Palaeoceanography of the mid-latitude North East

Pacific

during the late Pleistocene

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We accept this thesis as conforming to the required standard

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Abstract

Past climatic and oceanographic changes in the California Current region off western North America were investigated with the overall goal of contributing to a better understanding of natural ocean variability in the Pacific Ocean on glacial–interglacial and millennial-time scales. This was carried out by constructing downcore sedimentary records of past primary production (C_{org} , biogenic opal, Ba/Al ratio), the concentrations of redox sensitive metals (Mn, Re, Ag, Cd, Mo, U) and the stable isotopic composition of nitrogen ($^{14}N/^{15}N$) in two sediment cores from the continental margin off Oregon (at 2730 and 3111 m water depth). These data were then compared with previously published core records to build a synoptic picture of surface, subsurface and deep water conditions in the NE Pacific over the last 120 kyrs.

Isotopically enriched nitrate currently produced by denitrification in the Eastern Tropical North Pacific (ETNP) is exported northward along the continental margin via the California Undercurrent (CUC). Thus, the nitrogen isotopic composition (δ^{15} N) of subsurface nitrate is higher than the global deep water average (~4.5-5 ‰) and it decreases progressively from Mexico (18 ‰) to Vancouver Island (6 ‰) along the entire margin. Off Oregon, the similarity between the isotopic composition of subsurface (150 –600 m) nitrate (7.1 ‰), annual sediment trap material (7.0-7.4 ‰ on average) and surface sediments (6.5–8‰) implies that biological nitrate uptake is complete on an annual basis and that the surface sediments record the isotopic composition of subsurface nitrate without significant diagenetic bias. Together with similar findings from other sites along the margin, these results imply that the sedimentary δ^{15} N signal can be used as a tracer for the advection of isotopically enriched nitrate from the ETNP along the entire NW American margin from at least 20° to 45°N. Downcore δ^{15} N results off Oregon reveal a glacial-interglacial pattern that is remarkably similar in timing and amplitude to other records from the NW American margin. High values (7-10‰) during the Holocene, Stage 5 and some periods of Stage 3 at the Oregon sites are interpreted to reflect relatively strong denitrification in the ETNP and a strong CUC. High sedimentary concentrations of palaeoproduction indicators imply that coastal upwelling and northerly winds off Oregon were active at the same time. This is in marked contrast to lower δ^{15} N values (4-6 ‰) and reduced concentrations of palaeoproduction tracers during cold Stages 2 and 4. While palaeoproduction proxies and δ^{15} N vary approximately in phase in core records originating from outside the modern denitrification zone, δ^{15} N clearly leads palaeoproduction proxies in cores from within the ETNP after the last glacial maximum (LGM) and at the Stage 4/3 and 6/5 boundaries by several kyrs. This lead strongly implies that primary production in the ETNP cannot be the sole control on denitrification in this region.

Circulation changes in the equatorial Pacific are offered as an alternative explanation. Stronger trade winds during cold periods of the climate system (such as the LGM, Heinrich events and Dansgaard-Oeschger stadials) would force a stronger equatorial undercurrent (EUC) and increase oxygen advection into the ETNP, thereby reducing denitrification rates. During warm periods, oxygen advection by the EUC is low, denitrification rates in the ETNP are high and the CUC transports isotopically heavy nitrate towards the north, thereby synchronizing the sedimentary δ^{15} N signal along the continental margin of NW America. The proposed mechanism provides an atmospheric link between denitrification intensity in the eastern Pacific, horizontal

advection of isotopically heavy nitrate into the mid latitude N-Pacific and northern hemisphere climate change.

Furthermore, using sedimentary $\delta^{15}N$ as a quasi synchronous tracer along the margin, a latitudinal gradient in the onset of primary production (as recorded by %organic carbon in the same core records) after the LGM is evident. Thus, primary production and, by inference, upwelling favourable, northerly winds appear to have developed in a time transgressive fashion with those in the north (~40°N) starting several kyrs before those in the south (~20°N).

At 2730 m water depth off Oregon, the downcore authigenic enrichments of Re (up 60 times relative to crust), Ag and Cd (2-7 x) together with the absence of solid phase Mn imply that suboxic sediment conditions were maintained at shallow depth throughout the last 70 kyrs at this site. Similar to intermediate water depths, suboxic conditions at this deep site were most intense (i.e. the redox boundary was at its shallowest position) during the Holocene, a period possibly correlative with the Bølling-Allerød, and Stage 3 when organic matter flux was high. Although Mo and U in the same core are not significantly enriched over crustal reference values, their concentrations nevertheless correlate positively with production proxies, which possibly implies small amounts of authigenic Mo and U formation. No correlation was found between variations in the sedimentary concentrations of redox sensitive metals and the carbon isotopic composition (δ^{13} C) of the benthic foraminifera C. wuellerstorfi, which was previously interpreted to reflect short-term changes in deep water ventilation [*Mix et al., 1999; Lund and Mix 1998*]. While this does not contradict the δ^{13} C evidence that such ventilation changes might have occurred, it implies that they have not had an overriding control on the redox conditions of the sediment at this site.

Overall, the California Current region was vastly different from today under glacial climate conditions. Surface primary production and carbon export to the sediment were significantly reduced, as was the lateral advection of isotopically heavy nitrate from the ETNP by the California Undercurrent.

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Preface

Chapter 2 of this thesis is largely based on material published previously in *Kienast et al.* [2002]. The major part of the analytical work was carried out by myself with support from the technical staff at UBC. Biogenic opal flux data from the sediment trap time series and unpublished nitrogen isotope data (ODP core 1017) were kindly provided by Drs. Robert Collier (Oregon State University) and Thomas F. Pedersen (UBC), respectively. The interpretation of the data and the writing of the paper was entirely my work, my co- authors Drs. Stephen E. Calvert and Thomas F. Pedersen contributing editorial assistance and carefully reviewing the draft manuscript.

Appendix I includes a verbatim copy of a publication by *Kienast and McKay* [2001] as well as an addendum that compares this work with results that have been published subsequently. The determinations of alkenone abundances was based on my own expertise, and was carried out jointly with another doctorate student at UBC (Jennifer McKay), who also provided all AMS radiocarbon dates used in this work. Jennifer McKay contributed to the interpretation of the data, I wrote the manuscript, and Drs. Thomas F. Pedersen and Stephen E. Calvert carefully reviewed it.

Kienast, S.S., and J.L. McKay, Sea Surface Temperatures in the subarctic Northeast Pacific reflect millennial-scale Climate Oscillations during the last 16 kyrs, *Geophys. Res. Lett.*, 28 (8), 1563, 2001.

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Chapter 1: Introduction

1.1 Preamble

The ocean, covering 71% of the Earth's surface, affects the climate of the Earth in several ways. Most solar radiation received at the Earth's surface is absorbed by the ocean and warms the surface waters. As a result of its high heat capacity and its circulation, the ocean both stores and redistributes a large fraction of this heat before it is released back to the atmosphere. In addition, some of the heat indirectly affects the planetary albedo by changing the extent of sea ice cover. Besides playing a major role in the planetary energy cycle, biogeochemical cycles in the sea affect the storage and exchange of gases with the atmosphere and thereby influence its greenhouse gas content. The ocean consequently plays a major role in Earth's climate and climate variability.

Palaeoceanography, the study of the oceans and ocean climate in the past, is a relatively young field because the systematic collection of sediment cores from the sea floor only began in the 1950s, long after the initiation of modern oceanography with the CHALLENGER expedition (1872-1876). It is a highly interdisciplinary research endeavour, employing a large variety of methods originating in geology, physics, chemistry and biology to determine sets of sedimentary parameters that have known relationships to actual environmental parameters in the ocean. For example, the unsaturation patterns of membrane lipids (alkenones) in some algae change in a linear fashion with the growth temperature of the organism. Preserved in sediments, these molecular fossils provide a highly accurate tool for reconstructing past temperatures in the euphotic zone. The degree of nitrate utilization in the euphotic zone, on the other hand, can be reconstructed using the ratios of two stable isotopes of nitrogen in sedimentary organic matter, which are fractionated differently during photosynthesis.

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Other sediment parameters, referred to as proxy variables or "proxies", are used to estimate global sea level, export production, surface water pCO_2 , pH, sediment redox conditions, and the oxygen and nutrient contents of the deep waters. Using such proxies, palaeoceanographic studies can provide unique information on the physical and biogeochemical boundary conditions of past oceans and atmospheres. In light of the current debate on global warming, whether natural or manmade, a better understanding of the geographical extent, rate and frequency of natural climate change and its connection to changes in atmospheric greenhouses gases is urgently needed.

Palaeoceanographic results, in combination with ice core records, have been instrumental in establishing what we know about past climate change, especially that related to ice ages, which were the rule rather than the exception during the last two million years (the Quaternary). Orbitally driven variations in the amount and distribution of solar radiation are considered to be the ultimate pacemaker of the ice ages, but the mechanisms and feedbacks on the Earth that amplify the subtle insolation changes and lead to the buildup of up to 50×10^6 km³ of ice in the high latitudes are not well understood. And while a full explanation for the ice ages, which occurred with a frequency of roughly 100 kyrs, is still lacking, the last 15 years of research have shown that changes almost as dramatic as the ice ages have also occurred on a frequency of only 1500 years.

The last ice age, which ended approximately 20 kyrs ago, is relatively well recorded in marine and terrestrial geological sequences. Intensive palaeoceanographic research on the last glacial maximum (LGM) since the 1970s culminated in a series of maps prepared by the CLIMAP group in 1981 that depict global ice age conditions (e.g. sea surface temperature, ice cover). Until recently, CLIMAP results provided the main

boundary conditions in the majority of global climate models that have attempted to simulate ice ages and the associated environmental changes. These changes include lowered sea level (-120 m), decreased atmospheric CO₂ concentration (180 ppmv vs 260 ppmv during interglacials) and widespread air and sea surface temperature cooling.

The CLIMAP program was global in its scientific reach, but the database employed in the reconstructions was biased toward coverage in the Atlantic. In the Pacific, vast turbidite sequences and old, CO_2 -rich and thus carbonate-aggressive deep waters made it difficult to obtain continuous core records and to establish $\delta^{18}O$ stratigraphies during those early years of palaeoceanographic research. As a result, only ca. 130 sediment cores were available to CLIMAP in the Pacific versus ca. 230 in the Atlantic, an imbalance that appears even greater given that the Pacific has approximately twice the volume (700 x 10⁶ km³) and surface area (166 x10⁶ km²) of the Atlantic Ocean. Due to the scarcity of records in the Pacific, palaeoceanographic studies in the North Pacific are sometimes referred to as still "being in their infancy" [Alley and Clark, 1999; Mix et al., 1999]. Since CLIMAP, however, tremendous progress has been made in identifying suitable coring sites above the carbonate compensation depth (CCD) and away from the influence of turbidity currents on sea mounts and along the continental margins of western North America and Asia. This has yielded new albeit incomplete knowledge of the role the Pacific ocean might have played in global climate change (see Chap. 1.3). This thesis seeks to contribute to the growing understanding of Pacific palaeoceanography by presenting new proxy data for surface, subsurface and deep water conditions from a transect of sediment cores from the NE Pacific margin off Oregon. These data will be used to revaluate previously-published interpretations derived from research in this region.

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1.2 Modern Oceanographic conditions in the Pacific

The salinity-driven density contrast between surface and underlying waters is too large to allow deep water formation in the modern North Pacific [Warren, 1983]. Although the Ross Sea in the Pacific sector of the Southern Ocean is an important formation region of Antarctic Bottom Water, this water is prevented from flowing northwards by the combined effects of the Circumpolar Current and the topographic barrier of the Pacific Antarctic Ridge; it thus escapes the Antarctic region through the Drake Passage [Tomczak and Godfrey, 1994]. The abyssal Pacific is therefore only slowly ventilated by water leaving the Circumpolar Current (Circumpolar Deep Water, referred to as Antarctic Bottom Water (AABW) by some authors). This enters the southwest Pacific east of the New Zealand Plateau and Chatman Rise, mostly as a Deep Western Boundary Current [Mantyla and Reid, 1983; Tomczak and Godfrey, 1994; Schmitz, 1995; Talley, 1995]. Ultimately, this abyssal water is thought to be a mixture of Antarctic Bottom Water, North Atlantic Deep Water and Antarctic Intermediate Water [Mantyla, 1975; Broecker et al., 1985; Tomczak and Godfrey, 1994]. Moving gradually to the north, its oxygen content decreases, its nutrient content increases, and it is modified by vertical mixing with less saline water and by geothermal heating [Mantyla, 1975; Mantyla and Reid, 1983]. It is this modification that leads to the formation and upwelling of Pacific Deep Water (PDW) in the North Pacific basin, which then slowly returns southwards at mid-depths (1000 - 4000 m), separated from the northwards flowing bottom water by a stability maximum close to 4000 m water depth. The exact location and intensity of the abyssal upwelling is still an open question [Talley, 1995]. Due to the absence of new deep water formation, the North Pacific hosts the oldest and most CO₂-enriched waters in the world ocean.

Above the slowly moving old PDW, intermediate water masses with higher oxygen content and lower salinity are present in both hemispheres. North Pacific Intermediate Water (NPIW), defined by a prominent salinity minimum (at σ_{Φ} = 26.8 according to Reid [1965]), is present throughout the North Pacific subtropical gyre between 300-800 m [Reid, 1965; Talley, 1993; Talley et al., 1995]. Direct ventilation by sea ice formation in the Okhotsk Sea [Kitani, 1973; Talley, 1991] and vertical diffusion during winter in the Alaskan Gyre [Reid, 1965; Van Scoy et al., 1991; You et al., 2000] maintain the high oxygen content and low salinity at the density range of NPIW. The actual sinking of NPIW seems to take place east of Japan, where cold fresh waters from the Okhotsk Sea transported south by the Oyashio Current are overrun by warmer, more saline, less dense waters from the south [Talley et al., 1995]. NPIW has been observed as far east as the western boundary of the broad California Current region [Talley, 1993]. Antarctic Intermediate Water (AAIW), formed at the Antarctic Convergence, fills the intermediate depth range (700-1300 m) in all southern hemisphere ocean basins. Some AAIW also enters the northern hemisphere [Tsuchiya, 1991; Oudot et al., 1999]. Over the course of the 20th century, AAIW and NPIW have freshened, presumably as a consequence of an intensification of the global hydrological cycle [Wong et al., 1999]. This points to the sensitivity of intermediate waters to reacting to changes in the climate system.

The upper waters off western North America are part of the California Current System (CCS), which represents the eastern boundary current of the clockwise-rotating current gyre in the North Pacific (Fig.1.1). The CCS, as traditionally defined [*Hickey*, 1998], includes the broad (1000 km) but shallow (0-300 m) southward flowing California Current (CC) at the surface and the narrow (10-40 km) poleward flowing California Undercurrent (CUC) at greater depths. The CC transports cooler, low salinity and highly oxygenated water from the Subarctic equatorwards [*Hickey*, 1998]. Coastal jets, which meander offshore upon encountering coastal promontories such as e.g. Cape Blanco, have been shown to contain a large fraction of the overall equatorward flow and to transport coastal water and its constituents off the shelf into the more offshore CCS region [*Barth et al.*, 2000; *Barth et al.*, 2002]. Below the equatorwards flowing upper layer, the CUC carries warmer, salty, and oxygen-depleted water of equatorial origin to the north [*Wooster and Jones*, 1970; *Hickey*, 1979; *Gardner*, 1982; *Hickey*, 1998; *Pierce et al.*, 2000; *Kosro*, 2002]. In addition, the CUC exports a substantial amount of nitrogendeficient waters from the Eastern Tropical North Pacific (ETNP) to the north [*Castro et al.*, 2001].

The CCS is associated with intense coastal upwelling driven by northerly, alongshore winds that are generated by the pressure gradient between the North Pacific High pressure cell and a thermal low over California. The winds result in offshore Ekman transport of surface water and large-scale vertical movement of nutrient-rich subsurface water to the sea surface, supporting high primary production and a large fishery along the entire northwestern American coast [*Hickey*, 1998]. Onshore return flow of water to compensate offshore Ekman transport off Oregon occurs roughly from depths between 100 and 200 m [*Huyer*, 1983; van Geen et al., 2000]. This is within the depth range of strongest CUC flow (100-300 m) [*Wooster and Jones*, 1970; *Hickey*, 1979; *Gardner*, 1982; *Hickey*, 1998; *Pierce et al.*, 2000].

The oxygen minimum zone (OMZ) is a characteristic feature of much of the global ocean roughly between 150-800 m depth. In the N-Pacific, the OMZ is most intense at the southern end of the CCS (south of ~25°N) in the ETNP, where relatively old and oxygen-poor subsurface and intermediate waters impinge on the continental margin and the downward flux of organic matter derived from primary production at

the surface is high. In the upper part of the OMZ, roughly between 100 and 500 m, dissolved oxygen concentrations drop below 5 μ M, and water-column denitrification becomes the dominant respiratory process [*Cline and Kaplan*, 1975; *Brandes et al.*, 1998; *Voss et al.*, 2001]. During this process bacteria use dissolved nitrate, a major nutrient for phytoplankton growth, as an electron acceptor to degrade organic matter and produce N₂ and the greenhouse gas N₂O, both of which are lost to the atmosphere [*Cline and Kaplan*, 1975; *Codispoti and Christensen*, 1985; *Law and Owens*, 1990; *Naqvi et al.*, 1998; *Naqvi et al.*, 2000]. Water column denitrification in the eastern tropical North Pacific (ETNP), the eastern tropical South Pacific (ETSP) and the Arabian Sea (AS) represent a major sink in the marine nitrate reservoir of the present day ocean.



Fig. 1.1: Schematic overview of surface currents in the North Pacific. Abbreviations are used for the North Pacific Current (NPC), the California Current (CC), the California Undercurrent (CUC), the North Equatorial Current (NEC), the Equatorial Undercurrent (EUC), and the North Equatorial Countercurrent (NECC). Core locations of this study are indicated by the filled circle.

1.3 Previous Palaeoceanographic studies in the North Pacific

Relying mainly on siliceous plankton assemblage transfer functions on a limited number of sediment cores, CLIMAP [1981] inferred a southward migration of the polar front in the North Pacific from its present position at ~50°N to about ~40°N, associated with a decrease of sea surface temperatures (Δ SST~ 4°C) in the subarctic region. Since CLIMAP [1981], sea surface temperature change in the North Pacific has been studied in greater regional detail. In the Alaska Gyre region, LGM SST cooling was estimated to be 6 °C [de Vernal and Pedersen, 1997], which compares to only 2°C in the subtropical North Pacific gyre region close to Hawaii [Lee and Slowey, 1999]. In the California Current region, studies based on alkenone unsaturation patterns [Herbert et al., 1995; Prahl et al., 1995; Doose et al., 1997] and faunal assemblages [Sabin and Pisias, 1996; Pisias et al., 2001] point to an average glacial SST cooling of 2~ 4°C, with a greater cooling in the northern California Current region. In addition to a cooler LGM, higher temporal resolution records from the Santa Barbara Basin and the southern California Margin reveal SST oscillations of up to 4-8°C on millennial time scales. The pattern of these variations is reminiscent of, and within dating error possibly synchronous to, the deglacial warming pattern and the so-called Dansgaard-Oeschger temperature changes observed in the North Atlantic region [Mortyn et al., 1996; Hendy and Kennett, 1999, 2000]. However, the exact timing of SST events and their temporal and causal relationship to climate change elsewhere remains a highly controversial issue, whose complexity is just beginning to emerge. Using a north-south transect of several cores covering the last four full glacials in the CC region, for example, Herbert et al. [2001] showed that the onset of surface-water warming after glacials (based on alkenones) precedes sea level rise (based on $\delta^{18}O_{\text{benthic}}$) by several kyrs and, moreover, changes latitudinally in the CC region. Whereas the last deglacial warming trend observed in the eastern subarctic Pacific is interpreted to be in phase with North Atlantic temperature change [*Kienast and McKay*, 2001; *see appendix I*], the opposite conclusion has been reached in the western subarctic Pacific [*Kiefer et al.*, 2001].

With the exception of one study in a borderland basin [Mortyn and Thunell, 1997], biological production during the LGM was consistently found to be greatly reduced in the California Current area [Lyle et al., 1992; Sancetta et al., 1992; Dean et al., 1997; Gardner et al., 1997; Ortiz et al., 1997; Ganeshram and Pedersen, 1998] and in the far northwest Pacific [Narita et al., 2002; Sato et al., 2002] and the Alaska gyre region [McDonald et al., 1999]. Water column denitrification in the ETNP was reduced during the LGM [Ganeshram et al., 1995; Pride et al., 1999; Emmer and Thunell, 2000; Ganeshram et al., 2000], similar to that in the ETSP [Higginson et al., 2002] and the Arabian Sea [Altabet et al., 1995; 1999; 2002]. Based on this evidence, the glacial ocean would have contained more nitrate, which in turn might have stimulated higher phytoplankton growth. However, the regional extent of denitrification, the processes that lead to its weakening, and whether or not this had a global effect on climate, are still under debate.

Based on the assumption that the intensity of the OMZ in the NE Pacific is partly controlled by NPIW water properties, records of sedimentary laminations, oxygensensitive benthic faunal assemblages and redox-sensitive trace metals from the Santa Barbara Basin and the California Margin have been used to infer better NPIW ventilation during the Younger Dryas cold period, the LGM and cold stadials during oxygen isotope Stage 3 [*Kennett and Ingram*, 1995; *Behl and Kennett*, 1996; *Cannariato and Kennett*, 1999; *Cannariato et al.*, 1999; *Zheng et al.*, 2000, *Ivanochko and Pedersen, subm*. 2002]. The slow overturning circulation in the Pacific has been studied using vertical and horizontal gradients of carbon and oxygen isotope ratios (δ^{13} C and δ^{18} O) in foraminifera. The upper water column in the subarctic North Pacific appears to have been even more stable during the last glacial, making glacial deep water formation in this region highly unlikely [Zahn et al., 1991]. However, the O_2 and CO_2 contents of the deep and intermediate waters are more controversial. Studies based on $\delta^{13}C$ and $\delta^{18}O$ generally point to a better ventilated water mass at intermediate depths (above 2000 m) during the LGM and relatively small change at greater depths [*Keigwin*, 1987; *Duplessy* et al., 1988; *Herguera et al.*, 1991; *Mix et al.*, 1991; *Keigwin et al.*, 1992; *Gorbarenko*, 1996; *Keigwin*, 1998; *Lund and Mix*, 1998; *Matsumoto et al.*, 2002]. This is in general agreement with a limited amount of data on radiocarbon age differences between benthic and planktonic foraminifera [*Shackleton et al.*, 1988; *Duplessy et al.*, 1989; *Adkins and Boyle*, 1997]. However, the notion of unchanged, i.e. sluggish and old deep water, is in clear conflict with evidence for a better ventilated Pacific deep water from Cd/Ca ratios on benthic foraminifera [*Ohkouchi et al.*, 1994] and circumstantial evidence for increased bottom water flow based on reflection-profiler and high-frequency echograms [*Mangini et al.*, 1982; *Damuth et al.*, 1983; *Mammerickx*, 1985], thorium corrected ³He fluxes [*Marcantonio et al.*, 2001] and grain size proxies [*Hall et al.*, 2001].

In summary, a more detailed palaeoceanographic picture of the North Pacific has evolved since the 1980, but many issues still remain unresolved. With its high biological production and the resulting high sedimentation rates, the California Margin area has the potential to offer some new clues, in particular with regard to deep and intermediate water chemistry and circulation, the regional extend of denitrification and the connection of changes in the Pacific to climate changes observed elsewhere.

1.4 Objectives of this study

The primary production and nitrogen isotope proxies of two cores from the Oregon margin are examined in this study and placed in the context of published records from the California Current region (Chapter 2) with the goal to build a synoptic picture of changing surface and subsurface ocean conditions over the last climatic cycle along the northwest American margin. A new hypothesis for the control of denitrification in the ETNP and its connection to global changes elsewhere is presented. In Chapter 3, a record of redox-sensitive trace metal concentrations of one of the cores is interpreted in light of: a) the general question of deep water composition during the glacial; and b) postulated millennial scale deep water ventilation changes during oxygen isotope Stage 3 based on sedimentary δ^{13} C evidence published previously [*Lund and Mix*, 1998].

1.5 Materials

The sediment core and sediment trap material examined in this study is part of the Multitracers Experiment, which combined measurements of water column tracer fluxes with studies of downcore variations in sediment burial fluxes [*Lyle*, 1992] along a offshore transect off Cape Blanco on the Oregon coast (Fig. 1.2). Trap moorings were deployed 120 km ("Nearshore") and 270 km ("Midway") off the coast from September 1987 to September 1991. Box and piston cores at these sites (Table 1.1) were collected on board the R/V Wecoma in 1987. The traps collected particle flux at 1000, 1500, 1750, and 2300 m depth in cups that were changed automatically at bimonthly to biweekly time intervals (or after 6-12 months for bulk samples). Sodium azide was used as a preservative in the cups; more details of the trap design are given in *Dymond and Lyle* [1994]. In addition, water column samples for nitrate isotopic analyses were collected at 150 and 600 m off Oregon in July 1999 and at 200 and 400 m depth off Vancouver Island in August 2001 (Tab. 1.1). The time scales of the Nearshore and Midway cores are described in detail in Chap. 2.3. Average sedimentation rates in the Nearshore core are around 20 cm/kyrs from 30 to 0 kyrs and approximately 10cm/kyrs from 70- 30 kyrs B.P. (Fig. A.III.1 in appendix III). Sedimentation rates in the more offshore Midway core are lower and average 10 cm/kyrs over the last 110 kyrs (Fig. A.III.1).

			longitude (W)	latitude (N)	depth (m)
Nearshore	traps		125°45.00′	42°05.00′	1000, 1500,
					1750, 2300
	cores	W8709A-13PC	125°45.00′	42°07.01′	2712
		W8709A-9BC	125°49.28′	42°04.72′	2824
Midway	traps		127°35.00′	42°10.00′	1000, 1500,
					1750, 2300
	cores	W8709A-8TC	127°40.68′	42°15.74′	3111
		W8709A-8PC	127°40.68′	42°15.74′	3111
		W8709A-6BC	127°38.31′	42°15.24′	2914
Oregon	water		125°05.78′W	44°40.126'N	150, 600
Vanc. Is.	water		126°40.03′W	48°38.91′N	200, 400

Tab. 1.1: Location of sediment cores, sediment trap and water column samples used in this study



Fig. 1.2: Nearshore and Midway sediment core (filled squares) and sediment trap sites (inverted triangles) examined in this study. Location of other core sites mentioned in text are also shown.

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Chapter 2:

Nitrogen isotope and primary production variations along the northeast Pacific margin over the last 120 kyr: Surface and Subsurface Palaeoceanography

2.1 Introduction

The global carbon cycle is tightly coupled to that of nitrogen, and one of the current explanations for lower atmospheric CO₂ levels during the last glacial maximum (LGM) involves a stronger biological pump fueled by an increase in the store of oceanic nitrate [*McElroy*, 1983; *Altabet et al.*, 1995; *Ganeshram et al.*, 1995; *Falkowski*, 1997; *Altabet et al.*, 1999a; *Ganeshram et al.*, 2000; *Altabet et al.*, 2002]. Biologically available, fixed nitrogen is the main limiting nutrient in most of today's ocean [*Dugdale and Goering*, 1967; *Codispoti*, 1989], and changes in its oceanic reservoir size, which mainly consists of nitrate (NO₃-), may therefore play a key role in regulating Earth's climate via the uptake of CO₂ during photosynthetic primary production.

