 46299 50747 33241 41272 41006 39938 41514 33938 41514 3355 32598 33504 30481 36804	Cariaco Ba Mn ppm 159 158 208 216 167 135 139 195 369 464 288 462 462 443 324 308 291 302 250 250 250 250 220 267 243 241	Asin Mo ppm 79.4 80.7 38.7 47.1 80.7 122.0 55.4 96.1 108.8 1.8 2.5 2.6 4.3 6.7 6.8 54.5 22.2 25.3 11.8 22 53.3 11.8 22 79.9 68	V ppm 195 205 169 168 172 150 102 165 194 117 204 217 147 185 162 178 174 168 169 182 201 189	Ti ppm 2472 2503 2609 2837 2991 2525 2326 2474 3220 3607 5103 5798 3636 3828 4044 3976 3846 3195 3001 3155 2904 3489	K wt % 1.37 1.26 1.25 1.39 1.57 1.31 1.2 1.31 1.4 1.6 1.78 1.8 1.44 1.4 1.39 1.72 1.73 1.69 1.41 1.49 1.48 1.60	Terrigeno us wt% 48 49 50 55 57 46 42 47 62 68 90 99 99 67 69 70 74 73 62 58 61 57 67			88.33 89.66 91.00 92.24 93.59 94.82 96.17 97.58 99.12 100.57 101.95 103.27 104.08 105.10 106.41 107.68 108.95 110.27 111.55 112.80 113.55 114.50 115.99 117.12 118.43	-0.19 0.03 -0.83 -0.83 -0.37 -1.48 -1.16 0.03 0.38 -0.22 1.03 0.81 0.52 0.73 0.53 -0.02 -0.04 -0.75 -0.20 -0.17 -0.27 -0.21 -1.04 -1.21 -1.21	59.53 59.53 59.87 60.19 60.50 60.84 61.14 61.51 61.81 62.14 62.46 62.83 63.14 63.47 63.80 64.14 64.39 64.72 65.03 66.97 67.23 67.59 67.29 68.25 68.54 68.88	$\begin{array}{c} 11.60\\ 11.40\\ 3.92\\ 5.62\\ 6.87\\ 8.44\\ 6.02\\ 11.84\\ 11.15\\ 8.41\\ 17.65\\ 7.84\\ 9.21\\ 11.88\\ 5.82\\ 7.61\\ 7.04\\ 6.44\\ 8.35\\ 11.19\\ 10.61\\ 11.64\\ 16.11\\ 22.78\\ 23.37\\ 21.60\end{array}$	1.33 1.09 1.08 0.59 0.73 1.33 1.74 1.29 1.36 1.31 1.04 1.33 1.70 1.54 1.87 0.86 0.60 1.20 1.23 1.22 0.81 1.06 1.84 2.03 2.58	1.42 1.37 0.47 0.67 0.82 1.01 0.72 1.42 1.34 1.01 2.12 0.94 1.11 1.43 0.70 0.91 0.84 0.77 1.00 1.34 1.27 1.40 1.393 2.73 2.80 2.59

