

**Holocene climate evolution of the eastern tropical
Pacific told from high resolution climate records from
the Peru margin and equatorial upwelling regions**

By

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Preface

The Peru margin plays a significant role in global climate dynamics and biogeochemical cycling. The Peru coastal current merges with equatorial upwelling to form the eastern equatorial cold tongue [*Chavez, 1995; Strub et al., 1998*]. Instability of the tropical cold tongue drives the coupled oceanic- atmospheric El Niño Southern Oscillation (ENSO). This coupled mode has been described as a ‘globalizer’ for its ability to drive global climate on both millennial and orbital timescales [*Cane, 1998; Clement et al., 1999; Huybers and Molnar, 2007*].

The Peru margin is also one of the world’s three oxygen minimum/ denitrification zones [*Codispoti and Christensen, 1985*]. Fueled by coastal upwelling, the Peru Current is the most productive of the world’s eastern boundary currents; primary production exceeds $200 \text{ gC m}^{-2} \text{ yr}^{-1}$, [*Berger et al., 1987*]. This high surface productivity along with poorly ventilated subsurface waters lead to a persistent oxygen deficit at depth. Microbial denitrification under these oxygen-depleted conditions represents the major loss of nitrate from the global ocean [*Wyrski, 1973; Codispoti and Christensen, 1985*]. Peru margin upwelling represents the final stages of a ventilation process that begins in the southern high latitudes, extends to the western subtropics, and then travels across the Pacific basin to the eastern tropical Pacific [*Lukas, 1986 Wyrski, 1973; Toggweiler et al., 1991*]. As a result, Peru margin surface and subsurface climate parameters are connected to both the high and low latitudes.

Despite the significance of the Peru margin, little is known about how the climate evolved during the recent past. The work presented in this dissertation focuses on

understanding how Peru margin climate has evolved since the end of the Last Glacial Maximum, and on what the driving mechanisms of those climate changes were.

Chapter 1 looks at three sediment cores from a latitudinal transect in the Peru margin. Here we reconstruct the key environmental parameters of Peru margin climate: Sea surface temperature (U_k^{37} index [Prahl *et al.*, 1987; Müller *et al.*, 1998]), phytoplankton productivity (Alkenone- C_{37} total [Budziak *et al.*, 2000] and biogenic silica [Honjo *et al.*, 1982]) and subsurface ventilation ($\delta^{15}N$ of bulk organics [Libes and Deuser, 1988; Altabet *et al.*, 1995]). Chapter 1 focuses on the relationships between surface and subsurface proxies and their connection to the ventilation of the Peru undercurrent. Today the high respiration rates imposed by surface productivity are one of the drivers of the Peru oxygen minimum zone. Surprisingly our paleoreconstructions indicate that this was not always the case, during the early Holocene extreme oxygen deficits correspond to periods of low inferred surface production. This decoupling between surface and subsurface climate proxies indicates that the remote ventilation of the undercurrent dominated over the oxygen demand imposed by local productivity. Near the mid-Holocene we see evidence for a major increase in climate variance and a shift towards more locally driven climate.

This ‘ramping up’ in Peru margin variability occurs along with a regional enhancement of ENSO strength [eg. Moy *et al.*, 2002; Koutavas *et al.*, 2006; Conroy *et al.*, 2008]. Chapter 2 focuses on the relationship between proxies to evaluate whether these high amplitude climate oscillations of the late Holocene resemble ENSO forced climate. Rather than a regular increase in ENSO-like climate, the relationships between temperature, productivity and subsurface oxygen proxies indicate that the late Holocene

oscillated between ENSO-like and non-ENSO-like climate.

Chapter 3 focuses on a novel approach to reconstruct minute changes in subsurface oxygen. Using low oxygen benthic foraminifera assemblages we find evidence for close ties between Peru margin environmental conditions and foraminiferal species assemblages. Surface productivity and subsurface oxygen are the primary drivers of changes in foraminiferal abundance. Species diversity is driven only by modifications in subsurface oxygen. This work provides excellent confirmation for the use of $\delta^{15}\text{N}$ as a proxy for subsurface oxygen and introduces the utility of benthic foraminifera as proxies for both surface productivity and subsurface oxygen in Peru margin sediments.

Chapter 4 moves away from the Peru margin and towards the greater eastern tropical Pacific. Using cores collected at the boundary between the Peru margin and Equatorial upwelling regions we find evidence for major millennial-scale oscillations in surface temperatures, which are markedly different from those recorded in the Peru margin. This work highlights the differences between climates of the eastern tropical cold tongue and those of the Peru margin. Despite these differences, like Chapters 1 and 2, Chapter 4 highlights the importance of extra tropical climate forcing on the eastern tropical Pacific. Of particular significance, we find that long term changes in cold tongue sea surface temperatures are decoupled from local changes in upwelling.

Chapter 5 compares two proxies of sea surface temperature, TEX_{86} and $\text{U}^{\text{K}'}_{37}$ in Peru margin sediments. We find that the $\text{U}^{\text{K}'}_{37}$ temperature estimates are consistent with mean annual sea surface temperatures while TEX_{86} estimates record temperatures deeper in the water column where temperatures are cooler and more stable than the surface. Understanding the temperature gradients at the Peru margin may provide important

insight into the long term changes in local and remote climate forcings.

Each of these chapters highlights the importance of the extra tropics, most likely the high latitude southern ocean, in driving climate changes in the eastern tropical Pacific during the Holocene.

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Abbreviations used in text

BSi	Biogenic Silica
ECT	Eastern Cold Tongue
EEP	Eastern Equatorial Pacific
ENSO	El Niño Southern Oscillation
ETP	Eastern Tropical Pacific
EUC	Eastern Equatorial Undercurrent
HNLC	High nitrate low chlorophyll
ITCZ	Intertropical Convergent Zone
LGM	Last Glacial Maximum
NH	Northern Hemisphere
ODP	Ocean Drilling Project
OMZ	Oxygen minimum zone
PUC	Peru Undercurrent
PCC	Peru Coastal Current
R/V	Research Vessel
SAMW	Subantarctic Mode Waters
SST	Sea surface temperatures
SH	Southern Hemisphere
TOC	Total organic carbon

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CHAPTER ONE

Local and remote influences on Holocene Sedimentation along the Peru Margin

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Abstract

The Peru margin upwelling system is one of the most productive regions of the modern ocean. Persistent oxygen depletion in the Peru margin subsurface makes this region the strongest of the world's three Oxygen Minimum/Denitrification Zones. Changes in Peru margin upwelling are inextricably linked to Pacific basin circulation, ocean nutrient cycling and the global carbon cycle. Despite the significance of this region many outstanding questions remain about the state of Peru margin climate across the Holocene, including: 1) Are long term changes in the strength of the Peru oxygen minimum zone forced by climate mechanisms of the larger eastern tropical Pacific or do these climate fluctuations reflect factors originating outside the tropics in the southern high latitudes? and 2) Have these forcing mechanisms changed across the Holocene? We reconstruct changes in sea surface temperature (U_{37}^k), surface productivity (C_{37} total and biogenic silica) and subsurface oxygen ($\delta^{15}N$ and laminations), in a latitudinal transect (11-15°S) across the Peru margin upwelling zone during the Holocene. Using high sedimentation-rate, laminated marine cores with overlapping chronologies we capture a rare window into the evolution of the Peru margin climate both spatially and temporally. Comparison between proxies of surface and subsurface conditions enables us to separate the dual contribution of local and remote climate forcing. Our results suggest that the remote ventilation of the Peru thermocline dominated over the oxygen demand imposed by local productivity during the early Holocene. Near the middle Holocene a dramatic increase in climate variability was accompanied by a shift toward more locally driven climate dynamics, revealed through the relationship between our surface and subsurface climate proxies. The late Holocene section of our record oscillates between centennial-

scale periods of locally driven and non-locally driven subsurface ventilation. We therefore argue that the strength of the Peru oxygen minimum zone reflects a balance between high and low latitude climate forcings.

1. Introduction

The Peru upwelling system (4-16°S) provides a unique bridge between climates of the higher and lower latitudes in the Pacific basin. The poleward flowing Peru Undercurrent is derived from an extension of the Equatorial Undercurrent (EUC); Peru margin upwelling represents the final stages of a ventilation process that begins in the southern high latitudes, extends to the western subtropics, and then travels across the Pacific basin to the eastern tropical Pacific [Wyrki, 1973; Toggweiler *et al.*, 1991]. The strength of upwelling off of Peru is directly influenced by local wind strength, shoaling of the thermocline [Enfield and Allen, 1980; Enfield and Mestas-Nuñez, 2000; Vargas *et al.*, 2007], the position of the intertropical convergent zone (ITCZ) and the El Niño Southern Oscillation (ENSO) [Philander, 1983]. In turn, upwelling affects surface production, which, in combination with poorly ventilated source waters contributes to the subsurface oxygen deficit [Codispoti and Christensen, 1985]. Thus, the chemical, physical and biological properties of the Peru margin reflect the integration of processes linked to both high and low latitude climate dynamics [Strub *et al.*, 1998]. On decadal timescales Sea Surface Temperatures (SST) and the local carbon flux are primarily influenced by tropical climate dynamics, including the El Niño Southern Oscillation [Barber and Smith, 1981; Barber and Chavez, 1983; Sanchez *et al.*, 2000], while the intermediate water oxygen deficit is tied to both local production and remote ventilation of the subsurface

[Thomas *et al.*, 1979; 1966; Codispoti and Christensen, 1985; Ninnemann and Charles, 1997]. On centennial time scales SST and surface production can also be influenced by changes in the waters that feed the Peru undercurrent through an extension of the EUC [Wyrki, 1973; Toggweiler *et al.*, 1991]. Here, we evaluate whether remote (high latitude) or local (tropical) climate dynamics dominated the subsurface ventilation and surface temperature and productivity of the Peru margin across the Holocene.

The sediments underlying the Margin provide a unique record of high-resolution climate fluctuations across the Holocene. The combination of high sedimentation rates and hypoxic bottom water conditions yield excellent conditions for the preservation of organic matter. However, frequent hiatuses found in Margin sediment sequences and a lack of abundant carbonate materials has hindered previous work in this important region [De Vries and Schrader, 1981; Reinhardt *et al.*, 2002]. Using multiple sediment cores collected along the Peruvian shelf (11-15°S, 250-180mwd), with overlapping chronologies and a suite of geochemical proxies, we have overcome the stratigraphic challenges that have plagued previous studies at the Margin. We reconstruct parameters that define the key oceanographic variables of SST (U^k_{37} index [Muller *et al.*, 1998; Prahl *et al.*, 1988]), surface productivity (Alkenone- C_{37} total [Budziak *et al.*, 2000] and biogenic silica [Honjo *et al.*, 1982]) and subsurface oxygen (inferred from $\delta^{15}N$ of bulk organics [Libes and Deuser, 1988; Altabet *et al.*, 1995]). These cores include the first uninterrupted, high-deposition rate (70cm/kyr) Holocene (10-1.4ka) sediment archive ever recovered from the southern Peru margin [Chazen *et al.*, 2009] along with two additional high deposition rate cores collected from the central Margin (see Figure 1). For time periods where core chronologies overlap we can reconstruct how conditions in

the southern part of the Peru margin (15°S, PC-2) differ from those in the central Margin (11°S, cores 1228D and W7706-40K) and how these latitudinal gradients may have evolved over time.

Relative to the glacial-interglacial cycles of the Pleistocene epoch, the Holocene (last ~11ka years) was a stable period of Earth's history. The last of the large northern hemisphere ice sheets retreated by the early Holocene (~8ka) [Clark *et al.*, 1999] and major greenhouse gas concentrations were relatively stable [Indermühle *et al.*, 1999]. Tropical climate records from the Holocene Epoch however, are punctuated by a major increase in climate variability. Multiple paleoclimate reconstructions from the tropical [Moy *et al.*, 2002; Conroy *et al.*, 2008; Chazen *et al.*, 2009] and subtropical Pacific [De Pol Holz *et al.*, 2007; Lamy *et al.*, 2001; 2002] indicate that this climate shift resulted in a significant enhancement of high frequency climate variability. The prevailing explanation for this climate shift is the mid-Holocene strengthening of the El Niño Southern Oscillation, the primary mode of interannual variability in the Eastern Tropical Pacific [Philander, 1983]. Enhanced ENSO strength during the Holocene may be linked to modifications in the precession of Earth's orbit [Kutzbach *et al.*, 1998; Clement *et al.*, 1999]. Precession controls the summer-winter heating contrast in the tropics, an aspect fundamental to the underlying tendency of the tropical atmosphere-ocean instability to generate ENSO events [Fedorov and Philander, 2001; Cane, 2005] and also changes the intensity of seasonality between the hemispheres [Kutzbach *et al.*, 1998]. Paleoclimate reconstructions suggest that changes in precession caused a gradual drift in the position of the ITCZ from its most northerly extent in the early Holocene to a more equatorial location today [Haug *et al.*, 2001]. Changes in the position of the ITCZ may have also

played a role in allowing for the development of strong ENSO events near the mid-Holocene [*Moy et al.*, 2002; *Cane*, 2005; *Koutavas et al.*, 2006].

Many studies have described the tropical Pacific mid-Holocene climate transition in terms of tropical forcing mechanisms [*Clement et al.*, 1999; *Moy et al.*, 2002]. The role of the extra tropics however, which control a significant portion of the physical and biological properties of the tropical thermocline [*Wyrski*, 1973; *Toggweiler et al.*, 1991; *Strub et al.*, 1998] have received much less attention. Changes in the physical and biological properties of the EUC, which originates in the southern high latitudes and eventually provides the source of the Peru undercurrent, may be particularly important for Peru margin climate change. The EUC is vertically partitioned; the lower layers originate in the Antarctic Circumpolar region and provide the source of cool nutrient rich, oxygen depleted waters that impart a strong ‘upwelling’ signal off Peru today. The upper layer of the EUC originates in the Subantarctic region [*Toggweiler et al.*, 1991; *Wyrski*, 1973]. Compared to the lower layer of the EUC, the upper layer is warm and nutrient poor. What layer of the EUC eventually upwells off of Peru may have significant consequences on the biological, physical and chemical properties of Peru margin.