The major sources of fixed nitrogen to the ocean are terrestrial run off and marine nitrogen fixation. The main sink is sedimentary denitrification in shallow continental shelf sediments and water column denitrification in the Eastern Tropical North Pacific (ETNP), the Eastern Tropical South Pacific (ETSP), and the Arabian Sea (AS). In the oxygen poor subsurface waters ($[O_2] < 10 \mu$ mol) of these areas, bacteria use nitrate as an electron acceptor to degrade organic matter and produce N₂ and the greenhouse gas N₂O, both of which are lost to the atmosphere [*Cline and Kaplan*, 1975; *Codispoti and Christensen*, 1985; *Law and Owens*, 1990; *Naqvi et al.*, 1998; *Naqvi et al.*, 2000]. Isotopically lighter ¹⁴NO₃- is preferred over the heavier ¹⁵NO₃- during denitrification

with a substantial fractionation factor (ε =25-30 ‰; [*Cline and Kaplan*, 1975; *Brandes et al.*, 1998; *Voss et al.*, 2001]. Denitrification therefore leads to the accumulation of isotopically enriched nitrate, as evidenced by $\delta^{15}N_{nitrate}$ values of up to 18‰ in the ETNP (Fig. 2.1) at subsurface depths [*Cline and Kaplan*, 1975]. Biological nitrogen fixation, on the other hand, the conversion of the abundant, but inert, N₂ gas to NH₄⁺ by some marine cyanobacteria, adds new fixed nitrogen to the ocean. Almost no isotope fractionation occurs during N₂ fixation [*Wada and Hattori*, 1976], and newly fixed nitrate has an isotopic composition close to that of the atmospheric N₂ substrate, which is, by definition, 0‰. Sediments can be faithful recorders of the isotopic composition of oceanic nitrate when nitrate uptake by primary producers in the euphotic zone is complete and there is no diagenetic alteration of the isotopic signal as it sinks and is buried in sediments as particulate nitrogen (PN).

Observational support for glacial-interglacial (and higher frequency) changes in the marine nitrogen budget comes from sedimentary records from the Arabian Sea [*Altabet et al.*, 1995; 1999a; 2002; *Suthhof et al.*, 2001] and the ETNP and ETSP [*Ganeshram et al.*, 1995; 2000]. Glacial sediments in these regions are characterized by lower δ^{15} N (~5-6‰) compared with higher values (~8-9‰) during the Holocene. This pattern has been interpreted to reflect reduced denitrification and, by inference, an increased nitrate reservoir in the glacial ocean, an interpretation that has been challenged by sedimentary nitrogen isotope records from the South China Sea [*M. Kienast*, 2000]. Under conditions of complete nitrate utilization, changes in δ^{15} N of particulate nitrogen in the euphotic zone overlying an active denitrification area can potentially be affected by a) changes in the rate of denitrification at subsurface depths due to a variable supply of oxygen or of degradable organic matter, and b) changes in the strength of vertical transport of isotopically heavy NO₃ to the surface. Outside of denitrification zones, δ^{15} N of particulate nitrogen can additionally be influenced by changes in horizontal advection of nitrate with a preformed isotopic signature. Distinguishing between these different processes has not previously been attempted.

In this study new $\delta^{15}N$ and primary production records of sediment cores and sediment traps (Chp.1.5, Table 1.1) from the Multitracers Experiment off the Oregon margin [*Lyle et al.*, 1992] are presented. No local water column denitrification occurs in this region today; nevertheless, the sediment cores show a very similar glacialinterglacial $\delta^{15}N$ pattern to those from the ETNP and the AS. These $\delta^{15}N$ results are evaluated in light of the sediment trap results, regional $\delta^{15}N_{nitrate}$ data, and hydrographic conditions. Palaeo-export production is reconstructed using the sedimentary concentrations of biogenic opal and organic carbon (C_{org}) as well as Ba/Al ratios. The phase relationships between $\delta^{15}N$ and primary production proxies in the Multitracers cores are then compared to core records from within (off northwestern Mexico) and outside (off California) the denitrification zone in the ETNP. This comparison offers new insight into the effects of vertical and horizontal circulation changes on the $\delta^{15}N$ signal in marine sediments along the NW American margin. A full understanding of these processes may lead to the use of $\delta^{15}N$ as a water mass tracer for the present [*Brandes et al.*, 1998] and the past ocean.


Fig. 2.1: Map of the mid-latitude NE Pacific margin with Multitracers core (filled squares) and sediment trap (inverse triangles) sites Nearshore and Midway. Other core sites mentioned in the text are ODP Hole 1017E off California and NH22P off Mexico [*Ganeshram et al.*, 1995; 2000]. Other sediment trap sites include Monterey Bay, San Pedro Basin, and Carmen Basin in the Gulf of California [*Altabet et al.*, 1999b]. Numbers (filled circles) indicate maximal water column $\delta^{15}N_{nitrate}$ values between 100-350 m taken from *Cline and Kaplan* [1975] (ETNP); *Pride et al.* [1999] (Gulf of California); *Altabet et al.* [1999b] (San Pedro Basin and Monterey Bay). Stippled line (0.2 ml/1 O₂ at 400 m depth, from *Levitus et al.* [1994] indicates approximate boundary of the denitrification zone.

2.2. Productivity proxies

Past primary production has been reconstructed using three independent proxies: percent opal, percent organic carbon and the barium/aluminium ratio.

Opal

Cold, recently upwelled waters in the CCS region support a high biomass of various diatom species [Hood et al., 1990; Chavez et al., 1991; Hood et al., 1991], and diatoms overwhelmingly dominate the microfossil assemblage found in all Multitracers trap samples [Sancetta, 1992]. Although the presence of opal-rich sediments is clearly associated with high primary productivity in coastal upwelling areas [Calvert and Price, 1983; van der Weijden and van der Weijden, 2002], the relationship between silica production and opal accumulation is not straightforward, as sea water is undersaturated with respect to silicic acid [Archer, 1993; Ragueneau et al., 2000; Rickert et al., 2002]. Consequently, opal dissolves during settling through the water column and at the sediment surface. The physical and biological conditions of upwelling areas such as the CCS region, however, promote opal burial through pulsed upwelling events that support extensive blooms of large, heavily silicified and chain-forming diatom species with a tendency to form aggregates, as well as through grazing by zooplankton and subsequent fecal pellet production [Nelson et al., 1995; Ragueneau et al., 2000]. All of these factors effectively shorten the exposure time of opal particles to sea water by increasing their settling rate. Downcore enrichments in sedimentary opal are therefore used here as a qualitative indicator of past periods of relatively high diatom production.

Organic carbon

Along with biogenic opal, organic carbon is a direct product of marine primary production and its flux below the euphotic zone is a function of net primary production

at the surface and depth-dependent degradation [Suess, 1980]. Numerous studies in a variety of oceanic settings have demonstrated an overall positive relationship between primary production, organic carbon export and organic carbon burial [Müller and Suess, 1979; Sarnthein and Winn, 1988; Calvert et al., 1992; Pedersen et al., 1992; Calvert et al., 1995]. However, the exact conditions under which organic carbon supplied to the sediments is preserved are still subject to debate. High sedimentation rates [Müller and Suess, 1979] as well as physical protection of organic matter by the inorganic matrix of sinking particles [Hedges et al., 2001] have been suggested to enhance organic carbon preservation, whereas exposure to oxygen [Hartnett et al., 1998] has been proposed to reduce it. Recently, the rate at which fresh organic matter is degraded in the water column has been shown to be the same in anoxic basins and the open ocean [Thunell et al., 2000], indicating that exposure to oxygen is not the overriding control on the preservation of organic matter. In addition, the importance of surface productivity in controlling not only the sedimentary organic carbon content but also the local bottom water oxygen content was highlighted by Stott et al. [2000] in a recent study in the borderland basins of the NE Pacific. These authors showed that the superposition of bioturbated sediments (requiring bottom water oxygen) upon laminated sediments (deposited under anoxic or near anoxic bottom water) was caused by an overall reduction in coastal upwelling, i.e. marine production, over the course of the 20th century.

Comparing the C_{org} rain rate in the 1000 m sediment trap to the C_{org} accumulation rate at the sea floor at the Multitracer sites, *Lyle et al.* [1992] found that more than 20% of the entire C_{org} flux through the water column is preserved in the sediment. Moreover, sedimentation rate changes since the LGM seem to have been too small to have affected C_{org} preservation [*Lyle et al.*, 1992]. In LGM sediments, the total organic matter content is reduced and the terrestrial organic carbon fraction is about

twice as large as during the Holocene [Lyle et al., 1992]. Subtracting the terrestrial C_{org} input from the total organic carbon content will therefore only amplify the pattern of lower C_{org} values during glacials.

Barium

In addition to organic carbon and biogenic opal, barium (Ba) was quantified as a palaeoproduction proxy. The positive relationship between sedimentary Ba concentrations and surface ocean productivity has long been known [e.g. Goldberg and Arrhenius 1958]. Barite (BaSO₄) is precipitated in microenvironments containing decaying organic matter and the remains of siliceous plankton [Dehairs et al., 1980; Bishop, 1988], and is carried to the sea floor in settling organic detritus. A large set of sediment trap data has led to the definition of quantitative algorithms that allow the reconstruction of past new production in the euphotic zone from biogenic barium accumulation rates in sediments (e.g. Dymond et al. [1992], François et al. [1995], Dymond and Collier [1996]). However, rather than estimating biogenic barium as [bioBa] = ([Ba] -0.0075 x [A1]) in order to compute a quantitative estimate of past primary production, as adopted for example by Dymond et al., [1992]; François et al., [1995]; and Dymond and Collier [1996], I directly report the ratio of total barium to aluminium (Ba/Al) here. This more qualitative approach circumvents the problem associated with the correction for detrital Ba input, which can be substantial at continental margins [Dymond et al., 1992]. Given the rather constant supply of Al to the sediment ([Al] = 6-9 % in the Nearshore core, Chp. 3, Fig. 3.2, and the Midway core, not shown), changes in the Ba/Al ratio thus directly reflect the marine Ba contribution to the sediment. Barite is relatively unreactive in oxic and suboxic sediments [Church and Wolgemuth, 1972; Gingele, 1999], and the Ba/Al ratio is thus expected to be a reliable productivity indicator at the Multitracer sites.

Although both opal and organic carbon suffer from degradation and dissolution effects, the factors considered responsible for their preservation (e.g. opal solution vs. organic matter flux and/or oxygen exposure) are different. The combined use of these two proxies and their comparison with barium, a more refractory chemical species, should therefore help to reliably hindcast palaeoproduction changes in a semiquantitative manner.

2.3 Chronostratigraphy

The age model for Nearshore core W8709-13PC is presented in detail by *Mix et al.* [1999] and *Lund and Mix* [1998]. From 0-36 kyr (0-557 cm), it is based on 41 AMS ¹⁴C dates on planktonic and benthic foraminifera [*Mix et al.*, 1999]. From 36-59 kyr (557-760 cm) the age model is based on correlating millennial-scale oxygen isotope peaks to North Atlantic core V23-81 as well the identification of the marine oxygen isotope Stage (OIS) 3-4 boundary at 59 kyr [*Lund and Mix*, 1998]. The chronology of the remaining core length (760-858.5 cm) was approximated for this study by linearly extrapolating the sedimentation rate.

Piston core Midway (W8709A-8 PC) was spliced with its trigger core W8709A-8 TC based on a comparison of magnetic susceptibility and calcium carbonate (CaCO₃) records in both cores, which indicated that the piston core overpenetrated by 140 cm [*Lyle et al.*, 1992]. A new chronostratigraphy of this composite record was established for this study based on a correlation (Fig.2.2, table AIII.1) of its high resolution CaCO₃ content to a radiocarbon and oxygen-isotope dated, stacked carbonate record from the California margin [*Lyle et al.*, 2000]. Kiloyear-scale CaCO₃ and C_{org} events are a common feature in this area and can be used with care for chronostratigraphic control [*Karlin et al.*, 1992; *Lyle et al.*, 2000]. The resulting age model is considered accurate within a few

kyrs and corresponds to the previously used radiocarbon based chronology of W8709-8 PC [*Lyle et al.*, 1992; *Doose et al.*, 1997] for the last 30 kyrs, but is more robust in the older part of the record where the previous model was based on the assumption of linear sedimentation rates only.



Fig. 2.2: Correlation of the $CaCO_3$ record of the Midway core W8709-8 (bottom) to the stacked carbonate record of *Lyle et al.* [2000] (top). Named peaks in the stacked record have chronostratigraphic significance and are used as tie points for the new chronology of core W8709-8. The age datums and depths of the tie points are given in table A.III.1 in the appendix.

The age model of Mexican margin core NH22P is described in detail by *Ganeshram and Pedersen* [1998], and the age model of ODP Hole 1017E will be published elsewhere [*Hendy and Pedersen*, in prep.].

The absolute accuracy of the individual age models is not crucial in the context of this study. The conclusions are based on the phase relationship between a) different proxies within the same core and b) the same proxy relative to the benthic δ^{18} O signal in different cores. The glacial-interglacial δ^{18} O_{benthic} transition is assumed to be recorded simultaneously at comparable depths along the NW American margin.

2.4. Results

2.4.1 Water column and sediment trap results off Oregon

 $δ^{15}N_{nitrate}$ at the Multitracer sites at 150 and 600 m is 7.1 ± 0.2‰ (n=4, Fig. 2.3) whereas values of 6.1‰ and 6.3‰ are found off Vancouver Island at 200 and 400 m depth, respectively. For comparison, the global ocean average is estimated to be around 4.5 – 5‰ [*Sigman et al.*, 1997; 2000], and deep water values of 4 – 5‰ are observed in the NE Pacific [*Cline and Kaplan*, 1975; *Wu et al.*, 1997]. $δ^{15}N$ of settling particulate nitrogen ($δ^{15}N_{PN}$) collected in cups that were open for 6-12 months varies from 7.9 to 5.9‰ at the Nearshore site and from 8.8 to 5.4‰ at the Midway site with averages of 7.0 ± 1.0‰ and 7.4 ± 1.2‰, respectively (Fig. 2.3). These averages are similar to the $δ^{15}N$ of the surface sediment at both sites (6.5‰ and 8.0‰ at Nearshore and Midway, respectively, Fig. 2.3). The composite isotopic time series from September 1987 to September 1991 shows a distinct seasonal cycle of $δ^{15}N_{PN}$ depletion (4-6‰) and enrichment (8‰), with lighter values generally occurring in spring and fall and heavy values occurring in summer (Fig. 2.4). Maxima in opal flux (Fig. 2.4) occur shortly after $\delta^{15}N$ from 1987 to 1991.



Fig. 2.3: Nitrogen isotopic composition of dissolved nitrate off Oregon (diamonds, samples taken in July 1999 at 125°05.78′W, 44°40.126′N) compared with bulk sediment trap samples representing 6-12 months (circles) and boxcore surfaces (squares) at the Nearshore and Midway sites.



Fig. 2.4: a) Multitracers $\delta^{15}N_{PN}$ and opal flux trap time series off Oregon from September 1987 to September 1991. $\delta^{15}N_{PN}$ samples are from 1000 m (open diamonds), 1500 m (open circles), 1750 m (filled squares) and 2300 m (filled triangles). Note the lack of a systematic change with depth in $\delta^{15}N_{PN}$ and the increasing trend towards the end of the time series. Opal flux is from the 1000 m trap, data were kindly provided by R. Collier, OSU. Y axes are different for each site; b) Multitracers and the Monterey Bay sediment trap deployment periods (horizontal bars) relative to the Southern Oscillation Index (SOI). Negative SOI values indicate El Niño conditions.

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2.4.2 Sediment core results

The Multitracers cores show a clear glacial-interglacial pattern in export production over the last 120 ka, with low organic carbon, opal and barium contents during cold oxygen isotope Stages 2 and 4 and values almost twice as high during the Holocene and Stage 5 (Figs. 2.5 and 2.6). Stage 3 also shows several millennial-scale palaeoproduction proxy fluctuations with amplitudes approximately half as large as the glacial-interglacial contrast. In the higher resolution core W8709-13PC, organic carbon and opal percentages decrease to an intermittent minimum around 11 ka BP after an initial increase during the last termination. The increase to maximum Holocene values in organic carbon concentrations is quite abrupt in the Midway core, whereas opal and Ba/Al increase more gradually and reach maximum Holocene values slightly after %C_{org}. The three different palaeoproduction proxies consistently show reduced primary production during Stages 2 and 4 compared to the Holocene and Stage 5.

Sedimentary δ^{15} N values are low during the glacial (4-6‰), higher during the interglacials (7-10‰) and show millennial scale fluctuations during oxygen isotope Stage 3 (Fig. 2.5 and 2.6). Apart from a δ^{15} N maximum around 19 kyr BP, organic carbon and δ^{15} N covary closely in Nearshore core W9709-13PC and the transitions from oxygen isotope Stages 4 to 3 and from 2 to 1 as well as most fluctuations of both proxies during Stage 3 occur approximately synchronously. This is true for Midway core W8709-8PC as well, although from Stage 5 to Stage 2 the coupling between barium and δ^{15} N is tighter than that between C_{org} and δ^{15} N (Fig. 2.6). The relationship between opal and δ^{15} N is somewhat weaker. Thus, although maybe not strictly coupled, δ^{15} N covaries approximately in phase with palaeoproduction proxies off Oregon.



Fig. 2.5: Sedimentary δ^{15} N, organic carbon concentration, Ba/Al ratio and biogenic opal concentration versus age from Nearshore core W8709-13PC off Oregon. Time scale from *Mix et al.* [1999] and *Lund and Mix* [1998]. Diamonds on Y-axes indicate surface sediment values from corresponding boxcore. Italic numbers indicate marine oxygen isotope Stages. Ba/Al ratios around 66 kyrs B.P are likely to be erroneous (*see* Appendix II).



Fig. 2.6: Sedimentary δ^{15} N, organic carbon concentration, Ba/Al ratio, and biogenic opal concentration of Midway cores W8709-8PC and W8709-8TC off Oregon versus age. Time scale is described in text. Italic numbers indicate marine oxygen isotope Stages.

2.5 Interpretation

2.5.1 Water column and sediment trap data

Subsurface $\delta^{15}N_{nitrate}$ measurements from the NE Pacific are still sparse, but the available data from the NW American margin show that they progressively decrease from high values in the ETNP (18.3%) to lower values farther north (7.2% off Oregon; Fig. 2.1). Despite this decrease, they are still higher than the global ocean average of 4.5 - 5‰ [Sigman et al., 1997; 2000] and deep water values of 4 - 5‰ observed in the NE Pacific [Cline and Kaplan, 1975; Wu et al., 1997]. Using $\delta^{15}N_{nitrate}$ and salinity data, Liu and Kaplan [1989] suggested that the subsurface $\delta^{15}N_{nitrate}$ maximum observed in the San Pedro Basin off southern California is imported from the ETNP by the CUC. Based on the data compiled in Figs. 2.1 and 2.7 we argue that this transport continues to the Oregon coast, possibly even farther north to Vancouver Island. In Figure 2.7, $\delta^{15}N_{nitrate}$ in the CCS is plotted versus salinity. The ideal mixing lines for two depth ranges are constructed following the approach outlined by Liu and Kaplan [1989] and using data from the ETNP and from Oregon (for samples from 150-350m depth), and from the ETNP and Washington (for samples from 450-600 m depth) as end members (see Appendix A.III.2 for data and calculation). Most of the data fall on or near the ideal mixing lines, indicating that waters derived from the ETNP are indeed an important source of isotopically heavy nitrate for the northern CCS region. The CUC is most likely the main transport mechanism since it flows polewards from the ETNP to Vancouver Island along this coastline [Pierce et al., 2000; Castro et al., 2001]. Interestingly, the shallow water sample from Vancouver Island (200 m) does not fall on the calculated mixing line, whereas the deeper sample (400 m) does. Although it is possible that the salinity- δ^{15} N relationship observed further south breaks down at these latitudes, this observation is in agreement with long term current meter observations off Vancouver Island that consistently show undercurrent flow around 400 m, but not at 200 m [R.

Thomson, *personal communication*, 2003]. In addition to poleward export, heavy nitrate might also homogeneously spread northwards as well as westwards via lateral mixing from the ETNP. There are not enough $\delta^{15}N_{nitrate}$ data available yet to test this, however.



Fig. 2.7: Relationship between $\delta^{15}N_{nitrate}$ and salinity of samples from the California Current region. Open circles indicate samples originating from 150-350 m water depth, filled circles indicate deeper samples. The solid lines are ideal mixing lines following *Liu and Kaplan* [1989]. This mixing relationship illustrates that waters from the ETNP are an important source of isotopically heavy nitrate to the entire NW American margin. See figure caption 2.1 for $\delta^{15}N_{nitrate}$ references, salinity data are from *Liu and Kaplan* [1989] (ETNP and San Pedro Basin); F. Chavez and R. Michisaki, unpub. data (Monterey Bay); M. Lyle, unpub.data (Oregon) and *Brandes* [1996] (Washington). *Data can be found in appendix III*.

Additional support for the influence of the CUC comes from the three-year sediment trap time series off Oregon (Fig. 2.4). It shows a clear seasonal cycle in $\delta^{15}N_{PN}$, with lighter values in spring and fall most likely reflecting changes in relative nutrient utilization, i.e. the balance between physical supply of nitrate by upwelling and its consumption by phytoplankton uptake over the course of one year [Wada and Hattori, 1978; Altabet and François, 1994]. The relationship between opal flux maxima, indicating upwelling, and isotopic minima corroborates this assertion [Altabet, 1996]. However, there is also an overall trend towards higher $\delta^{15}N_{PN}$ values from 1987 to 1991, which is superimposed on the seasonal $\delta^{15}N_{PN}$ pattern. Sediment traps from Monterey Bay, ca. 400 km farther south, also show heavier $\delta^{15}N_{PN}$ values from late 1991 to early 1992 compared with the two previous years [Altabet et al., 1999b]. The end of the Multitracers time series coincides with the beginning of the 1991-1992 El Niño period. During El Niño events, CUC flow is unusually strong [Hickey, 1998], and increased undercurrent flow has been directly observed off Oregon [Huyer and Smith, 1985; Huyer et al., 2002; Kosro, 2002. Corwith and Wheeler [2002] observed a lower N:P ratio in the poleward moving southern water compared to typical coastal water during the 1997-8 El Niño, indicating the presence of waters that have lost nitrate by denitrification. The increased import of heavy nitrate caused by a stronger CUC may therefore explain the trend towards higher $\delta^{15}N_{PN}$ observed in sediment trap time-series off Oregon and Monterey Bay.

Although there is some year-to year $\delta^{15}N_{PN}$ variation in the bulk sediment trap samples (Fig. 2.3), the sediment surface $\delta^{15}N$ values (6.5 and 8.0 ‰ at Nearshore and Midway, respectively) fall within the range of the trap samples and are very close to their average composition (7.0 and 7.4 ‰ at Nearshore and Midway, respectively). This indicates that there is no significant diagenetic offset at the sediment water interface. We note, however, that the more offshore Midway site does have a 1.5 ‰ heavier core top δ^{15} N despite no large difference in %C_{org} (Fig. 2.6). The average composition of settling PN is in turn very similar to that of dissolved nitrate (7.1 %) off Oregon (Fig. 2.3). Surface nitrate concentrations over the annual cycle at the Nearshore and Midway sites are low (1-2 μ mol/l, [Levitus et al., 1994]). If all upwelled nitrate is taken up by primary producers and converted to PN, and if sinking PN is the only significant loss term, then mass balance dictates that the isotopic composition of the product equals that of the substrate [Altabet and McCarthy, 1985; Altabet, 1988]. These conditions of complete nitrate utilization over the course of one year seem to apply at the Multitracers sites. Complete nitrate utilization and the absence of diagenetic alteration of the isotopic signal has also been inferred at Monterey Bay, San Pedro Bay, and Carmen Basin farther south in the CC region [Altabet et al., 1999b; Pride et al., 1999], and they most likely represent regional phenomena along the North American coast. This means that the seasonal differences in relative nitrate utilization seen in the time series will not be recorded in the sediment. Rather, the $\delta^{15}N$ composition of the Multitracers cores is a recorder of the mean $\delta^{15}N$ of subsurface nitrate imported from the ETNP by the CUC.

2.5.2 Down core records

Primary production

The sedimentary concentrations of opal, organic carbon and the Ba/Al ratio consistently show reduced primary production during Stages 2 and 4 compared to the Holocene, Stage 3 and Stage 5. Reduced coastal upwelling and primary production during the LGM have previously been inferred off Oregon [Lyle et al., 1992; Sancetta et al., 1992; Ortiz et al., 1997], California [Dean et al., 1997; Gardner et al., 1997] and Mexico [Ganeshram and Pedersen, 1998]. Building on model simulations [COHMAP, 1988], Lyle et

al. [1992] and *Ganeshram and Pedersen* [1998] argue that the semi-permanent high pressure cell over the Laurentide ice cap caused a weaker and more southerly North Pacific high pressure cell during the LGM, which can explain the widespread reduction of upwelling favourable winds along the entire Northwest American margin.

The deglacial rise in C_{org} is interrupted by three intermittent C_{org} minima in the higher resolution core W8709-13PC (Fig. 2.5). The third and most pronounced minimum occurs between 13.6 and 11.6 ka BP, supporting findings by Mix et al. [1999] and Pisias et al. [2001] that coastal upwelling off Oregon and northern California was significantly lower during a period possibly correlative to the Younger Dryas event. During Stage 3, periods of relatively intense production every 5-10 kyrs are interrupted by four periods of reduced upwelling. In a model of the response of the Pacific North West to the North Atlantic Heinrich events [Hostetler and Bartlein, 1999], lowering the Laurentide ice sheet during ice surges induces changes in upper level and surface winds over western North America, which in turn significantly reduce northerly, upwelling-favorable summer winds over Oregon and northern California. Similarly, *Pisias et al.* [2001] infer that at wavelengths > 3000 yrs, warm events in Greenland are correlated to intervals of increased coastal upwelling off Oregon. A direct correlation of the millennial-scale upwelling events recorded in the Multitracers cores to events elsewhere is difficult because of the errors associated with marine sedimentary chronologies, but in light of the results of Hostetler and Bartlein [1999] and Pisias et al. [2001] we suggest that the periods of reduced upwelling might correspond to Heinrich events and that the periods of stronger upwelling might correspond to the most pronounced Dansgaard-Oeschger interstadials as recorded in GISP2.

In the Midway core, primary production during Stage 5 was higher than during the cold Stages 2 and 4 (Fig. 2.6). However, the signals are quite variable and, for example, an increase in %opal between 100 and 94 ka B.P coincides with a decrease in %C_{org} in W8709-8PC. This is similar to findings from nearby ODP Site 1020 during this time and probably reflects the individual signature of MIS 5 compared to the Holocene [*Lyle et al.*, 2001].

$\delta^{15}N$

In principle, the glacial-interglacial δ^{15} N variations observed in the Multitracers cores could reflect differences in nutrient utilization and/or denitrification. However, given that nitrate uptake is complete under modern conditions of intense coastal upwelling, nitrate uptake most likely was complete during the LGM as well when upwelling was reduced [*Lyle et al.*, 1992; *Sancetta et al.*, 1992; *Ganeshram and Pedersen*, 1998]. Therefore, changes in relative nitrate utilization over time can be discounted as an explanation for the observed sedimentary δ^{15} N variations. Local denitrification during the Holocene, Stage 3 and Stage 5 is unlikely, as the lowest dissolved O₂ concentrations in subsurface waters off Oregon today (~18 µM, between 500-1000m; *Levitus et al.* [1994]) are not low enough to support local denitrification. During the glacial Stages, lower organic matter flux through the water column would have diminished oxygen consumption, possibly leading to even higher dissolved O₂ concentrations.

The Multitracers sediment traps and surface sediment data together with the isotopic composition of modern subsurface nitrate strongly suggest that the $\delta^{15}N$ composition of the Multitracers cores record the $\delta^{15}N$ of subsurface nitrate, which today is characterized by an isotopically heavy signature imported from the ETNP by the

CUC. Higher sedimentary δ^{15} N values during the Holocene, parts of Stage 3 and during Stage 5 therefore imply that the CUC and the processes that drive it have most likely been in existence during these times. Simultaneously, palaeoproduction proxies indicate that northerly winds drove coastal upwelling during at least part of the year. Thus, during the Holocene, parts of Stage 3 and Stage 5, these components of the CCS seem to have been working in a similar fashion as today.