46.15	7.15	32019	194	20.4	132	3716	1.62	67	121.06	-0.36	69.58	30.06	2.63	3.61
46.55	6.77	31869	217	27.9	134	3589	1.45	64	122.70	0.79	69.84	34.67	2.25	4.16
47.23	7.34	46091	373	4.8	177	3616	1.49	67	123.53	0.85	70.19	31.83	2.19	3.82
47.79	7.4	37462	755	2.3	160	3693	1.48	68	124.84	0.85	70.53	35.34	2.01	4.24
48.73	10.25	59375	551	9.9	196	5191	1.97	95	126.14	0.37	70.88	39.46	1.01	4.74
49.18	7.38	35054	849	2.1	160	3633	1.50	67	127.50	0.47	71.17	26.32	0.92	3.16
50.23	7.89	41152	898	4.1	168	3930	1.54	72	128.87	0.41	71.51	19.09	0.63	2.29
50.79	7.58	34631	615	1.4	167	3844	1.49	70	133.12	-0.06	71.86	23.59	0.60	2.83
51 72	7.81	36975	508	0.6	157	4031	1.52	73	134 45	-0.58	72 21	25.52	0.69	3.06
52.28	8 35	42480	717	5.0	185	4332	1.52	78	135 72	-1 17	72.47	9.92	0.58	1 19
53 27	7.82	34213	711	2.2	171	3901	1.58	72	137.02	-0.70	72.82	12.05	0.95	1.10
53.84	7 74	34970	440	17	161	4235	1.50	74	138 35	-0.40	73.16	18.84	2.08	2.26
5/ 82	8 36	56679	404	62.8	176	4200	1.61	82	130.55	-0.70	73.40	37.64	2.00	4.52
55 38	8.80	18907	373	50.5	189	4579	1.00	83	1/0 79	-0.70	73 77	26 35	0.30	3 16
56 31	8.58	40307	352	21.7	171	4379	1.74	83	140.75	-0.40	74.10	20.33	1 45	2 77
56.25	0.00	40744	460	56.0	171	4700	1.71	77	141.73	-0.57	74.10	23.07	1.40	2.11
56.52	0.2	43003	409	50.9	139	4304	1.04	00	142.24	-0.15	74.42	27.90	2.27	2.55
50.55	9.31	49002	442	42	175	4974	1.07	00	143.02	-0.72	75.39	20.74	3.27	3.43
57.13	9.2	40301	374	20.0	159	3114	1.04	09	145.10	-0.27	75.72	29.75	1.91	3.57
58.0Z	8.64	47340	433	38.9	100	4575	1.75	81	146.50	-0.10	75.94	28.33	1.92	3.40
58.63	8.33	45659	444	27.1	105	4587	1.72	80	147.81	-0.95	76.23	27.00	1.49	3.32
59.58	9.26	38558	432	1.6	168	4710	1.86	86	149.17	-0.55	76.57	28.97	1.90	3.48
60.31	8.69	48248	495	38.6	181	4590	1.71	82	150.45	-0.52	76.90	34.55	1.54	4.15
61.12	9.4	56911	346	18.7	195	5020	1.90	89	151.59	-0.01	77.23	31.45	1.72	3.77
61.7	9.55	35495	300	2.3	163	4940	1.89	89	153.07	-0.31	77.57	26.04	2.71	3.12
62.59	8.83	48032	379	27.5	183	4609	1.80	83	154.54	-1.18	77.90	20.45	2.83	2.45
63.14	7.95	42091	498	8.6	146	4064	1.65	74	156.03	-0.02	78.23	21.42	2.28	2.57
64.25	8.84	54481	382	21.2	191	4513	1.70	82	157.49	-0.92	78.56	23.61	1.89	2.83
64.84	8.51	47659	470	59.4	173	4202	1.67	78	158.90	-0.83	78.93	19.39	2.36	2.33
65.64	9.36	45315	344	66.8	174	4552	1.89	85	159.83	-0.82	79.30	21.78	2.64	2.61
66.15	9.84	46939	593	2.6	168	4729	2.00	89	161.10	-0.63	79.63	15.28	1.77	1.83
66.78	9.76	47844	571	1.9	161	4885	2.06	90	162.54	-0.96	79.73	18.26	1.80	2.19
65.58	9.32	44386	477	19.8	188	4154	1.87	81	163.97	-1.47	80.07	18.36	2.25	2.20
66.12	8.13	42020	395	37.7	192	3779	1.72	72	165.87	-0.99	80.31	21.01	2.59	2.52
67.28	8.73	43803	375	27.9	165	4087	1.77	78	167.26	-1.08	82.11	32.17	1.04	3.86
67.62	9.13	43886	387	21.8	155	4221	1.85	81			82.58	45.00	0.71	5.40
68.76	7.36	41682	383	26.4	180	3622	1.42	67			82.85	30.73	0.70	3.69
69.12	8.69	47824	404	43.1	185	4214	1.71	79			83.28	19.74	0.75	2.37
70.27	6.88	38000	255	45.8	184	3226	1.45	61			83.61	19.40	0.79	2.33
70.62	6.68	34537	294	34.2	180	3087	1.43	59			84.02	16.55	0.57	1.99
71.77	6.25	32470	278	6.3	130	2858	1.23	55			84.32	16.63	0.46	2.00
72.15	6.29	34464	287	6.8	137	3046	1.36	57			84.60	19.05	1.20	2.29
73.21	7.32	37757	405	7.1	145	3922	1.49	69			84.95	45.36	1.81	5.44
73.65	8.47	42577	437	6.5	171	4522	1.78	80			85.93	33.24	2.11	3.99
74.13	7.06	37783	274	46.6	193	3388	1.45	64			86.29	34.03	2.32	4.08
74.8	6.91	40372	283	71.9	172	3475	1.38	64			86.44	27.06	2.48	3.25
75.12	6.81	34678	273	53.2	153	3062	1.45	60			86.78	27.59	2.18	3.31
75.15	7.35	36563	288	3.7	157	3540	1.47	66			87.16	25.03	2.39	3.00
75.56	6.69	34270	249	67.8	201	3061	1.35	59			87.47	26.83	2.34	3.22
76.53	6.01	28355	191	33.6	154	2946	1.07	55			87.81	35.25	2.17	4.23
77	6.76	32096	212	34.7	162	3228	1.40	61			88.13	24.02	0.90	2.88
77.97	6.12	28866	184	31.1	93	3038	1.39	56			88.49	36.77	0.95	4.41
78.62	6.34	32932	326	44.8	148	3267	1.36	59			88.85	24.71	1.66	2.97
79.54	7.72	41275	296	23.6	188	4052	1.50	72			89.06	29.92	1.39	3.59
80.21	7.23	40177	298	37	179	3943	1.52	69			89.40	24.68	0.56	2.96