Using a suite of climate proxies that record both surface and subsurface climate indices in the Peru margin, we identify climatic signatures consistent with locally driven climate processes and those that appear to be influenced by remote processes. Using three individual sediment cores in a latitudinal transect allows us to assess whether the climate changes recorded in our sediment records reflect a regional signal or are restricted at an individual core site. In order to distinguish locally driven from remotely driven climate dynamics we establish end members of each idealized state based on observations from

the modern Peru margin. In the locally driven state, we anticipate surface productivity and subsurface oxygen to be closely related. Enhanced organic matter production imparts a strong oxygen demand at depth. Additionally, periods of high local productivity should accompany cooler temperatures due to the relationship between upwelling and nutrient supply. In the remotely forced end member the physical properties of the subsurface are inherited outside the tropics. In this state, local climate indices are decoupled from subsurface oxygenation. The goal of this paper is to outline the dual contributions of the physical and biological properties that influence local upwelling and remote ventilation of the Peru upwelling system across the Holocene.

2. Modern Oceanographic Setting

The Peru margin is situated at the interface between the poleward Peru Undercurrent (PUC, 50-500 m depth) and the equatorward Peru Coastal current (PCC). Equatorward along-shore winds are deflected offshore by the Coriolis effect, which forces cold nutrient-rich, thermocline waters to the surface. The poleward flowing Peru Undercurrent is derived from an extension of the Equatorial Undercurrent (EUC), which originates in the Antarctic polar region before it is transported across the Pacific basin and ultimately surfaces near the Galapagos [Toggweiler *et al.*, 1991; Strub *et al.*, 1998; Wyrtki, 1973]. What remains of this transport is deflected along the South American continent and eventually upwelled off of Peru [Lukas, 1986]. The poor ventilation of the surface waters along with high respiration rates make the intermediate waters of the Peru margin the largest of the world's 3 oxygen minimum zones (OMZ). Oxygen minimum/denitrification zones describe regions of the subsurface ocean (150 to 800 mwd) with persistent oxygen deficits (suboxic, $[O_2] < 10 \mu\text{mol kg}^{-1}$). The formation of OMZs

depends on geography, ocean circulation and surface productivity. The poor ventilation of the Peru Undercurrent [Toggweiler *et al.*, 1991; Bernhard and San Gupta, 1999] in combination with large quantities of sinking organic debris impose a high oxygen demand and lead to a persistent oxygen deficit in the subsurface [Toggweiler and Carson, 1995; Pennington *et al.*, 2006].

Oxygen minimum zones occupy over 1% of the global ocean [Kamykowski and Zentara, 1990] and have major impacts on the ocean nitrogen cycle and global carbon. In the open-oxygenated ocean the isotopic signature of nitrate is near 4-6‰ [Altabet *et al.*, 1999; Sigman *et al.*, 1999]. By comparison $\delta^{15}\text{N}$ from sediments underlying OMZs are significantly heavier, 8-10‰ [Libes and Deuser, 1988; Prospero, 1996; Altabet *et al.*, 1999]. In oxygen depleted environments microbial bacteria reduce (NO_3^-) into nitrogen gas (N_2), which is lost to the atmosphere. Microbial denitrification represents the major loss of nitrate from the global ocean [Wyrski, 1973; Codispoti and Christensen, 1985]. During denitrification, light nitrate ($\text{N}^{14}\text{NO}_3^-$) is preferentially removed leaving the remaining nitrate pool enriched in heavy nitrate ($\text{N}^{15}\text{NO}_3^-$). This heavy nitrate signal is transferred to the surface through upwelling where it is used by biota and eventually transferred to the underlying sediments.

The strength of upwelling off Peru is highly sensitive to changes in the position of the ITCZ and the strength of Walker circulation [Strub *et al.*, 1998; Lavin *et al.*, 2006]. Along shore winds are deflected off shore by the Coriolis effect- leading to strong Ekman pumping along the southern coast of Peru. The thermocline resides < 40 m below the surface and can break the surface during periods of enhanced upwelling [Fiedler and Talley, 2006; Pennington *et al.*, 2006]. During peak divergence (boreal summer) the

equatorward Peru Current merges with equatorial upwelling to form the eastern equatorial cold tongue [Barber, 1995; Strub *et al.*, 1998; Scheidegger and Krissek, 1981]. The cool surface waters of the eastern Pacific increase in temperature as they migrate westward along the equator, resulting in a significant west to east temperature gradient in the tropical Pacific surface waters. This surface gradient overlies and helps to maintain a perched thermocline that is significantly shallower in the east than the west [Toggweiler *et al.*, 1991; Barber and Smith, 1981].

The PCC supports one of the world's most abundant pelagic fisheries [Smith, 1983; Berger *et al.*, 1987]. Primary production exceeds $200 \text{ gC m}^{-2} \text{ yr}^{-1}$ [Berger *et al.*, 1987], making the PCC the most productive of the world's eastern boundary currents. As much as 50% of the global ocean's new biological production originates in the eastern tropical pacific (ETP) [Chavez and Barber, 1987]. Despite these high rates of new production the Peru margin is classified as a high nitrate low chlorophyll (HNLC) region due to the year round surplus of nitrate in the surface waters [Smith, 1983]. Biological production and efficiency at the Margin is influenced by upwelling strength, thermocline properties and the availability of micro and macronutrients [Dugdale and Wilkerson, 1998; Nixon and Thomas, 2001]. The availability of micro nutrients (dissolved Fe) and over-grazing by zooplankton appear to be the most critical factors limiting new production [Bruland *et al.*, 2005; Sarmiento *et al.*, 2004]. HNLC regions play an importance role in global nutrient cycling and atmospheric CO_2 . The Peru margin surface waters are supersaturated with respect to CO_2 , making the Margin an important source for atmospheric CO_2 [Stramma *et al.*, 2008].

3. Site Locations

At present, Peru margin SST, productivity, subsurface [O₂] and sedimentation rates vary with latitude and longitude. SSTs increase moving towards the equator and away from the coast; the average annual SST in the central margin (~11° S, ~21.5 °C) is ~2.5 °C warmer than that of our southern core site (~15° S, ~19 °C) (see Figure 1 for core locations). While upwelling persists year-round, local wind strength and corresponding changes in SSTs vary seasonally with the migration of the ITCZ [*Philander, 1990*]. Peak divergence, and the coolest temperatures occur during boreal summer between June and November, which corresponds to the period of maximum trade wind strength [*Barber and Smith, 1981; Scheidegger and Krissek, 1981; Strub, 1998*]. Although the average mean annual SST varies with latitude, the seasonal range is similar between the central Margin (~18-24°C) and the southern Margin core site (~16.5-23°C) [*Pennington et al., 2006; USGS SST program (Tcl/Tk version 1.3)*].

Annual average *chlorophyll a* maps indicate that surface productivity is slightly higher in the central margin (near sites 1228D and 40K) than the southern margin site (core PC-2, see Figure 1). The seasonal range in primary production is also stronger in the northern and central Margin than the south [*Chavez, 1995; Strub et al., 1998; Pennington et al., 2006*]. Surprisingly, peak productivity blooms are offset from maximum upwelling by several months [*Calienes et al., 1985*]. This delay may be the result of light limitation during boreal winter when upwelling is the strongest but the exact cause is unclear [*Calienes et al., 1985; Chavez, 1995; Pennington et al., 2006*]. Large centric diatoms dominate the biomass in both the central and southern Margin [*Rojas de Mendiola, 1981*]. El Niño events are associated with increases in Peru margin

SSTs (1-3 °C) and dramatic decreases in surface productivity. While the opposite pattern occurs during the La Niña end-member of the southern oscillation the changes in temperature and productivity are less dramatic compared to El Niño events [*Chavez and Barber, 1987*].

The climate of coastal Peru is hyperarid, dominated by barren landscapes and broad coastal deserts. The small amount of rainfall that does reach western Peru is largely restricted to the Andes and falls mostly during the austral summer months but rarely reaches the coast [*Hebbeln et al., 2000*]. This changes during El Niño events, when the air warms and rises along the western coast of Peru- leading to heavy rainfall and increased sediment transport along the coast [*Chavez and Barber, 1987; Philander, 1990; Hebbeln et al., 2000*]. While macronutrients are supplied through upwelling, micronutrients reach the surface waters primary through contact with the underlying sediments, aeolian transport or river transport. The availability of micronutrients is an important factor for surface productivity [*Strub et al., 1998*]. Along the Peru margin, the availability of micronutrients is largely restricted to aeolian transport (during non El Niño conditions) or supplied through contact with the underlying sediments. The broad Peruvian shelf provides a ready source for dissolved Fe, which is transported to the surface by the Peru undercurrent, which intersects the slope in some areas before being upwelled to the surface [*Bruland et al., 2001, 2004; Hutchins et al., 2002*]. The shelf narrows between the northern and southern margin. As a result, dissolved Fe is more abundant in the northern and central margin than the southern margin [*Bruland et al., 2004*].

The south Pacific oxygen minimum zone extends off the Peruvian coast into the

eastern equatorial pacific [*Garcia et al.*, 2005]. Oxygen levels are lowest in the core of the OMZ between 14-16° S, where core PC-2 was collected. In the heart of the OMZ, laminated sediments indicate that oxygen concentrations are low enough to preclude bioturbation. Cores ODP1228D and W7706-40K were collected in the central margin near the northern boundary of the oxygen minimum/ denitrification zone (11 to 12° S). Subsurface oxygen concentrations vary seasonally with upwelling strength and interannually with El Niño Southern oscillation [*Barber and Chavez*, 1983].

While the high deposition rates and suboxic bottom water conditions of the Peru margin provide an ideal environment for the preservation of organic materials, the majority of sediment cores from this region suffer from major gaps in Holocene sedimentation [*Rein et al.*, 2002]. The bathymetry of the Peru slope is complex; water depths range from 180-400m but are interspersed with sharply dipping trenches and more shallow sections of sea floor [*Reinhardt et al.*, 2002]. Winnowing and erosion can introduce hiatuses in the sediment record, but are for the most part recognizable by gypsum layers [*Reimers*, 1982]. To overcome the difficulties in reconstructing continuous climate records imposed by frequent hiatuses in Margin sediments we present data from three sediment cores (see Fig. 1).

4. Methods

4.1. Age Models

We constructed age models from multiple AMS ^{14}C age estimations from bulk organics and alkenone specific analysis (see Fig. 1). A uniform reservoir correction of 450 years was used for each sediment core [*Bard et al.*, 1993; 1999]. Sedimentation rates range from 20-70cm/kyr in the three sediment cores. Core PC-2 was dated using 8 AMS

^{14}C age estimations and exhibits the highest sedimentation rates (70cm/kyr) with essentially linear accumulation rates between ~10ka and ~1.4ka (Figure 1b). Core W7706-40K contains a major hiatus in sedimentation between 13ka and 4ka; only the most recent section of this core (4ka-0.2ka) is presented here with 5 AMS ^{14}C age estimations (Figure 1c). The sedimentation rate (50cm/kyr) for 40K is somewhat lower than core PC-2 but typical of the central Peru margin [Reinhardt *et al.*, 2002]. Age models for cores PC-2 and W7706-40K were constructed using a linear curve fit of calendar ages (see Figures 1b,d). The age model for core 1228D is divided into two sections, 0.4ka-3.5ka and 7.6ka-14ka, which are separated by a major hiatus. Each section is dated with 4 AMS ^{14}C age estimations (Figure 1c).

4.2. *Laminations: X-radiograph/ Visual inspection*

Visual and x-ray inspection of sediment cores reveals important information about the depositional history of the Margin. Prior to destructive sampling, each sediment core was inspected carefully for the presence of laminations. These alternating layers of light and dark sediments are visible in each of the three sediment cores (see Figure 3b); their presence can provide clues to modes of production at the Margin and subsurface oxygen conditions. For example, the presence of annual lamination precludes the possibility of bioturbation and points to anoxic conditions during sedimentation. In modern OMZ environments animals capable of bioturbating sediments are rare when $[\text{O}_2] < 0.3\text{ml/l}$ and absent when $[\text{O}_2]$ fall below 0.1ml/l [Thompson *et al.*, 1985]. Laminated sediments are commonly found in environments where $[\text{O}_2]$ is below 0.2ml/l [Calvert, 1964]. The thickness (millimeter to multi-centimeter) and composition of these laminations varies

with time and with core location. A more detailed description of the composition and resolution of the laminations is outlined in section 5.3. Interspersed with laminated core sections are intervals of non-laminated homogenized sedimentation. In addition to visual inspection, core PC-2 was examined under medical x-ray (Figure 3a).

4.3. Benthic Foraminifera

We reconstruct Benthic Foraminiferal assemblages with two primary research objectives, 1) the presence/absence of benthic foraminifera, in addition to the preservation of calcareous tests can provide important information about changes in bottom water chemistry during the Holocene, and 2) variations in foraminiferal assemblages in low oxygen environments are reliable recorders of fluctuations in subsurface [O₂] [*Chazen et al.*, 2010 (dissertation chapter 3); *Bernhard et al.*, 1997]. Thus, benthic foraminifera can provide, among other things, confirmation of our use of $\delta^{15}\text{N}$ as a proxy for subsurface oxygen.

Samples were taken at a sample spacing corresponding to every 30-40 years to determine presence/absence of benthic foraminifera in cores 1228D and 40K. Core PC-2 was sampled at an estimated 20 year resolution and sampling was further increased to ~7-8 year resolution across intervals with abundant (>10 individuals/gram) benthic foraminifera. Figure 4 indicates where benthic foraminifera were found in core PC-2. Each sample was carefully homogenized, sieved and picked wet to prevent damage of thin-shelled foraminifera (following method of *Bernhard et al.*, 1997). Benthic foraminifera identification to the species level was conducted using a portion (~0.1-0.5g) of each homogenized sample under dissection microscopy (detailed information about species assemblages is summarized in *Chazen et al.*, 2010 (dissertation chapter 3)).