In contrast, the lower $\delta^{15}N$ values during glacial Stages 2 and 4 can be interpreted in several ways. First, the glacial reduction in coastal upwelling [Lyle et al., 1992; Sancetta et al., 1992; Ganeshram and Pedersen, 1998] would have caused a diminished supply of isotopically heavy nitrate to the euphotic zone. A deepening of the thermocline would have had the same effect (see discussion below). Secondly, as denitrification in the ETNP was weakened [Ganeshram et al., 1995; Ganeshram et al., 2000], the isotopic signal exported from the ETNP would have been lower than today and, by the time it reached Oregon, too diluted to be distinguishable from that of average oceanic nitrate. Thirdly, the CUC was most likely weaker because of a weaker CC during the LGM [Doose et al., 1997; Herbert et al., 2001] and because the CUC is strongest today in the summer when the surface-flowing CC is strongest [Hickey, 1998]. A weaker CUC would have led to reduced importation of heavy nitrate to the Oregon site. We cannot currently distinguish between the above scenarios because the minimal δ^{15} N values in the Oregon cores (4-6‰) are similar to the isotopic composition of mean oceanic nitrate. Most likely, a combination of them (i.e. a reduction in production, horizontal and vertical advection of heavy nitrate) caused the CCS region to lose its distinctive isotopic signature during the glacials and instead to be indistinguishable from the mean oceanic nitrate pool. Information on the $\delta^{15}N_{nitrate}$ in the glacial ocean outside of denitrification zones is still quite limited, although it might not have been very different from today [*M. Kienast*, 2000]. Thus, the Oregon margin was no longer connected to the denitrification zone via the CUC but was part of a different regime. At the same time, denitrification in the ETNP was reduced, leading to lower sedimentary δ^{15} N values off Mexico. Interestingly, the glacial-interglacial amplitude of 2-3 ‰ is the same in both regions. This, however, is most likely fortuitous.

2.6 Discussion

2.6.1 Comparison of the Oregon sites with other records from the NE Pacific

In spite of covering a distance of over 2000 km, the transect of $\delta^{15}N$ variations from Oregon and California to Mexico displays a remarkably similar and most likely synchronous (see below) pattern over the last 60 kyr (Fig. 2.8). Comparable to the spatial trend in modern $\delta^{15}N_{\text{nitrate}}$ values, sedimentary $\delta^{15}N$ decreases with distance from the ETNP. The record from ODP Hole 1017E off California can also be explained by variations in the advection of isotopically heavy nitrate from the ETNP, similar to the Oregon cores (see above, and Emmer and Thunell, [2000]). During the Holocene and during Stage 3, δ^{15} N values in core 1017E are 0.5-1 ‰ higher than in core W8709-13PC off Oregon, whereas both cores show the same minimal values between 26-30 kyrs BP. Changes in δ^{15} N and palaeoproduction proxies in the Oregon cores are closely in phase on a sample to sample basis, and the same is true for $\delta^{15}N$ and C_{org} in ODP Hole 1017E off California [see Fig. 3 in Ganeshram et al., 2000] and also for $\delta^{15}N$ and biogenic opal in core JPC-56 from the central Gulf of California [Pride et al., 1999]. While palaeoproduction tracers therefore appear to respond more or less in phase with sedimentary $\delta^{15}N$ outside the ETNP, the two proxies are out of phase within the denitrifying zone off the Mexican margin. In this area, the rise in C_{org} during the last termination lags that of δ^{15} N by several kyrs (Fig. 1 in Ganeshram et al., 1995; Fig. 3 in

Ganeshram et al., 2000) and the same lag is observed at the Stage 4/3 and 6/5 boundaries. In view of this considerable lag, variations in primary production in this region cannot have been the sole control on the intensity of denitrification in this area.



Fig. 2.8: Sedimentary δ^{15} N records from the Mexican (NH22P), Californian (ODP 1017E) and Oregon margin (W8709-13PC) over the last 60 kyrs plotted according to their independent age models. The δ^{15} N record of ODP Hole 893A from the Santa Barbara Basin [*Emmer and Thunell*, 2000; *not shown*] is similar to that of Hole 1017E.

2.6.2 What drives glacial-interglacial variations in sedimentary $\delta^{15}N$?

Changes in the isotopic composition of PN in the euphotic zone overlying an active denitrification area such as the ETNP can be governed by two different processes. The first is a change in the vertical transport of isotopically heavy nitrate to

the surface where it is then assimilated by phytoplankton and incorporated into sedimenting particles. The second process is a variation in either the supply of oxygen or of organic matter, both of which induce a change in the intensity of denitrification. Both of these mechanisms, changing thermocline depth and changing denitrification intensity, can be tested as possible candidates for explaining the glacial-interglacial δ^{15} N variations in the NE Pacific.

2.6.3 Thermocline hypothesis

Changes in the vertical upward flux of isotopically heavy nitrate can be achieved by deepening the thermocline, thereby allowing less water from the subthermocline denitrification zone to be tapped and upwelled. Conversely, raising the thermocline would increase the vertical transport of isotopically heavy nitrate into the euphotic zone. Consistent with this hypothesis, *Altabet et al.* [1999b] observed that the δ^{15} N of new nitrogen delivered to the sea surface in the modern Gulf of California decreased during the 1991-92 El Niño event, when the main thermocline in the eastern tropical Pacific deepened [*Philander*, 1990]. However, in areas such as the ETNP, where organic matter flux is important in maintaining low subsurface O₂ concentrations, this mechanism can only operate on short (interannual) time-scales. On longer time-scales, an increase in thermocline depth will also reduce the upward flux of subthermocline nutrients and consequently primary production will decrease. Such a deepening of the thermocline should therefore be recorded as a synchronous decrease in sedimentary δ^{15} N and primary production, which is not observed at the Mexican margin sites.

2.6.4 Equatorial and California Undercurrent hypothesis

The depletion of O_2 and the potential for denitrification at a particular location depend on the flux of oxidizable material present and the supply of O_2 to this location by circulation and diffusion [Wyrtki, 1962; 1967]. In the modern ETNP, the secondary nitrite maximum and the heavy $\delta^{15}N_{nitrate}$ peak, both of which are results of active denitrification, are observed between 100-500 m depth with maximal values at around 250 m [Cline and Kaplan, 1975; Garfield et al., 1983] and 350-400 m [Brandes et al., 1998], respectively. The water mass in this depth range is Subtropical Subsurface Water [SSW, after Wyrtki, 1967]. It is characterized by its high salinity (>34.6) and has the identical temperature, salinity, and density properties as the "13°C Water" described by Tsuchiya [1981]. 13°C Water acquires its initial properties in the western South Pacific and is transported to the ETNP by the Equatorial Undercurrent [Tsuchiya, 1981; Tsuchiya et al., 1989; Toggweiler et al., 1991]. At the Galapagos Islands, most of the water from the EUC spreads south and north and continues to flow poleward along the eastern boundaries of the Pacific Ocean [Tsuchiya, 1981; Lukas, 1986]. The initially high oxygen content of EUC water is consumed rapidly under the highly productive surface waters in the eastern tropical Pacific [Wyrtki, 1967]. As pointed out by Ganeshram et al. [2000], only circulation or ventilation changes in this subsurface water mass have the potential to affect denitrification rates in the ETNP, not changes the North Pacific Intermediate Water, which is deeper and forms the lower part of the OMZ.

The EUC mostly owes its existence to the easterly trade winds. They force the oceanic upper layer to pile up at the western boundary of the Pacific basin and thereby establish a zonal horizontal pressure gradient towards the east. The trade winds form the lower limb of the thermally produced Hadley cell, which in the northern hemisphere is strongest in winter when the equator-pole temperature gradient is

intensified. Cooling of the polar regions is thought to compress and intensify the Hadley cell [Nicholson and Flohn, 1980; Flohn, 1982] and a variety of palaeoceanographic data indeed suggest stronger atmospheric circulation and trade winds during the LGM [Molina-Cruz, 1977; Sarnthein et al., 1981; Pedersen, 1983; Little et al., 1997; Perks et al., 2002]. The model based results of Bush and Philander [1999] and Andreasen et al. [2001] suggest that stronger glacial easterlies increased the E-W tilt of the tropical thermocline in the central Pacific and doubled the speed of the EUC. The computed changes in thermocline depth agree with foraminiferal evidence collected from sediments deposited during the LGM [Andreasen and Ravelo, 1997]. An increase in EUC speed should increase O₂ advection into the ETNP and reduce denitrification during cold Stages, independent of local productivity changes. The decrease in the intensity of denitrification in the ETNP would be in concert with the millennial-scale climate coolings such as the Dansgaard-Oeschger stadials and Heinrich events observed in the North Atlantic region since the injection of O2 in this hypothesis is an atmospheredriven mechanism. During warm Stages, on the other hand, with little O2 advection and intense denitrification in the ETNP, the CUC could easily propagate the heavy nitrate signal northward along the entire NW American margin within a few months. As ODP site 1017 is located closer to the source region, it shows slightly higher δ^{15} N values (by 0.5-1 ‰) than in the core records off Oregon during these times (Fig. 2.8). During cold periods and reduced denitrification in the ETNP, however, $\delta^{15}N$ values in the Oregon and the California cores are the same as both most likely recorded the isotopic composition of mean oceanic nitrate. The suggested scenario would result in a synchronous, continental-margin wide sedimentary $\delta^{15}N$ response reaching far beyond the boundaries of the ETNP that is in phase with the transition from glacial (stadial) to interglacial (interstadial) periods.

In the southern hemisphere, the poleward Peru Undercurrent is the equivalent of the CUC and its connection with the EUC is well documented [*Tsuchiya*, 1981; *Lukas*, 1986; *Toggweiler et al.*, 1991, *Fedele Razon*, 1993]. The mechanism described above could therefore operate in the southern Hemisphere as well and thereby synchronize δ^{15} N records along the NE and SE Pacific margins. Preliminary results from the Peru margin [*Higginson et al.*, 2002], however, possibly indicate a lead of the southern hemisphere δ^{15} N rise after the LGM.

As pointed out above, our model depends on a stronger EUC, driven by intensified trade winds during the LGM. Although there is palaeoceanographic and model-based evidence for such an assertion (see above references), it should be pointed out that the relationship between trade wind intensity and primary production in the equatorial region is still controversial. Recent work by *Stott et al.* [2002] and *Koutavas et al.* [2002] possibly suggests that the trade winds were actually weaker during the LGM, and palaeo-productivity estimates based on benthic foraminiferal transfer functions highlight a previously unrecognized degree of spatial heterogeneity in this region [*Loubere*, 2002]. Focussing and redistribution of sediments due to bottom currents in the equatorial region [*Marcantonio et al.*, 2001] also severely complicate the interpretation of palaeo-records. Whether the EUC was indeed stronger during the glacial cannot currently be resolved. However, if the proposed O_2 injection by the glacial EUC is discounted, an alternative mechanism has to be found to decouple denitrification intensity from primary production in the ETNP.

The glacial-interglacial δ^{18} O transition in benthic foraminifera should be recorded at the same time off Mexico and off Oregon. The timing of the δ^{18} O change in Mexican core NH 22P based on its radiocarbon chronology [*Ganeshram and Pedersen*, 1998] indeed corresponds to that in core 13PC off Oregon, independently dated using radiocarbon dates (Fig. 2.9, top). This good correspondence in turn indicates that the chronologies of both cores are sufficiently accurate to allow an intercomparison between both records (within an error margin of \pm 0.5 kyrs). Comparing δ^{15} N in both cores shows that the glacial-interglacial $\delta^{15}N$ variations occur approximately synchronously at these two sites (Fig. 2.9, middle), giving support to the vital role of the CUC in transporting isotopically heavy nitrate northwards. Comparing downcore organic carbon concentration profiles, on the other hand, indicates that the glacialinterglacial %Corg transition in Mexico lags that off Oregon by several thousand years (Fig. 2.9 bottom). Acknowledging that organic carbon burial might be affected by changes in sediment accumulation rate at each site, we also compare organic carbon concentrations normalized to aluminium (C_{org} /Al) and C_{org} mass accumulation rates in both cores (Fig. 2.10). Changes in C_{org} /Al ratios confirm the temporal offset between both sites. Comparing mass accumulation rates is more ambiguous. The close spacing of ¹⁴C dates in Nearshore core W8709-13PC leads to abrupt changes in sedimentation rates, which directly translate into abrupt changes in Corg mass accumulation rates. Nevertheless, the general Corg accumulation rate increase after the last glacial seems to occur earlier off Oregon than off Mexico. Taken together, these records strongly suggest that the temporal offset between the two sites is a robust feature. It seems to indicate a so far undescribed time-transgressive development of upwelling-favourable northerly winds along the NW American coast after the last glacial, with those in the north $(\sim 40^{\circ}N)$ increasing several kyrs earlier than those in the south ($\sim 20^{\circ}N$).



Fig. 2.9: Comparison of benthic δ^{18} O, δ^{15} N, and C_{org} of Mexican margin core NH22P and Oregon core W8709-13PC plotted according to their independent chronologies. NH22P data and time scale are from *Ganeshram et al.* [2000] and *Ganeshram and Pedersen* [1998]. W8709-13PC δ^{18} O data are from *Lund and Mix* [1998] and chronology is from *Mix et al.* [1999] and *Lund and Mix* [1998]. Diamonds on Y-axes in middle and lower panel indicate surface sediment values at the Oregon site. Note that the Y-axis is different for both sites in the lower panel. The glacialinterglacial δ^{18} O transition is recorded at the same time at both sites (± 500 yrs). Note the synchronous response in δ^{15} N but the lag in C_{org} off Mexico

Relative to δ^{18} O benthic, %C_{org} increases approximately synchronously off Oregon (Fig. 2.9) but lags δ^{18} O off Mexico [Fig. 3 in Ganeshram et al., 2000]. Recently, Herbert et al. [2001] found that sea surface temperatures (SSTs) in the CC region warmed 10,000 to 15,000 years in advance of deglaciation as recorded by benthic δ^{18} O. This earlier SST warming is most pronounced in the central CC (32°N) and somewhat smaller at the northern limb of the CC (41°N). It is thought to represent a collapse of the relatively cool CC during maximum glaciation, allowing the warmer gyre waters to move shorewards. South of the modern CC (22°N), early deglacial warming is absent and SST rose in concert with deglaciation and benthic $\delta^{18}O$ [Herbert et al., 2001]. Combining our findings with those of Herbert et al. [2001] south of the CC, it follows that primary production and upwelling-favourable winds lag SST and δ^{18} O benthic by several kyrs after the LGM in this region. At the northern limb of the CC, however, primary production rises synchronously with $\delta^{18}O$ and only slightly lags SST. As the Cordilleran and Laurentide ice sheets melted back (and δ^{18} O benthic rises), one would expect to see an increase in upwelling along the NW American margin [Kutzbach, 1987; COHMAP, 1988; Lyle et al., 1992]. The Oregon records thus fit this picture but the apparent delay of upwelling to the south is not easily explained within the current understanding of climate evolution after the LGM. There does not seem to be a significant difference in mean insolation forcing between 40°N and 20°N [Laskar, 1990]. We speculate that the more northern latitudes might be more sensitive to atmospheric changes caused by the melting ice sheet. Alternatively, there might be yet unknown conditions in the tropical ocean that prevent northerly winds from developing in concert with the melting ice. Hindcasting these regionally diverse responses of single components in the ocean atmosphere system and examining their apparent decoupling using climate modeling will eventually lead to a better understanding of the climate system.



Fig.2.10: C_{org} /Al ratio and C_{org} accumulation rate records of Mexican margin core NH22P and Oregon core W8709-13PC plotted according to their independent chronologies. W8709-13PC C_{org} /Al data are from *Dean et al.* [1997] and *Gardner et al.* [1997], *see* Fig. 2.9 for other references. Thick black line in the bottom panel is the smoothed average accumulation rate in Oregon core W8709-13PC (calculated using the software KaleidaGraph). Note that Y-axes are different for each site.

7. Summary and Implications

Annual nitrate utilization off Oregon is complete and there is no significant diagenetic alteration of the $\delta^{15}N_{PN}$ signal in the water column or at the sediment-water interface. Combined with similar findings farther south, this observation makes sedimentary $\delta^{15}N$ a reliable tracer of subsurface nitrate along the NW American margin from at least 20° to 45°N. Isotopically heavy nitrate generated in the ETNP today is exported northward along the NW American coast via the CUC to at least 45°N. Although subsurface $\delta^{15}N_{nitrate}$ values decrease progressively towards the north, they are still higher than the global deep water average in the entire CCS region. Consequently, isotopically heavy nitrate is recorded at sites far beyond the boundaries of the denitrification zone in the ETNP.

The glacial-interglacial pattern in sedimentary δ^{15} N is remarkably similar in timing and amplitude along the entire NW American margin, despite a general decrease in δ^{15} N values away from the ETNP. High values during the Holocene, OIS 5 and some periods during OIS 3 at the Oregon sites most likely reflect relatively strong denitrification in the ETNP and a strong CUC. Approximately at the same time, palaeoproduction indicators imply coastal upwelling was active off Oregon. During glacial Stages 2 and 4, δ^{15} N values are relatively low and coastal upwelling strength off Oregon was significantly reduced. To a lesser degree, upwelling was also reduced between 13.6 and 11.6 ka BP, a period possibly correlative with the Younger Dryas and during millennial-scale intervals in OIS 3 which seem to occur on a similar frequency as Heinrich events in the North Atlantic. While sedimentary δ^{15} N and palaeoproduction indicators vary approximately synchronously in records outside the modern denitrification zone, δ^{15} N clearly leads palaeoproduction proxies within the ETNP after the LGM and at the Stage 4/3 and 6/5 boundaries by several kyrs. This lead implies a

decoupling in the vertical dimension of surface and subsurface processes during the glacial-interglacial and stadial/interstadial transitions.

Circulation changes in the equatorial Pacific offer an explanation for this decoupling. Stronger easterlies during cold periods, such as the LGM, Heinrich events and Dansgaard-Oeschger stadials, would force a stronger EUC and increase oxygen advection into the ETNP, thereby reducing denitrification. During warm periods of low O_2 advection and strong denitrification, the CUC could transport heavy nitrate northwards in a similar fashion as today. In contrast to local productivity change by itself, this mechanism can accommodate the decoupling of local surface production and denitrification rates in the ETNP. At the same time, it provides an atmospheric link between denitrification intensity in the eastern Pacific, horizontal advection of heavy nitrate into the mid-latitude eastern Pacific and global climate change.

Along the northwest American margin, northerly, coastal upwelling favourable winds have intensified in a time-transgressive fashion after the LGM, with those in the north (~40°N) starting several kyrs before those in the south (~20°N). Together with recent results by *Herbert et al.* [2001], this points to a regionally diverse response of single components of the ocean-atmosphere system within the NE Pacific.

8. References

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Chapter 3:

Sedimentary redox conditions on the northeast Pacific margin over the last 70 kyrs as reflected in the distribution of redox-sensitive trace elements

3.1. Introduction

3.1.1 Scope of this Chapter

Due to its vast size, the deep ocean has a large capacity to store heat and certain dissolved chemical species, both of which can play a role in the planetary climate system. Acknowledging that changes in deep water circulation influence Earth's climate, palaeoceanographers have tried to reconstruct changes in deep water formation and movement during the Quaternary. In this context, the deep Pacific Ocean, albeit volumetrically the most important ocean basin, has received the least attention, mainly because of the poor preservation of traditional calcium carbonatebased palaeoceanographic proxies, such as the carbon and oxygen isotopic composition $(\delta^{13}C \text{ and } \delta^{18}O)$ and the Cd/Ca ratio of benthic foraminifera. The sedimentary concentration of redox sensitive trace metals potentially offers an alternative proxy for reconstructing deep water conditions, and has shown great promise in identifying periods of reduced O2 concentration in deep waters during various periods of Earth's history [e.g. Calvert and Pedersen, 1993; Piper and Isaacs, 1995; Piper and Isaacs, 1996; Crusius et al., 1999; Pailler et al., 2002]. One goal of this thesis was to generate a record of variations in redox sensitive trace metals in the deep Pacific and to compare it with existing deep water proxy data(δ^{13} C) from the same core [Lund and Mix, 1998; Mix et al., 1999], as well as with trace metal records from shallower sites along the California margin. This chapter will present such comparisons and interpret geochemical similarities and contrasts in terms of oceanographic processes that have influenced the margin during the last 70,000 years.

3.1.2 The Deep Circulation of the Pacific Ocean in the past: Status quo and open questions

The nature of deep water circulation in the Pacific on glacial-interglacial or even millennial time scales is still an open question. The upper water column in the subarctic NE Pacific appears to have been even more stable during the last glacial maximum (LGM) compared with today [Zahn et al., 1991], and glacial deep water formation in that region thus appears highly unlikely. However, benthic δ^{13} C data throughout the Pacific Ocean consistently point to a better ventilated (i.e. younger) water mass at intermediate depths (ca. 800-2000 m) during the LGM, possibly originating from the modern NPIW source region in the far NW Pacific. By contrast, no significant change is seen in benthic for a miniferal δ^{13} C at deeper sites, indicating that there was no significant ventilation change during the LGM deeper than approximately 2000 m [Duplessy et al., 1988; Duplessy et al., 1989; Keigwin, 1998; Matsumoto et al., 2002]. However, these isotopic results are in conflict with Cd/Ca ratios of benthic foraminifera, which point to reduced Cd concentrations, and thus better ventilated water in the glacial deep North Pacific [Ohkouchi et al., 1994]. Based on grain size as well as isotopic proxies, Hall et al. [2001] recently inferred a stronger Deep Western Boundary Current and intensified Antarctic Deep Water injection into the Southwest Pacific during glacials. A stronger inflow of deep water from the south could potentially lead to a faster turnover rate of Pacific Deep Water, thus ventilating the deep Pacific from below, as suggested by Lund and Mix [1998], thereby reducing its carbon storage potential.

At intermediate water depths, evidence from lamination patterns, benthic faunal assemblages, and trace metal enrichments from the Santa Barbara Basin and the

California Margin points to a weakening of the NE Pacific Oxygen Minimum Zone (OMZ) during the Younger Dryas cooling (YD, 12.9-11.6 kyrs B.P.), the LGM and during the cold stadials of oxygen isotope Stage 3 [*Keigwin*, 1987; *Kennett and Ingram*, 1995; *Behl and Kennett*, 1996; *van Geen et al.*, 1996; *Cannariato and Kennett*, 1999; *Mix et al.*, 1999; *Zheng et al.*, 2000b; *Ivanochko and Pedersen*, 2003 submitted; *Hendy and Pedersen*, 2003, in preparation]. Conversely, the OMZ is thought to have intensified during the Bølling-Allerød warming (BA, 14.7-12.9 kyrs BP) and warm interstadials of Stage 3. The changes in O₂ concentration at this depth range are thought to reflect changes in 1) NPIW ventilation 2) the depth of intermediate water masses and/or 3) large scale biological productivity that modifies the intensity of the region's OMZ.

Relatively little is known about the history of the deep waters along the California Margin. Carbon isotopic data from core 13 PC ([Lund and Mix, 1998; Mix et al., 1999] Fig. 1.2) indicate repeated millennial-scale changes in PDW ventilation, whereby PDW appears to become better ventilated during stadial events in the North Atlantic between 20-60 kyrs BP as well as during a period centered at 13 kyrs BP. The latter is possibly in phase with the Antarctic Cold Reversal (ACR, 12.2 –13.7 kyrs BP). These authors propose that changes in the northward flow rate of Pacific Bottom Water and return southward flow of deep water could modify the properties and age of PDW from below. Such changes could be caused by 1) increased bottom water formation near Antarctica (AABW) during cold intervals [Rahmstorf, 1995; Hall et al., 2001], 2) an increased burden on the Pacific to export deep water to the Antarctic when input of North Atlantic deep water to the Antarctic Common Water is reduced during glacials [Lund and Mix, 1998; Mix et al., 1999] and 3) the formation of new deep water in the NW Pacific itself [Curry et al., 1988; Ohkouchi et al., 1994].

Given the scarcity of deep water data from the western North American margin, the downcore concentrations of a select group of redox sensitive trace metals were studied in a deep-water core from this area, in order to understand better glacialinterglacial changes in sedimentary redox conditions along the deep California Margin. Determination of the history of the deep waters in the NE Pacific over the same time frame added a further dimension to the study. To accomplish these objectives, analytical results from core 13PC are compared in this chapter to a nearby record from an intermediate water depth (ODP Site 1019, 977 m depth, Fig.1. 2). The comparison is intended to allow separation of the effects on the sedimentary record of regional organic carbon input from the surface and far-field deep water ventilation changes. These records are then compared to the benthic foraminiferal δ^{13} C signal which, as will be shown, provides a lower boundary for the scale of past variability in ventilation and allows to asses the biasing effect of locally derived, isotopically light carbon on the δ^{13} C signal of the benthic foraminifera *C. wuellerstorfi* and *Uvigerina spp*.

3.2 Geochemistry of redox sensitive metals

3.2.1 General overview

The concentrations of manganese (Mn), rhenium (Re), silver (Ag), cadmium (Cd), molybdenum (Mo), and uranium (U) in core 13PC (125°45.00'W/42°07.01'N, 2712 m) were determined by isotope dilution ICP-MS using the analytical methods described in Appendix II. The soluble forms of Ag and Cd in sea water are precipitated in anoxic sediments (defined here as containing H₂S but no O₂) as insoluble sulfides. Mo is sequestered in anoxic sediments either by progressive sulphidation of molybdate and adsorption of thiomolybdate species or reduction of Mo(VI) to Mo(IV) and coprecipitation in sulphide phases [Helz et al., 1996; Erickson and Helz, 2000]. Re is reduced under suboxic conditions (defined as no H_2S , no O_2) and precipitates, possibly as ReO_2 (T.F. Pedersen, personal communication 2003) while U is reduced at a lower redox potential (thus under anoxic conditions) and precipitates possibly as uraninite, UO_2 [Langmuir, 1978; Anderson and Fleischer, 1991; Chase et al., 1991]. The sedimentary concentrations of all metals are directly affected by their different behaviours in sea water: Re and Mo (and to a large extent U) behave conservatively, i.e. their concentration covaries only with salinity (Table 3.1). Cadmium, on the other hand, is a micronutrient and is quantitatively removed from the surface ocean by plankton growth and released in deeper parts of the ocean and the upper part of the sediment during the remineralization of organic matter. Silver is incorporated into the frustules of coccolithophorids and especially diatoms [Fisher and Reinfelder, 1995], the latter being the main primary producers in the coastal upwelling regime off Oregon [Hood et al., 1990; Chavez et al., 1991; Hood et al., 1991; Sancetta et al., 1992]. Silver and Cd are thus mainly delivered to the sediment during the remineralization of organic matter.

	abundance in	concentration	behaviour in	main processes controlling accumulation
	upper crust ¹	in sea water ²	sea water	suboxic sediments
Re	0.5 ppb	40 pmol/kg	conservative	diffuses across sediment-water interface
				to precipitation depth, exact removal
				mechanism unknown
Ag	50 ppb	0.5 – 35 pmol/kg	nutrient-type	probably delivered to sediment during
				organic matter diagenesis, especially that
				of diatom-derived organic matter,
				precipitation as sulphide and/or selenide
Cd	0.098 ppm	0.002 -1 nmol/kg	nutrient -type	delivered to sediment via organic matter
				diagenesis, precipitates in the presence of
				microquantities of HS ⁻
Мо	1-2 ppm	100 nmol/kg	conservative	diffuses across sediment-water interface
				to precipitation depth, HS ⁻ required at
				threshold levels to precipitate
U	2.8 ppm	14 nmol/kg	conservative	diffuses across sediment-water interface
				to precipitation depth, precipitation
				controlled by kinetic factors
Al	8.04 %		scavenged	supplied by terrigenous input (alumino
				silicates), behaves conservatively in the
				sediment
Mn	600 ppm		scavenged	accumulates as Mn-hydroxide on
				sediment surface under oxygenated
				conditions
Ba	550 ppm		nutrient -type	precipitates as BaSO₄ in
				microenvironments containing decaying
				organic matter

Table 3.1: Overview of Re, Ag, Cd, Mo and U geochemistries

¹: Taylor and McClennan [1985]
²: Nozaki [2001], see text for additional references.