80.89	6.67	38076	274	80.3	168	3540	1.29	63	89.65	21.83	0.91	2.62
81.11	7.48	41679	342	35.8	178	3976	1.48	71	90.01	23.02	1.78	2.76
81.76	7.95	43945	293	47.4	188	4352	1.61	76	90.46	25.65	1.17	3.08
81.84	6.85	34625	421	4.9	134	3482	1.47	63	90.75	30.59	2.14	3.67
82.43	6.12	32434	302	2.3	117	2983	1.23	55	91.10	36.08	1.95	4.33
83.09	5.91	31195	386	0.7	105	2929	1.28	54	91.45	29.72	0.72	3.57
83.94	7.87	41529	418	6.1	173	4078	1.56	73	91.78	26.92	1.61	3.23
84.72	8.65	35362	332	2.3	170	4464	1.69	80	92.12	26.19	1.76	3.14
85.44	6.58	35653	441	41.5	138	3209	1.37	60	92.38	30.62	1.57	3.67
85.45	7.45	40895	318	37.1	169	3689	1.48	68	92.73	33.15	2.17	3.98
86.23	4.57	25592	348	54.9	113	2184	1.08	41	93.01	31.78	1.75	3.81
86.89	7.15	38220	304	36.5	167	3455	1.38	65	93.42	27.39	2.14	3.29
87.7	6.63	39681	341	54.9	167	3153	1.28	59	94.88	32.96	2.48	3.96
88.49	6.39	32590	306	30.1	148	2939	1.29	56	95.21	31.56	3.12	3.79
89.25	7.92	36372	313	10	153	3795	1.50	71	95.53	26.82	4.52	3.22
89.99	6.86	36098	283	14	136	3309	1.40	62	95.90	22.56	2.73	2.71
90.8	7.38	41799	308	42.7	170	3636	1.44	67	96.24	21.54	2.61	2.58
91 57	673	36851	257	28.7	169	3194	1 29	60	96.62	23.32	1 92	2.80
92.66	7 24	37074	385	4.5	169	3509	1.20	65	97.01	32.85	1.02	3.94
93.09	7.65	41620	274	15.9	195	3599	1.10	65	97.39	26.96	1.60	3 24
93.95	6.72	35610	307	30.3	170	2947	1.33	58	97.00	30.02	1.02	3.60
94.65	6.93	33531	376	15.7	151	3118	1.30	61	98 14	43.67	1.00	5 24
04.00 04.33	7 89	40230	421	41.6	203	3391	1.62	68	98.45	3.68	0.33	0.24
95.00	6.2	30025	318	47.7	184	2832	1.00	55	98 79	9.11	0.00	1.09
96.08	6.27	28630	18/	65.7	130	2890	1.33	55	90.15	1 02	0.70	0.23
96.88	5.54	27/30	184	65.2	133	3009	1.34	53	99.10	5.47	1.00	0.25
90.00	4.06	21352	137	/3.1	90	2108	0.00	30	00 0/	2 47	0.81	0.00
97.27	4.00	22040	156	31.5	103	2467	1 15	43	100.27	2.47	0.01	0.00
08 31	4.04	22340	107	64	81	2407	0.07	40	100.27	2.10	0.10	0.20
00.12	4.09	23440	224	0.4	107	5473	1 00	95	100.03	1.52	0.42	0.10
00.97	9.0 8.70	44473	224	1.4	197	1815	1.55	90	101.00	31.42	1.67	3 77
100.86	0.79	43070	230	24	210	5451	1.71	04	101.44	22.45	1.07	2.60
100.00	9.90	43431	273	2.4	200	5310	1.07	90	101.77	17 / 8	1.30	2.09
101.43	9.90	42320	422	20.0	203	4225	1.70	34 76	102.22	21.40	1.70	2.10
102.72	0.19	40124	423	20.3	201	4220	1.55	70	102.49	17 94	1.74	2.00
103.20	7.4	41030	370	30.3	103	3004	1.50	09 70	102.04	17.04	2.20	2.14
103.30	1.31	43070	447	44.7	202	4222	1.59	79	102.97	12.22	2.05	1.47
103.03	0.74	40003	334	23.7	203	3901	1.41	71	104.12	10.39	0.60	2.21
104.52	0.04	3/000	-999	1.0	104	4114	1.50	74	104.42	17.00	0.00	2.14
105	7.91 0 EE	41297	600	1.9	102	3939	1.00	72	104.55	20.20	1.21	2.07
105.70	0.00	42394	699	1.0	103	4400	1.70	00	104.02	20.20	1.07	2.42
100.04	0.02	44090	527	3.9	191	4402	1.72	01	105.44	14.23	1.15	1./1
107.41	8.09	40004	591	21.1	183	4031	1.55	74	105.87	15.59	1.42	1.87
100.09	9.19	42221	393	0.C	203	4/42	1.00	00	100.21	13.93	1.25	1.67
108.80	0.21	55990	380	17.4	183	4179	1.54	76	106.55	13.23	0.98	1.59
109.5	8.24	51455	441	32.7	183	4218	1.01	76	106.89	10.70	0.89	1.28
110.44	8.63	44529	330	7.1	192	4320	1.64	79	107.06	11.15	0.90	1.34
111	7.89	45524	324	74.4	184	4145	1.55	74	107.40	13.31	0.57	1.60
111.98	7.81	39729	298	15.3	165	3668	1.54	70	107.75	11.04	0.82	1.32
112.78	8.09	43313	364	21.9	1/5	3/45	1.57	72	108.07	11.47	1.22	1.38
113.41	8.18	43852	362	24.6	183	3937	1.60	/4 70	108.34	13.07	1.06	1.5/
113.92	8.16	43566	379	25.3	183	3907	1.55	73	108.64	14.27	1.19	1./1
113.4	8.69	40559	339	10.5	160	4234	1.76	79	108.98	13.43	1.14	1.61
113.79	9.02	40475	368	14.5	162	4270	1.85	81	109.32	13.62	1.18	1.63
114.28	7.81	37552	294	39.4	172	3574	1.66	69	109.71	15.69	1.26	1.88
1