4.4. Alkenones

We use two proxies to reconstruct surface productivity: C_{37} total, which is an alkenone based proxy and biogenic silica (discussed below). Alkenones are widely used to reconstruct sea surface temperatures [Conte *et al.*, 2006; Herbert *et al.*, 1998; Muller *et al.*, 1998; Brassell *et al.*, 1993] but their utility in productivity reconstructions has also proved robust [Bolton *et al.*, 2010]. Compared to other phytoplankton lipids, alkenones are highly refractory [Brassell *et al.*, 1993; Budziak *et al.*, 2000]. While degradation of alkenones has been observed in a variety of oceanographic settings [Prahl *et al.*, 1998] these factors are most exaggerated in older sediments and in regions with low sedimentation rates [Sun and Wakeham, 1994; Rontani *et al.*, 2006]. Recent work from the eastern equatorial Pacific and Atlantic upwelling regions demonstrate that on orbital cycles alkenone accumulation rates are closely tied not only to alkenone-synthesizing haptophyte concentrations but also to total phytoplankton productivity [Bolton *et al.*, 2010].

High-resolution alkenone analysis was conducted on each of the three sediment cores. Samples for alkenone analysis were extracted using 0.8-1.2g of sediment in a Dionex 200 Accelerated Solvent Extractor and analyzed with a Gas Chromatograph Flame Ionization Detector, using a modified method of Herbert *et al.* 1998. Alkenone $C_{37:2}$ and $C_{37:3}$ identification was confirmed using a Gas Chromatograph- Mass Spectrometer. Lab analytical error, $\pm 0.2^\circ\text{C}$, is calculated based on a laboratory sediment standard, which is extracted and measured every few months. Temperature error based on sample replicates ($\sim 10\%$ of samples were duplicated) is $\pm 0.1^\circ\text{C}$, within our lab analytical error. Alkenone concentrations (C_{37} di- and triunsaturated ketone mass/grams

of dry sediment = “C₃₇total”) were calculated by normalizing to an internal standard (C₃₇ and C₃₆ n-alkanes). C₃₇total provides a qualitative estimate of haptophyte production, which is closely linked to total phytoplankton productivity [Brassell *et al.*, 1993; Budziak *et al.*, 2000]. The relative error for C₃₇total is $\pm 10\%$, calculated from 10% sample replication. Independent validation of our C₃₇total proxy comes from comparison to %N (see supplemental Figure 1), another frequently used indicator of total phytoplankton productivity.

Several alkenone derived records from the Eastern Equatorial Cold Tongue show evidence of a monotonous late Holocene warming [Koutavas and Sachs, 2008; Pahnke *et al.*, 2007; Kienast *et al.*, 2006]. This has led some researchers to conclude that the U^K₃₇ index is biased towards certain seasons [Leduc *et al.*, 2007]. However, a recent high resolution alkenone record from 3°S refutes this assumption and alternately suggests that rather than a monotonous warming these other records may be undersampling millennial scale temperature oscillations [Chazen *et al.*, 2010 (dissertation chapter 4)]. In a global core top survey Prahl *et al.* [2010] found a significant ($\sim 2\text{--}3^\circ\text{C}$) warm residual in samples from Peru margin. The authors attribute this offset to enhanced alkenone production during the warm season. Despite these observations we find no evidence of a strong seasonal bias in alkenone temperatures.

4.5. Biogenic Opal

In addition to alkenones, we reconstruct biogenic silica (BSi), a widely used proxy for marine surface productivity. The primary source of BSi in this study comes from diatoms (and in smaller part radiolarians and sponges) [De Vries and Schrader, 1981]. In the modern ocean, opal production varies seasonally with upwelling intensity.

The strongest diatom blooms occur during late-boreal summer when upwelling is strong but waters are relatively clear [Strub *et al.*, 1998]. In many highly productive regions, annual opal production is closely associated with organic carbon flux [Treguer *et al.*, 1995]. However, biogenic opal in marine sediments is also affected by the availability of dissolved silica in the surface waters and the silicic acid saturation of the water column, both of which can effect opal preservation [Ragueneau *et al.*, 2000]. Another potential complication in interpreting down-core opal concentrations is the availability of micronutrients. Hutchins and colleagues argue that iron availability can have major consequences on the export and preservation of opal by altering the thickness of diatom tests [Hutchins *et al.*, 2002].

Biogenic silica (BSi) was measured every 8cm in cores 1228D and 40K and every 2cm in core PC-2. BSi for core PC-2 was obtained from splits of the sediment samples used for alkenones. BSi was measured using a continuous flow analysis, using a Molybdate spectrometry method modified from Mortlock and Froelich [1989]. Approximately, 0.3g of sediment was extracted in a hot alkaline digestion at 85 °C in 0.5 M NaOH for 2 hours. Relative analytical error of, $\pm 5\%$ BSi is calculated from 10% of sample duplicates.

4.6. Nitrogen Isotopes

Reconstructing changes in subsurface oxygen enables us to distinguish between the influences of local climate from remote ventilation of the Peru margin subsurface. We use changes in nitrogen isotopes ($\delta^{15}\text{N}$) in sediments to track subsurface oxygen across the Holocene. In low oxygen environments [$\text{O}_2 < 0.5 \text{ mg/L}$] heterotrophic bacteria reduce NO_3^- to N_2 , which is termed denitrification. During denitrification, light nitrate

(N^{14} - NO_3^-) is preferentially removed, leaving the remaining nitrate pool enriched in heavy nitrate (N^{15} - NO_3^-). This heavy nitrate signal is transferred to the surface through upwelling where it is used by biota and eventually buried in the underlying sediments. While, $\delta^{15}\text{N}$ has been used as an indicator of changing subsurface oxygen in a number of studies [Codispoti *et al.*, 1986, 2001; Agnihotri *et al.*, 2008], many factors can contribute to the sedimentary $\delta^{15}\text{N}$ signal, including secondary fractionation during euphotic assimilation [Altabet and Francois, 1994], incomplete nitrate utilization and preexisting nitrogen pools [Altabet and Francois, 1994; Sigman *et al.*, 1999]. To validate the use of $\delta^{15}\text{N}$ as a proxy for subsurface $[\text{O}_2]$ we consider the multiple factors that may have contributed to the $\delta^{15}\text{N}$ signal and compare the down core $\delta^{15}\text{N}$ records with two independently derived proxies of anoxia, the presence/absence of laminations and low oxygen benthic foraminiferal assemblages [Chazen *et al.*, 2010 (dissertation chapter 3)].

Nitrogen isotopes ($\delta^{15}\text{N}$) were measured on bulk sediments following the procedure established by Altabet *et al.* [1999]. Samples for nitrogen analysis were sampled at an estimated resolution of every 26 years in PC-2, 40 years for core 1228D and 30 years for core 40K. Particulate nitrogen is converted into N_2 using a CN analyzer attached to an isotope-ratio Mass Spectrometer, which uses He as the carrier gas. $\delta^{15}\text{N}$ values are referenced to atmospheric N_2 with an uncertainty of $\pm 0.2\%$.

5. Results

5.1. Peru Margin Sedimentation

Previous studies along the Peruvian shelf have revealed frequent hiatuses in sedimentation, apparently related to periods of low deposition or erosion [De Vries and Schrader, 1981; Reinhardt *et al.*, 2002]. Continuous Holocene records from this region

are particularly sparse; among the possible Holocene records that we consulted, radiocarbon dating suggests that a period of no or extremely low sedimentation took place between ~8 and 4ka [Skilbeck *et al.*, 2004; Rein *et al.*, 2002; Makou *et al.*, 2010]. This observation has been erroneously interpreted as evidence for widespread sediment starvation across the Margin in response to persistent La Niña-like conditions (or a lack of El Niño events) during the early Holocene [Rein *et al.*, 2002]. In contrast, the nearly linear sedimentation rate of core PC-2 indicates that in certain regions of the Margin sedimentation rates were remarkably stable over the course of the Holocene (see Figure 1]. We therefore postulate that the frequent hiatuses are the result of winnowing and post depositional erosive events, which are common in this region, rather than the absence of sedimentation. The existence of the continuous, high-deposition rate Holocene records from core PC-2 suggests that selective coring based on high resolution shallow seismic surveying [c.f. Reinhardt *et al.*, 2002] may yield many more windows into mid-Holocene deposition along the Peru margin.

5.2. *Laminations and Stratigraphy*

Alternating sequences of laminated and non-laminated sediment sequences reflect fluctuations in the strength of the Peru OMZ with time. Laminations are more common in the southern core (PC-2) than either of the central Margin cores, which is consistent with the modern day position of the OMZ. The occurrence of laminations also varies with time; laminated sequences are more common during the late Holocene (5.5-1.4ka) section of the sediment cores than the early Holocene intervals (see Figure 3). Based on the PC-2 age model (Figure 1b) the finest laminations (see black boxes in Figure 3) appear to

represent annual couplets. These annual laminations are only found in the southern core location (PC-2) during the late Holocene (5.5-1.4ka) and intervals during the early Holocene where $\delta^{15}\text{N} > 7.5\text{‰}$ (9.5-9.7ka, 7.7-7.8ka) (Figure 3a). The occurrence of the laminations pictured in Figure 3c are highly irregular; in a single laminated section adjacent bands fluctuate between 1cm and 4cm (or 2-8 yr time scale, see gray boxes in Figure 3a. c). The early Holocene (10-5.5ka) sections of 1228D and PC-2 (when $\delta^{15}\text{N} < 7.5\text{‰}$) are predominantly non-laminated (see white boxes in Figure 3a, d).

Individual laminae consist of alternating layers of pale, porous sediments, with well preserved diatom frustules and dark, tightly packed, clay rich diatomaceous mud. The non-laminated core sections are medium in color, crumbly and contain abundant diatom debris (Figure 3d). The observation that laminations tend to occur during periods of inferred low $[\text{O}_2]$ (high $\delta^{15}\text{N}$, Figure 3a) is consistent with the expectation of diminished bioturbation in low oxygen environments and provides independent confirmation of our $\delta^{15}\text{N}$ proxy [Chazen *et al.*, 2009].

5.3. Benthic Foraminifera

Benthic foraminifera were found in all three sediment cores. The species assemblages are typical of low oxygen environments, with a dominance of small thin shelled forams, predominantly *Nonionella* and *Stanforthia* genera [Bernhardt *et al.*, 2006; Bernhard and Bowser, 1999]. Benthic foraminifera are more abundant (number of individuals /gram of sediment) in the southern Margin core (PC-2) than the central Margin cores (1228D and 40K); core PC-2 contains approximately 10 times the number of individuals per gram than cores 1228D and 40K. It is unclear whether these

differences reflect changes in preservation between the core sites or subsurface oxygen gradients. Subsurface oxygen is more depleted in the southern Margin (near the location of site PC-2) than the central Margin where cores 1228D and 40K are located. Bernhard and Reimers [1991] have demonstrated that preservation along the perimeter of oxygen minimum zones can be significantly reduced compared to the center of the OMZ, therefore it is difficult to distinguish whether the differences in benthic foraminifera between sites reflects in situ changes in foraminiferal environmental preferences or post depositional preservation differences. Foraminiferal presence/ absence data for core PC-2 is shown in Figure 4.

In addition to these regional differences, benthic foraminiferal abundances vary significantly over the course of the Holocene. They are more abundant in the late Holocene (post-5.5ka) than in the early Holocene (10-5.5ka) in both cores 1228D and PC-2 (Fig. 4). In the early Holocene section of core PC-2, benthics are only present during the short intervals where $\delta^{15}\text{N}$ exceeds 7.5‰. During the late Holocene, foraminiferal presence and absence also relates to $\delta^{15}\text{N}$; intervals without forams tend to coincide with lower than average $\delta^{15}\text{N}$ (<5‰). However, in contrast to the early Holocene, the majority of the late Holocene section of PC-2 contains benthic foraminifera, including periods where $\delta^{15}\text{N}$ is between 5-7.5‰ (Fig. 4).

Only a few intervals during the early Holocene (see Fig. 4) contain measurable amounts of benthic foraminifera. Similarly, only the late Holocene section of core 1228D contains measurable amounts of foraminifera. The intervals that contain benthics in the early Holocene section of core PC-2 coincide with periods of extreme oxygen deficits (inferred from high $\delta^{15}\text{N}$ and laminations, Figures 3, 4). Reductions in subsurface oxygen

appear to benefit select species of benthic foraminifera. The foraminifera identified during the early Holocene section of PC-2 tend to show greater dissolution (for example see Figure 5a) than those found during the late Holocene (for example see Fig. 5b). This supports the assertion that the lack of benthic foraminifera in early Holocene sediments may be partially attributed to preservation.

5.4. Sea Surface Temperature

Seasonal and interannual variability in sea surface temperature, productivity and water column stratification of the Peru Coastal Current is closely tied to the strength of Walker circulation, the position of the ITCZ and contraction and expansion of the South Pacific Subtropical High [Enfield and Allen, 1980; Strub *et al.*, 1998]. Peru Margin (8° to 16 °S) surface temperatures range from 16-24° C annually. The coolest temperatures occur during boreal summer when the ITCZ is positioned furthest north. During austral summer the ITCZ migrates south and Walker circulation weakens, causing a reduction in upwelling and a warming of surface waters. Despite the persistent upwelling across the Margin, a latitudinal temperature gradient is maintained throughout the year. Modern temperatures increase by nearly 1.5°C between 15°S (location of core PC-2) and 11°S (location of cores 1228D and 40K) [USGS SST program (Tcl/Tk version 1.3)].