Each of the metals is immobilized in the sediment at specific redox boundaries depending on their redox characteristics, and this causes the more or less continual supply of dissolved metal by diffusion from bottom waters or from the surficial layers of the sediment along a concentration gradient established by their removal depths. Metal accumulation is thus intrinsically linked to the early diagenetic degradation of organic matter, during which pore water O₂ and NO₃, solid phase MnO₂ and FeOOH, and lastly pore water SO_4^{2-} are sequentially depleted [Froelich et al., 1979]. The depth range over which these redox reactions take place is controlled, in principle, by the rain of organic matter to the sea floor and the consumption of oxidants within the sediment. A high organic matter rain will cause a shallow redox boundary, and result in a steep concentration gradient and elevated metal accumulation. At steady state and constant organic carbon flux, the redox boundary will move upwards at the same rate as the accumulating sediment, resulting in continuously elevated metal concentrations. Metals precipitated under these conditions are referred to as authigenic, in contrast to the detrital metal fraction delivered to the sediment within terrigenous aluminosilicate phases. Under steady state conditions, metal enrichments can thus be used to infer past redox conditions of the sediments. However, a sudden change in sedimentary conditions, such as a decrease in the organic carbon flux or sedimentation rate, or an increase in the supply of O2 via bottom water, can lead to a fixation or deepening of the redox boundary [Wilson et al., 1986]. Whereas a fixation of the redox boundary will result in reduced metal precipitation, a deepening of the redox boundary will lead to redissolution or "burn down" of authigenic metals [Rosenthal et al., 1995b; Thomson et al., 1995; 1996; 1998; Crusius and Thomson, 2000, 2003]. It is also important to keep in mind that because metal precipitation occurs below the sediment water interface, the. same palaeoceanographic event will be recorded at greater depth (up to a few cm) by redox-sensitive metals than by other proxies, such as organic carbon or foraminifera [Donnadieu et al., 2002].

3.2.2 Modern redox conditions at the Nearshore site

Core site W8709-13PC at 2712 m water depth is bathed by PDW. The concentration of dissolved oxygen in the bottom water is ~100 µM [Levitus et al., 1994], and the organic carbon flux from the surface averages 4 g $/m^2/yr$ [Lyle et al., 1992]. No pore water measurements are available from this site with which we could assess modern redox conditions. However, a colour change from dark brownish gray to olive gray occurs at 1 cm depth in boxcore W8709-9BC at the same site [Lyle, 1987 unpub.]. This colour change, which most likely represents the FeOOH (i.e. $Fe^{3+}to Fe^{2+}$) redox boundary [Lyle, 1983], is often used as a convenient visual marker of the oxic/suboxic boundary [Thomson et al., 1996; Thomson et al., 1998]. Consistent with this observation, solid phase Mn (the presence of which in the common oxyhydroxide form requires O₂ in bottom waters) is present at the boxcore surface, but drops to crustal background values in a 1 cm thick sample taken between 2-3 cm core depth (Fig. 3.1). These two lines of evidence suggest a maximal O_2 penetration depth of ~ 1.5 cm, which is consistent with pore water oxygen measurements at sites at comparable depths within the California Current system (sites F and G at 36°16' N/ 122°20'W, 2000 m and 36°10' N / 122°40′W, 3250 m, respectively; [Jahnke et al., 1990]). Below this depth, the sediment is suboxic. The approximate depth of the suboxic-anoxic boundary can be inferred from pore water sulphate measurements at sites F and G and ODP site 1020 (41°00.05' N/ 126° 26.07'W, 3038 M, [Lyle et al., 2000]). At sites F and G, sulphate concentrations do not decrease within the top 30 to 40 cm of the sediment, and this finding most likely suggests minimal sulphate reduction and HS⁻ generation above 40 cm. Low resolution pore water measurements at nearby ODP site 1020, however, reveal that sulphate concentrations have already markedly declined from sea water values of 28 mM to 25 mM at 5 m depth below the sea floor. By analogy with these sites, the onset of

sulphate reduction and HS- generation at the Nearshore site probably occurs deeper than 40 cm, but significantly shallower than 5 m.



Fig.3.1: Total Mn concentration of box core W8709-9BC at the Nearshore site versus depth. Dashed vertical lines indicate depth range averaged in the uppermost 3 samples; the remaining samples average 2 cm intervals. Arrow on x-axis marks the abundance of Mn in average crust [*Taylor and McClennan*, 1985]. The decrease in solid phase Mn represents the onset of suboxic conditions in the sediment (shaded).

3.2.3 The marine geochemistries of Mn, Re, Ag, Cd, Mo, and U

Manganese

In oxygenated sea water, Mn occurs predominantly as the divalent species in dissolved form and as Mn^{3+} and Mn^{4+} in solid MnOOH and MnO₂, collectively referred to as Mn-oxyhydroxides [Calvert and Pedersen, 1996]. Mn oxyhydroxides are reduced under suboxic conditions, and soluble Mn²⁺ is the dominant species. Manganese enrichments are observed in deep sea sediments where the accumulation rate of biogenic and detrital material is low compared to the accumulation rate of authigenic Mn oxyhydroxides and a low supply rate of organic matter allows oxic conditions to persist to great sediment depths [e.g. Finney et al., 1988; Calvert and Pedersen, 1996]. In areas of high productivity, where oxic (sediment surface) and suboxic (subsurface) conditions are juxtaposed, Mn is actively recycled between the two horizons. The burial of solid Mn oxyhydroxides transports Mn^{4+} into the suboxic layer, and the dissolved Mn^{2+} released into the pore waters diffuses down into the sediment and up into the overlying oxic zone where it is reprecipitated. This process (the "manganese pump") traps Mn passing through the accumulating sediment into a layer highly enriched in solid Mn oxyhydroxides close to the sediment surface. It can also build up Mn²⁺ concentrations in the suboxic part of the sediment until a mixed Mn carbonate phase precipitates [e.g. Froelich et al., 1979; Middelburg et al., 1987; Calvert and Pedersen, 1993, 1996]. All authigenic Mn enrichments in marine sediments hence require oxygenated bottom water and oxic conditions in the surface sediments.

Rhenium

Rhenium is present at relatively high concentrations (40 pmol/kg) in sea water relative to other trace metals of similar crustal abundance because of the high solubility of the oxyanion (ReO₄) in aqueous environments [Koide et al., 1986; Anbar et al., 1992; Colodner et al., 1993]. It behaves conservatively in oxygenated [Koide et al., 1987; Anbar et al., 1992] and possibly even anoxic [Colodner et al., 1993; Colodner et al., 1995] sea water with an estimated residence time of 780 kyrs [Morford and Emerson, 1999]. The metal is highly enriched in mildly reducing, suboxic sediments and perhaps to a lesser extent in anoxic sediments [Morford and Emerson, 1999; Crusius and Thomson, 2000; Nameroff et al., 2002]. Its precipitation does not appear to be controlled by the formation of a sulphide species [Colodner et al., 1993], and occurs before that of Mo, which requires HS⁻, in the diagenetic sequence [Crusius et al., 1996]. Given its extremely low detrital concentrations (0.5 ppb; Taylor and McClennan [1985]) Re is an ideal tracer for authigenic accumulation under suboxic conditions.

Silver

Although Ag does not appear to have an essential role in cell metabolism [Fisher and Wang, 1998], it displays a typical nutrient-type profile with low concentrations at the sea surface (~0.5 pmol/kg) and higher concentrations at greater depths [35 pmol/kg; Murozumi, 1981; Martin et al., 1983; Zhang et al., 2001]. Its depth distribution correlates significantly with that of silicic acid [Flegal et al., 1995; Zhang et al., 2001], and this is consistent with the results of laboratory experiments which have shown that marine algae, especially diatoms, posses an extraordinary ability to accumulate Ag from sea water with concentration factors (concentration in organism/concentration in medium) of 10⁴ [Fisher and Reinfelder, 1995]. Silver uptake evidently occurs by passive absorption to the cell wall of living and dead cells. Once absorbed, Ag remains very strongly bound to the cell membrane, and sinking phytoplankton aggregates are thus thought to export the metal efficiently out of the surface ocean [Connell et al., 1991; Fisher and Wente, 1993]. Preliminary evidence suggests a positive correlation between diatom production and Ag accumulation in marine sediments (Friedl, Pedersen, Crusius, *unpub. data*, 2000). This appears to indicate that, upon degradation of biogenic material, Ag is released to the pore water and sequestered as an authigenic phase. As a type-B metal cation, Ag (I) exhibits a high affinity for sulphur and can be strongly bound to inorganic and organic sulphur S(II-) groups [*Stumm and Morgan*, 1996; *Bell and Kramer*, 1999]. Moreover, Ag (I) exchanges for other metals (e.g. Fe, Zn, Pb, Cd, As) more weakly bonded to S(II-) in metal sulphides [*Bell and Kramer*, 1999] and appears to sorb rapidly onto amorphous FeS [*Adams and Kramer*, 1998]. It is thus highly likely that Ag is sequestered into reducing sediments as the sulphide (e.g. AgS₂) in the presence of HS⁻. Additional binding, presumably to organic matter, has also been demonstrated [*DiToro et al.*, 1996]. Alternatively, *Crusius and Thomson* [2003] suggest that Ag may be sequestered by precipitation of a silver selenide species in mildly reducing environments.

Cadmium

Like Ag, Cd displays a nutrient-type distribution in the ocean with very low concentrations (~0.002 nmol/kg) in oligotrophic surface waters and higher concentrations in (~1.1 nmol/kg) in intermediate and deep waters [*Bruland*, 1980; *Knauer and Martin*, 1981]. This distribution most likely reflects the biological requirement of cadmium during carbon fixation through the formation of the enzyme carbonic anhydrase [*Morel et al.*, 1994; *Lee et al.*, 1995]. The concentrations of Cd and phosphorus in the open ocean (below the mixed layer [*Knauer and Martin*, 1981; *Boyle*, 1988]) and in newly upwelled water [*van Geen and Husby*, 1996] are highly correlated. The estimated residence time of Cd with respect to riverine inflow is 30-150 kyrs [*Morford and Emerson*, 1999]. The metal only has only one redox state (Cd²⁺) and occurs principally as CdCl⁻ in oxygenated sea water.

Cadmium is enriched over its crustal abundance (0.1 ppm, [Taylor and McClennan, 1985]) in anoxic, sulphide bearing-sediments [Calvert and Pedersen, 1993], as well as in suboxic sediments from continental margins [Pedersen et al., 1989; McCorkle and Klinkhammer, 1991; Rosenthal et al., 1995a; Rosenthal et al., 1995b; van Geen et al., 1995]. In these environments, its removal is probably related to its strong tendency to form insoluble sulphides [Elderfield, 1981; Gobeil et al., 1987; Jacobs et al., 1987; Gobeil et al., 1997], even when HS is present only in small amounts ($\leq 4 \mu mol/kg$).

Cadmium is delivered to the sediment both by diffusion from bottom waters and, due to its role in the biological cycle, via sinking organic matter [*Collier and Edmond*, 1984]. Concentrations typically increase sharply over bottom water values just below the sediment water interface, then decrease to lower values at greater depths [*Gobeil et al.*, 1987; *McCorkle and Klinkhammer*, 1991; *Gobeil et al.*, 1997]. This pattern is consistent with the release of Cd from decomposing organic matter at the sedimentwater interface, whence it then diffuses upward into the bottom waters as well as downward into the sediment where it is subsequently precipitated near the top of the anoxic zone.

Although both Ag and Cd are involved in the biological cycle and are transported to the sediment via sinking particles, Ag is most likely mainly supplied by frustule-bearing phytoplankton such as diatoms, whereas Cd is supplied by all species of phytoplankton due to its involvement in carbon fixation.

Molybdenum

Although Mo is a biologically essential element [Williams, 1994], it is sufficiently abundant (100 nmol/kg) relative to biological requirements that its distribution in the ocean is almost entirely conservative, with a small depletion is surface waters [Collier, 1985]. Molybdenum (VI) is the stable oxidation state in oxygenated seawater, and the metal occurs as the molybdate ion (MoO_4^{2-}) . The unreactive nature of Mo in oxygenated sea water is reflected in its long residence time of 800 kyrs [Morford and Emerson, 1999]. The marine geochemistry of Mo is characterized by 1) its removal into HS⁻-containing sediments under anoxic conditions and 2) its association with manganese oxides under oxygen replete conditions. Thus, solid phase Mo is strongly enriched over average crustal values in surface sediments from anoxic basins, [e.g. Jacobs et al., 1987; Francois, 1988; Emerson and Huested, 1991; Crusius et al., 1996] and in highly oxygenated sediments containing high concentrations of solid phase MnO₂ [Shimmield and Price, 1986]. Mo is also enriched in subsurface sediments from the deeper, stagnant part of the Santa Barbara Basin and the Santa Monica Basin at ~600 m depth [Shaw et al., 1990; Zheng et al., 2000a]. A compilation of sediment surface Mo and bottom water O_2 concentrations indicates that Mo tends to be enriched in surface sediments where bottom water O₂ levels fall below 10 μ M [\cong 0.25 mL/L; Zheng et al., 2000a].

The fundamental control on Mo precipitation under anoxic conditions appears to be the amount of sulphide available in the water column or in the sediment pore water. When HS⁻ concentrations reach critical levels, tetrathiomolybdate (MoS_4^{2-}) forms, which is very susceptible to scavenging by Fe phases and organic substances [*Helz et al.*, 1996; *Erickson and Helz*, 2000]. This "geochemical switch" occurs under laboratory conditions (anoxic solution at 25° C and 1 atm) at ~11 µM [*Erickson and Helz*, 2000]. The results of an independent field study [*Zheng et al.*, 2000a] are in good agreement with these laboratory studies. Based on trends of solid phase Mo and dissolved Mo, Fe and H_2S in several box cores from contrasting redox conditions, there appear to be two thresholds for the formation of authigenic Mo in marine sediments. Thus, a sulphide concentration of 0.1 μ M close to the sediment water interface seems to be sufficient for the onset of Mo precipitation (presumably Mo-Fe-S co-precipitation), whereas a higher threshold sulphide concentration between 100 and 300 μ M is required for Mo precipitation in the absence of dissolved Fe (possibly as a sulphide phase or as particle bound Mo).

Under oxygenated conditions, manganese oxyhydroxides capture Mo by surface adsorption and facilitate its transport to the sediment surface [Bertine and Turekian, 1973; Berrang and Grill, 1974; Calvert and Pedersen, 1993]. The fate of Mo is then coupled to that of the Mn oxyhydroxide host, which is stable only in the presence of oxygen. Manganese enrichments are found in pelagic sediments as well as in continental margin sediments under high productivity regimes. In the latter environment, Mo is released to pore water when Mn oxyhydroxides redissolve reductively during burial into more reducing subsurface sediments. It is recaptured by renewed Mn oxide formation near the sediment water interface when O_2 becomes available. The metal may then be removed from the pore water where HS- is produced at greater depths. Recycled Mo has a constant ratio to Mn [Mo/Mn ~ 0.002, Shimmield and Price, 1986].

Uranium

Uranium behaves conservatively in oxygenated and anoxic sea water and is present as U(VI) in the stable and highly soluble uranyl carbonate complex $[UO_2(CO_3)_3^4]$] [*Ku et al.*, 1977; *Langmuir*, 1978]. Its estimated residence time is 250-500 kyr [*Morford and Emerson*, 1999]. U is enriched in sediments underlying anoxic bottom waters (e.g.

[Francois, 1988; Anderson et al., 1989]) and in sediments underlying oxygenated waters where oxygen is consumed within the upper few centimeters [Klinkhammer and Palmer, 1991; Branes and Cochran, 1993; Morford and Emerson, 1999; Nameroff et al., 2002]. These observations are consistent with thermodynamic predictions that U should be reduced to insoluble UO2 (uraninite) under reducing conditions [Langmuir, 1978]. Diffusion of U (VI) from bottom waters into reducing sediments, followed by its reduction to U (IV), and subsequent absorption or precipitation is considered one of the main sources of authigenic U in these settings [Anderson and Fleisher, 1991; Chase et al., 2001]. Uranium reduction occurs after iron reduction in the diagenetic sequence [Klinkhammer and Palmer, 1991] but the exact nature of U immobilization is yet to be determined. Potential mechanisms are the specific adsorption of uranyl and Fe (II), which acts as the reductant, to mineral surfaces [Liger et al., 1999] and/or the reduction by iron and sulphate reducing microorganisms [Lovley et al., 1991; 1993]. Recent work indicates that labile, particle bound, non-lithogenic U (PNU), can contribute significantly to the sedimentary U inventory in ocean margin settings, where dissolved O₂ concentrations are low [Zheng et al., 2002]. According to this study, the contribution of PNU to the total authigenic U in sediments can be as high as 70% at shallow water depths, but is insignificant (10%) at depths comparable to the Nearshore site.

3.3 **Results and Interpretation**

The trace metal data obtained in this study are reported as absolute concentrations and as metal/aluminium (Al) ratios in Figs 3. 2 to 3. 5. Normalization of trace element concentrations to those of an immobile element (such as Al) in the same sample is common practice in geochemical studies in order to correct for dilution of the bulk sediment by mineral phases containing low concentrations of the trace element of interest (e.g. carbonates, biogenic silica, detrital components; see *Van der Weijden* [2002] for a recent review). The results are often compared to upper crust composition [*Taylor and McClennan*, 1985, *not referenced here after*] to infer the presence or absence of authigenic enrichments. In the case of core 13PC, the relatively constant downcore variations in concentration of Al (Fig. 3.2) suggest that variations in detrital sources (or dilution by other, non Al-bearing, phases) should not affect the interpretation of variability of redox sensitive metals. For this reason, the data are mainly discussed in terms of absolute metal concentrations in this chapter.

As in Chapter Two, the age model for the core analyzed is based on *Mix et al.* [1999] and *Lund and Mix* [1998]. In addition, the inferred correlation [*Mix et al.*, 1999] of the deglacial SST trend in 13PC (based on %*N. pachyderma* (sinistral), Fig. 3.6) with the Bølling-Allerød warming (14.7 –12.9 kyrs BP) and the Younger Dryas cooling (12.9 –11.6 kyrs BP) observed in Greenland ice cores is adopted here. This is done for consistency with other publications [*Mix et al.*, 1999; *Ivanochko and Pedersen*, 2003 submitted; *Hendy and Pedersen*, 2003, in preparation] only; evaluating whether or not these events are truly synchronous with climate changes in the N-Atlantic region is beyond the scope of this chapter.



Fig.3.2: Total Al concentration of core W8709-13 PC versus age. During the sample preparation, a white precipitate, presumably AlF₃, was observed in a samples at around 66 kyrs B.P. These values are likely to be erroneously low, similar to Ba analyses on the sample digests (compare Ba/Al ratio in Fig. 3.9 and see appendix II for more details).

3.3.1 Trace metal variations

Manganese

Total Mn values (500-900 ppm) are close to crustal abundance (600 ppm) throughout the core (Fig. 3.3). There is consequently little evidence for the presence of authigenic Mn phases, such as Mn carbonate. The Mn/Al ratio shows sporadic elevated values at around 16 and 18 kyrs and before 66 kyrs. The spikes around 66 kyrs, however, are most likely caused by analytical problems with the determination of Al, rendering them too low (see Fig. caption 3.2 and Appendix II). The absence of solid

phase Mn enrichment downcore, together with the Mn cap (1800 ppm) at the boxcore surface (Fig. 3.1), indicate that the balance between organic matter flux and bottom water oxygen was such as to maintain a shallow redox boundary at this site over the last 70 kyrs. Under these conditions, solid phase Mn accumulates in the presence of O_2 at the sediment surface but is dissolved upon burial into the suboxic deeper layers [e.g. *Calvert and Pedersen*, 1996]. The magnitude of the Mn enrichment at the surface coupled with its rate of burial have apparently been insufficient to boost the porewater Mn concentration to the level of supersaturation required to cause Mn carbonate precipitation.



Fig.3.3: Total Mn and Mn/Al of core W8709-13 PC versus age. Arrows on Y axis of the upper panel indicate the Mn concentrations in the corresponding box core (bc; see Fig. 3.1). Peak values in the Mn/Al ratio around 66 ka B.P are likely to be in error due to analytical problems with Al determinations at these depths (*see* Fig. caption 3.2)

Rhenium

Total Re concentrations range from 5-30 ppb (Fig. 3.4a), making Re the most enriched (10-60 x) metal compared to crustal values (0.5 ppb) of the group of metals studied here. Rhenium precipitation requires suboxic conditions close to the sedimentwater interface, and this condition appears to have been maintained over the last 70 kyrs, in agreement with the Mn data. Rhenium enrichment is particularly strong during the Holocene and at the beginning of Stage 3, between 50 and 60 kyrs B.P. There is no significant difference in the Re record between stages 2 and 3, which is in marked contrast to the Ag record and the productivity proxies (*see below*). Following a period of moderately high values centered around 13 kyrs BP, minimal values occur around 11.5 kyrs BP (Figs. 3.4a and b).

Silver and Cadmium

Silver concentrations range from 50 to 350 ppb (compared to 50 ppb in the crust) and Cd values range from 0.3 to 0.7 ppm (compared to 0.1 ppm in the crust, Fig. 3.4a). Both metals are thus mildly enriched (2-7 fold) during certain time intervals, implying that small amounts of HS- were available at these times. Silver values are elevated during the Holocene, and during most of Stage 3 (from 30 to 60 kyrs BP), with lower values during Stages 2 and 4. Cadmium, on the other hand, displays a different pattern. Similar to Ag, Cd shows high values around 66 kyrs BP, but it does not follow the marked decrease from the high values centered on 54 kyrs BP through Stage 3 seen in the Ag profile. The behaviours of the two metals are most dissimilar during the LGM, where Ag remains low and Cd increases abruptly, and during the deglaciation and the Holocene, where Cd values decline and Ag values remain high (Fig. 3.4b). In contrast to Re, Cd shows a relative maximum towards the end of the Younger Dryas period and relative minimum towards the end of the Bølling-Allerød. Note also that Ag and Re concentrations do not change at the exact same time, that is in the same depth interval.

The Re minimum during the deglaciation (at 11.5 kyrs BP) starts slightly later and lasts longer than the corresponding Ag minimum. This might be caused by slightly different precipitation depths for both metals.

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Fig.3.4: see next page



Fig.3.4: Re, Ag, and Cd concentrations of core 13 PC and the same data normalized to Al for **a**) the last 70 kyrs and **b**) the last 25 kyrs; Thin lines represent raw data, thick lines are 5 point moving averages for better visualization of overall trends; italic numbers in a) indicate oxygen isotope Stages. Arrows on Y-axes in a) indicate crustal values.

Molybdenum and Uranium

Total Mo and U concentrations range from 0.7 to 1.5 ppm and from 2.5 to 4 ppm, respectively (Fig. 3.5). Relative to reported crustal abundances (Mo: 1.5 ppm, U: 2.8 ppm, *but see below*), these metals therefore show no, or very little, enrichment. The absence of significant enrichments is strong evidence against anoxic conditions at or close to the sediment water interface at any time during the last 70 kyrs. However, the degree of enrichment of a metal obviously depends on the crustal (or other) reference value chosen, which might not always be a good representation of the detrital sedimentation in a given setting. Molydenum and U concentrations determined in Russian River and Columbia River particulates [Mo: 0.96 –1.5 ppm; U: 2 ppm, *Morford and Emerson*, 1999], are close to the crustal reference values used here, which would corroborate the very low authigenic enrichments observed (*but see* 3.3.4 *for further discussion*).



Fig. 3.5: Mo and U concentrations of core 13 PC versus age and the same data normalized to Al. Thin lines represent raw data, thick lines are 5 point moving averages for better visualization of overall trends; italic numbers indicate oxygen isotope Stages and arrows on Y-axes indicate crustal values.



Fig.3.6: Sea surface temperature (SST) estimates of core W8709-13 PC and nearby ODP Site 1019 based on the abundance of the cold water dwelling, planktonic foraminifera *N.pachyderma* (left coiling). Note that the % N.pachyderma axes are inverted to visualize SST, i.e. low percentages correspond to warm temperatures. Data and time scales of both cores are from Mix et al. [1999]. Lower panel shows Greenland Summit (GISP-2) ice core δ^{18} O data from Stuiver and Grootes [2000] on the time scale from Meese et al. [1997]. Note the good temporal agreement of the Younger Dryas (YD) cooling between all records. The onset of the interval interpreted as the Bølling-Allerød (BA) appears to lead in the marine records; however, the error associated with the marine chronologies is +/- 600 yrs at this interval so that this warming event may well be synchronous with the warming in Greenland [Mix et al., 1999].

3.3.2. Possible effects of post-depositional burndown and diagenetic redistribution of metals

Oxidative burndown and redissolution (see 3.2.1) of authigenically precipitated metals during renewed exposure to pore water O₂ has been shown to affect the distributions of the trace metals studied here [Rosenthal et al., 1995b; Thomson et al., 1996; Thomson et al., 1998; Crusius and Thomson, 2000, 2003]. Burndown typically leads to the formation of distinct re-immobilization peaks immediately below the O2 penetration depth, which is thought to be caused by downward diffusing dissolved metal upon reencountering suboxic conditions. A schematic illustration of characteristic burndown peaks is shown in Fig.3.7. Silver [Crusius and Thomson, 2003] and Cd [Rosenthal et al., 1995b] form sharp, narrow burn-down peaks (few cm), most likely related to their high affinity for HS-, which the dissolved metals encounter below the oxidation front. Uranium on the other hand forms a much broader (>10 cm) peak if burndown occurs [Rosenthal et al., 1995b; Thomson et al., 1996; Crusius and Thomson, 2000]. The shape of the Re re-immobilization peak appears to be proportional to the organic carbon content of the sediment [Crusius and Thomson, 2000]. In turbidite sequences from the Maderia Abyssal Plain that contain at least 1.5 % Corg, the Re burndown peak has a similar shape to that for U. At lower Corg concentrations, the Re burndown peak spreads over an even wider depth range (Fig. 3.7). Comparison of the positions in core 13 PC of the Ag and Cd profiles (Fig. 3.8) with the uppermost boundaries of the prominent Re maxima (at 12 kyrs and 53 kyrs BP) is instructive in assessing any influence attributable to burn down. The two Re maxima could qualify as burndown peaks, but there are no corresponding sharp (and shorter) Ag or Cd peaks at either of the two depths where Re contents are highest. Hence, no convincing evidence of burn-down peak patterns can be found in this core. This is consistent with previous findings along other continental margins, where higher sedimentation rates (>5 cm/kyrs) and shallow O₂ penetration depths help to preserve the original authigenic signal [Crusius and Thomson, 2000, 2003]. For comparison, the sedimentation rate in core 13 PC is at least between 10-20 cm/kyrs (*see Chapter* 1.5).



Fig.3.7: Schematic illustration of expected burndown peaks. Ag and Cd form sharp peaks (few cm), whereas re-immobilization peaks of U and Re tend to be broader (>10 cm, *see* 3.3.2)



Fig. 3.8: Re, Ag, and Cd concentrations versus age. Vertical lines are drawn at the upper boundaries of the prominent Re maxima at 12 kyrs and 53 kyrs BP. No corresponding peaks in the Ag or Cd record are obvious (compare Fig. 3.7), suggesting that burndown effects have not altered the metal record of 13 PC.

3.3.3 Comparison between trace metal and productivity proxies

Past primary production was estimated using the sedimentary concentrations of organic carbon, biogenic opal and total barium (see Chp. 2.2). Analytical methods are described in appendix II. The positive relationship between sedimentary Ba concentrations and surface ocean productivity has long been known [e.g. Goldberg and Arrhenius, 1958]. Barite (BaSO4) is precipitated in microenvironments containing decaying organic matter and the remains of siliceous plankton [Dehairs et al., 1980; Bishop, 1988], and is carried to the sea floor in settling organic detritus. A large set of sediment trap data has led to the definition of quantitative algorithms that allow the reconstruction of past new production in the euphotic zone from biogenic barium accumulation rates in sediments [e.g. Dymond et al., 1992; François et al., 1995; Dymond and Collier, 1996]. However, rather than estimating biogenic barium as [bioBa] = ([Ba] - $0.0075 \times [Al]$ in order to compute a quantitative estimate of past primary production, as adopted for example by Dymond et al. [1992], François et al. [1995] and Dymond and Collier [1996], the ratio of total barium to aluminium (Ba/Al) is reported here. This more qualitative approach circumvents the problem associated with the correction for detrital Ba input, which can be substantial at continental margins [Dymond et al., 1992]. Given the rather constant supply of Al to the sediment over the last 70 kyrs (Fig.3.2), changes in the Ba/Al ratio thus primarily reflect the marine Ba contribution to the sediment. Barite is relatively unreactive in oxic and suboxic sediments [Church and Wolgemuth, 1972; Gingele et al., 1999], and the Ba/Al ratio is thus expected to be a reliable productivity indicator at the Nearshore site. Downcore enrichments of biogenic opal can also be used as a qualitative indicator of past periods of high production, in this case particularly of diatoms [Nelson et al., 1995; Ragueneau et al., 2000]. Furthermore, organic carbon, like biogenic opal, is a direct product of marine primary production. Its flux below the euphotic zone is a function of net primary production at the surface and depth-dependent degradation [Suess, 1980]. Indeed, despite degradation effects in the water column and at the sediment surface, numerous studies in a variety of oceanic settings have demonstrated an overall positive relationship between primary production, organic carbon export and organic carbon burial in marine sediments [Müller and Suess, 1979; Sarnthein and Winn, 1988; Calvert et al., 1992; Pedersen et al., 1992; Calvert et al., 1995]. The three productivity tracers give a coherent picture of reduced production during the glacial Stages 2 and 4, as well as during some millennial-scale periods in Stage 3 (Fig.3.9.a). Note that the Ba/Al ratio and opal agree particularly well at the transitions from lower glacial values to higher interglacial values at 10 and 60 kyrs. Organic carbon and opal show relative maxima and minima approximately correlative with the Bølling-Allerød and the Younger Dryas, respectively (Fig. 3.9.b). Although the three proxies generally agree well, organic carbon is offset from opal and the Ba/Al ratio at the beginning of the Holocene where it appears to rise somewhat earlier than the other two proxies. The reason for this offset is not understood, but it could possibly be related to the different residence times and reactivities of the individual tracers within the upper mixed layer of the sediment [Donnadieu et al., 2002].