115.22	7.05	34799	262	61.8	189	3202	1.43	62
115.67	6.57	36206	242	127.2	179	2993	1.28	58
116.72	6.07	32717	229	65.4	190	2669	1.22	53
117.29	6.29	32065	207	76.8	191	2818	1.28	55
118.22	5.59	29116	183	84.2	186	2380	1.19	48
118.87	6.05	29792	192	91.6	191	2765	1.37	53
119.72	6.48	32741	223	44.7	178	2936	1.38	57
120.3	6.22	32879	191	95.3	191	2929	1.32	56
121.25	7.66	41851	257	96.9	196	3800	1.52	70
121.66	6.72	30233	243	59.3	180	3036	1.38	59
122.73	8.41	41369	243	22.9	186	4181	1.62	77
122.63	8.21	48956	423	64.8	229	4311	1.60	77
123.35	7.91	43525	384	54.7	197	3918	1.55	72
124.26	8.53	48311	386	51.1	223	4185	1.63	78
124.85	8.45	46486	393	23.3	209	4243	1.61	78
125.76	8.22	44531	359	74	226	4157	1.52	76
126.35	7.73	43599	279	55.7	177	3898	1.48	71
127.26	8.82	46721	319	20	189	4576	1.54	82
127.92	8.84	47422	-999	4.4	204	4529	1.65	82
128.83	8.86	54421	685	9.3	199	4540	1.59	82
129.51	8.82	49583	312	9.9	218	4410	1.63	81