Our paleoclimate reconstructions indicate that this latitudinal temperature gradient and the modern seasonal range of temperatures were maintained for the past 3kyrs (see Figure 2a). The fact that this SST gradient is preserved in the paleo record suggests that alkenones from the Peru margin reliably record SSTs from the overlying surface waters rather than drift in from adjoining areas. Since cores PC-2, 1228D and 40K are missing the most recent sediments we cannot directly compare core tops with modern mean

annual SSTs. However, the temperatures recorded from the most recent sediments in each of the sediment cores are within 1°C of modern mean annual SST (see Figure 2a). These results are inconsistent with a recent global survey that reports significant warm residuals in $U^{K'}_{37}$ from Peru margin core tops [Prahl *et al.*, 2010]. Without finding any evidence of a significant seasonal bias in our alkenone temperature reconstructions we speculate that these apparent warm biases may be the result of sample handling rather than a $U^{K'}_{37}$ seasonal bias. Warm biases in $U^{K'}_{37}$, related to preferential degradation of the $C_{37:3}$ alkenone have been found in sediments subject to prolonged oxygen exposure [Kim *et al.*, 2009] and samples left at room temperature for extended periods of time [Chazen and Herbert, unpublished]. Preliminary work suggests that Ocean margin sediments may be more sensitive to this preferential degradation than sediments with lower TOC values [Chazen and Herbert, unpublished].

Early Holocene SSTs at 11°S (core 1228D) are ~1.5°C warmer than SSTs at 15°S (PC-2) over the same time period (Figure 2a). During the late Holocene, centennial trends between sediment cores are remarkably similar. A prominent warming occurs in all three sediment cores between ~2.2ka and 1.5ka. A mid Holocene increase in variance is visible in both cores 1228D and PC-2 (see Figure 2). In core PC-2, this change is abrupt (~5ka) but the character and timing of the change in 1228D is obscured by the sedimentation hiatus (Figure 2a).

5.5. Surface Productivity

At present, surface productivity varies with upwelling intensity; enhanced upwelling corresponds to enhanced surface production [Strub *et al.*, 1998]. Modern seasonal fluctuations in surface productivity are subtle but reductions in upwelling

strength (for example El Niño events) are coupled to decreases in phytoplankton productivity [Chavez, 1995]. Our paleoclimate reconstructions are consistent with modern productivity gradients where production (inferred from $C_{37}total$ and BSi) are higher in the central Margin, sites 1228D and 40k (11°S) than the southern Margin, site PC-2 (15°S) [Dugdale and Wilkerson, 1998; Bruland *et al.*, 2004] (Fig. 2b, c). The difference in surface productivity between the central and southern Margin is not entirely clear but may be the result of differences in the availability of micronutrients. Regardless of its cause our data suggests that this gradient persisted into the past. In our paleoclimate reconstructions we see a reduction in the $C_{37}total$ and BSi variance moving backward in time (towards the early Holocene, see Figure 2b, d) similar to what we observed in our temperature reconstructions (Figure 2a). The late Holocene section of our southern margin site (PC-2) is characterized by high amplitude centennial-scale fluctuations which are significantly reduced by ~4.5ka (see Figure 2b, d) and absent from the early Holocene section of the record. These changes in surface productivity describe a shift from a more stable early Holocene climate to a more variable late Holocene. Overall our $C_{37}total$ and BSi records are remarkably similar, which provides support for the use of both $C_{37}total$ and BSi as proxies for paleoproductivity. The inconsistencies that do exist between proxies may reflect the availability of dissolved silica in the surface waters and the silicic acid saturation of the water column, both of which can effect opal preservation [Ragueneau *et al.*, 2000].

5.6. Nitrogen Isotopes

In low oxygen environments, sedimentary $\delta^{15}\text{N}$ can provide a reliable record of subsurface $[\text{O}_2]$ [Codispoti *et al.*, 1986, 2001; Agnihotri *et al.*, 2008]. However, other environmental factors, including nitrate utilization by phytoplankton [Altabet and Francois, 1994], fractionation during organic matter delivery, post-burial diagenesis [Altabet *et al.*, 1999], surface productivity [Brandes *et al.*, 1998] and changes in source water nitrate [Altabet *et al.*, 1999; Loubere, 2000]. Here, we review the potential factors that affect the down-core $\delta^{15}\text{N}$ signal and assess its utility as a proxy for subsurface $[\text{O}_2]$ in Peru margin sediments.

Secondary fractionation during assimilation in the euphotic zone [Altabet and Francois, 1994] can bias the $\delta^{15}\text{N}$ signal recorded in the sediments. If the degree of nitrate utilization varied with time (possibly a result of Fe availability), $\delta^{15}\text{N}$ recorded in the sediments may reflect a combination of subsurface nitrate removal and surface utilization [Altabet and Francois, 1994; Sigman *et al.*, 1999]. While the Peru Current is classified as an HNLC region, there is little evidence to suggest an annual surplus of unused nitrate [Conkright *et al.*, 2002]. Furthermore, modern surveys of the Peru Current do not support Fe-limited conditions that would lead to an excess of nitrate in the euphotic zone [Ganeshram *et al.*, 2000; Bruland *et al.*, 2005]. Therefore, it seems unlikely that changes in nitrate utilization imparted a significant bias on our $\delta^{15}\text{N}$ reconstructions during the Holocene.

Another possible factor that can alter $\delta^{15}\text{N}$ records down-core is the potential for isotopic alterations as particles settle out of the waters column or post-burial diagenesis. The absence of a down core trend in $\delta^{15}\text{N}$ indicates, among other things, that diagenesis is

not a major factor on sedimentary $\delta^{15}\text{N}$ in Peru margin sediments. The shallow water column position (180-250m) of our sediment cores and the extremely high sedimentation rates (20-70cm/kyr) make the risk of fractionation during diagenesis minimal [Altabet *et al.*, 1999].

Comparison between $\delta^{15}\text{N}$ reconstructions from individual core sites (Figure 2d) provides further support for the use of $\delta^{15}\text{N}$ as a proxy for subsurface $[\text{O}_2]$. There is a 1‰ offset between the mean $\delta^{15}\text{N}$ of the central Margin core sites (40K and 1228D) and the southern Margin core site (PC-2, see Figure 2d). This gradient is consistent with modern oceanographic conditions, where subsurface oxygen is more depleted in the southern margin (PC-2) than the central Peru margin [Strub *et al.*, 1998; Garcia *et al.*, 2005; Stramma *et al.*, 2008]. Additionally, comparison between independent proxies for anoxia and our $\delta^{15}\text{N}$ reconstructions are remarkably consistent. The occurrence of annual laminations and $\delta^{15}\text{N}$ enrichment (i.e. $\delta^{15}\text{N} > 7.5\text{‰}$, see Figure 2a) are closely associated throughout the Holocene (see Figure 3a). Finally, oscillations in species assemblages of low oxygen benthic foraminifera correspond exceptionally well with $\delta^{15}\text{N}$ [Chazen *et al.*, 2010 (dissertation chapter 3)]. The combination of each of these factors gives us confidence in the use of $\delta^{15}\text{N}$ as a proxy for subsurface oxygen in Peru sediments.

Peru margin $\delta^{15}\text{N}$ reconstructions between 11-15°S reveal significant changes in subsurface oxygenation across the Holocene. The $\delta^{15}\text{N}$ offset (~1‰) between the central and southern core sites suggests that the OMZ was centered in the southern Margin and weakened moving towards the North; this is consistent with modern Peru margin conditions [Strub *et al.*, 1998; Stramma *et al.*, 2008].

In the southern Margin (core PC-2) $\delta^{15}\text{N}$ values reach their Holocene maximum ($\sim 9\text{‰}$) near 9.7ka and steadily decrease until 5.7ka where they reach the Holocene minimum ($\sim 4.7\text{‰}$). This steady decline in $\delta^{15}\text{N}$ is punctuated by two major departures; dramatic increases in $\delta^{15}\text{N}$ occur at $\sim 6.9\text{ka}$ and $\sim 7.8\text{ka}$ both of which last for approximately 100 years (see Figure 2c). Near the middle Holocene $\delta^{15}\text{N}$ variance increases dramatically; this increase in variance occurs near 5.7ka in the southern core site (PC-2). The timing of the change in variance in the central Margin is obscured from the sediment hiatus but must have occurred sometime between 8-4ka. During the late Holocene section of PC-2 (5.7ka to 0.2ka) $\delta^{15}\text{N}$ values oscillate irregularly in 50-200 year intervals.

5.7 Mid-Holocene Variance Shift

Climate proxies that record the key environmental parameters of the Peru upwelling region (i.e. inferred surface temperature and productivity and subsurface oxygen) display increased variance near the mid-Holocene (see Figure 2). To evaluate the significance of this change in variance we must first establish whether it is related to changes in sedimentation rates, sedimentation character or the result of smearing due to bioturbation. While both cores 1228D and PC-2 show changes in variance across the Holocene, PC-2 provides the most reliable record since it is continuous from $\sim 10\text{ka}$ - 1.4ka (see Figures 1 and 2). Each sediment core was sampled with a constant sampling interval throughout the length of the core; the sampling interval for PC-2 for example, was 0.5cm, which integrates 6-7 years of sedimentation (according to our age model, see Figure 1). Because these sampling intervals stay constant a change in sedimentation rates between the early and late Holocene would change the amount of time captured in each sample

and thus could potentially alter the variance. Core PC-2 shows a nearly constant sedimentation rate across the length of the Holocene (see Figure 1) thus, we can rule out changes in sedimentation rates as causing the mid-Holocene change in variance. Another potentially complicating factor is bioturbation from benthic organisms including, annelids, bivalves and other infaunal organisms. Bioturbation disturbs stratigraphic layers and can mix up to several centimeters of sediment [see *Henderson et al.*, 1999; *Thompson et al.*, 2000]. This is particularly relevant in core PC-2 where the presence of laminations (indicating a lack of bioturbators) varies across the length of the core (see Figure 3). Therefore, a 0.5cm-sampling interval would integrate a longer time period in bioturbated sediments than in laminated sediments. Annual laminations are more common in the late Holocene section of PC-2 than the early Holocene section (see Figure 3), which introduces the possibility that the increased variance is related to changes in sedimentation character (ie bioturbated vs. laminated sediments) rather than an actual change in variance. However, if this were the case we would expect all laminated intervals to display higher variance than samples from the bioturbated sections of PC-2, which is not the case (see Figure 3). Instead, climate variance (of SST, C_{37}^{total} and $\delta^{15}N$) is higher in both the laminated and non-laminated sections of the late Holocene compared to the early Holocene. For all of these reasons we are confident that the mid-Holocene shift in climate variance is the result of enhanced climate variability rather than changes in sedimentation.

The sampling interval becomes particularly important when assessing ENSO in paleoclimate reconstructions. In evaluating ENSO related temperature gradients during the Pliocene, Wunsch [2009] demonstrates that under-sampling or smearing can result in

aliasing of high frequency climate events. Specifically, Wunsch [2009] points out that seasonal bias in climate proxies may result in spurious variability by recording seasonal changes rather than changes in mean climate conditions. This is particularly relevant to ENSO reconstructions since El Niño and La Niña anomalies are highly seasonal [Barber and Smith, 1981; Enfield and Mestas-Nuñez, 2009]. We are confident for a number of reasons that the high amplitude swings during the late Holocene section of our record (see Figure 2) reflect changes in mean conditions rather than an aliased seasonal signal. The $U^{K'}_{37}$ index has been shown to faithfully record mean annual SST rather than temperatures specific to a certain season [Conte *et al.*, 2006; Herbert *et al.*, 1998; Muller *et al.*, 1998; Brassell *et al.*, 1993] (refer to section 5.4 for further discussion on the $U^{K'}_{37}$ index). Furthermore, if the mid-Holocene change in variance were an aliased seasonal signal we would expect to see a shift in the mean state of our climate proxies along with a shift in variance. Instead, we see little change in the mean values of inferred SST, productivity and subsurface oxygen between the early and late Holocene despite the major change in variance [Chazen *et al.*, 2009]. The high amplitude fluctuations in inferred SST, productivity and subsurface oxygen that characterize the late Holocene (see Figure 2) consist of multiple data points indicating alternating periods of prolonged warm and cool conditions. Finally, it is unlikely that all of our climate proxies, both surface (SST - $U^{K'}_{37}$, productivity - $C_{37}total$ and BSi) and subsurface ($\delta^{15}N$ and the presence/absence of benthic foraminifera) would reflect the same seasonal bias.

Wunsch [2009] also posits that periods of enhanced ENSO strength cannot be distinguished from changes in the mean state of the Pacific temperature gradient. Similarly, we are unable to distinguish between periods of more frequent ENSO events

from periods that contain stronger El Niño/La Niña events. However, we argue that the relationship between proxies in combination with changes in variance can be used to assess potential changes in ENSO strength and/or frequency over time.

6. Discussion

6.1. *Did local upwelling drive the Peru margin OMZ?*

Coastal upwelling is the conduit between the cool nutrient-rich thermocline waters and the warm surface ocean; the physical and biological properties of the Peru surface waters vary with upwelling strength [Strub *et al.*, 1998; Chavez, 1995]. As a result, Peru surface productivity, temperature and subsurface oxygen vary seasonally with the migration of the ITCZ and interannually with ENSO [Strub *et al.*, 1998; Philander, 1990]. By analogy we might expect changes in upwelling strength to influence productivity and subsurface oxygenation over longer timescales; periods of enhanced wind strength should have accompanied cooler SSTs and higher surface productivity and lower subsurface oxygen. However, this ‘local’ view of Peru climate fails to account for extra tropical influences, in particular the waters that feed the Peru undercurrent. Here we examine whether local wind induced upwelling or modifications in circulation impart the strongest signal on the Peru margin oxygen minimum zone over the course of the Holocene.