The maxima in Re at the beginning of Stage 3, during the Holocene, and around 13 kyrs BP generally correspond to higher inferred fluxes of productivity tracers (Figs. 3.9 a and b). However, there is a generally poor correlation between Re and the productivity tracers at the transitions from Stage 4 to 3 and 2 to 1. Consistent with the geochemical behaviour of Re (3.2.3), Re enrichments thus increase during periods of high organic carbon flux, but the response is not linear.



Fig. 3.9: see next page



Fig.3.9: Percent $C_{org'}$ % biogenic opal and the Ba/Al ratio compared to the concentrations of Re, Ag, Cd for **a**) the last 70 kyrs and **b**) the last 25 kyrs. Italic numbers in a) indicate oxygen isotope Stages. Thin lines in the Re, Ag and Cd panels represent raw metal data, thick lines are 5point moving averages for better visualization of overall trends. Note that the low cut off Ba/Al ratios at the end of the record in **a**) are most likely erroneous (*see* caption to Fig. 3.2).

The downcore Ag profile generally compares favourably with the variations in the productivity proxies (Figs. 3.9.a and 3.9.b). High values are thus interpreted here to reflect enhancement of subsurface suboxic conditions and HS- availability when organic matter flux, probably that supported by diatoms (*see* 3.2.3), was high. Note that the peaks of Ag and Re during the Bølling-Allerød are offset from each other. Ag concentrations are maximal at a deeper depth (13.6 kyrs B.P or 179.5 cm) than Re (12.8 kyrs B.P or 162 cm). This is consistent with the notion that Re precipitation does not require HS⁻ [*Colodner et al.*, 1993; *Crusius et al.*, 1996] and should thus occur at a shallower depth than Ag precipitation.

The Cd record is more difficult to interpret because there is no obvious correlation to the productivity proxies. The metal values are maximal during the deglaciation, when the productivity proxies increase from low glacial to high interglacial values. However, Cd has an intermittent minimum at the end of the Bølling-Allerød period, when %opal and the Ba/Al ratio as well as Ag and Re concentration ratios are relatively high (Figs. 3.9a and 3.9b). Conversely, Cd concentrations are maximal towards the end of the Younger Dryas, when % opal and $\%C_{\rm org}$ are much lower. This is difficult to explain with the current geochemical understanding of Cd precipitation in marine sediments (3.2.3). Whereas Ag may be predominately delivered to the sediment via diatom production, Cd is an essential element for all phytoplankton groups. The Cd pattern, and the Cd/Ag ratio (Fig. 3.10), might thus represent shifts in the predominance of diatoms over other groups of phytoplankton. If glacial primary production was simply lower, but without an ecosystem change, the Cd/Ag should remain constant. During the Younger Dryas, Stage 2 and at the end of Stage 3, however, when overall production was diminished, the Cd/Ag ratio is higher, possibly implying that phytoplankton groups other then diatoms were more important. This interpretation of the Cd/Ag ratio remains highly speculative until the palaeoceanographic significance of Ag is better understood. However, it is consistent with other lines of evidence for an ecosystem shift in the California Current region. Planktonic foraminiferal assemblages in glacial sediment sections along the Multitracer transect resemble those currently observed in the low export ecosystem of the modern Gulf of Alaska [*Ortiz et al.*, 1997]. Similarly, during glacial periods of reduced California Current flow, the migration of relatively warmer waters from the low export open gyre system towards the coast has been inferred based on SST records along this margin [*Herbert et al.*, 2001]. Such shifts could have been accompanied by ecosystem adjustments.



Fig. 3.10: The Cd/Ag ratio of core 13 PC compared to % Corg of the same core. Note the coincidence of productivity minima (low C_{org}) and maxima in the Cd/Ag ratio.

In summary, the record of redox-sensitive trace metals at the Nearshore site indicates that suboxic conditions prevailed at shallow subsurface depths over the last 70 kyrs. The depth of the suboxic-oxic redox boundary, however, has varied during this time period. The redox boundary was shallowest (about 1.5 cm by analogy with modern conditions) during the Holocene, the Bølling-Allerød, and parts of Stage 3, especially at the beginning of Stage. 3. These periods are also characterized by high organic matter flux.

3.3.4. The behaviour of Mo and U

By comparison with published average crustal values, it could be concluded that there are no authigenic Mo enrichments in core 13PC (Fig.3.5, Table 3.1). However, apart from a molybdenum maximum centered around 25 kyrs, the downcore Mo distribution is generally coherent with the Ag profile (which shows significant enrichment), C_{org} and opal concentrations and the Ba/Al ratio, (Fig. 3.11). As Mo has no direct biological source for the sediment, changes in the various detrital sources, possibly linked to glacial-interglacial climate changes, would have to be invoked to generate fortuitously a Mo record similar to that of the biogenic proxies. An alternative explanation is that the slightly higher Mo concentration in 13 PC during the Holocene and Stage 3 represents a small authigenic addition to the sediments in the presence of trace amounts of HS- that diffused upwards in the deposits during periods of high organic matter flux. The generally accepted crustal reference value of 1.5 ppm is based on colorimetric and photometric studies from the 1930s to 1950s on basic and acidic rocks, which quote an analytical detection limit of 0.2 ppm Mo [Wedepohl, 1978, and references therein].


Fig. 3.11: Downcore changes in % C_{org} , % biogenic opal, and the Ba/Al ratio compared with the of Mo and Ag records. Note the general agreement between the distribution of Mo and the productivity proxies, except for a broad maximum centered at ca. 24 kyrs B.P.

Coincidentally, 1.5 ppm is close to the detection limit for Mo determination by X-ray fluorescence (XRF, 2 ppm), a commonly used technique in geological and sedimentological studies. This might have led to the synonymous use of "below crustal abundance" and "below detection limit" in parts of the geochemical literature (T. F. Pedersen, personal communication 2002). With the advent of more sensitive analytical techniques, such as ICP-MS, the detection limits for Mo and other metals have significantly decreased (the Mo detection limit in this study was 0.5 ppm, see Table A.II.5). Consequently, the broad-scale agreement observed here between Mo and the productivity proxies might be an indication that authigenic enrichments occur, albeit in minute amounts, at concentrations below commonly accepted crustal background values. This would mean that there were sufficient pore water HS- concentrations to permit authigenic Mo precipitation at the Nearshore site during periods of enhanced organic fluxes to the sea floor. Similar to Mo, U shows elevated values around 66 kyrs, at the beginning of Stage 3, and during the Holocene (Fig. 3.5) and the same reasoning might apply to this metal. These findings imply that the commonly used crustal reference values, and also the Mo and U value observed by Morford and Emerson [1999] in local river particulates are not actually relevant to the detrital aluminosilicate background at the Nearshore site.

3.4. Comparison with ODP Site 1019

ODP Site 1019A is located very close to the Nearshore site (41°40. 963'N, 124°55.979', Fig. 1.2) at a water depth of 977m, closer to the coastal upwelling system than the more offshore site 13PC, and close to the depth range of NPIW (300-800 m). The bottom water O_2 content at present is ~20 μ M [Levitus et al., 1994], and sedimentation rates during the last deglaciation were approximately twice as high at

Site 1019 (50cm/kyrs, [Lyle et al., 2000] than at the Nearshore site (mean 20 cm/kyrs). Trace metal data from this core were kindly provided by Tara Ivanochko; *N. pachyderma* (left) abundances and $%C_{org}$ data are published in *Mix et al.* [1999], and were kindly provided in electronic form by Alan C. Mix, Oregon State University.

3.4.1 Sea Surface Temperature, C_{org} and trace metals

During the deglaciation, the dominance of the cold water dwelling foraminiferan *N. pachyderma* (sinistral) at Site 1019A and the Nearshore site provides strong support for a cold event, which, according to *Mix et al.* [1999], is essentially synchronous with the Younger Dryas cooling interval as documented in the Greenland ice cores (Fig. 3.6).

Organic carbon concentrations are similar at both sites, except for peak concentrations at Site ODP 1019 between 14-15 and 10-11.5 kyrs BP (Fig. 3.12.a). The transition from lower glacial to higher Holocene C_{org} values appears to be more gradual in the more offshore setting of 13 PC. Nevertheless, both sites show some similarity with respect to elevated C_{org} values during the Bølling-Allerød and lower values during the Younger Dryas. Although the apparent timing of the organic carbon peak at Site 1019 appears to lead the Bølling-Allerød warming by a few hundred years, *Mix et al.* [1999] point out that the error associated with the time scale of ODP Site 1019 is +/- 600 years in this time interval and that the productivity maxima observed at 1019 and 13 PC may well be synchronous with the Bølling-Allerød warming.



Fig. 3.12: Comparison of **a**) C_{org} records and **b**) Re, Ag and Mo records in core 13 PC and nearby ODP Site 1019; data and time scale for Site 1019 are from *Ivanochko and Pedersen* [2003 subm.], which is based on the calibrated radiocarbon ages tabulated in *Mix et al.* [1999]. However, it differs slightly (<300 yrs, not shown) from the one by *Mix et al.* [1999] used in Fig. 3.6 due to interpolation uncertainties. Note the difference in Y-axis at both sites. Horizontal lines in b) are drawn at the same levels of metal concentration for 1019 and 13 PC in each panel as a visual aid.



Fig. 3.12.b: see previous page

Total Re values are higher in core 13PC (3-35 ppb) compared to Site 1019 (5-15 ppb), which could be attributed to a lower dilution factor due to reduced bulk sedimentation rates at this deeper site (Fig. 3.12.b). Both records show elevated values during an interval approximately correlative with the Bølling-Allerød period. Silver concentrations are similar in both cores (200 ppb) prior to the Bølling-Allerød when productivity was lower. However, absolute Ag values are significantly higher (>500 ppb) at Site 1019 during periods of high productivity associated with the Bølling-Allerød and the early Holocene. This is consistent with the closer proximity of this site to the coastal upwelling front and the planktonic source of Ag to the sediment (see Section 3.2.3). The Ag maximum at 15 kyrs B.P. at Site 1019 appears to slightly lead that in 13 PC, however, this apparent lead is also seen in the C_{org} profile (Fig. 3.12.a) and is thus most likely caused by a slight mismatch between the age models of the cores. Since 13 PC is less than 100 km farther offshore than Site 1019, both locations most likely record the same productivity increase at that time. In summary, despite the difference in absolute values and the much more subtle Ag signal in 13 PC, Re and Ag display a consistent pattern at both sites.

The Cd trends, however, are substantially different. Cadmium concentrations at ODP Site 1019 are significantly higher at the onset of the Bølling-Allerød (2.5 ppm) and the Holocene (1 ppm) compared to 13 PC, which shows maximal values of only 0.7 ppm towards the end of the Younger Dryas. The reason for the different trends at each of these sites is possibly related to the more offshore position of core 13 PC and the inferred dominance of open ocean phytoplankton groups during periods of reduced coastal upwelling such as the Younger Dryas (*see 3.3.3*). For the time interval covered by both cores, the overall similarity between Ag and Re at both locations, however, reinforces the conclusion that the elevated Re and Ag concentrations during the

Bølling-Allerød and the Holocene in 13 PC are caused by changes in the local organic matter flux and not by changes in deep water circulation.

The Bølling-Allerød is characterized by sedimentary anoxia and high concentrations of redox sensitive trace metals in the semi-enclosed Santa Barbara Basin and the Gulf of California [Keigwin, 1987; Kennett and Ingram, 1995, Cannariato and Kennett, 1999] as well as on the open California margin at intermediate water depths [<1 km, van Geen et al., 1996; Gardner et al., 1997; Ganeshram et al., 1999; Zheng et al., 2000b; Ivanochko and Pedersen, 2003 subm.; Hendy and Pedersen, 2003, in prep.]. The low O_2 conditions have been attributed to an intensification of the OMZ caused by a reduction in NPIW ventilation [e.g. Zheng et al., 2000b] and/or lateral advection of oxygen poor waters from the ETNP by the California Undercurrent [Ivanochko and Pedersen, 2003 submitted], supported by high fluxes of surface-derived organic matter [Mix et al., 1999]. Core 13 PC at the Nearshore site is located in PDW, well below the depth range of NPIW. Its organic carbon and trace metal records should thus be unaffected by changes in NPIW ventilation. However, the productivity changes during the Bølling-Allerød at this deeper site were sufficient to elevate metal concentrations (Ag, Re). This is inconsistent with the inferred *improved* deep water ventilation shortly after the Bølling-Allerød (see below), which should have diminished the potential for metal enrichments.

3.5 Comparison of the benthic δ^{13} C signal with the trace metal record

A high resolution benthic carbon isotopic record of core 13 PC [Lund and Mix, 1998 and Mix et al., 1999; Fig. 3.13.a and b] shows repeated excursions of δ^{13} C of *Cibicidoides wuellerstorfi* towards heavier values between 10-60 kyrs BP, which were interpreted to represent periods of better PDW ventilation. These events are recorded during cold stadials of OIS 3 and during the deglaciation at around 13 kyrs BP according to the most recent chronology of this core [Mix et al., 1999]. They are superimposed on the more gradual, well known glacial-interglacial δ^{13} C shift of 0.3 ‰, which is generally attributed to glacial-interglacial changes in a) terrestrial biomass [*Shackleton*, 1977; *Curry et al.*, 1988], and also, more recently b) water column pH and carbonate ion concentration [*Spero et al.*, 1997]. To what extent is this conclusion supported by the downcore record of redox sensitive trace metal concentrations in the same core?

In most of the ocean a negative linear correlation is observed between the isotopic composition of total inorganic carbon ($\delta^{13}C_{2CO2}$) and nutrient concentrations of deep and bottom waters. The distribution of both is controlled by the interaction of biological uptake (at the surface) and decomposition of organic matter in deeper waters with the large scale circulation of the ocean [*Kroopnick*, 1985; *Mackensen*, 1999]. During photosynthesis, phytoplankton preferentially incorporate the lighter carbon isotope (12 C), leaving surface waters enriched in 13 C. Upon sinking and traveling along the path of the abyssal circulation, the remineralization of isotopically light phytoplankton detritus adds isotopically depleted carbon to deeper waters. The oldest waters in the ocean are thus characterized by the lightest δ^{13} C values [*Kroopnick*, 1985]. The δ^{13} C signal of a given water mass is recorded in the calcite tests of benthic foraminifera and

is widely used as a nutrient proxy to infer past changes in the residence time of deep and bottom waters [e.g. Curry et al., 1988; Duplessy et al., 1988; Boyle, 1992; Sarnthein et al., 1994; Keigwin, 1998; Matsumoto and Lynch-Stieglitz, 1999; Matsumoto et al., 2001; Matsumoto et al., 2002]. These reconstructions can be confounded by two effects, however. During gas exchange between surface water and the atmosphere, carbon isotopes are fractionated in a strongly temperature-dependent way such that, at isotopic equilibrium, colder water has a higher δ^{13} C composition than warmer water. This thermodynamic effect is independent of nutrient-related changes in δ^{13} C [Broecker] and Maier-Reimer, 1992; Zhang et al., 1995]. High positive deviations of $\delta 13C_{\Sigma CO2}$ from the expected correlation between phosphate and $\delta^{13}C$ occur, for example, in the source regions of AAIW [Charles and Fairbanks, 1990; Broecker and Maier-Reimer, 1992] and AABW [Mackensen et al., 1996]. Sea surface temperature cooling and stronger winds in these regions should lead to an even heavier $\delta^{13}C$ signal [Broecker and Maier-Reimer, 1992]. In addition, the δ^{13} C signal recorded in benthic foraminifera can be complicated by direct input of phytoplankton detritus in areas of high productivity, which adds isotopically light carbon to the bottom and pore waters. Originally, this phytodetritus effect (often referred to as "Mackensen effect") was observed to bias benthic species that prefer deep and shallow infaunal habitats (i.e. living below sediment water interface, such as *Uvigerina* species; towards lighter δ^{13} C values [Zahn et al., 1986]. However, this effect can also bias the carbon isotopic composition of Cibicides and Cibicidoides species [Sarnthein and Winn, 1988; Mackensen et al., 1994], but to a lesser degree. These species prefer an epibenthic or even an elevated position above the sediment water interface and are thus generally considered the most reliable foraminiferal recorders of deep water δ^{13} C.

All benthic δ^{13} C data from the original publications by *Mix et al.* [1999] and *Lund* and *Mix* [1998] as well as additional, unpublished data (δ^{13} C of *Uvigerina* from 20-60 kyrs) were kindly provided by Allan C. Mix, Oregon State University.

In theory, enhanced deep water ventilation, thus heavier $\delta^{13}C_{\text{benthic}}$, should lead to a deepening of the redox boundary and reduced precipitation of Re, Ag, and Cd in the sediment. If, on the other hand, the phytodetritus effect alters the benthic $\delta^{13}C$ signal, lighter $\delta^{13}C$ values should correspond to high fluxes of organic matter (thus increased productivity tracers) and greater metal enrichments. The data generated here, however, cannot be used to distinguish between greater gas exchange in deep water source regions (due to higher wind speed and cooler SSTs) and lower nutrient contents in deep water (due to faster circulation). Both scenarios result in the same far field effect of higher dissolved O₂ concentrations in deep water.

Assuming no other changes, the increased ventilation recorded in the δ^{13} C record of *C. wuellerstorfi* should have led to a deepening of the redox boundary and reduced precipitation of Re, Ag, and Cd. However, no clear overall correlation between heavy δ^{13} C events and reduced metal concentrations is evident during the last 70 kyrs (Fig. 3.13.a). The δ^{13} C *C. wuellerstorfi* maximum at 13 kyrs BP actually corresponds to relative minima in Ag and Cd, but in contrast to the above prediction it also corresponds to elevated Re values. Taken at face value, the elevated Re values are in conflict with the inferred ventilation event at 13 kyrs BP. However, they can be reconciled with the δ^{13} C data if a relatively shallow redox boundary was maintained during the ventilation event, mutually allowing the epibenthic *C. wuellerstorfi* to record a heavier δ^{13} C signal while Re precipitation continued at shallow sediment depth. This scenario is consistent with the light δ^{13} C values of *Uvigerina* (Figs. 3.13.a and b),

reflecting the increased input of phytodetritus at this time. As Re precipitation does not require HS⁻, this scenario is also consistent with the presence of relative minima in Cd and Ag at that time.

Relatively light δ^{13} C C. wuellerstorfi values and high productivity and trace metal values are poorly correlated over the last 70 kyrs in core 13PC (Figs. 3.13.b). This confirms the contention that C. wuellerstorfi is not affected by local phytoplankton detritus [Lund and Mix, 1998; Mix et al., 1999] and justifies its use as a monitor of deep water δ^{13} C. However, the lightest δ^{13} C Uvigerina values between 13.8 -12 kyrs BP indeed correspond to intervals of high concentrations of Re (Fig. 3.14a), high biogenic opal contents and high Ba/Al ratios (Fig. 3.13b). This would imply that the Uvigerina record has been altered by the input of isotopically light phytoplankton detritus, a conclusion different from that presented by Mix et al. [1999]. Based only on % C_{org} data, these authors inferred that the δ^{13} C record of Uvigerina, similar to that of C. wuellerstorfi, is unaltered by phytodetritus. As observed by Mix et al. [1999], Corg concentrations are already in decline when δ^{13} C Uvigerina is at a minimum, but the additional data presented here show that the Corg decline actually precedes the corresponding decreases in biogenic opal and the Ba/Al ratio. The reason for this is possibly related to the different preservation mechanisms (see 2.2) and the different residence times and reactivities of the individual productivity proxies within the sedimentary mixed layer [Donnadieu et al., 2002]. This difference highlights the value of using multiple proxies to reconstruct primary production from downcore records.



Fig. 3.13.a: see next page



Fig. 3.13: δ^{13} C records of C.*wuellerstorfi* and *Uvigerina spp.* [*Lund and Mix*, 1998] compared with **a**) Re, Ag, and Cd concentrations and **b**) C_{org}, Ba/Al and biogenic opal in core W8709-13PC. Thin lines in the Re, Ag and Cd panels represent raw metal data, thick lines are 5 point moving averages. Heavy δ^{13} C excursions superimposed on the gradual glacial-interglacial δ^{13} C shift (0.3 ‰) are thought to represent increased deep water ventilation events.

Overall, the ventilation changes inferred from the δ^{13} C record of C. wuellerstorfi have not left a marked imprint on the accumulation of redox sensitive trace metals. However, trace metal precipitation at the deep Nearshore site might not be sensitive enough to respond to moderate bottom water ventilation changes. Modern O_2 concentrations at this site are around 100 µM. Maximum carbon isotope excursions observed by Mix et al. [1999] and Lund and Mix [1998] are 0.2 ‰ vs. PDB. Such changes can be converted to changes in bottom water oxygen concentrations by using the relationship between sea water $\delta^{13}C$ and the apparent oxygen utilization (AOU) in the modern ocean given by *Kroopnick* [1985]: $\delta^{13}C = 1.5 - 0.0075^*$ AOU (R²= 0.86, *n* =2059). The 0.2 $\% \delta^{13}$ C anomalies thus translate to a ca. 20 μ M/kg change in AOU, or *in situ* O₂ concentration, assuming no other changes. This change, relative to the modern value, might not be sufficient to decrease bottom and pore water O₂ concentrations to levels that would cause the precipitation of redox-sensitive metals in the sediment. In other words, there might have been changes in deep water ventilation, but the recorder did not see them. In the case of Mo, for example, authigenic enrichments (compared to crustal abundance) at the sediment surface have not been detected in sediments under bottom water O_2 levels >10 μ M [Zheng et al., 2000a]. At the same time, the trace metal data presented here strongly suggest that the redox boundary in the sediment has migrated vertically in the sediment over the last 70 kyrs. In light of the good overall agreement between metal enrichments and productivity tracers, changes in organic carbon flux from the surface, rather than deep water ventilation changes, appear to have been the dominant control on the sedimentary redox conditions at the Nearshore site over the last 70 kyrs.

3.6 Conclusions

At the Nearshore site on the Oregon continental margin at 2712 m water depth, suboxic conditions close to the sediment-water interface have been maintained throughout the last 70 kyrs. Such conditions (as recorded by Re and Ag) were most intense (i.e. the redox boundary was at its shallowest position) during the Holocene, the Bølling-Allerød, and near the beginning of Stage 3, when organic matter flux was high. This is consistent with enrichment patterns observed at intermediate water depths along the California Margin [*van Geen et al.*, 1996; *Zheng et al.*, 2000b; *Ivanochko and Pedersen*, 2003 subm.; *Hendy and Pedersen*, 2003, in prep.], and implies that, even at almost 3000 m, subtle changes in the redox conditions caused by productivity related organic carbon flux are recorded.

The high resolution records of trace metal concentrations presented here do not show evidence of *significant* deep water ventilation changes over the last 70 kyrs. The multiproxy records do not contradict the evidence for deep water ventilation variations inferred from the δ^{13} C *C. wuellerstorfi* record, but they provide a lower boundary condition for the scale of historical variability in ventilation. Thus, the absence of high Mo and U enrichments clearly excludes the possibility that bottom water O₂ concentrations dropped to levels <10µM during the last 70 kyrs. This is in marked contrast to the sedimentary records from intermediate water depth along the California Margin [*Keigwin*, 1987; *Kennett and Ingram*, 1995; *Behl and Kennett*, 1996; *van Geen et al.*, 1996; *Cannariato and Kennett*, 1999; *Mix et al.*, 1999; *Zheng et al.*, 2000b; *Ivanochko and Pedersen*, 2003 subm.; *Hendy and Pedersen*, 2003, in prep.]. While the trace metal results presented here confirm that the δ^{13} C record of *C*. wuellerstorfi is unbiased by the phytodetritus effect, they also imply that the δ^{13} C record of *Uvigerina spp*. is affected by it during a period of increased organic matter flux between 12-13 kyrs BP.

Although Mo concentrations in core 13 PC are close to crustal abundance values, the Mo pattern over the last 70 kyrs resembles that of %Corg, biogenic opal and the Ba/Al ratio and Ag, which is authigenically enriched. This might be an indication that small authigenic enrichments (below the commonly accepted crustal abundance value) occur, and can potentially be exploited in palaeoceanographic studies.

3.7 References

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Appendix I:

Sea Surface Temperatures in the subarctic Northeast Pacific reflect millennial-scale Climate Oscillations during the last 16 kyrs

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Abstract

Changes of sea surface temperature (SST) in the subarctic NE Pacific over the last 16,000 calendar years before present (16 kyr BP) have been inferred from the study of C_{37} alkenone unsaturation in a sediment core from the western Canadian continental slope. Between 16.0 and 11.0 kyr, three distinct cold phases (6-7°C) interrupt two warmer periods (9-10°C). Within the 2 σ range of the radiocarbon based time control, the observed SST oscillations correspond to the Oldest Dryas, the Bølling, the Older Dryas, the Allerød, and the Younger Dryas periods in the GISP2 δ^{18} O record. These results represent the first high resolution marine palaeo-temperature estimates off the northern west coast of North America and imply that the climate of this region may be very strongly coupled to that of the North Atlantic. Given the fast rates of SST change (1°C/40-80 yr), such coupling must be controlled by atmospheric transmission of the climate signal.

Introduction

When the ice sheets of the Northern Hemisphere retreated during the termination of the last ice age, the climate of the North Atlantic region was subjected to a series of cold/warm oscillations known as the Oldest Dryas, the Bølling, the Older Dryas, the Allerød, and finally the Younger Dryas period. These millennial-scale oscillations are well recorded in European pollen sequences and in Greenland ice cores and may be linked to changes in the freshwater discharge of mid-latitude ice sheets into

the North Atlantic and its effect on North Atlantic Deep Water production. With the exception of the Younger Dryas cold event, the geographical extent of these climate flickerings beyond the North Atlantic area is only beginning to be explored. Evidence is emerging that the deglacial warming trend was interrupted by several cold reversals in various parts of North America. The Owens Lake record in the southwestern United States, for example, shows repeated desiccations in phase with cool episodes in Greenland (Benson et al., 1997). Evidence for a cold spell in north-western North America coeval with the Younger Dryas comes from terrestrial records in Alaska, the Canadian Rocky Mountains, as well as the Cascade Range (e.g. Engstrom et al., 1990; Reasoner et al., 1994; Grigg and Whitlock, 1998). Mathewes et al. (1993) inferred cool SSTs from peak abundances of cold-water dwelling benthic foraminifera on the western Canadian shelf during the time of the Younger Dryas.

This paper presents a direct record of SST change during the deglaciation in the NE Pacific. We analyzed di- and tri- unsaturated C_{37} alkenones which are biosynthesized in the ocean by some Prymnesiophyte algae, mainly the cosmopolitan coccolithophorid *Emiliania huxleyi*. The degree of alkenone unsaturation, defined as the $U^{K'}_{37}$ index ($U^{K'}_{37} = [C_{37:2}]/([C_{37:2}]+[C_{37:3}])$, where $[C_{37:2}]$ and $[C_{37:3}]$ denote the sedimentary concentrations of the di- and tri- unsaturated alkenone, respectively), changes linearly with growth temperature of the algae (Brassell et al., 1986; Prahl and Wakeham 1987, Müller et al., 1998).