10.04	19.60	1.50	2.35
10.38	16.03	1.34	1.92
10.64	21.91	1.74	2.63
10.94	14.45	0.90	1.73
11 25	17 90	1.30	2 15
11.20	18.45	1.00	2.10
13.22	13.46	0.95	1.64
13.22	12.00	0.95	1.04
13.35	21.81	2.00	2.62
10.00	21.01	2.00	2.02
14.10	20.10	2.10	2.14
14.04	20.92	2.22	2.11
15.11	20.05	2.50	3.13
15.22	31.32	3.12	3.70
15.57	36.62	2.83	4.39
16.04	29.00	3.18	3.48
16.29	30.11	3.16	3.61
16.63	31.92	3.42	3.83
16.98	35.36	2.96	4.24
17.33	35.47	3.32	4.26
17.68	35.54	3.60	4.26
18.01	36.58	3.46	4.39
18.49	34.85	3.48	4.18
18.73	30.35	3.07	3.64
19.06	35.95	3.64	4.31
19.41	30.47	4.14	3.66
19.80	22.71	3.58	2.73
20.11	26.33	3.07	3.16
20.46	26.78	4.59	3.21
20.71	24.31	2.52	2.92
21.11	30.54	1.78	3.66
22.47	19.11	1.38	2.29
22.71	10.84	1.79	1.30
23.05	12.95	1.66	1.55
23.40	14.77	1.55	1.77
24.03	10.72	1.16	1.29
24.38	18.41	1.32	2.21
24.88	13.36	1.42	1.60
25.17	10.13	1.68	1.22
25.53	10.60	1.64	1.27
25.87	42.61	1.40	5.11
26.16	17.72	1.62	2.13
26.49	29.51	1.18	3.54
26.89	9.85	1.00	1.18
27.25	10.13	0.76	1.22
27.55	10.28	0.82	1.23
27.85	11.35	0.92	1.36
28.34	14.63	0.86	1.76
28.68	13.61	1.54	1.63
28.92	6.72	1.00	0.81
29.21	8.62	1.75	1.03