Examining correlations between proxies for surface and subsurface climate allow us to distinguish time periods dominated by local climate from those more influenced by remote climate. If local, wind-induced upwelling were the primary control on the physical and biological properties of the Peru surface waters across the Holocene we

would expect to find predictable relationships between our proxies. For example, upwelling brings cool, nutrient-rich waters to the surface and thus, temperature proxies should be inversely correlated with productivity proxies, which should be positively correlated with proxies for subsurface oxygen. At present, the El Niño Southern Oscillation (ENSO) is the primary source of interannual climate variability at the Peru margin. ENSO oscillates between reduced wind-strength (El Niño) and enhanced wind strength (La Niña). Thus, periods where our proxies exhibit ENSO-like correlations can be described as locally forced climate. Similarly, if the oxygen demand imposed by the local carbon flux persists into the past we anticipate a positive correlation between local productivity and subsurface oxygen.

Climate properties of the southern high latitudes are communicated to the Margin through an extension of the equatorial undercurrent, the ocean ‘tunnel’ pathway. If this ‘remote’ mechanism of climate change dominated during the Holocene we would expect a decoupling between surface and subsurface climate parameters. For example, if the oxygen content of the Peru subsurface waters was inherited before these waters reached the Peru margin there is no reason to expect any correlation between surface and subsurface climate parameters. Additionally, if the nutrient content or temperature of the Peru subsurface waters varied with time the simple ‘local’ view of Peru margin climate would no longer apply.

Based on the relationships between proxies for surface productivity, SST and subsurface oxygen we find evidence that the dominant control of the Peru margin OMZ alternated between local and remote climate forcings. The lack of a correlation between proxies for surface productivity (BSi and C_{37}^{total}) and subsurface oxygen ($\delta^{15}N$) during

the early Holocene (Figure 6b) indicates a clear disconnect between surface productivity and subsurface oxygen during this period. This suggests that the subsurface oxygen signal was tied to the ventilation of the Peru subsurface rather than the oxygen demand imposed by local productivity. Additionally, we see little evidence to support cooler temperatures or higher productivity during the early Holocene (see Figure 2a,b). This lack of a strong upwelling signal during the early Holocene is inconsistent with model results from the Eastern Equatorial Pacific (EEP), which predict enhanced upwelling when forced by changes in orbital precession [*Clement et al.*, 1999; *Cane*, 2005]. Our results also conflict with paleoreconstructions from the Galapagos which show a $\sim 1^{\circ}\text{C}$ cooling in the early Holocene, which the authors attribute to enhanced upwelling [*Koutavas et al.*, 2006]. The discrepancy between other EEP work and our results indicate one of two possibilities: (1) Peru margin upwelling during the early Holocene was not enhanced compared to today and/or the position of trade winds during the early Holocene did not produce upwelling favorable conditions along coastal Peru; (2) Upwelling strength alone does not account for the biological and physical properties of the Peru Current across the Holocene. The latter suggestion points to modifications in the physical and biological properties of the Peru Undercurrent.

The mid-Holocene marks a dynamic time in the Peru margin climate system; we see a change in the relationship between surface and subsurface proxies- indicating a shift towards a more locally driven oxygen minimum zone (see Figure 6b), along with a substantial increase in climate variance (see Figure 2). This increased variance is consistent in timing with other records from the eastern tropical Pacific (ETP) and has been described as a response to enhanced El Niño strength [*Moy et al.*, 2002; *Conroy et*

al., 2008; *Makou et al.*, 2010]. Using the relationships between proxies, we can evaluate whether the mid-Holocene enhancement of El Niño strength was responsible for the dramatic increase in Peru margin climate variance. As variance increases, we find more periods that can be described as ENSO-like. For example, in Figure 7 periods highlighted in blue show La Niña-like correlations between proxies (i.e. reduced SST, increased productivity, reduced subsurface oxygen) and periods highlighted in red show El Niño-like relationships between proxies (i.e. increased SST, reduced productivity, increased subsurface oxygen). However, rather than a linear increase in ENSO-like climate the late Holocene is best described as oscillating between periods of ENSO-like and non ENSO-like climate.

The late Holocene (3ka to present) also shows SST gradients between core locations similar to what we find today (see Figure 2a). If upwelling were much stronger during the early Holocene we might expect to see a reduction in the latitudinal temperature gradients between sites during the mid to early Holocene. While the overlap in our temperature records between core locations is not sufficient to examine how these gradients may have changed over time, the offset between SSTs at 1228D and PC-2 (see Figure 2a) during the early Holocene is not consistent with a major expansion in coastal upwelling.

Near the mid-Holocene we also see a dramatic change in the correlations between inferred surface productivity and inferred subsurface oxygen in both the central and southern Margin (see Figures 6a, c), indicating that the local oxygen demand has a stronger impact on subsurface oxygen in the late Holocene than the early Holocene. Each of these correlations appears to support a shift towards a more locally driven climate

regime in the late Holocene. However it is important to emphasize that this change is best described as a climate that alternates between local and remote periods on roughly centennial time scales (see Figure 7). An important outstanding question regarding Peru margin climate is what controls the flickering between local and remote climate during the late Holocene. And why are these oscillations restricted to the late Holocene? The answers to these questions likely lie in the climate of the southern high latitudes where the waters that ventilate the Peru undercurrent originate.

6.2. Ventilation of the Peru undercurrent

Peru margin subsurface oxygen is influenced by both local primary productivity [Altabet *et al.*, 1995, 1999; Agnihotri *et al.*, 2008] and variations in the physical properties of the waters that ventilate the Peru undercurrent [Loubere *et al.*, 2001, 2003; De Pol-Holz *et al.*, 2007]. Our results indicate that the dominant influence on subsurface oxygen varied across the Holocene. Previous work from the Peru margin has established a long-term link between subsurface oxygen and local productivity; the strength of the Peru OMZ has been found to track changes in phytoplankton growing seasons, which oscillate with precession cycles [Dezileau *et al.*, 2004; Agnihotri *et al.*, 2008]. However, the decoupling between inferred surface productivity and subsurface oxygen in our study region, particularly during the early Holocene (see Figure 2, Figure 6), suggests that the remote ventilation of the Peru undercurrent dominated over the oxygen demand imposed by local productivity. Even more intriguing is that the dominant control on subsurface [O₂] appears to have changed over the course of the Holocene, shifting from a system clearly dominated by remote ventilation during the early Holocene and gradually shifting towards more locally driven OMZ during the late Holocene.

The low $[O_2]$ signature of the Peru subsurface results from prolonged isolation from the surface, as waters are transferred from the high to low latitudes. At present this low $[O_2]$ signal is enhanced by the high respiration rates imposed by the local carbon flux. However, the lowest subsurface $[O_2]$ during the Holocene (inferred from the presence of laminations and high $\delta^{15}N$) coincides with a regional low in surface productivity (see Figures 2 and 3). As productivity increases near the mid-Holocene the correlation between local productivity and inferred subsurface oxygen strengthens (see Figure 6a, c), indicating a shift towards more locally driven subsurface ventilation. This suggests that the extra tropical factors that influence Peru ventilation changed across the Holocene; specifically that the oxygen demand imposed by local productivity was minimal during the early Holocene. Subantarctic temperature changes have been linked to the ventilation and nutrient dynamics of the tropical thermocline on millennial time-scales via the ocean tunnel pathway [Ninnemann and Charles, 1997; Spero and Lea, 2002; Pena et al., 2008]. Recent work from Euler and Ninnemann [2010] and Chazen et al. [2009] indicates that this connection between the subantarctic and the tropical thermocline may also affect high frequency (centennial-scale) climate variability in the Peru margin [Euler and Ninnemann, 2010]. Modifications in the strength and/or position of the subtropical gyre may have also played an important role in the ventilation of the tropical undercurrent [Yang and Liu, 2005]. The ‘shadow zone’ theory states that in order to conserve potential vorticity in a multi-layered model the layers outside the direct contact of Ekman pumping must be stagnant [Luyten et al., 1983]. If the south Pacific shadow zone was enhanced during the early Holocene, possibly due to changes in the position of the subtropical gyre, early Holocene ventilation could be reduced as a result of a pronounced stagnant water

layer. Changes in orbital precession across the Holocene may have altered the latitudinal position of atmospheric pressure system, which can alter the position and/or strength of the subtropical gyre and shadow zone [*Fine et al.*, 1994; *Lamy et al.*, 1998; *Liu et al.*, 2000].

6.3. *Modifications of the Equatorial Undercurrent*

The cool waters and high productivity that characterizes the modern Peru upwelling system originate from an extension of the eastward flowing Equatorial Undercurrent (EUC). The EUC is vertically partitioned between the cool, oxygen depleted, nutrient rich lower layers, which are tied to the subantarctic mode waters (SAMW) and the warmer nutrient depleted upper layer, which originates in the western subtropics [*Toggweiler et al.*, 1991; *Goodman et al.*, 2005]. After traveling east across the equator a portion of the EUC surfaces near the Galapagos before the remaining transport, now termed the Peru undercurrent, is deflected south along the South American continent and eventually upwelled off of Peru [*Lukas*, 1986]. At present, the deeper layer of the EUC upwells off Peru, providing the rich productive regime [*Toggweiler et al.*, 1991; *Loubere et al.*, 2003] while the comparatively nutrient-poor upper portion of the EUC surfaces before reaching the Margin. If the proportions of the nutrient poor/nutrient rich end members of the EUC were to change over time the physical and biological properties of the waters upwelled off of Peru would change as well [*Loubere*, 1991; *Toggweiler and Carson*, 1995]. The low surface productivity (Figures 2a, b) of the early Holocene may be a response to a reduced nutrient delivery to the Peru undercurrent. If this were the case we would also expect to see a related increase in subsurface oxygen. With the exception of three pronounced anoxic episodes (inferred from the presence of laminations and

elevated $\delta^{15}\text{N}$, see shaded bars in Figure 3) proxies for subsurface oxygen suggest that on average early Holocene $[\text{O}_2]$ was slightly lower than that of the late Holocene.

Why would the physical and biological properties of the EUC change during the Holocene? One possibility is that changes in seasonal insolation altered the physical properties of the equatorial undercurrent and thus, the properties of the waters that eventually compose the Equatorial and Peru thermocline. During the early Holocene austral winters were warmer than they are today. The physical properties of the equatorial undercurrent depend on the partitioning between the shallower subtropical component [*Liu et al.*, 1994] and the deeper nutrient rich subantarctic component [*Toggweiler et al.*, 1991]. Modification in the structure of these two layers can result in changes in the physical and biological properties of the equatorial undercurrent [*Liu et al.*, 2000; *Timmermann*, 1999; *Loubere et al.*, 2003] and thus, alter the Peru undercurrent. Modeling results from Liu et al. [2000] suggest that warming of the equatorial undercurrent during the early-mid Holocene led to a deepening of the tropical thermocline and thus reduced the influence of local wind strength on eastern tropical pacific sea surface temperatures. If this were the case it might help to explain why Peru margin climate shifted toward a more locally driven system over the course of the Holocene.

We speculate that this mid Holocene shift in proxy correlations marks a major reorganization in Peru margin climate forcing that can be summarized by two significant changes: (1) Modifications in the composition of the equatorial undercurrent resulted in a greater contribution of the subantarctic mode waters rather than the subtropical end member [*Liu et al.*, 1994; 2000; *Toggweiler et al.*, 1991]; (2) Reduced walker circulation led to a strengthening of the El Niño Southern Oscillation [*Clement et al.*, 1999; 2000].

7. Conclusions

Climate reconstructions of sea surface temperature (U_{37}^k), surface productivity (C_{37} total and biogenic silica) and subsurface oxygen ($\delta^{15}N$, laminations), in a latitudinal transect (11-15°S) across the Peru margin upwelling/ oxygen minimum zone reveal a unique window into the forcing mechanisms of tropical productivity, SST and subsurface ventilation across the Holocene.

Near the middle Holocene a dramatic increase in climate variability was accompanied by a shift toward more locally driven climate dynamics revealed through the relationships between our surface and subsurface climate proxies. We speculate that this mid Holocene shift results from the combination of remote and local climate forcings. Locally, changes in tropical insolation led to the weakening of walker circulation and enhanced ENSO strength [*Clement et al.*, 1999], which likely contributed to the increased variance of the late Holocene. Additionally, an increase in the subantarctic mode water end-member of the EUC [*Toggweiler et al.*, 1991] and by extension to the Peru undercurrent may have increased the ETPs sensitivity to local climate dynamics including the El Niño Southern Oscillation by cooling and thus shoaling the thermocline [*Liu et al.*, 1994; 2000].

The tendency of the late Holocene climate to flicker between ENSO-like and non-ENSO like climate remains elusive. The answer likely lies in the connection between the southern high latitudes and the climate of the eastern tropical pacific but a greater regional perspective is needed to address these questions.

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Figure Captions

Figure 1. (a) Shaded relief map of the Peru Margin with corresponding age models. Triangles indicate the location of sediment cores. Age models are based on multiple AMS ^{14}C age estimation, which were converted into calendar ages using the IntCal4.0 calibration program [Reimers *et al.*, 2007] with a reservoir correction of 450 years [Bard *et al.*, 1993]. (b) Age model for core PC-2; (c) Age model for W7706-40K; (d) Age model for core ODP1228D.

Figure 2. Holocene time series for cores PC-2 (black), W7706-40K (blue) and ODP1228D (red); (a) Alkenone derived sea surface temperature; arrows indicate the modern mean annual SST at each core location [Levitus *et al.*, 2002]. The temperature offsets between cores are consistent with modern day temperature gradients; (b) $\text{C}_{37}\text{total}$: alkenone derived productivity proxy; (c) $\delta^{15}\text{N}$: Subsurface oxygen proxy, we interpret high $\delta^{15}\text{N}$ values as period of depleted subsurface oxygen and; d) Biogenic silica: productivity proxy.

Figure 3. (a) $\delta^{15}\text{N}$ record superimposed on a reversed X-ray image of core PC-2. Red dots indicate the location of ^{14}C AMS dates for core PC-2. Shaded bars indicate the presence or absence of laminations. Black bars mark annual laminations (pictured on upper left, panel b), grey bars represent the presence of centennial laminations (for example see panel c) and the white bars indicates the absence of laminations (see panel d for visual example). The $\delta^{15}\text{N}$ record correlates with the presence/absence of laminations; higher $\delta^{15}\text{N}$ corresponds with more annual laminations, while lower $\delta^{15}\text{N}$ is associated with an absence of laminations.