Material and Methods

Piston core JT96-09pc and its corresponding multicore (JT96-09mc) were retrieved from 920 m water depth on the western Canadian continental slope (48°54.7′N/126°53.4′W) off Vancouver Island, British Columbia. The piston core consists of 3.74 m of undisturbed hemipelagic sediments with a distinct 16 cm thick sandy turbidite (136-152 cm). After the addition of an internal standard, freeze-dried and manually ground sediment (3-10 g) was solvent extracted according to Villanueva et al. (1997). The extracts were analyzed by manual injection into an HP 5880 gas chromatograph. An extract of a pure *E. huxleyi* culture was used to identify the C₃₇ alkenones by their retention times. Selected samples were examined by GC-MS to confirm compound identification and to check for possible coelutions. Duplicate extractions yielded temperatures within \pm 0.3°C of each other. SST values were calculated using the relationship U^K₃₇ = 0.033T+0.044 obtained in a global core top calibration, which leads to an overall accuracy of the SST estimates of \pm 1.5°C (Müller et al. 1998). JT96-09pc was spliced with its multicore based on a comparison of several proxies (CaCO₃, C_{org}, δ^{15} N) as well as one accelerator mass spectronomy (AMS) ¹⁴C date in each core (*McKay, unpubl. data*) that show that the piston core overpenetrated by ~20 cm. The 16 cm thick turbidite is considered an instantaneous deposit and 16 cm were thus subtracted from all composite depths greater than 156 cm for the age model.

Chronostratigraphy

The chronostratigraphy of this composite, turbidite-corrected record was constructed using 9 AMS ¹⁴C dates (Tab. A.I.1, Fig. A.I.1) of mixed planktonic foraminifera (mainly *N. pachyderma* with subordinate *G. bulloides*; picked from relative abundance maxima). Based on marine shells and associated wood from coastal sediments in British Columbia, the estimated reservoir age of the surface mixed layer in the NE Pacific is taken to be ~800 years for the Holocene extending into the Younger Dryas (0 to 11 ¹⁴C kyr, Southon et al., 1990), and ~1100 years from 12.1 and 13.1 ¹⁴C kyr (Kovanen and Easterbrook 2002). The radiocarbon dates of core JT96-09 have been corrected for reservoir effects and calibrated to calender years using the software CALIB 4.3 (Stuiver et al. 1998). CALIB's marine calibration incorporates a time-dependent global ocean reservoir correction of ~400 years. To account for the higher local reservoir age, we added 400 years (" Δ R") to the reservoir correction for all ¹⁴C ages younger than 12 ¹⁴C kyr, and 700 years for all the remaining ¹⁴C dates. In doing so, we assume that the reservoir ages found by Southon et al. (1990) and Kovanen and Easterbrook (2002) are also valid between 11-12 ¹⁴C kyr and 13-15 ¹⁴C kyr, respectively. To account for potential changes in the local reservoir age through time, we allowed an error of ±200 years in Δ R. Based on this input, CALIB computes a calibrated calendar age taking into account variations of ¹⁴C activity in the atmosphere and reservoir age through time (Tab. A.I.1).

CompDepth (cm)	¹⁴ C Age (kyr)	Res.Cor.	Cal Age ³ (kyr)	2σ range ⁴
		¹⁴ C Age (kyr)		(kyr)
55.5	9.76±0.07	8.96 ¹	10.03	10.59-9.46
85.5	11.21±0.12	10.41 ¹	12.29/12.24/12.12	12.91-11.32
95.5	11.50±0.11	10.70 ¹	12.80/12.73/12.65	13.74-11.68
110.5	11.60 ± 0.08	10.80 ¹	12.84	13.74-11.76
120.5	12.46±0.12	11.36 ²	13.17	13.82-12.68
150.5	12.64±0.09	11.54^{2}	13.43	14.02-12.99
185.5	10.09±0.05	9.29 ¹	10.32 *	
190.5	13.24±0.2	12.14 ²	14.08 *	
285.5	13.41±0.08	12.31 ²	14.14	15.44-13.66
310.5	13.52±0.07	12.42^{2}	14.30	15.52-13.70
370.5	14.14±0.07	13.04 ²	15.57	16.23-14.35

Table A.I.1. Radiocarbon data of core JT96-09

1) reservoir corrected -800 years (Southon et al. 1990)

2) reservoir corrected -1100 years (Kovanen and Easterbrook, 2002)

3) calibrated using CALIB 4.3 (Stuiver et al. 1998)

4) 2σ ranges from intercepts

* not included in age model



Fig. A.I.1: U^K′₃₇ SST of JT96-09mc (dashed) and pc (solid). Bold numbers indicate AMS ¹⁴C dates (kyr) determined on mixed planktonic foraminifera. Question marks indicate suspect dates and suspect SST estimates.

The 2σ range represents the combined propagated standard deviations of the ¹⁴C dates, the calibration curve and the uncertainty in the reservoir age at an 95% confidence interval (Fig. A.I.2). The age reversal at 185.5 cm comp. depth is most likely due to a mislabeled sample. The adjacent date (190.5 cm comp. depth) was analyzed to check the age reversal, but it has a large analytical error bar because it is based on a small sample. We chose to ignore these two ¹⁴C dates in the age model. The age model for core JT96-09 was constructed by linearly interpolating between the calibrated ages and assuming that the multicore top equals zero years. Two of the ¹⁴C dates (85.5 and 95.5 cm comp. depth) fall within age plateaus on the radiocarbon calibration curve and three, relatively similar, calibrated dates are possible for each of these ¹⁴C dates. In these instances, we chose the middle age for the age model. In addition to this age model, we calculated an "oldest extreme" and a "youngest extreme" age model by linearly interpolating between all the oldest and all the youngest 2σ range extremes (Fig. A.I.3, thin lines).

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Fig. A.I.2: Calibrated ages for the ¹⁴C dates (diamonds) with 2σ standard deviation. For two ¹⁴C dates (85.5 and 95.5 cm), 3 calibrated ages each are possible due to plateaus in the radiocarbon calibration curve. Question marks indicate suspect dates excluded from the age model.

Results and Discussion

Average sedimentation rates decrease from >130 cm/kyr in the older part of core JT96-09 to 4-6 cm/kyr in the upper section. The most prominent changes in SST, however, are not paralleled by major changes in sedimentation rates, thus the inferred ages of abrupt temperature events are not significantly affected by interpolation errors. Moreover, the sedimention rate is sufficiently high that bioturbation effects are not a serious concern. The sedimentation rates translate to an average time resolution of less than 100 years per sample during the deglaciation and ~500 years during the Holocene. In three samples in the lower section of the core (Fig. A.I.1) alkenone concentrations are close to an analytical threshold below which $U^{K'}_{37}$ deviations towards warmer SST occur (Villanueva and Grimalt, 1997), and old organic carbon is present, evidenced by a ~7000 yr age difference between ¹⁴C dates of bulk organic carbon and those of

planktonic foraminifera (*McKay, unpubl. data*). In light of these two conspiring factors, we believe these three SST estimates to be erroneous.

The overall SST trend of core JT96-09 resembles the pattern of deglacial temperature fluctuations recorded in the GISP2 ice core in Greenland (Fig. A.I.3). Plateaus in the radiocarbon calibration curve introduce uncertainties in any ¹⁴C based chronology during the deglaciation. Although the reservoir age of the surface mixed layer is well constrained for parts of our record (*see above*) there is no field data to cover the entire record and this might introduce additional errors. The calculation of the 2σ time scales is an attempt to address these uncertainties in a conservative fashion. Within these error bars, SST changes off Vancouver Island are coveal with δ^{18} O oscillations in the GISP2 ice core record.

SST estimates off Vancouver Island drop from ~9°C during the Allerød to ~6°C during the Younger Dryas period. After ~1400 years, they rapidly rise from ~7°C to ~12°C in less than 400 years. This direct and quantitative evidence for cool SSTs in the NE Pacific between 13.0-11.4 kyr confirms previous findings based on δ^{18} O and microfossil data that indicate a two-step deglaciation in the subarctic North Pacific (Kallel et al., 1988; Zahn et al. 1991). The SST rise that terminates the inferred Younger Dryas (1°C/80 yr) is greater than the 2-3°C rise in air temperature inferred from pollen transfer functions 300 km north of our study site (Mathewes et al., 1993), but its amplitude is very similar to the \geq 5°C SST rise observed at the end of the Younger Dryas in the Norwegian Sea at the same latitude (50°N; Lehman and Keigwin, 1992).

Today, annual SSTs of <6°C are confined to the far north-western parts of the Pacific in the western Pacific subarctic Gyre and the Bering Sea Gyre. The occurrence of SSTs as low as 6°C off the coast of Vancouver Island might represent a southeastwards expansion of these cold water systems during the Younger Dryas period, in agreement with a coupled ocean atmosphere model that predicts a strengthening and eastwards

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expansion of the Aleutian Low pressure system in response to freshwater input into the North Atlantic (Mikolajewicz et al., 1997). However, our Holocene-Younger Dryas SST



Fig. A.I.3: Comparison of $U^{K'}_{37}$ SST from core JT96-09 (thick line) and the GISP2 δ^{18} O record (Grootes and Stuiver, 1997). Triangles indicate calibrated ¹⁴C dates. Thin SST lines are shifted by +4° and -4°C and indicate the oldest and youngest possible age models based on the 2 σ standard deviation, respectively.

difference (~4°C) is significantly higher than the control vs. freshwater-event SST anomalies (max. 2°C) predicted by Mikolajewicz et al. (1997) and Manabe and Stouffer (2000) for the NE Pacific. This discrepancy corroborates findings from northern California (Mix et al., 1999) and the Santa Barbara Basin (Hendy and Kennett, 2000), where SST changes associated with the Younger Dryas are 2-3°C and 4-8°C, respectively. Taken together, these three marine SST reconstructions indicate that the models that have investigated the effect of a freshwater discharge into the North Atlantic, underestimate the Younger Dryas cooling along the entire NE Pacific margin.

The importance of the Pacific Ocean with its vast surface area may have been previously neglected in climate change studies. Peteet et al. (1997) designed a climate model that specifically tests the sensitivity of the Northern Hemisphere to changing SSTs in the North Pacific. A cooling of only -2°C (compared to today) is sufficient to decrease temperatures and increase snowcover over most of mid-latitude Europe, parts of Asia and, most importantly, the Laurentide ice sheet. By affecting the growth of the ice sheet, the Pacific "water vapor control" has the potential to influence thermohaline circulation in the North Atlantic, where the mechanisms driving global climate change are usually sought. In light of the >2°C cooling that we observe along the NE Pacific margin, the impacts on Northern Hemisphere climate described by Peteet et al. (1997) might be even stronger than suggested by their model.

In addition to the Younger Dryas, all deglacial climate reversals seen in the GISP2 δ^{18} O record seem to have a SST equivalent in the NE Pacific Ocean. The inferred Allerød in the NE Pacific is interrupted by a SST drop of ~1.5°C. We speculate that this might correspond to the intra-Allerød cold period (IACP) in the Norwegian Sea (Lehman and Keigwin, 1992). However, this cooling is only corroborated by one sample in core JT96-09.

The cooler SST in the NE-Pacific during the Oldest, the Older and the Younger Dryas would have lowered annual precipitation over the southwestern United States (Peteet et al., 1997), possibly accounting for the desiccations of Owens Lake in central northern California (Benson et al., 1997) during these periods. If the temporal correlations of this terrestrial record and our marine record to GISP2 are valid, they reveal a very dynamic climate history of North America. SSTs rise from ~6°C at the end of the Oldest Dryas to ~10°C at the beginning of the Bølling period within ~150 years (~1°C/40 yrs). During the Older Dryas, SSTs decrease to ~7°C and again rise to ~9°C during the Allerød in ~100 years.

SSTs off Vancouver Island reach a maximum of ~12°C during a 400 year period centered at ~10.7 kyr BP. NE Pacific SST maxima at the beginning of the Holocene are also inferred at 50°N (Sabin and Pisias, 1996) and at 42°N (Doose et al., 1997; Mix et al., 1999). The SST maximum is most likely related to the summer insolation maximum at 50°N around 11 kyr BP (Laskar, 1990). Interestingly, this temperature maximum is not evident in the ice core record.

Summary & Conclusions

Past SST estimates have been derived for the last 16 kyr in the subarctic NE Pacific based on the U^K[']₃₇ index. Between 16 and 11 kyr BP, the observed SST changes between ~6° and ~12°C correspond to the Oldest Dryas, the Bølling, the Older Dryas, the Allerød, and the Younger Dryas periods in the GISP2 δ^{18} O record (within the 2σ error of the radiocarbon based age control). Current model-based investigations of the response of a freshwater discharge in the N-Atlantic during the Younger Dryas period underestimate the SST cooling along the entire NE Pacific margin (Mix et al. 1999; Hendy and Kennett, 2000; this study). A modelling study focusing on the NE Pacific itself, on the other hand, indicates that SST changes in the North Pacific Ocean have a Northern Hemisphere-wide climate impact (Peteet et al. 1997). The cool spells off Vancouver Island are terminated by rapid SST rises of 1°C in 40-80 years. For a 400 year long period around 10.5 kyr, SST reaches maximal values of ~12°C. After this early Holocene maximum, SST values remain fairly stable around 10°C. These findings of millennial-scale SST changes during the de-glaciation complement other high resolution marine records from the California Margin which indicate oscillations in surface ocean conditions that seem synchronous with climate variability in Greenland (Hendy and Kennett, 2000). The fast rate of SST change off Vancouver Island seems to suggest a strong atmospheric coupling between the subarctic NE Pacific and the North Atlantic, possibly via the Arctic region. Our paleo-SST results are in excellent qualitative agreement with striking evidence that large-scale warmings and coolings over the North Pacific in the 20th century are preceded by similar SST behavior off the southern tip of Greenland (Moron et al., 1998).

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Addendum

Since the palaeotemperature record examined in this thesis was published (see previous pages), more SST records from the N Pacific have become available (Fig. A.I.4). A high resolution $U^{k'}_{37}$ record from ODP site 1019 off northern California [Barron et al., 2002 accepted] shows a high degree of similarity to the SST record off Vancouver Island during the last deglaciation, both in amplitude and in timing (Fig. A.I.5). At this site, the deglacial temperature changes as recorded by both the alkenone unsaturation patterns [Barron et al., 2002 accepted] and by the abundance of the cold water dwelling foraminiferan N. pachyderma (sinistral) ([Mix et al., 1999]; see Chp. 3.3) are interpreted to be synchronous to the Bølling-Allerød warming and the Younger Dryas cooling observed in Greenland ice cores [Mix et al., 1999; Barron et al., 2002 accepted]. Similarly, Seki et al. [2002] interpret a deglacial warm period observed at ODP site 1017E off southern California to represent the Bølling-Allerød warm period (Fig. A.I.5). As with the record off Vancouver Island, the chronologies of these sediment records are based on AMS ¹⁴C dates, which are reservoir corrected by ~800 years [1110 at certain periods in JT96-09; see Kienast and McKay, 2001] and calibrated to calendar years using the calibration provided by Stuiver et al. [1998].

Insight into the temporal relationship between climate changes in different regions, such as the North Pacific and the North Atlantic, potentially offers significant insight into the mechanisms of past and present climate change. It is generally assumed that synchronous changes which are in phase (i.e. warming in both regions) are evidence of a rapid, or almost instantaneous, atmospheric teleconnection. In the case of the N. Pacific and the N. Atlantic, this connection could presently operate via the Arctic region, and via the massive Laurentide and Cordilleran ice sheets during the LGM. Conversely, a pattern of temperature change that is synchronous, but anti-phased (i.e.

warming here and cooling there) has recently been inferred between the NW Pacific (ODP site 883, Fig. A.I.4) and the N. Atlantic region during Stage 3 [*Kiefer et al.*, 2001]. These authors propose an oceanic connection between the two regions and suggest that a shutoff or slowdown of N. Atlantic deep water formation during Dansgaard-Oeschger stadials led to a reduction in the upwelling of cold Pacific deep water and thus to surface ocean warming in the NW Pacific. The anti-phased pattern between SST in the NW Pacific and N. Atlantic appears to continue into the last deglaciation (T. Kiefer, *personal communication* 2002), which is the opposite from what is inferred at sites ODP 1019 and JT96-09 at the northern continental margin of NW America (*see above*). An anti-phased pattern between JT96-09 and the N. Atlantic might also be seen at 14.5 and 13.5 kyrs [M. Sarnthein, *personal communication* 2001]. Given the limitation of radiocarbon chronologies [see error bars in *Kienast and McKay* 2001] this question cannot be fully resolved at this time.



Fig. A.I.4: Location of recently published sea surface temperature records (large black circles) in the N-Pacific relative to site JT96-09 examined in this thesis and the Greenland ice core GISP 2. Grey line along the Californian coast indicates latitudinal transect of cores (small black circles) examined by *Herbert et al.* [2001]. See text for additional references.

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A SST record from the Alaskan Gyre region based on dinocyst assemblages shows a warm period between 20 and 17 kyrs and a return to glacial conditions centered around 15 kyrs B.P. (Fig. A.I.5). In contrast to the records from the continental margin (ODP site 1019 and JT6-09), the Younger Dryas cooling is absent in the Alaska Gyre record. Assuming that SST reconstructions based on dinocyst assemblages are directly comparable to those based on alkenones (i.e. assuming that they record the annual temperature of the euphotic zone with the same degree of sensitivity) this possibly points to regional differences of deglacial temperature evolution within the different domains of the N-Pacific.

Recent work by Herbert et al. [2001] highlights the regional dynamics of SST development in a single region. Using a N-S transect of cores in the California Current (CC) region (Fig. A.I.4), these authors found that SST started to increase several kyrs in advance of the deglaciation (as recorded by benthic δ^{18} O in the same cores) in the central CC (32°N). This earlier warming gradually weakens towards the southern (22°N) and the northern (40°N) end of the CC, i.e. it does not seem to affect sites OPD 1019 and JT96-09. It is thought to represent the intrusion of warmer offshore waters to the coast at times of maximal glaciation when the California Current was weaker. While the different climatological and oceanic mechanisms implied for deglacial warming by the three different SST records [Herbert et al., 2001; Kiefer et al., 2001; Kienast and McKay, 2001] are not mutually exclusive, they all critically depend on the precision of the age model and on the degree of sample resolution. Increased coverage of AMS dating and the application of a multitude of stratigraphic tools (such as benthic δ^{18} O, AMS radiocarbon dating, and magnetostratigraphy), will possibly help to resolve this issue in the future.



Fig. A.I.5: Comparison of sea surface temperature estimates for the last 20 kyrs from the N Pacific, *see next page*

Fig. A.I.5: Comparison of sea surface temperature estimates for the last 20 kyrs from the N Pacific. SST reconstructions at OPD sites 1017E [*Seki et al.*, 2002] and 1019 [*Barron et al.*, 2002 accepted] as well as at site JT96-09 [*Kienast and McKay*, 2001] are based on alkenone unsaturation patterns. SST reconstruction of Alaskan Gyre core PAR87-10 is based on dinocyst assemblages [*de Vernal and Pedersen*, 1997]. The three alkenone records are plotted according to their individual time scales as published by *Kennett et al.* [2000] (1017); *Mix et al.* [1999] (1019) and *Kienast and McKay* [2001] (JT96-09). The time scale of Alaskan Gyre core PAR87-10 used here is based on the raw AMS radiocarbon dates given in *de Vernal and Pedersen* [1997], which were reservoir corrected[-800 years, *Southon et al.*, 1990] and calibrated to calendar years for this comparison using the calibration software CALIB [ΔR = 400 ± 200 yrs; *Stuiver et al.*, 1998]. Note that Y-axes are different in all panels. Lower panel shows Greenland Summit (GISP-2) ice core δ^{18} O data from *Stuiver and Grootes* [2000] on the time scale from *Meese et al.* [1997]. Light and dark gray shadings indicate the duration of the Bølling-Allerød warming and the Younger Dryas cooling in the ice core record, respectively.

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Appendix II: Analytical methods

The Multitracers sediment cores and sediment trap samples were subsampled for this study at the Oregon State University core depository in March 1998. The core samples were freeze dried and manually homogenized in an agate mortar prior to all chemical analyses carried out at UBC. Details of the sediment trap design and the sample preservation with sodium azide are described by Dymond and Lyle [1994]. Below are descriptions of the analytical methods used in this study and estimates of method precision ([standard deviation/average]*100) and accuracy ([(certified value measured value)/ certified value]* 100). The organic carbon, Ba/Al, biogenic opal and δ^{15} N data of cores W8709-13PC and W8709-8PC, as well as δ^{15} N data of the sediment available electronic form time series are in at trap www.ngdc.noaa.gov/paleo/contributions by_author/kienast2002. The data presented in chapter 3 (Aluminium and redox sensitive metals) are listed in Appendix 4.

Total and inorganic carbon

Total carbon was determined by combustion gas chromatography with a Carlo Erba NA1500 elemental analyzer using operational conditions similar to those described by Verardo et al. [1990]. Approximately 20 mg of sample were accurately weighed into tin cups using a microbalance (Mettler M3), and stored in desiccators until analysis. The cups were introduced into the sample tray of the elemental analyzer and completely and instantaneously combusted ("flash combustion") in a stream of oxygen and helium at a temperature >1600°C. The combustion products were quantitatively oxidized in a heated (1050°C) column of granulated chromium trioxide (CrO₃) overlying silvered cobaltous cobaltic oxide (CO₃O₄ + Ag). Excess O₂ was

removed in a heated copper (650 °C) column and excess H_2O was removed in a filter containing magnesium perchlorate. The resulting gases were separated chromatographically and total carbon was quantified by a thermal conductivity detector. Sulfanilamide was used to calibrate the instrument. Based on several certified rock standards analyzed along with each batch of samples, precision and accuracy for total carbon were ± 2.0 % and ± 2.6 %, respectively.

Inorganic carbon was determined by coulometry. Five-10 mg of sample were weighed into glass cups, placed into the sealed reaction vessel of the instrument and digested with hot 10% HCl. The evolving CO₂ was swept by a CO₂ free air stream into the coulometer cell containing an aqueous solution of ethanolamine and a coulorimetric indicator. The cell is located between a photo detector and a light source. When the gas stream passes through the solution, CO₂ is quantitatively absorbed, it reacts with ethanolamine to form a strong titratable acid which causes the indicator colour to fade (% transmittance increases). As the percentage of transmittance increases, a titration current is turned on which electrically generates base. When the solution returns to its original color, the current stops. The total amount of current required for the titration is electronically integrated and the results displayed as μ g C. Analytical precision and accuracy based on an internal calcium carbonate standard are ± 2.3 % and ± 1.20 %. Organic carbon was estimated by subtracting inorganic from total carbon, with a combined analytical precision of ± 3 %.

Biogenic opal

Biogenic opal was determined by alkaline extraction of silica following a method described by *Mortlock and Froelich* [1989]. A subsample containing 20 mg of sediment was treated with 10% H_2O_2 and 10% HCl (2 ml each) to remove organic matter and

carbonate carbon. Excess reagents were removed with distilled, deionized water (DDW) and the samples were dried overnight at 60 °C. Silica was extracted with 20 ml of 2M Na₂CO₃ solution in a hot water bath maintained at 85°C for 5 hours. Dissolved Si concentrations in the extract were determined by molybdate-blue spectrophotometry as described by *Mortlock and Froelich* [1989] and are assumed to be exclusively derived from biogenic opal. Percent opal is calculated as 2.4 x % Si_{opal}. The precision based on a laboratory sediment standard was ± 4.3 %.

Nitrogen isotopes

Nitrogen isotope ratios were determined using a Fisons NA1500 elemental analyzer coupled to a VG prism mass spectrometer in a continuous flow of helium. A weighed sediment subsample in a tin cup was flash combusted as described above. The generated N₂ gas was separated chromatographically and introduced online into the mass spectrometer in a stream of helium. Masses 28, 29, and 30 were monitored as the N₂ pulse passed through the ion source. Isotopic data are expressed in the delta notation as

$$\delta^{15}N \ \% = \left[{\binom{15}{N}}^{14}N \right]_{sample} - {\binom{15}{N}}^{14}N \right]_{standard} \left] / {\binom{15}{N}}^{14}N \right]_{standard} * 10^{3}$$

with air N_2 as standard.

Analytical precision based on a laboratory standard (acetanalide) was \pm 0.2 ‰ (1 σ R.S.D.). Isotopic analyses on dissolved nitrate were carried out after extraction of nitrate from sea water followed by diffusion onto acidified glass fiber filters [*Sigman et al.*, 1997]. Data were kindly provided by M. Altabet (Oregon samples) and J. Needoba and M. Kienast (Vancouver Island samples). Details of the analytical method can be found in *M. Kienast* [2002].

Minor and major elements (Ba, Al and Mn)

Barium (Ba) and aluminium (Al) in core W8709-8TC and PC were determined using a Philips 2400 wavelength-dispersive sequential automatic X-ray fluorescence (XRF) spectrometer using the procedures outlined for major and minor element determination described in *Calvert et al.* [1985] and *Calvert* [1990]. Briefly, 400 mg of sediment was mixed with Spectroflux 105 ($Li_2B_4O_7$, La_2O_3 and Li_2CO_3) and fused at 1100°C in a muffle furnace. Weight loss after fusion was compensated by adding Spectroflux 100 ($Li_2B_4O_7$). The mixture was remelted and cast into a glass disk for Al analyses. For Ba determination, four grams of sample were pressed into a borax backed pellet using a hydraulic press. Precision for both elements was better than ± 4%.

There was not enough sample material to carry out XRF analysis on core W8709-13PC. Thus a digestion technique that requires less sample material was developed for this thesis. Five to ten mg of sediment was weighed into 6ml teflon savillex vessels of known weight. Concentrated acids (300 μ l HNO3, 50 μ l HF and 100 μ l HCl) were added, the vessels were sealed and the total weight was recorded (dilution factor or DF 1, *see below*). Twelve samples at a time were digested for 40 minutes at 50 psi (% 50 power) in a CEM 205 microwave system. Following digestion, the closed vessels were weighed again to check for possible loss of sample during the digestion. Using a precision balance, an aliquot of the digested sample was transferred into a 15ml Nalgene container and diluted with 10 ml of 1 % HNO₃ (DF 2). Aluminium, Ba, and Mn concentrations of the diluted sample were determined by a commercial laboratory (ALS Chemex, Vancouver) using ICP-OES (inductively coupled plasma optical emission mass spectrometry). Metal (Me) percentages in the sediment were calculated as

%Me = (DF 1 * DF2 * [Me]) / 10 000

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where

DF 1: (weight of concentrated acid cocktail + sediment) / weight of sedimentDF 2: weight of the final 10 ml sample / weight of the aliquot[Me]: metal concentration in diluted sample in ppm as analyzed by Chemex

Occasionally, a white-grayish precipitate was observed at the bottom of the Savillex container after the digestion of sediment samples or PACS-2 reference material. This precipitate was more frequently observed when performing sediment digestions (10-250 mg) in various acids mixtures in a MILESTONE Mega 1200 microwave system at powers ranging from 550-650 W (S. Kienast and M. Soon, unpub. data, 2000-2002). The nature of this precipitate and the exact analytical conditions that lead to its formation were not further examined. However, it fits the description of aluminum fluoride (AlF_3) which forms during digestions of rock samples in the presence of HF at high microwave pressures and co-precipitates a suite of other trace metals Takei et al. [2001]. Al concentrations in digested reference material (PACS-2) samples showing the precipitate were consistently too low (by ~ 20- 50%, Table A.I.1). Most samples in which precipitate formation initially occurred could be repeated (under the same analytical conditions !) without precipitate formation. However, there are a few samples in which precipitate formation occurred but for which no repeat measurements were carried out (see 3.3.1 and Fig. 3.2 caption). The Al and Ba numbers derived from these samples are likely to be in error, while Mn did not seem to affected by this problem. Accuracy and precision of the Al measurements were calculated excluding samples containing the precipitate (4 out of 32) and are given in Table A.II.1).

• •		certified value	measured	n	precision	accuracy
Al	PACS-2	6.61 ± 0.3 %	6.60 ± 0.77	28	12 %	0.2 %
	PACS-2*		2.89 ± 0.85	4		
	JB1a	7.69 %	7.57 ± 0.92	14	12 %	1 %
Ва	JB1a	490 ppm	506 ± 32	14	6 %	3 %
Mn	PACS-2	440 ± 19 ppm	439 ± 68	32	15 %	0.3 %
	JB1a	1238 ppm	1148 ± 84	14	7 %	7 %

Table A.II.1: Al and Ba data for PACS-2 and JB-1a (certified reference materials) obtained by ICP-OES analyses. Asterisk marks digestions which showed precipitate formation.