Oxburgh et	al. (2007)		DISSOLVE	D METALS IN	CARIACO BA	SIN WATER	COLUMN (Jac	obs et al. 198	7)
Depth	¹⁸⁷ Os/ ¹⁸⁸ Os		Depth						
(mbsf)	(‰)	Os (pg/g)	(mbsl)	Mn nmol L-1	Fe nmol L-1	Co nmol L-1	Ni nmol L-1	Cu nmol L-1	Cd pmol L-1
0.3	1.045	8 252	5	30	26	0.11	2.53	1.95	21.5
2.3	1.045	3 254	30	55	212		2.50	1.60	53.0
4.3	1.044	8 165	60	25	72	0.66	2.30	2.70	54.5
6.3	1.0	2 247	90	15	46	0.05	2.60	1.60	27.0
8.3	0.9773	3 139	120	13	60	0.09	2.35	1.50	61.5
10.3	0.9823	3 126	150	13	26	0.05	2.50	1.40	77.0
12.3	0.980	6 133	180	13	46	0.30	3.10	1.30	129.0
14.3	0.988	1 124	210	12	64	0.06	2.40	1.40	
16.3	0.990	6 127	240	18	34	0.11	2.40	1.00	117.0
18.3	1.012	7 149	240	28	64	0.05	2.80	0.80	101.0
20.3	0.983	2 108	250	13	32	0.05	2.30	0.90	111.0
22.3	0.942	5 99	260	23	88	0.05	3.10	1.30	109.0
24.3	0.954	6 119	270	25	32	0.08	2.70	0.80	113.0
26.3	0.951	9 117	280	49	28			1.20	91.0
28.3	0.914	7 93	280	21	36	0.06	2.70	0.80	96.0
30.3	0.968	9 141	290	33	36		2.80	1.10	96.0
32.4	1.032	6 103	300	74	46	0.08	2.45	0.85	49.5
36.5	1.032	6 90	310	364	116	0.37	2.60	0.75	27.0
38.3	1.045	7 141	320	384	108	0.42		0.35	27.0
40.3	1.047	2 142	340	400	228	0.35			27.0
42.3	1.054	6 178	370	408	230	0.41	2.30	0.24	17.0
44.3	1.060	B 190	390	415	312	0.40			7.0
46.3	1.047	1 94	410	425	320		2.60	0.25	10.0
47.1	0.965	4 139	430	420	280	0.35	2.60	0.49	5.0
50.3	0.984	2 165	450	435	254		2.40	0.20	
51.1	0.982	3 106	470	440	264		2.50	0.29	4.0
53.1	0.989	1 167	490	435	286	0.28	3.25	0.78	13.0
56.3	1.004	5 95	530	420	240		3.00	0.41	9.0
57.6	1.047	2 90	560	410	256		2.80	0.44	7.0
59.7	1.018	4 122	620	400	200	0.27	3.00	0.33	18.0
60.7	0.96	5 118	690	390	192		2.90	0.68	11.0
61.8	0.968	8 89	800	385	176	0.13	2.50	0.52	4.5
62.8	1.018	6 120	855	375	132		2.50	0.27	5.0
63.8	1.020	8 142	910	375	134	0.15	2.50	0.46	4.5
64.9	1.031	3 108	965	375	116		2.90	0.41	9.0
2.10			1065	365	120	0.21	2.80	0.47	7.5
			1120	360	164	0.21	2.50	0.45	7.0
			1175	370	104	0.11	2.40	0.37	4.0

1230

365

116

bs et al. 1987)

0.79

2.60

21.5 53.0

54.5

27.0 61.5

77.0

129.0

117.0

101.0

111.0 109.0

113.0

91.0

96.0 96.0

49.5 27.0

27.0 27.0

17.0 7.0 10.0

5.0

4.0

9.0 7.0

18.0

11.0

4.5 5.0

4.5

9.0

7.5

7.0

4.0

16.0

13.0

Appendix 5

Published Abstract

Shore A., 2008. Selenium isotopes: a new oceanic paleoredox proxy?. *Geochimica et Cosmochimica Acta*, **72**, 12S, A863.

Selenium isotopes: a new oceanic paleoredox proxy?

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Previous work on selenium has tended to focus on understanding the biogeochemical cycle of selenium, driven by the need to understand and manage its environmental behaviour due to its toxicity in moderate concentrations. Due to their redox-sensitive nature, and the tendency for massdependent fractionation to be induced by redox reactions, some authors have begun investigating whether the isotopes of elements such as Mo, Fe and Se can be used in palaeoredox studies (e.g. Mo [1]).

A record of sedimentary selenium isotope ratios (^{82/76}Se), spanning the last 500 ka, has been produced. We propose differences in the cycling of Se due to variations in water column oxygen content will affect seawater selenium isotope ratios and sediment components deposited from the seawater. Sediments deposited under an anoxic water column are dominated by organically - bound Se which has little fractionation with the water. In contrast, samples deposited under an oxic water column of authigenic Se which should be enriched in light isotopes relative to the water.

Oxygenation of the oceans is difficult to constrain. Determination of past ocean oxygenation provides important constraints on atmospheric O_2 and the overall "health" of the oceans, information crucial for understanding the development of life.

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