Figure 4. Core PC-2 $\delta^{15}\text{N}$ times-series is overlain with shaded bars indicating the presence/ absence of benthic foraminifera. Shaded bars indicate core sections where foraminifera are present in sufficient abundances for taxonomic work (i.e. > 10 individuals /gram). Hatched lines show regions of the core that were surveyed but not benthic foraminifera were found. Benthics are much more common during the late Holocene section of the core and appear restricted to regions with elevated $\delta^{15}\text{N}$ during the early Holocene.

Figure 5. (a) Photograph of foraminifera from the early Holocene section of core PC-2 when preservation is poor. (b) Photograph of foraminifera from the late Holocene section of core PC-2 when preservation is excellent.

Figure 6. Scatter plots. (a) PC-2: late Holocene, BSi- $\delta^{15}\text{N}$ (b) PC-2: early Holocene, BSi- $\delta^{15}\text{N}$ (c) 1228D: late Holocene, BSi- $\delta^{15}\text{N}$ (d) 1228D: early Holocene, BSi- $\delta^{15}\text{N}$.

Figure 7. (a) PC-2 time series of SST (red) $\text{C}_{37}\text{total}$ (green) and $\delta^{15}\text{N}$ (blue). The shaded bars indicate periods that exhibit El Niño (blue) or La Niña (red) correlations between proxies. (b) Inset of El Niño time correlations between proxies and (c) Non- ENSO correlations between proxies.

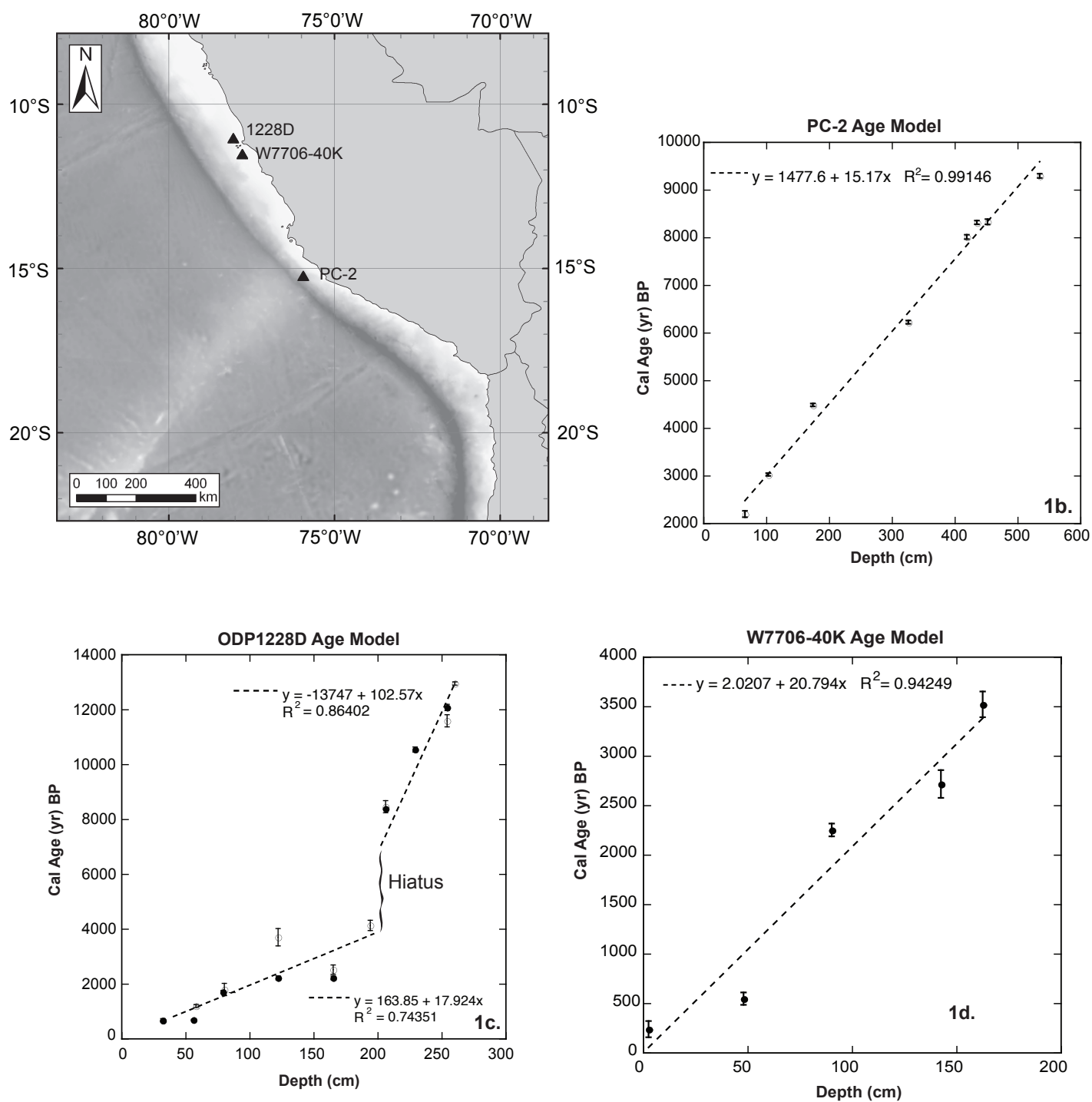


Figure 1.

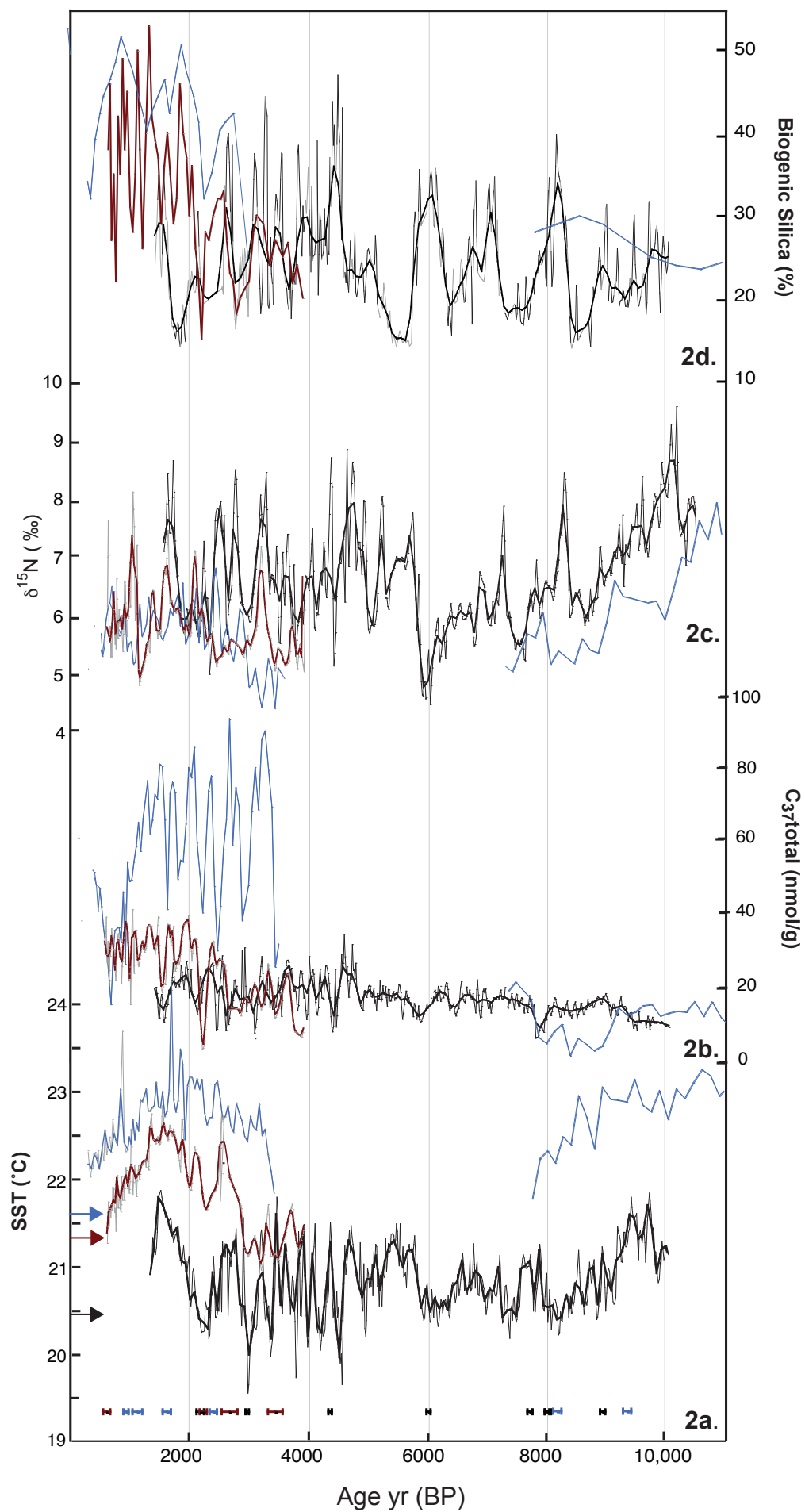


Figure. 2

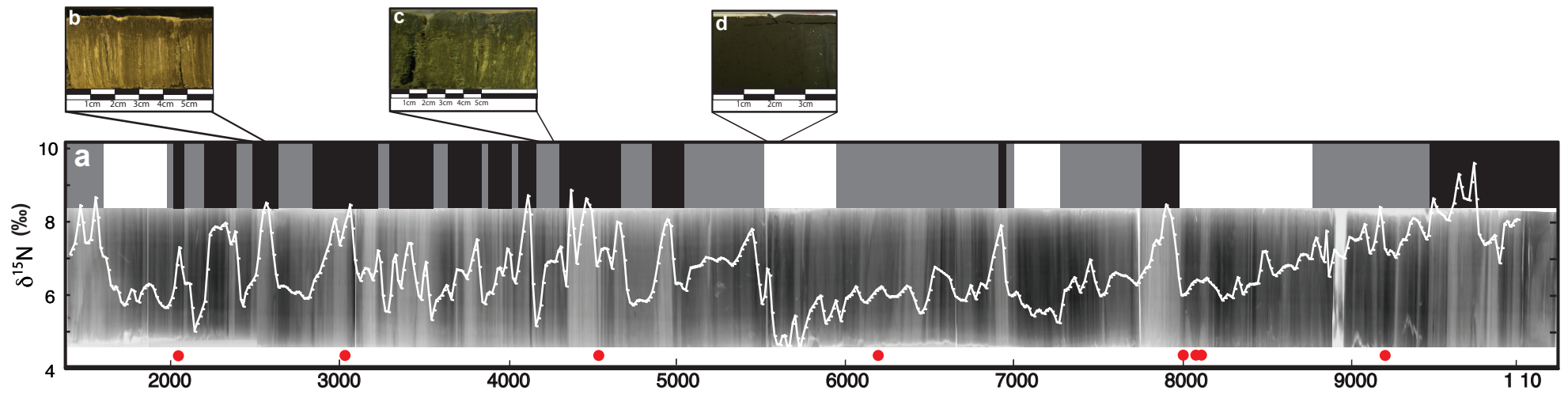


Figure 3.

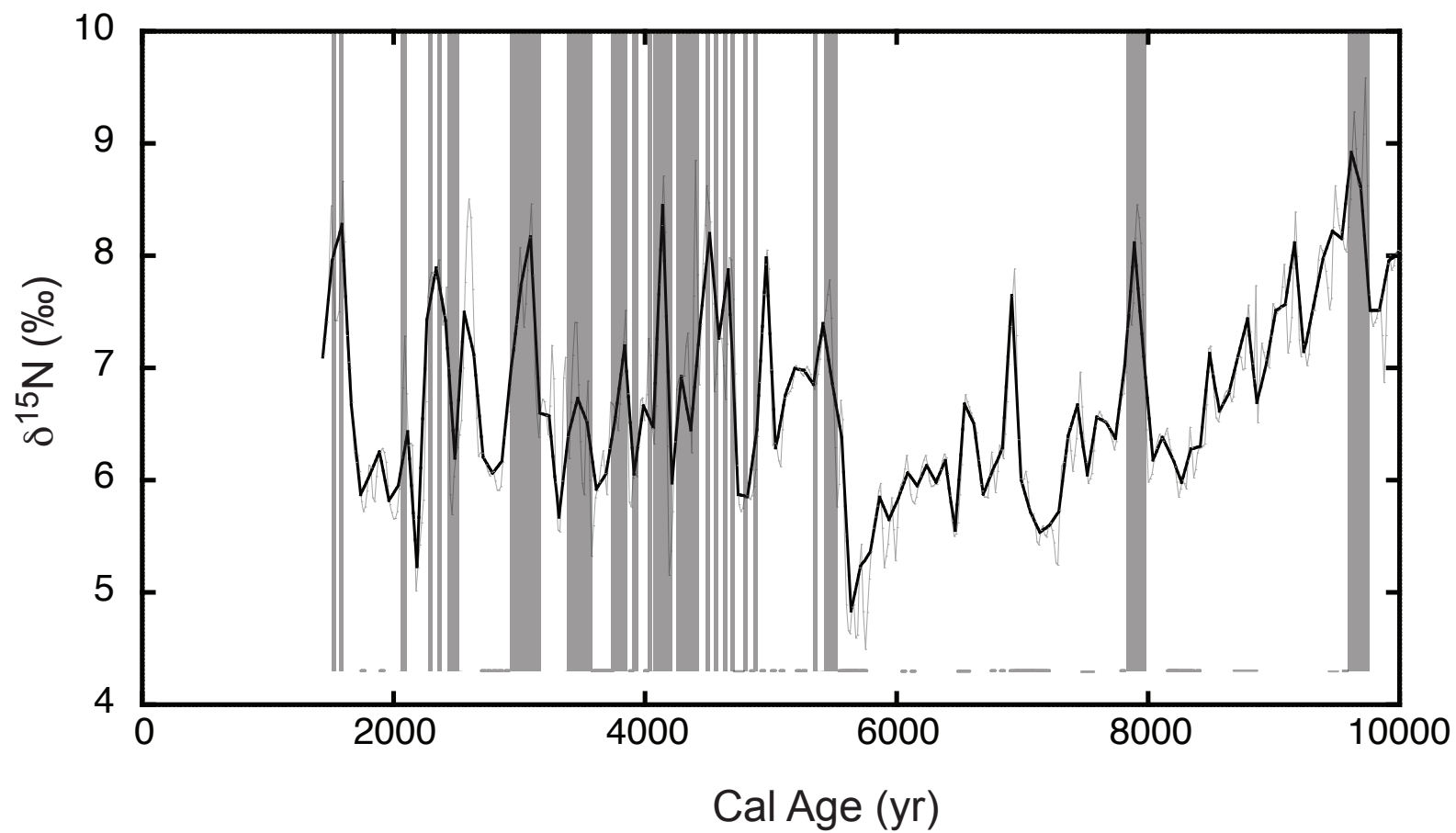


Figure 4.