Trace metals analysis (Ag, Cd, Re, Mo, and U)

Ten to fifteen mg of sediment were accurately weighed into a 6 mL teflon screwcap vial (Savillez Inc., Minnetonka, MN) and spiked with known amounts of isotopically labeled Ag, Re, Cd, Mo, and U stock solutions (see table A.II.2). A cocktail of concentrated acids (0.8 μ l HNO₃, 0.1 μ l HCl, 0.2 μ l HF) was added and the vessels were sealed. Microwave digestion was performed using a CEM 205 microwave system equipped with a caroussel of 12 pressure bombs accommodating 2 vials per bomb. To counteract excessive pressure build up in the vials, a round teflon spacer (3 cm diameter screw cap) was placed in the bottom of the bomb and covered with DDW. The samples were digested for 40 min at 50 psi (50% power). After digestion, the samples were evaporated to complete dryness on a hotplate to remove HF. The residue, a reddish-brown precipitate, was redissolved by adding 1.5 ml of 0.5N HCl and microwaved for 20 min at 50 psi (50% power) to obtain a clear a solution. An aliquot (0.1 ml) was taken for Mo and U analyses, and diluted with 0.5 ml of 1N HNO₃. The remaining solution was run through an anion exchange column (Dowex 1-X8 resin, 100-200 mesh) in order to remove potential polyatomic interferences of Nb, Zr and Mo with Ag and Cd isotopes, and to concentrate Re in the sample following a method developed elsewhere [Colodner, 1991; Crusius et al., 1996]. The column was connected to a peristaltic pump set at 47 rmp, and remaining solution was taken up in 0.5 N HCl and eluted with 8 N HNO₃. The eluent was diluted with 0.5 ml of 1N HNO₃ prior to analysis. Blanks, standard reference material (MESS-2) and an in house standard (Saanich bulk sediment) were run with every batch of 24 samples.

		natural abundance	spike abundance %
		%	-
Ag	107	51.80	0.30
0	109	48.20	99.70
	109/107	0.93	332.33
Re	185	37.40	96.66
	187	62.20	3.34
	185/187	0.60	28.94
Cd	111	12.80	96.50
	113	12.20	0.44
	111/113	1.05	219.32
Мо	95	15.90	96.47
	98	24.10	0.63
	95/98	0.66	153.13
U	235	0.72	49.70
_	233	0	100
	235/233		0.497

Table A.II.2: Isotopic abundances of the spike solution used in this study

Trace metal measurements were performed on a Plasmaquad II+ inductively coupled plasma mass spectrometer (ICP-MS) in peak jumping mode using a flow injection system. Blanks within every batch of samples were averaged and subtracted from the mass count of each element. Results are also corrected for instrument mass bias, which was determined at the beginning of each session at the ICP-MS.

Accuracy and precision

Precision is approximately 10 % for Ag, Mo and U (Tables A.II.3 and A.II.4) based on repeatedly analyzed standards. Re and Cd show lower precisions for MESS-2

(16 and 13.5 %, respectively, Table A.II.3), which in the case of Re might be due to the low metal concentration in the standard (close to limit of detection, 1 ppb). Re concentrations in the core material studied are significantly higher (5-30 ppb) than in MESS-2. The accuracy of the analyses (Table A.II.3) was determined for metals that have certified values. Ag and Cd analyses are accurate to 2 and 4 %, respectively. In contrast, Mo displays a much lower accuracy (18%) and appears to be systematically biased towards lower values. The reason for this is unclear, but a similar bias (15% too low based on PACS-2) has been observed elsewhere [Morford et al. 2001]. Since MESS-2 does not have certified values for Re and U, accuracies *sensu stricto* could not be determined for these metals. However, the average Re and U values found in this study compare well with long-term averages observed in the UBC laboratory ("expected" values in tables A.II.3 andA.II.4).

Table A.II.3 : Data for Canadian National Research Council certified reference material Mess-2 (\pm standard deviation, 1 σ)

	MESS-2				
	certified	expected	this study	precision %	accuracy %
Ag (ppb)	180 ± 20		176 ± 18	10.3	. 2.2
Re (ppb)		2.98 ± 0.52^{1}	2.84 ± 0.46^{2}	16.1	
Cd (ppm)	0.24 ± 0.01		0.23 ± 0.03	13.5	4.2
Mo (ppm)	2.85 ± 0.12		2.34 ± 0.24	10.4	17.9
U (ppm)		2.62 ± 0.25^{1}	2.67 ± 0.29	10.9	

¹: based on long term replicate measurements at UBC (*n*>20, K. Gordon, personal communication 2002) ²: close to limit of detection

Table A.II.4: Data for Saanich bulk sediment standard (not certified), values \pm standard deviation (1 σ)

	Saanich bulk		
	expected ³	measured	precision %
Ag (ppb)	$1\hat{6}8 \pm 24$	169 ± 14	8.6
Re (ppb)	5.7 ± 0.86	5.05 ± 0.45	8.9
Cd (ppm)	4.81 ± 0.48	4.8 ± 0.43	9.0
Mo (ppm)	54 ± 6.36	49.69 ± 4.12	8.3
U (ppm)	4.46 ± 0.41	4.27 ± 0.49	11.37

³: expected based on long term replicate measurements at UBC (n > 40, K. Gordon personal communication 2002)

Detection limits

The detection limit (DL) is usually defined as the metal concentration that corresponds to $3*s_{blank}$ based on a calibration curve, where s_{blank} is the standard deviation of the blank. For this study, a calibration curve was kindly provided by K. Gordon (UBC). The detection limit was calculated by determining the metal concentration that corresponds to $3*s_{blank}$ and then multiplying this number with the final dilution factor of the sediment sample (100 for Ag, Re, Cd and 750 for Mo and U). Metal variations in this study above these conservative estimates are considered to be real.

Table A.II.5: detection limits of Ag, Re, Cd, Mo and U

	DL
Ag	57 ppb
Re	<1 ppb
Cd	0.1 ppm
Мо	0.5 ppm
U	0.04 ppm

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Appendix III: Ancillary information for Chapter 1 and 2



Fig. A.III.1: Linear sedimentation rates of cores 13PC and 8 PC (Nearshore and Midway, respectively) versus age. Sedimentation rates are about twice as high in the Nearshore setting compared to the more offshore Midway setting. Note that the close spacing of radiocarbon dates in core 13 PC leads to abrupt changes in sedimentation rates after 13 kyrs B.P.

Table A.III.1 : De	pth and age of tie	points used for new	chronology of Midwa	y core W8709-8
			0,	

W8709-8 PC & TC	Age (ka)	CaC03 events
(comp. cm)		
0	0	
159	16.6	CC 2-1
374	36.5	CC 3-3
464	49.3	CC 3-5a
594	56.9	CC 3-5c
674	65.2	CC 4-2
744	72.3	CC 4-4
804	78.9	CC 5-2

The ideal mixing lines are constructed from two end members following *Liu and Kaplan* [1989]. Salinity is linearly related to the fraction of an end member

$$S=S_2 + (S_1-S_2)X_2$$

Where S_1 and S_2 are the salinities of the two end members and X_2 is fraction of end member 2. $\delta^{15}N$ is not linearly related to a fraction because the fraction of each end member must be weighted with its nitrate concentration:

$$\delta^{15}N = [\delta_1 + (\delta_2C_2/C_1 - \delta_1)X_2] / [1 + (C_2/C_1 - 1)X_2]$$

where δ_1 and δ_2 are the δ_{15} N values of nitrate and C1 and C2 are concentrations of nitrate in each end member. Curvature depends on the C2:C1 ratio; the more this ratio departs from unity, the greater is the curvature.

							•		
· · · · · · · · · · · · · · · · · · ·	water depth	lat (°N)	long (°W)	$\delta^{15}N_{nitrate}$	salinity (PSU)	[NO ⁻ ₃]		data source	1
	(m)	()	· · /	(‰)	· · ·				
							$\delta^{15}N$	sal	[NO ⁻ ₃]
Vanc.Is.	200	48.5	126.75	6.1	33.9487	31.4	1	10	1
· unicity	400	2010		6.3	34.0139	39.5	1	10	1
Washington	450	46.75	126.13	6.59	34.037	36	2	7	7
Oregon	150	44.66	125.8	7.23	33.92	29.3	1	8	11
0100011	150		1000	7.04	33.92		1	8	
	600			6.91	34.21		1	7	
	600			7.36	34.21		1	7	
Monterey	150	36.75	122.05	7.75	34.05		3	9	
Bay									
San Pedro	350	33.66	118.35	11.6	34.38		4	4	
Basin									
Delfin Basin	100-500	29.83	113.88	11			5		
Carmen	500	26.22	110.6	14			5		
Basin									
ETNP	275	19.77	107.1	18.3	34.76	24.3	6	6	6
	325			17.5	34.72		6	6	
	200			17.3	34.79		6	6	_
	600			9.25	34.55	35.8	6	6	7

Tab. A.III.2: δ^{15} N_{nitrate}, salinity, and nitrate data from the California Current region

1 : kindly provided for this study by J. Needoba, M. Kienast and M. Altabet

2 : Brandes, J.A.G, Ph.D. thesis, Univ. of Washington, Seattle, 1996 3 : Altabet et al., Deep Sea Research, I 46, 655-679, 1999

4 : Liu, K.-K., and I.R. Kaplan, Limnology and Oceanography, 34 (5), 820-830, 1989. 5 : Pride et al., Paleoceanography, 14 (3), 397-409, 1999 6 : Cline, J.D., and I.R. Kaplan, Mar. Chem., 3, 271-299, 1975

7 : Levitus et al. 1994, http://ferret.wrc.noaa.gov/las1/climate_server 8 : Lyle et al. 1987 cruise report W8709, *unpub*.

9: Chavez and Michisaki, unpub. data 2002

10: Courtesy of Institute of Ocean Sciences, Sidney, OSAP group

11: P. Wheeler, OSU, unpub. data 1998

Appendix IV: Data

All data presented in chapter 2 (organic carbon, Ba/Al, biogenic opal and $\delta^{15}N$ data of cores W8709-13PC and W8709-8PC, as well as $\delta^{15}N$ data of the sediment trap time series) are available in electronic form at <u>www.ngdc.noaa.gov/paleo/contributions_by_author/kienast20</u>02. The alkenone sea surface temperature data (*see Addendum*) are also available electronically at the above archive. The data presented in chapter 3 (aluminium and redox sensitive metals) are listed here.

13	kyrs	Al	Ва	Mn	sed rate	dbd	Ag	Re	Мо	Cd	U
PC	,	(%)	(ppm)	(ppm)	(cm/kyr)	(g/cm^3)	(ppb)	(ppb)	(ppm)	(ppm)	(ppm)
cm		. ,									
3.0	6.34	7.58	1180	545	17.70	0.40	384	35.99	1.21	0.45	3.32
5.5	6.43	7.54	1160	555	17.70	0.40	308	9.61	1.28	0.41	3.51
9.0	6.55	7.54	1110	550	17.70	0.43	269	14.90		0.39	3.26
13.0	6.69	7.74	1160	565	17.70	0.45	328	21.18	1.27	0.44	3.91
15.0	6.76	7.63	1120	560	17.70	0.46	348	28.65		0.36	3.17
18.0	6.87	7.87	1160	575	17.70	0.47	323	27.67		0.38	3.38
20.5	6.96	7.76	1110	560	17.70	0.47	257	18.45	1.15	0.33	2.84
24.0	7.08	7.76	1130	560	17.70	0.48	314	11.19	1.10	0.37	3.30
27.0	7.18	7.89	1140	575	17.70	0.49	309	9.83		0.45	2.97
30.0	7.29	7.37	1010	530	28.65	0.50			1.02		2.56
33.0	7.39	6.77	930	480	28.65	0.50	285	13.97	1.16	0.48	3.00
36.0	7.50	6.92	960	500	28.65	0.51	335	8.06	1.23	0.33	3.28
39.0	7.60	6.60	890	455	28.65	0.51	320	13.43	1.11	0.31	2.59
42.0	7.71				28.65	0.51	291	13.10	1.22	0.48	3.45
45.5	7.83	7.05	980	520	28.65	0.52	265	9.29	1.21	0.28	3.03
48.0	7.92	5.90	830	440	28.65	0.52	260	19.54	1.14	0.36	2.65
51.0	8.02	7.14	990	535	28.65	0.52	267	14.70	1.30	0.47	3.44
54.0	8.13	7.27	1000	550	28.65	0.53	259	11.34		0.33	3.03
57.0	8.23				28.65	0.53	360	12.51		0.38	3.08
60.0	8.33	6.14	880	470	28.65	0.53	247	12.48	1.24	0.40	2.73
63.0	8.44	5.89	840	440	28.65	0.54	266	9.38	1.46	0.49	3.35
67.0	8.58	5.66	830	435	28.65	0.54	340	11.56		0.43	3.40
69.0	8.65	5.65	800	430	28.65	0.54	298	16.68	1.36	0.38	3.03
72.0	8.75				28.65	0.54	257	10.06	1.46	0.47	3.53
74.0	8.82	6.01	890	465	28.65	0.55	345	7.94		0.37	3.39
78.0	8.96	3.28	480	255	28.65	0.55	325	11.11	1.45	0.41	4.03
81.0	9.07	7.09	1010	540	28.65	0.55	270		1.46	0.42	3.92
84.0	9.17	6.86	970	525	28.65	0.55	271	12.04	1.46	0.40	3.29
87.0	9.28	7.76	1100	595	28.65	0.55	337	14.13	1.22	0.31	3.26
90.0	9.38	7.26	1070	570	28.65	0.56	233	5.54	1.10	0.26	2.87
93.5	9.50	7.37	1060	565	28.65	0.56	257	9.26	1.68	0.43	3.85
96.0	9.59	7.34	1020	555	28.65	0.56		16.03	1.28	0.31	2.94
99.0	9.71	7.04	940	525	12.50	0.56	300	18.47	1.41	0.32	3.48
102.5	9.78	6.78	930	515	12.50	0.56	296	23.78	1.51	0.43	3.53
105.0	9.84	6.85	900	520	12.50	0.57		10.31		0.36	2.68
108.0	9.90	6.81	900	525	12.50	0.57	259	11.88		0.40	3.06
111.0	9.97	8.22	1010	620	12.50	0.57	299	18.11		0.62	2.56
114.0	10.03	7.37	920	550	12.50	0.57		9.88		0.48	

Table.A.IV.1: Sedimentation rate and metal concentration data of core 13 PC at the Nearshore site

117.0	10.10	7.50	950	575	12.50	0.57		13.08	1.20	0.56	3.73
120.0	10.16	7.50	970	580	12.50	0.57	267	14.68	1.02	0.54	2.49
122.0	10.10	7 20	030	550	12.50	0.57	231	6 78	1 01	0.42	3 14
122.0	10.21	7.20	930	550	12.50	0.57	201	6.26	1.01	0.52	2 21
125.0	10.27	7.29	960	500	12.50	0.57	209	0.30	1.09	0.52	2.05
128.0	10.44	7.60	960	590	12.81	0.58		6.48	1.02	0.43	3.05
131.0	10.68	7.93	980	600	15.00	0.58	304		1.05	0.63	2.82
135.0	10.99	7.46	880	560	15.00	0.58		6.73	0.89	0.61	2.60
140.5	11.40	7.61	930	580	16.50	0.58	315	4.87	1.03	0.60	2.95
144.0	11.63	7.42	910	565	16.50	0.58	262			0.46	2.51
147.0	11.83	7.63	980	575	16.50	0.58		5.25		0.78	2.55
150.0	12 03	7.19	900	525	16.50	0.59	296	5.38		0.69	3.18
152.5	12 20	6 52	810	480	16.50	0.59		8 44		0.67	2.83
152.5	12.20	7 42	020	555	25.00	0.59	214	7 72	0.01	0.53	2.00
100.0	12.42	7.40	. 930	555	25.00	0.59	214	19 12	0.71	0.00	2.74
162.0	12.70	7.40	940	505	35.00	0.59	237	10.13		0.45	2.07
167.0	13.09	7.56	950	570	35.00	0.59	217	15.51		0.44	3.07
170.5	13.30	6.29	780	480	35.00	0.59	258	11.84		0.45	3.40
173.5	13.39	7.52	970	580	35.00	0.59	282	15.12	0.92	0.46	2.63
177.0	13.49	7.84	1020	610	35.00	0.59	260		1.44	0.38	3.18
179.5	13.56	6.94	900	535	35.00	0.60	367		1.61	0.53	3.11
183.0	13.66	7.26	930	575	23.75	0.60	291	10.40	0.95	0.45	2.62
186.0	13.74	7.12	920	565	23.75	0.60			1.32		2.69
189.0	13.83	7.14	910	560	23.75	0.60		12.01		0.47	3.47
192.0	13.92	7 54	960	600	25.00	0.60	319		1.04	0.35	3.12
195.0	14 05	7 58	960	600	25.00	0.60	017	10.83		0.37	3.09
102.0	14.00	7 20	020	505	10.58	0.00	202	8 48		0.57	3 32
190.0	14.17	7.37	920	595	22 50	0.00	225	770	0.95	0.07	2 55
201.0	14.41	7.00	090	090	22.50	0.00	235	6.09	1.02	0.62	2.00
204.0	14.70	0.11	910	620	22.50	0.60	200	0.00	1.03	0.02	2.27
207.0	14.98	7.19	790	585	22.50	0.60	200	12.20	1.02	0.55	3.30
210.0	15.26	6.74	760	555	22.50	0.50	165	4.65	0.80	0.45	2.4/
213.0	15.52	7.01	840	565	22.50	0.60	152	14.23	0.78	0.49	3.29
216.0	15.66	7.29	900	590	22.50	0.61	170	6.01	0.82	0.47	4.00
219.0	15.79	8.10	1000	660	22.50	0.61	201	8.99	0.75	0.44	2.78
221.0	15.88	7.20	870	580	22.50	0.61	198	5.72	0.79	0.56	2.98
224.0	16.09	7.22	830	920	2.68	0.61	231	6.12	0.97		2.71
227.0	17.21	7.18	810	600	2.68	0.61	130	8.88	0.71	0.45	3.24
230.0	17.45	7.08	600	590	46.09	0.50	203	3.67	0.72	0.30	2.38
233.0	17 52				46.09	0.61	221	8.50	0.87	0.50	3.83
236.0	17 58	7 27	870	575	46.09	0.61	221	3.83	0.91	0.53	3.18
220.0	17.50	676	810	545	46.09	0.61	221	4 51	0.81	0.43	3.03
237.0	17.00	7 51	000	405	46.00	0.61	100	1 96	0.01	0.45	2 52
241.0	17.09	7.51	900	600	46.00	0.01	190	9.00	0.77	0.52	2.02
244.0	17.70	0.00	800	550	40.09	0.61	005	0.20	0.77	0.32	2.71
247.0	17.82	7.20	890	<i></i>	46.09	0.61	205	5.64	0.02	0.57	5.10
250.0	17.89	7.86	850	615	46.09	0.61	193	5.10	0.75	0.28	2.76
253.0	17.95	7.72	700	625	46.09	0.50	130	5.91	0.59		2.39
256.0	18.02	7.30	79 0	585	46.09	0.61			0.59		2.63
259.0	18.08	7.70	830	590	46.09	0.62	175	10.11	0.75	0.28	2.83
262.0	18.15	4.52	510	510	46.09	0.62	198	6.24	0.73		2.49
265.0	18.21	7.55	830	590	46.09	0.62			0.95		2.57
268.0	18.28	7.38	810	580	46.09	0.62	140	5.99	1.04	0.30	2.56
272.5	18.38	7.28	830	580	46.09	0.62	163	6.52	0.80	0.39	2.55
275 5	18 44	7 50	830	605	46.09	0.62	166	10.73	1.21	0.33	3.34
275.5	19 51	7.50	000	000	46.09	0.62	179	5 61	0.89	0.24	2 77
202.0	10.51				46.00	0.62	167	5 11	0.07	0.39	297
202.0	10.00	(= (770	FOF	40.09	0.02	107	6 59	0.05	0.32	2.00
284.5	18.64	6.36	.770	505	46.09	0.62	101	0.00	0.90	0.33	2.77
289.0	18.73	6.75	800	530	40.09	0.62	1/0	7.00	0.91	0.29	3 70
293.5	18.83	6.80	800	525	46.09	0.62	168	5.60	0.95	0.35	2.70
296.5	18.90	5.26	640	440	46.09	0.62	139	5.79	0.71		2.77
299.5	18.96	7.12	850	555	46.09	0.62	181	6.63	0.66		2.36
303.0	19.70	7.29	860	570	2.50	0.62		8.50	0.83	0.34	2.99
306.5	20.09	7.19	810	570	31.94	0.62	222	4.49	0.78	0.40	3.10
310.0	20.20	7.39	840	580	31.94	0.63	192	14.34	0.64		2.95
313.0	20.29	7.44	850	590	31.94	0.63	223	8.58	0.76	0.39	3.13
316.5	20.40	8.15	890	650	31.94	0.63	172	5.24	0.81	0.34	3.00
310.0	20.40	8 4 2	950	675	31 94	0.63	157	13.05	0.96	0.30	3.06
222.0	20.40	7 60	820	580	31 94	0.63	159	12 46	0.94	0.30	2.72
544.0	20.57	7.00	020	000	51.74	0.00	107	12.10	5.7.1	5.50	

325.0	20.67	9.03	970	675	31.94	0.63	261	9.58	0.82	0.30	2.76
327.5	20 74	9 40	1080	715	31 94	0.63	189	3.86	0.88	0.36	2.37
221.0	20.71	0 57	000	645	21.04	0.00	210	7.00	1 1 1	0.00	2.29
331.0	20.85	8.57	980	645	31.94	0.63	210	7.92	1.11	0.42	2.30
336.5	21.24	6.91	790	555	11.79	0.63	197	6.90	0.92	0.33	2.74
240.0	21 54	7.95	010	600	11 70	0.63	107	5 78	0.87	0.38	2 54
340.0	21.04	7.00	910	000	11.79	0.05	197	5.76	0.07	0.50	2.54
344.5	21.92	7.18	840	530	11.79	0.63	185	8.26	0.76	0.30	2.58
346 5	22.09				11 79	0.63	287	766	0 94	0.40	2.64
040.0	22.07			< 1 F	11.77	0.00	207	7.00	0.94	0.10	2.01
349.5	22.34	8.16	920	645	11.79	0.63	197		0.82	0.40	2.18
354.0	22.72	8.30	940	635	11.79	0.63		5.41		0.34	2.60
257.0	22.00	6.00	(00	400	11 70	0.62	261	0.01			2.45
357.0	22.98	6.30	680	400	11.79	0.05	201	0.51			2.05
359.5	23.19	10.44	1120	800	11.79	0.63	195	10.17	1.05	0.37	2.37
363.0	23 10	8 3 2	920	635	11 79	0.63	223	9 54	1 04	0.40	2 76
505.0	23.49	0.52	720	000	11.77	0.00	220	2.54	1.04	0.47	2.70
366.0	23.74	6.45	730	465	11.79	0.63	244	8.46		0.47	2./8
369.0	24.00	7.94	870	580	11.79	0.64	207	11.25	0.98	0.53	3.08
271 5	24 21	8 20	060	630	11 70	0.64	233	16.00	1.00	0.49	3 31
371.5	24.21	0.20	900	050	11.79	0.04	255	10.02	1.00	0.47	0.01
	24.51				11.79	0.64	202	5.38	1.89		3.42
377 5	24 72	9.84	1160	715	11.79	0.64	225	8.60	0.97	0.47	3.15
201.0	05.00	0.01	020	(15	11 70	0.01	206	E 00	1 1 6	0.44	2.07
381.0	25.02	8.31	930	615	11.79	0.64	206	5.99	1.10	0.44	2.97
384.0	25.16	7.87	870	590	35.00	0.64	188	12.55	1.17	0.44	2.82
287.0	25.24	8 71	030	660	35.00	0.64	204		1 07	0.36	2.68
307.0	23.24	0.71	950	000	33.00	0.01	204	0.50	1.07	0.00	2.00
390.0	25.33	8.53	950	655	35.00	0.64		2.73	0.97		2.94
393.0	25 42	8.62	940	670	29.17	0.64	179	5.17	1.15	0.48	3.09
200.0	20.12	0.02	070	670	20.17	0.01	150	776	0.09	0.29	2.62
396.0	25.52	9.33	970	645	29.17	0.64	159	1.76	0.98	0.58	2.02
399.5	25.64	7.18	780	525	29.17	0.64	163	8.59	1.30	0.42	3.69
402.5	25 70	7 76	880	570	25.00	0.64	186	7 55	0.91	0.41	3 29
403.5	23.79	7.70	000	570	25.00	0.04	100	7.00	0.71	0.41	0.27
407.5	26.04	7.94	920	585	15.70	0.64	188	5.01	0.90	0.40	2.85
410.0	26.20	7.16	810	530	15.70	0.64					
412.0	26.20	0 10	0.0	610	15 70	0.64	244	214	1 01	0.52	2 1 1
415.0	20.39	0.40	900	010	15.70	0.04	244	5.14	1.01	0.52	5.11
416.0	26.58	8.47	950	615	15.70	0.64	222	12.42	0.82	0.50	3.29
410 N	26 77	8 21	970	625	15 70	0.64	168	7.83	0.75	0.34	2.71
419.0	20.77	0.21	270	020	15.70	0.01	100	0.00	0.70	0.01	2.20
423.5	27.06	8.22	970	625	15.70	0.64	226	8.80	0.84	0.33	3.28
425.0	27.15	7.91	920	585	15.70	0.64	171	13.31	0.78	0.36	3.61
420.0	27.24	0 11	000	620	15 70	0.64	206	0.51	1 10	0.30	2 94
420.0	27.34	0.44	990	030	15.70	0.04	200	9.51	1.10	0.39	2.74
431.0	27.54	8.12	950	590	15.70	0.64	70	11.57	0.79	0.34	2.74
434.0	27 73	8 21	960	665	15 70	0.64	122	9 77	1.09	0.33	2.48
434.0	27.75	0.21	200	000	15.70	0.04	1/0	10.00	1.07	0.00	2.10
437.0	27.92	8.34	930	610	15.70	0.64	169	10.20	0.94	0.41	2.88
440.0	28.11				15.70	0.65		6.99	0.96	0.42	3.27
440 5	20.24	0 50	020	645	14.01	0.65	140	6 66	0.97	0.20	2 03
443.5	28.34	0.55	920	043	14.21	0.05	100	0.00	0.07	0.29	2.95
445.5	28.48	9.03	1030	615	14.21	0.65	106	9.29	1.05	0.32	3.49
116.0	28 51	8 30	950	630	14 21	0.65	74	7.00	0.99	0.39	3.28
440.0	20.01	0.50	250	500	14.01	0.00	100	10.04	0.77	0.02	0.20
448.0	28.65	7.25	850	520	14.21	0.65	199	12.04	0.98	0.38	2.74
449 0	28 72	8.86	1010	625	14.21	0.65	91	8.78	0.98	0.44	3.38
450.0	20.02	0.00	1000	(20	14.01	0.65	00	1704	1 07	0.42	1 06
452.0	28.93	0.02	1000	630	14.21	0.05	90	17.90	1.07	0.42	4.00
455.0	29.14				14.21	0.65	87	11.70	1.28	0.40	3.22
458.0	20.36	7 84	830	550	14 21	0.65	136	4 76	0 79	0.32	3.11
400.0	27.50	7.01	500	500	14.01	0.00	100	4 00	1 10	0.44	214
461.0	29.57	7.16	780	505	14.21	0.65	218	4.30	1.10	0.40	3.14
464.0	29.78	8.34	900	590	14.21	0.65	149	6.25	0.67	0.36	2.64
467.0	20.00	8 70	010	605	14 21	0.65	117	873	0.83	0.30	2 52
407.0	27.77	0.79	910	005	14.41	0.00	117	0.75	0.00	0.50	2.52
470.0	30.20	8.54	880	575	14.21	0.65	149	4.03	0.63	0.31	2.57
471 5	20 21	8.07	850	540	14 21	0.65	198	7 68	0 70	0.46	2.94
471.5	00.01	0.07	000	FOF	14.01	0.00	171	12 50	0.04	0.20	2.26
4/4.5	30.52	8.97	950	595	14.21	0.65	1/1	13.52	0.84	0.30	5.50
477.5	30.73	8.32	930	570	14.21	0.65	201	8.07	0.78	0.39	2.80
180 5	20.04	767	880	525	14 21	0.65	270	15 12	1.05	0.48	3 13
400.0	30.94	7.07	000	555	17.41	0.00	2/0	10.12	1.00	0.10	0.10
483.5	31.15	8.73	1010	600	14.21	0.65	205	9.41	0.78	0.36	2.86
486.0	31 33	7 44	820	520	14 21	0.65	138	3.71	0.51	0.33	2.97
400.0	21.00	7 67	050	FOF	14.01	0.00	100	10 17	0.07	0.40	3 55
489.5	31.57	1.57	006	525	14.21	0.05	224	12.1/	0.97	0.49	3.55
492.5	31.78	8.15	910	560	14.21	0.65	144	9.35	0.90	0.40	3.10
105 5	21.00	g 12	030	555	14 21	0.65	212	16 10	1 11	0.38	3 14
493.3	31.99	0.15	930	555	14.21	0.05	<u> </u>	10.10	1.11	0.00	0.14
498.5	32.21	8.43	950	580	13.95	0.65	180	7.90	1.07	0.47	3.53
502 5	32 49	8.57	960	575	13.95	0.65	213	3.77	0.89	0.46	3.06
502.5	00 71	0.47	1000	0.0	12.05	0.00	200	10.94	0.00	0 50	2.24
505.5	32.71	ð.46	1000	605	13.95	0.65	289	10.84	0.82	0.50	5.50
508.5	32.92	8.35	980	600	13.95	0.65	309	11.50	1.00	0.48	3.29
511 E	22 14	0 20	070	575	13.05	0.65	100	7 01	0 02		3 20
511.5	33.14	0.00	7/0	3/3	13.73	0.00	177	7.71	0.93	o	0.20
515.5	33.43	8.48	980	585	13.95	0.65	223	8.75	0.94	0.44	3.03
518.5	33.64	5.72	680	405	13.95	0.65	312	12.92	1.48	0.56	3.82
									-		