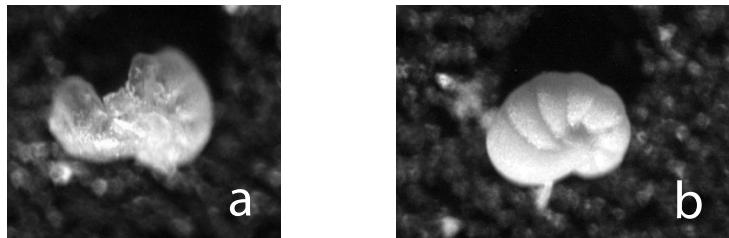


Figure 5.

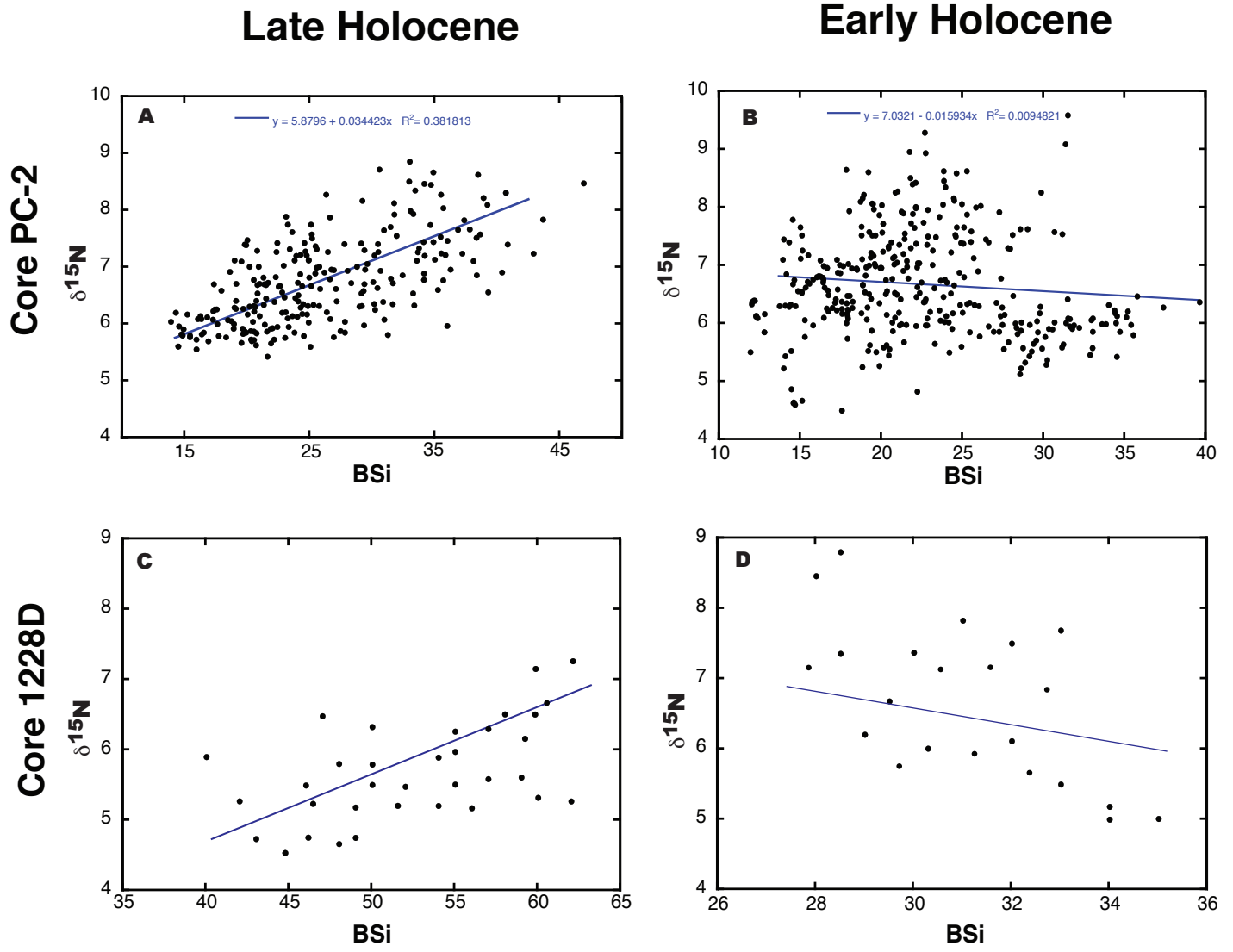


Figure 6.

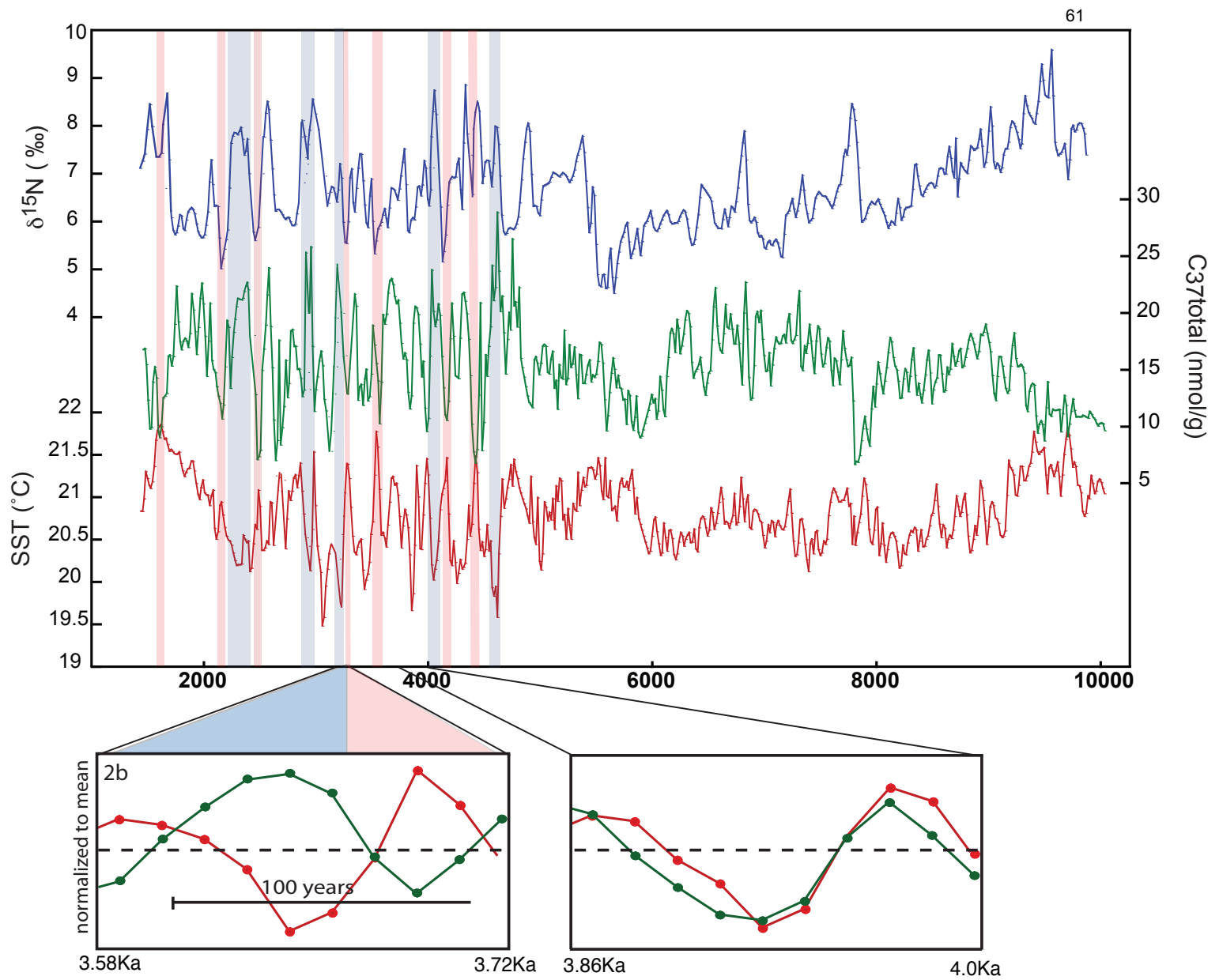


Figure 7.

CHAPTER TWO

Abrupt Mid-Holocene onset of centennial scale climate variability on the Peru-Chile Margin

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Abstract

Understanding the natural climate variations in the eastern tropical Pacific (ETP) is crucial for predicting the evolution of the El Niño-Southern Oscillation (ENSO). Here we present the first continuous, decadal-resolution Holocene climate record from the Peru-Chile Margin, near the epicenter of the modern ENSO system. Geochemical proxies allow us to reconstruct sea surface temperature, phytoplankton productivity, and thermocline ventilation, variables that are tightly correlated to ENSO events today. Despite the observation that the mean state of all three variables did not change over the past 10,000 years, our data reveal a dramatic increase in climate variability near 5 ka; represented by prolonged periods (50 – 200 yrs) of climate extremes, which are absent in the early Holocene. These centennial-scale oscillations do not show typical El Niño-La Niña correlations between proxies. We therefore posit that a significant fraction of super-ENSO variance may originate outside the tropics, through processes that ventilate the ETP subsurface waters.

1. Introduction

The Peru-Chile Margin plays a role of global climatic and biogeochemical importance. The equatorward Peru (Humboldt) Current merges to the north with equatorial upwelling to form the eastern equatorial Pacific cold tongue. The latter feature provides the instability to drive atmospheric-oceanic oscillations of the ENSO system and their global teleconnections, and may also, on longer time- scales, explain the persistence of Northern Hemisphere glaciations over the course of the Plio-Pleistocene ice ages [Huybers and Molnar, 2007]. The Peru Current is driven by along-shore winds, which are

deflected offshore by the Coriolis effect, forcing cold, nutrient-rich thermocline waters to upwell to the surface. Primary production exceeds $200 \text{ gC m}^{-2} \text{ yr}^{-1}$, making the Peru Coastal Current the most productive of all eastern boundary currents [Berger *et al.*, 1987]. The physical and biogeochemical properties of the waters upwelled off Peru are highly sensitive to changes in the position of the intertropical convergence zone (ITCZ) and the strength of Walker circulation [Strub *et al.*, 1998; Lavin *et al.*, 2006]. In the subsurface, waters at 200 to 800 meters depth are depleted in oxygen through a combination of high respiration rates driven by upwelling- induced surface productivity, and poor ventilation. Microbial denitrification under these oxygen-depleted conditions represents the major loss of nitrate from the global ocean [Wyrski, 1973; Codispoti and Christensen, 1985]. All of these aspects of the eastern tropical Pacific (ETP) oscillate strongly on the ENSO timescale (4 – 7 years), the primary mode of interannual variability [Philander, 1983] deduced from instrumental records.

Here, we seek to determine whether the long-term climate trends across the Holocene (last 11,000 yrs) and the centennial-millennial-scale climate variability within the Holocene followed tropical insolation forcing, which can produce long-term changes in ETP oceanography through changes in the frequency and intensity of ENSO [Clement *et al.*, 1999, 2000; Cane, 2005]. The backdrop for this time period includes the final meltback of Northern Hemisphere ice sheets by about 8,000 yrs BP [Clark *et al.*, 1999] and nearly constant atmospheric CO_2 levels [Indermühle *et al.*, 1999]. Earth's orbital configurations have, however, changed significantly enough over the Holocene to force changes in ETP climate. Changes in orbital precession could modulate ENSO frequency and intensity in at least two ways over the course of the Holocene. Precession controls the

summer-winter heating contrast in the tropics, an aspect fundamental to the underlying tendency of the tropical atmosphere-ocean instability to generate ENSO events [Cane, 1998, 2005; Fedorov and Philander, 2001] and also changes the intensity of seasonality between the hemispheres [Kutzbach *et al.*, 1998]. Precessional variations should also have induced a gradual drift in the position of the ITCZ from its most northerly extent in the early Holocene to a more equatorial location today, a prediction born out of paleoclimatic reconstructions [Haug *et al.*, 2001]. It is also possible, however, that remote forcing might dominate ETP conditions, perhaps through variations in the subduction and ventilation of Sub-Antarctic source waters that ultimately flow into the equatorial Pacific thermocline [Toggweiler *et al.*, 1991] or through the interaction of the Asian monsoon with Pacific trade winds [Liu *et al.*, 2000].