5215 34.00 6.77 780 4.65 13.95 0.66 11.19 0.84 0.83 3.67 53105 34.50 8.39 960 565 13.95 0.66 193 11.19 0.77 0.80 3.04 5315 34.72 8.20 960 560 13.95 0.66 192 11.65 0.94 0.43 3.01 5335 34.72 8.20 960 560 13.95 0.66 244 1.45 0.47 0.444 3.10 542.5 35.36 8.23 1200 565 13.95 0.66 244 1.45 0.31 3.25 551.0 5.79 6.40 395 1.462 0.66 223 4.43 1.25 0.20 3.34 555.5 3.65 97.73 1150 695 1.462 0.66 224 1.45 0.31 3.25 565.5 7.69 0.65 21.91 0.20 3.63	521.5	33.86	7.87	920	560	13.95	0.65	166	7.39	0.66	0.42	2.84
527.0 54.25 8.39 960 557 13.05 0.66 193 11.24 0.77 0.50 3.14 530.5 34.72 8.20 960 565 13.95 0.66 155 8.85 1.03 0.51 3.17 533.5 34.72 8.20 960 565 13.95 0.66 220 1.23 0.44 3.14 530.5 34.35 510 295 1.395 0.66 244 1.54 0.47 3.14 531.5 7.66 1020 585 13.95 0.66 244 1.54 0.41 3.48 555.5 36.35 59.9 64.0 395 13.95 0.66 224 4.54 1.45 0.31 3.25 565.5 37.05 7.56 900 14.62 0.66 244 1.165 1.32 0.42 3.61 571.5 37.50 7.43 9.40 540 550 7.59 0.66	523.5	34.00	6.77	780	465	13.95	0.65	205	11.19	0.84	0.38	3.67
5315 3450 8450 560 1505 1305 1005 1317 3335 3417 820 960 500 1305 1066 192 11.65 0.94 0.33 3.01 3335 3417 820 960 500 1305 0.66 129 11.65 0.94 0.43 3.01 3420 335.6 7.66 1000 855 13.95 0.66 244 1.13 3.05 551.0 3576 81.0 950 13.95 0.66 248 1.13 3.05 551.0 3577 81.0 950 14.62 0.66 223 4.43 1.25 0.21 3.20 565.0 36.28 82.9 980 14.62 0.66 244 1.45 0.36 3.41 571.0 7.67 975 128 970 975 128 970 975 130 940 7.69 0.66 291 10.91	527.0	34 25	8.38	960	575	13.95	0.66	193	11.24	0.77	0.50	3.04
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	530 5	34 50	8.39	960	565	13.95	0.66	155	8.85	1.03	0.51	3.17
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	533 5	34 72	8 20	960	560	13.95	0.66	192	11.65	0.94	0.43	3.01
$ \begin{array}{c} \begin{array}{c} c_{0}c_{0}c_{0}c_{0}c_{0}c_{0}c_{0}c_{0}$	536 5	34 92	4 35	510	295	13.95	0.66	260	9.85	1 18	0.47	3.14
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	520 F	35 15	7.06	1020	585	12.95	0.00 0 66	200	15 40	1.10	0.4/	3.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	542 5	35.10	8.72	1020	565	12.95	0.00	207	10.40	1 22	0.79	3.14
black black <td>551.0</td> <td>35.30</td> <td>0.23 8 10</td> <td>050</td> <td>580</td> <td>13.95</td> <td>0.00</td> <td>348</td> <td></td> <td>1 1 2 3</td> <td>0.27</td> <td>3 05</td>	551.0	35.30	0.23 8 10	050	580	13.95	0.00	348		1 1 2 3	0.27	3 05
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	551.0 552 5	26 1E	6.10	740	155	12.55	0.00	760		1 50	0.41	3 48
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	555.5 554 5	26.13	0.42 5 50	740 610	400 20E	13.93	0.00	200	4 54	1.09	0.41 () 21	3 25
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	550.5 550 5	30.30	0.09	1150	60F	13.93	0.00	722	4 4 2	1.50	0.01	3.20
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	559.5 549 E	26.09	7./J Q 10	1120	500	14.02	0.00	200	4.43 6 10	1.20	0.27	3 43
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	302.3 E4E E	27.05	0.27	900	590	14.02	0.00	229	7 20	1.02	0.30	3 30
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	505.5	37.03	2.00 Q /1	700 1070	505	14.02	0.00	261	7.2 7 17 14	1.00	0.50	3 41
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	509.0	37.32 37.50	0.41 7/2	040	540	14.02 7.60	0.00	344	12.10	1.20	0.00	3 61
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	571.5	27.30	7.43 0.75	74U 1000	705	7.09	0.00	365	16 74	1 30	0.42	3 50
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5/4.0	27.0/	7./J 7.45	1200	703	7.09 7.40	0.00	202	10.74	1.30	0.40	3.50
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	577.0	20,00	7.00	900 1010	500	7.09	0.00	271	7 14	1.41	0.47	3.02
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	500.0	20.00	0.30	1010	060	7.09 7.40	0.00	220	7.40	1.00	0.00	3.47
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	503.0	30.29	6.40	000		7.09	0.00	201	10.00	1.04	0.20	3.20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	586.0	38.49 28.47	0.49	800		7.09	0.00	1/4	10.20	1.00	0.44	3 01
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	E01 5	38.67	0 22	020	EON	7.09	0.00	191	14.23 5 92	1 00	0.4/	5.04 2.04
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	591.5	38.8/	ð.32	930	580	7.69	0.00	1/3	0.00 1 04	1.00	0.33	2.90 2 91
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	594.0	39.04	8.50	950	580	7.69	0.66	184	4.20	1.20	0.35	2.01
	597.0	39.25	8.85	1010	580	7.69	0.66	251	7.90	0.88	0.39	3.05 3.97
	600.0	39.45	8.16	960	575	7.69	0.66	137	0.18 14 50	0.84	0.35	2.00
	603.0	39.66	8.19	980	575	7.69	0.66	201	14.59	0.97	0.33	2.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	606.0	39.86	7.31	880	490	7.69	0.66	210	9.24 7.05	1.11	0.38	2.90
	609.5	40.19	7.52	880	520	7.69	0.66	311	7.95	1 00	0.45	3.30 2.09
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	612.5	40.58	8.25	1000	555	7.69	0.66	243	9.50	1.22	0.14	3.Uð 2.02
	615.5	40.97	8.27	990	595	7.69	0.66	194	0 1 2	1.12	0.30	2.73 2 91
	618.0	41.30	6.48	750	445	7.69	0.66	248	0.13	1 17	0.29	2.01
	621.0	41.69	6.84	770	4/5	7.69	0.66	234	0.39	1.17	0.27	2.73
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	624.0	42.08	8.41	1050	575	7.69	0.66	309	9.88	1.33	0.39	3.13 2.15
	627.0	42.47	8.37	1090	575	7.69	0.66	273	16.84	1.05	0.50	3.13 2.16
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	630.5	42.92	8.36	1040	570	7.69	0.67	071	1.77	1.00	0.57	3.10
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	633.0	43.25	8.38	1070	585	7.69	0.67	2/1	7.63	1.31	0.55	3.07
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	636.5	43.71	8.78	1040	595	7.69	0.67	252	8.09	1.25	0.50	3.13
642.5 44.49 8.82 1050 590 7.69 0.67 209 4.20 1.09 0.41 2.85 645.5 44.87 7.99 970 565 7.69 0.67 259 8.66 1.20 0.49 3.00 648.5 45.26 8.56 1050 595 7.69 0.67 238 8.82 1.01 0.45 3.22 651.5 45.65 8.54 1120 570 7.69 0.67 307 11.77 1.13 3.21 654.5 46.04 7.95 1040 540 7.69 0.67 204 7.22 0.93 3.02 660.5 46.81 8.45 1100 585 8.00 0.67 254 9.58 1.44 2.94 663.5 47.19 9.07 1160 635 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.94 9.96 1160 690 8.00 0.67 228 6.29 0.37 3.09 672.5 48.69 8.72 970 605 8.00 0.67 278 5.11 1.11 0.33 3.17 666.5 47.94 9.96 1160 690 8.00 0.67 278 5.11 1.11 0.33 3.19 672.5 48.69 8.72 970 585 8.00 0.67 184 5.47 1.36 2.99 675.5 49.06 <td>639.5</td> <td>44.10</td> <td>8.67</td> <td>1010</td> <td>595</td> <td>7.69</td> <td>0.67</td> <td>299</td> <td>15.16</td> <td>1.43</td> <td>0.64</td> <td>2.98</td>	639.5	44.10	8.67	1010	595	7.69	0.67	299	15.16	1.43	0.64	2.98
645.5 44.87 7.99 970 565 7.69 0.67 259 8.66 1.20 0.49 3.00 648.5 45.26 8.56 1120 570 7.69 0.67 238 8.82 1.01 0.45 3.22 651.5 45.65 8.54 1120 570 7.69 0.67 207 7.63 1.33 0.37 2.98 657.5 46.44 8.60 1190 625 7.69 0.67 204 7.22 0.93 3.02 660.5 46.81 8.45 1100 585 8.00 0.67 254 9.58 1.44 2.94 633.5 47.19 9.07 1160 635 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.56 8.90 1090 625 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.56 8.90 1006 690 8.00 0.67 225 9.08 1.19 0.31 3.17 666.5 47.94 9.96 1160 690 8.00 0.67 225 6.29 0.37 3.09 675.5 48.69 8.72 970 605 8.00 0.67 271 7.29 1.56 0.38 2.80 678.5 9.06 8.61 880 585 8.00 0.67 271 7.29 1.56 0.38 2.80 <th< td=""><td>642.5</td><td>44.49</td><td>8.82</td><td>1050</td><td>590</td><td>7.69</td><td>0.67</td><td>209</td><td>4.20</td><td>1.09</td><td>0.41</td><td>2.85</td></th<>	642.5	44.49	8.82	1050	590	7.69	0.67	209	4.20	1.09	0.41	2.85
648.5 45.26 8.56 1050 595 7.69 0.67 238 8.82 1.01 0.45 3.22 651.5 46.04 7.95 1040 540 7.69 0.67 207 7.63 1.33 0.37 2.98 657.5 46.44 8.60 1190 625 7.69 0.67 204 7.22 0.93 3.02 660.5 46.44 8.60 1190 625 7.69 0.67 224 9.58 1.44 2.94 663.5 47.19 9.07 1160 635 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.56 8.90 1090 625 8.00 0.67 258 1.29 0.32 3.00 669.5 47.94 9.96 1160 690 8.00 0.67 278 511 1.11 0.33 3.17 666.5 47.94 9.96 1160 690 8.00 0.67 278 511 1.11 0.33 3.19 672.5 48.49 8.72 970 605 8.00 0.67 278 511 1.11 0.33 3.19 678.5 49.06 8.61 880 585 8.00 0.67 184 547 1.36 2.94 681.5 49.46 8.12 970 585 8.00 0.67 184 547 1.36 2.94 681.5 50.19	645.5	44.87	7.99	970	565	7.69	0.67	259	8.66	1.20	0.49	3.00
651.5 45.65 8.54 1120 570 7.69 0.67 307 11.77 1.13 3.21 654.5 46.04 7.95 1040 540 7.69 0.67 272 7.63 1.33 0.37 2.98 657.5 46.44 8.60 1190 625 7.69 0.67 272 7.63 1.33 0.37 2.98 660.5 46.81 8.45 1100 585 8.00 0.67 254 9.58 1.44 2.94 663.5 47.19 9.07 1160 635 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.56 8.90 1090 625 8.00 0.67 226 12.69 1.29 0.32 3.00 669.5 47.94 9.96 1160 690 8.00 0.67 278 5.11 1.11 0.33 3.19 675.5 48.69 8.72 970 605 8.00 0.67 271 7.29 1.56 0.38 2.80 678.5 49.44 8.41 970 585 8.00 0.67 124 1.36 2.94 681.5 49.44 8.41 970 585 8.00 0.67 124 1.36 2.94 687.5 50.19 7.92 900 530 8.00 0.67 10.40 0.98 2.86 690.5 51.31 7.27 950 525 <td>648.5</td> <td>45.26</td> <td>8.56</td> <td>1050</td> <td>595</td> <td>7.69</td> <td>0.67</td> <td>238</td> <td>8.82</td> <td>1.01</td> <td>0.45</td> <td>3.22</td>	648.5	45.26	8.56	1050	595	7.69	0.67	238	8.82	1.01	0.45	3.22
654.5 46.04 7.95 1040 540 7.69 0.67 272 7.63 1.33 0.37 2.98 657.5 46.44 8.60 1190 625 7.69 0.67 204 7.22 0.93 3.02 660.5 46.81 8.45 1100 585 8.00 0.67 254 9.58 1.44 2.94 663.5 47.19 9.07 1160 635 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.56 8.90 1090 625 8.00 0.67 225 9.08 1.19 0.32 3.00 669.5 47.94 9.96 1160 690 8.00 0.67 225 6.29 0.37 3.09 672.5 48.31 8.56 1040 590 8.00 0.67 278 5.11 1.11 0.33 3.19 675.5 48.69 8.72 970 605 8.00 0.67 271 7.29 1.56 0.38 2.80 678.5 49.06 8.61 880 585 8.00 0.67 192 9.38 1.00 2.90 681.5 49.44 8.41 970 585 8.00 0.67 10.40 0.98 2.86 690.5 50.19 7.92 900 530 8.00 0.67 10.40 0.98 2.86 690.5 51.31 7.27 950 525 <td>651.5</td> <td>45.65</td> <td>8.54</td> <td>1120</td> <td>570</td> <td>7.69</td> <td>0.67</td> <td>307</td> <td>11.77</td> <td>1.13</td> <td>o</td> <td>3.21</td>	651.5	45.65	8.54	1120	570	7.69	0.67	307	11.77	1.13	o	3.21
657.5 46.44 8.60 1190 625 7.69 0.67 204 7.22 0.93 3.02 660.5 46.81 8.45 1100 585 8.00 0.67 254 9.58 1.44 2.94 663.5 47.19 9.07 1160 635 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.56 8.90 1090 625 8.00 0.67 252 9.08 1.19 0.32 3.00 669.5 47.94 9.96 1160 690 8.00 0.67 225 6.29 0.37 3.09 672.5 48.31 8.56 1040 590 8.00 0.67 278 5.11 1.11 0.33 3.19 675.5 48.69 8.72 970 605 8.00 0.67 271 7.29 1.56 0.38 2.80 678.5 49.06 8.61 880 585 8.00 0.67 192 9.38 1.00 2.90 684.5 49.44 8.41 970 585 8.00 0.67 10.40 0.98 2.86 690.5 50.56 6.32 720 420 8.00 0.67 10.40 0.98 2.86 690.5 51.31 7.27 950 525 8.00 0.67 10.87 1.10 3.18 695.5 51.69 7.66 7.69 1.45 3.65 3.65 <	654.5	46.04	7.95	1040	540	7.69	0.67	272	7.63	1.33	0.37	2.98
660.5 46.81 8.45 1100 585 8.00 0.67 254 9.58 1.44 2.94 663.5 47.19 9.07 1160 635 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.56 8.90 1090 625 8.00 0.67 252 9.08 1.19 0.31 3.17 666.5 47.94 9.96 1160 690 8.00 0.67 225 6.29 0.37 3.09 672.5 48.31 8.56 1040 590 8.00 0.67 278 5.11 1.11 0.33 3.19 675.5 48.69 8.72 970 605 8.00 0.67 271 7.29 1.56 0.38 2.80 678.5 49.06 8.61 880 585 8.00 0.67 184 5.47 1.36 2.94 681.5 49.44 8.41 970 585 8.00 0.67 192 9.38 1.00 2.90 684.5 49.41 8.41 970 585 8.00 0.67 10.40 0.98 2.86 690.5 50.19 7.92 900 530 8.00 0.67 10.40 0.98 2.86 690.5 50.56 6.32 720 420 8.00 0.67 10.40 0.98 2.86 690.5 51.31 7.27 950 525 8.00 0.67 <td>657.5</td> <td>46.44</td> <td>8.60</td> <td>1190</td> <td>625</td> <td>7.69</td> <td>0.67</td> <td>204</td> <td>7.22</td> <td>0.93</td> <td></td> <td>3.02</td>	657.5	46.44	8.60	1190	625	7.69	0.67	204	7.22	0.93		3.02
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	660.5	46.81	8.45	1100	585	8.00	0.67	254	9.58	1.44		2.94
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	663.5	47.19	9.07	1160	635	8.00	0.67	252	9.08	1.19	0.31	3.17
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	666.5	47.56	8.90	1090	625	8.00	0.67	268	12.69	1.29	0.32	3.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	669.5	47.94	9.96	1160	690	8.00	0.67	325	6.29		0.37	3.09
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	672.5	48.31	8.56	1040	590	8.00	0.67	278	5.11	1.11	0.33	3.19
678.5 49.06 8.61 880 585 8.00 0.67 184 5.47 1.36 2.94 681.5 49.44 8.41 970 585 8.00 0.67 192 9.38 1.00 2.90 684.5 49.81 8.25 930 580 8.00 0.67 206 8.98 0.91 2.81 687.5 50.19 7.92 900 530 8.00 0.67 10.40 0.98 2.86 690.5 50.56 6.32 720 420 8.00 0.67 16.01 1.16 0.37 3.34 693.5 50.94 7.61 960 535 8.00 0.67 10.87 1.10 3.18 696.5 51.31 7.27 950 525 8.00 0.67 6.69 1.04 0.50 2.77 699.5 51.69 7.96 1100 650 8.00 0.67 341 1.24 3.47 702.5 52.06 7.72 1020 565 8.00 0.67 344 15.31 1.39 3.36 705.5 52.44 7.95 1050 585 8.00 0.67 304 7.26 1.30 3.12 710.5 53.08 7.32 1010 530 6.25 0.67 381 23.50 1.53 0.54 4.03 714.5 53.72 8.54 1180 635 6.25 0.67 365 31.63 1.52 <	675.5	48.69	8.72	970	605	8.00	0.67	271	7.29	1.56	0.38	2.80
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	678.5	49.06	8.61	880	585	8.00	0.67	184	5.47	1.36		2.94
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	681.5	49.44	8.41	970	585	8.00	0.67	192	9.38	1.00		2.90
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	684.5	49.81	8.25	930	580	8.00	0.67	206	8.98	0.91		2.81
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	687.5	50.19	7.92	900	530	8.00	0.67		10.40	0.98		2.86
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	690.5	50.56	6.32	720	420	8.00	0.67		16.01	1.16	0.37	3.34
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	693.5	50.94	7.61	960	535	8.00	0.67		10.87	1.10		3.18
	696.5	51.31	7.27	950	525	8.00	0.67		6.69	1.04	0.50	2.77
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	699.5	51.69	7.96	1100	650	8.00	0.67	341		1.24		3.47
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	702.5	52.06	7.72	1020	565	8.00	0.67		7.69	1.45		3.65
708.5 52.81 7.98 1100 580 8.00 0.67 304 7.26 1.30 3.12 710.5 53.08 7.32 1010 530 6.25 0.67 381 23.50 1.53 0.54 4.03 714.5 53.72 8.54 1180 635 6.25 0.67 406 30.06 1.29 3.70 717.5 54.20 7.90 1120 600 6.25 0.67 365 31.63 1.52 0.53 3.22	705.5	52.44	7.95	1050	585	8.00	0.67	344	15.31	1.39		3.36
710.5 53.08 7.32 1010 530 6.25 0.67 381 23.50 1.53 0.54 4.03 714.5 53.72 8.54 1180 635 6.25 0.67 406 30.06 1.29 3.70 717.5 54.20 7.90 1120 600 6.25 0.67 365 31.63 1.52 0.53 3.22	708 5	52 81	7.98	1100	580	8.00	0.67	304	7.26	1.30		3.12
714.5 53.72 8.54 1180 635 6.25 0.67 406 30.06 1.29 3.70 717.5 54.20 7.90 1120 600 6.25 0.67 365 31.63 1.52 0.53 3.22	710 5	53.08	7.32	1010	530	6.25	0.67	381	23.50	1.53	0.54	4.03
717.5 54.20 7.90 1120 600 6.25 0.67 365 31.63 1.52 0.53 3.22	714 5	53.72	8.54	1180	635	6.25	0.67	406	30.06	1.29		3.70
	717.5	54.20	7.90	1120	600	6.25	0.67	365	31.63	1.52	0.53	3.22

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720.5	54.68	7.48	1080	565	6.25	0.67	323	15.07	1.24		3.88
723.5	55.16	8.09	1150	620	6.25	0.67	253	13.59	1.30	0.41	3.86
726.5	55.64	9.58	1390	735	6.25	0.67	435	15.20	1.09		3.37
729.5	56.12	6.61	870	490	6.25	0.67	279	16.34	0.98		2.93
732.5	56.60	7.95	990	585	6.25	0.67	224	14.72	0.96	0.47	3.15
735.5	57.04	8.48	1030	620	12.50	0.67	226		1.00	0.45	2.92
738.5	57.28	7.34	900	525	12.50	0.67	209	8.78	0.87	0.39	3.18
741.5	57.52	8.42	1080	620	12.50	0.67	277	13.50	0.81	0.39	3.31
744.5	57.76	8.07	1010	605	12.50	0.67	160	6.19	0.60	0.40	
747.5	58.00	8.16	1060	610	12.50	0.67		4.62	0.58		
750.5	58.24	8.10	1090	605	12.50	0.67	255	11.42	0.77	0.35	2.98
753.5	58.48	8.36	1140	640	12.50	0.68	313	11.82	0.77		2.15
756.5	58.72	7.32	900	535	12.50	0.68	314	12.90	0.74	0.26	2.78
759.5	58.96	7.84	900	525	12.50	0.68	195	4.84	1.19		2.70
762.5	59.20	7.61	910	565	3.12	0.68	219	15.20	0.77		2.73
765.5	59.44	7.29	840	535	3.12	0.68	241	13.69	0.72	0.37	2.80
768.5	59.68	6.82	830	500	3.12	0.68		9.07	0.72	0.32	2.62
771.5	59.92	7.35	810	530	3.12	0.68		5.73	0.76	0.37	2.45
774.5	60.16	9.26	1020	680	3.12	0.68	209	5.02	0.92	0.29	2.54
777.5	60.40	8.47	890	595	3.12	0.68	251	6.93	0.81	0.36	2.62
780.5	60.64	7.07	730	485	3.12	0.68	122	6.03	0.67		2.32
783.5	60.88	7.83	780	530	3.12	0.68	169	6.47	0.72		2.58
786.5	61.12	9.43	950	630	3.12	0.68	165	3.98	0.61		2.24
789.5	61.36	9.35	950	605	3.12	0.68	144	7.25	0.91	0.27	2.23
792.5	61.60	10.29	990	685	3.12	0.68	161	10.31	0.67	0.36	2.23
795.5	61.84	8.78	730	575	3.12	0.68	168	4.34	0.73	0.35	
798.5	62.08	9.43	950	610	3.12	0.68	201	7.19	0.74	0.25	2.04
801.5	62.32	9.17	930	610	8.64	0.68	204	5.60	0.72	0.47	2.41
804.5	62.56	8.19	840	550	8.64	0.68	296	6.82	1.18		2.61
807.5	62.80	9.19	910	605	8.64	0.68	193	6.95	0.73	0.28	2.47
810.5	63.04	8.62	870	580	8.64	0.68	306	9.66	0.87	0.26	2.78
813.5	63.28	0.02	0/0	000	8.64	0.68	257	4.86	0.76	0.27	2.41
816.5	63.52	8.34	810	570	8.64	0.68	215	4.60		0.37	2.65
819.5	63 76	9.53	930	645	8.64	0.68	229	5.87	0.58	0.37	2.09
822.5	64 00	9.35	910	630	8.64	0.68	186	9.27	0.81	0.41	2.64
825.5	64.24	9.89	1000	675	8.64	0.68	235	5.38	0.82	0.37	2.44
828.5	64.48	8.55	870	590	8.64	0.68	213	5.12	0.68	0.43	2.88
831.5	64 72	8.07	810	550	8.64	0.68	180	5.89	0.68	0.36	2.59
834 5	64 96	0.07	010	000	8.64	0.68	205	4.96	0.56	0.37	2.70
837.5	65.20	8.34	820	595	8.64	0.68	156	5.91	0.68	0.41	2.79
840 5	65 44	8.55	950	635	8.64	0.68	178	5.84	0.76	0.36	2.87
842 5	65 68	6 53	290	870	8.64	0.68	159	3.48	0.91	0.36	2.72
846 5	65.92	3.91	190	745	8.64	0.68	106	8.16	0.65	0.28	2.54
849 5	66 16	4 34	230	660	8.64	0.68	***	5.69	0.64	0.40	2.34
852 5	66 40	4.04	240	910	8 64	0.68		0.07	0.67		2.52
855 E	66 64	702	1020	655	8 64	0.68	236	4 51	1.38		3.24
858 F	66.89	1.72	1020	000	8 64	0.68	300	845	1 40	0.37	4.16
861 E	67 10	4 57	170	820	8 64	0.00	352	13 32	1.30	0.50	1.10
864 E	67 26	4 25	280	865	8.64	0.00	211	6 4 8	1 19	0.55	4.17
967 F	67.60	0.55	1170	710	8.64	0.68	274	5 10	0.97	0.53	2.80
007.0 970 E	07.0U 47.04	5.13	200	600	861	0.00	122	0.10	1 00	0.00	3 11
0/0.5	07.84	0.42	300	090	0.04	0.00	100	7.30	1.00	0.00	2.11

W8709-A 9BC	Mn (ppm)
0-1	1788.5
0-2	1011.5
2-3	661.6
2-4	647.2
4-6	694.4
6-8	665.0
8-10	657.4
10-12	616.9
12-14	659.8
14-16	643.9
16-18	637.7
18-20	613.4
20-22	619.9
22-24	614.8
24-26	627.3
26-28	617.4
28-30	623.6
30-32	617.2
32-34	636.4
34-36	667.9
36-38	649.6
38-40	651.2
40-42	687.4
42-44	659.8

Table A.IV.2: Mn data of box core W8709-9BC at the Nearshore site