An outstanding question is whether climate change in the eastern tropical Pacific over the Holocene follows modes of variability observed during the instrumental period. Clement *et al.* [1999] argue that Milankovitch forcing alters the atmospheric-ocean interactions of the tropical Pacific on timescales of centuries to millennia through changes in the seasonal forcing of the ENSO cycle. The two most important aspects of this hypothesis for our study are 1) the tendency for alterations in solar radiation to produce long-term (hundreds to thousands of years) SST anomalies analogous to those associated with El Niño and La Niña events and 2) the prediction that ENSO variability can alter the state of the tropical Pacific on timescales longer than the typical ENSO period itself (e.g., >4 – 7 years). Multiple paleoclimate reconstructions from the tropical Pacific support the prediction that ENSO-like variability can ‘scale up’ to centennial and millennial climate changes. In the western Pacific, Stott *et al.* [2002] demonstrate that

salinity anomalies between stadial and interstadial periods were similar to El Niño /La Niña-like changes of today's climate but occurred on time scales of centuries to thousands of years. In the ETP, Koutavas et al. [2002] find evidence for a reduction in Walker circulation during the LGM followed by enhanced Walker circulation in the early and middle Holocene. The authors link this long-term shift in ETP SST to a multi-millennial El Niño /La Niña-like pattern. Continental climate reconstructions of rainfall events recorded in an Ecuadorian lake are interpreted to reflect millennial-scale (2 ka) fluctuations in ENSO strength, a pattern that is superimposed on a gradual increase in El Niño strength across the Holocene [*Moy et al.*, 2002]. Each of these climate reconstructions demonstrates that ENSO-like variability can produce coherent climate fluctuations at centennial to millennial time scales in the tropical Pacific.

We reconstruct surface and subsurface climate parameters from the heart of the modern ENSO system using the first high-deposition rate (70 cm/kyr), uninterrupted Holocene sediment archive ever recovered from the Peru- Chile Margin. This remarkable sediment core has a nearly constant sedimentation rate and contains annual laminations. While our sampling resolution (12 yr) is extremely high for marine environments, we note that our records are not sampled at the resolution required to reveal individual El Niño or La Niña events. The variables we reconstruct are, however, highly correlated to ENSO in the modern system. At present, El Niño events are characterized by increases in SST, reductions in primary productivity and increases in subsurface oxygen (and the opposite pattern for La Niña events). If ENSO-like variability persisted into centennial-millennial time scales across the Holocene we would expect, by analogy, to see the same proxy relationships that characterize interannual ENSO variability 'scaled up' over longer

time periods. Our records indicate that an abrupt increase in Peru Margin climate variability took place at the mid-Holocene (5 ka), which is only in part consistent with ENSO-like climate patterns. Despite this increase in climate variability, we see no evidence for a change in mean oceanographic conditions at the Peru-Chile Margin, as might be expected if increased ENSO variability was the major determinant of tropical Pacific oceanography over the past 10,000 years.

2. Site Location

Although the high productivity of the Peru-Chile Margin promotes high deposition rates, and the suboxic bottom water conditions inhibit sediment mixing by benthic organisms, nearly all sediment cores recovered from this region suffer from major gaps in Holocene sedimentation [*Reinhardt et al.*, 2002] (see auxiliary material for further discussion of Peru chronology). Here, we present data obtained from a ~6 meter piston core collected from the mid-Peruvian shelf at a water depth of ~250 meters (Figure S1) in the heart of the oxygen minimum zone (OMZ) [*Codispoti and Christensen*, 1985] that provides the first uninterrupted archive of conditions from ~10 ka to 1.5 ka. As constrained by eight AMS ^{14}C dates, the core accumulated at a high and nearly constant rate (70 cm/kyr, Figure S2) and contains annually laminated couplets of diatomaceous and non- diatomaceous layers (Figure S3).

3. Methods

We analyzed the core for geochemical parameters that define the key environmental variables of SST (U_{37}^k index [Prahl *et al.*, 1988; Muller *et al.*, 1998]), phytoplankton productivity (Alkenone- C_{37} total [Budziak *et al.*, 2000] and biogenic silica [Honjo *et al.*, 1982]) and subsurface ventilation ($\delta^{15}N$ of bulk organics [Libes and Deuser, 1988; Altabet *et al.*, 1995]). The core was sampled at 12 year time steps (every 1 cm) for alkenones and biogenic silica; the thickness of each sample (0.5 cm) results in an integrated picture of 6–7 years. Samples were freeze-dried and homogenized. Alkenones were extracted using 0.8–0.9g of sediment in a Dionex 200 accelerated solvent extractor and analyzed by gas chromatography, using a modified method of Herbert *et al.* [1998]. Laboratory analytical error, $0.2^{\circ}C$, is calculated based on a composite sediment standard, which is extracted and analyzed every 3 months. We also report an error that is specific to this study of $0.08^{\circ}C$ based on replicate GC analyses of individual PC-2 sample extracts (10% of samples were duplicated). Alkenone concentrations (C_{37} di- and triunsaturated ketone mass/grams of dry sediment = “ C_{37} total”) as a fraction of sediment dry weight are calculated by normalizing C_{37} total to an internal standard (C_{37} and C_{36} alkanes). C_{37} total provides a qualitative estimate of haptophyte production, which is closely linked to total phytoplankton productivity [Brassell, 1993; Budziak *et al.*, 2000]. Biogenic silica was determined using a modified method from Mortlock *et al.* [1989]. Analytical error for %BSi $\pm 3\%$, is calculated based on sample duplicates (20% of samples were duplicated). Nitrogen isotopes ($\delta^{15}N$) were sampled at 24 year time steps and measured on bulk sediments following the procedure established by Altabet *et al.* [1995]. Particulate nitrogen was converted into N_2 using a CN analyzer attached to an isotope-

ratio mass spectrometer using He as the carrier gas. $\delta^{15}\text{N}$ values are referenced to atmospheric N_2 and have an uncertainty of $\pm 0.2\%$.

4. Results

While the core is missing the most recent millennium, the average SST and SST range in the late Holocene section of the core (19.5 to 22 °C, Figure 1a) is consistent with modern conditions [Reynolds *et al.*, 2007]. Large centennial- scale variability has been observed at nearby sites on the Peru Margin over the last two millennia [Agnihotri *et al.*, 2008; Gutiérrez *et al.*, 2008]. The extended Holocene record presented here, however, shows a striking change in variability in each proxy record near 5 ka, such that late Holocene climate is characterized by significantly more variability than the early Holocene (see Figure 1a). SST displays the most dramatic increase in variance, averaging $0.25 \sigma^2$ in the early Holocene (10–5 ka) to $0.5 \sigma^2$ in the late Holocene (5–1.4 ka). This change in variability took place without a significant change in the mean values of the proxies before and after 5 ka: for example, mean SST, averaged over 4 kyr windows before and after the increase in variance changed by 0.06°C , below our analytical error. The onset of this shift in variance was not synchronous between proxies (SST and $\delta^{15}\text{N}$ lead $\text{C}_{37}\text{total}$ and biogenic silica: Figures 1 and S4) but occurred between 5.4 and 4.6 ka. The high amplitude events present in the latter half of the record are defined by multiple data points and clearly represent sustained (50–200 year) swings in time-averaged conditions (Figure 1b). There is a weak correlation ($r = 0.35$) between SST and $\text{C}_{37}\text{total}$ (productivity proxy) in the late Holocene, consistent in sign with an ENSO-like pattern: El Niño events are characterized by high SST, low productivity and

increased subsurface oxygen (decreased $\delta^{15}\text{N}$), and the opposite case is true for La Niña events (see Table S1). Laminations are more common in the late Holocene section of the core but also occur in the early Holocene when $\delta^{15}\text{N}$ is high (above 7‰). The correlation between $\delta^{15}\text{N}$ and %BSi is consistent with an ENSO pattern in the late Holocene ($r = 0.29$) but opposite in sign during the early Holocene (Table S1). The productivity proxies therefore argue that the local carbon flux was weakly tied to subsurface oxygenation in the late Holocene, and not linked to the strength of the OMZ in the early Holocene.

5. Discussion and Conclusions

Our results provide the first direct confirmation that conditions on the Peru-Chile Margin became more variable in the late Holocene. Moy et al. [2002] interpret the increase in pulses of terrigenous material in an Ecuadorian lake as evidence for increased El Niño-related rainfall events across the Holocene. Along the equator, stronger east–west gradients may have prevailed in the early Holocene and weakened toward the present [Koutavas et al., 2006]. A stronger SST gradient during the early-mid Holocene presumably accompanied stronger Walker circulation, and suppressed El Niño strength. Koutavas et al. [2006] also demonstrated that the variability in the range of temperatures recorded by oxygen isotopes of individual planktonic foraminifera in the eastern equatorial Pacific increased in the late Holocene, as would be expected if the extremes of the ENSO cycle intensified toward the present. While our record is consistent with other climate reconstructions showing a more variable ETP in the late Holocene, we emphasize the importance of the abrupt onset of climate variability evident in our climate reconstruction (Figure 1). The ‘ramping up’ in variability occurs between 5.4 and 4.6 ka (Figure S4), significantly faster than the gradual increase in variability found in other

climate reconstructions from ENSO sensitive regions [e.g., *Moy et al.*, 2002; *Koutavas et al.*, 2006; *Conroy et al.*, 2008]. Mechanistically, an abrupt change in climate variability may be linked to an alteration in the position of the ITCZ. Until the ITCZ migrated south of its early Holocene position the Bjerknes feedback between SST and wind strength was incomplete and anomalies were insufficient to generate strong ENSO events. Pulling convergence off of the equator is a requirement in the completion of the Bjerknes feedback loop [*Cane*, 2005]. A gradual shift in the position of the ITCZ could therefore produce an abrupt response in climate. Interestingly, this abrupt increase in variability is not synchronous between proxy records; the productivity proxies (C_{37} total and Biogenic Silica) lag SST and $\delta^{15}N$ by 400 yrs. This lag suggests that the mid-Holocene climate forcing of the Peru-Chile Margin is more complex than a gradual shift in the position of the ITCZ alone and may additionally require a mechanism that influenced surface and subsurface proxies at different rates. Paleo-temperature reconstructions from the Chilean margin, at the southern extension of the Peru-Chile Current (41°S) show strong coherence with temperature changes in the Ross Sea, which are attributed to latitudinal shifts in the position of the Antarctic Circumpolar Current [*Lamy et al.*, 2002] while fluctuations in paleoproductivity, rain fall and wind strength are better correlated with changes in tropical forcing through intensification of Hadley cell circulation [*Lamy et al.*, 2001]. The lag between paleoproductivity and SST and $\delta^{15}N$ may also represent the competing influences of high and low latitude forcing, where productivity is strongly tied to local wind strength and $\delta^{15}N$ and SST are influenced by both local climate and the climate of the high latitudes where source waters of the tropical thermocline originate [*Strub et al.*, 1998].

We also examine our record in light of two related questions: to what degree does the evolution of environmental variables at the centennial to millennial time scale within the Holocene represent “scaled-up” ENSO variations, and to what degree do the geological records resemble climate model simulations that attempt to capture the evolution of the tropical Pacific over the Holocene? It is intriguing to observe that, while all proxies increase their variability near 5 ka, the expected associations of high SST, low productivity, and depressed $\delta^{15}\text{N}$ that should accompany El Niño states (and the opposite case for La Niña conditions) do not persist into the centennial-millennial scale of our records. Many climate reconstructions [e.g., *Tudhope et al.*, 2001; *Koutavas et al.*, 2002; *Stott et al.*, 2002; *Moy et al.*, 2002; *Cobb et al.*, 2003] and model predictions [e.g., *Clement et al.*, 1999; *Philander and Fedorov*, 2003] have found evidence for ENSO-like patterns on centennial-millennial time scales. But our records suggest that the centennial fluctuations during the late Holocene in the Peru-Chile Margin do not show consistent ENSO-like variability. Instead the late Holocene section of our record fluctuates between ENSO-like and non-ENSO-like climate patterns. We also note that the late Holocene centennial fluctuations in our SST record (2°C) are substantially larger than previous reconstructions of Holocene climate. We suggest that the sediment archive hints at processes important to ETP oceanography that may not be observed or simulated at the ENSO timescale. Contrary to tropics-only model simulations [*Clement et al.*, 1999, 2000], the orbital changes of the Holocene did not produce changes in the mean SST of this region, although they may have promoted changes in variance. The decoupling of SST, carbon flux (productivity) and subsurface ventilation that we observe, particularly in the early Holocene, instead hints at the importance of climatic processes originating

remotely, for example, changes in the source of the equatorial undercurrent waters that enter the Peru-Chile thermocline, or in the circulation of the south Pacific gyre, which could influence the thermocline density structure and ventilation of the OMZ over time [Toggweiler *et al.*, 1991; Strub *et al.*, 1998; Lamy *et al.*, 2002]. The importance of gyre scale processes is indicated by, among other observations, the lack of a positive relationship between local indicators of high productivity and the expected consequence of low oxygen (high $\delta^{15}\text{N}$) conditions. Instead, the $\delta^{15}\text{N}$ record indicates that the OMZ was strongest when surface productivity was lowest (Figure 1). It would appear that on centennial to millennial timescales, the ventilation of the OMZ by remote processes dominates over the oxygen demand imposed by regional productivity to determine the intensity of oxygen depletion and nitrate removal along the Peru-Chile Margin. We also note that the expected Holocene southward migration of the ITCZ did not change the mean SST or biological productivity along the Peru-Chile Margin. Early to mid Holocene SSTs did not cool, as expected in some climate models [Clement *et al.*, 1999, 2000] although it is possible that coastal SSTs could have followed a different pattern from the heart of the equatorial cold tongue [Liu *et al.*, 2000]. In the aggregate, our paleoclimatic data argue for the necessity of including extra-tropical processes into investigations of tropical Pacific climate variability, and raise unanswered questions as to the relationship of centennial changes in the mean state of the eastern Pacific to the frequency and intensity of ENSO events.

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Figure Caption

Figure 1. Time series of proxy records. (a) Alkenone derived SST (red), C_{37} total (green), %BSi (blue) and $\delta^{15}N$ (black). (b) Inset shows an example (from 3.92 ka to 3.76 ka) of the high-amplitude events that are typical of the late Holocene section of the record.

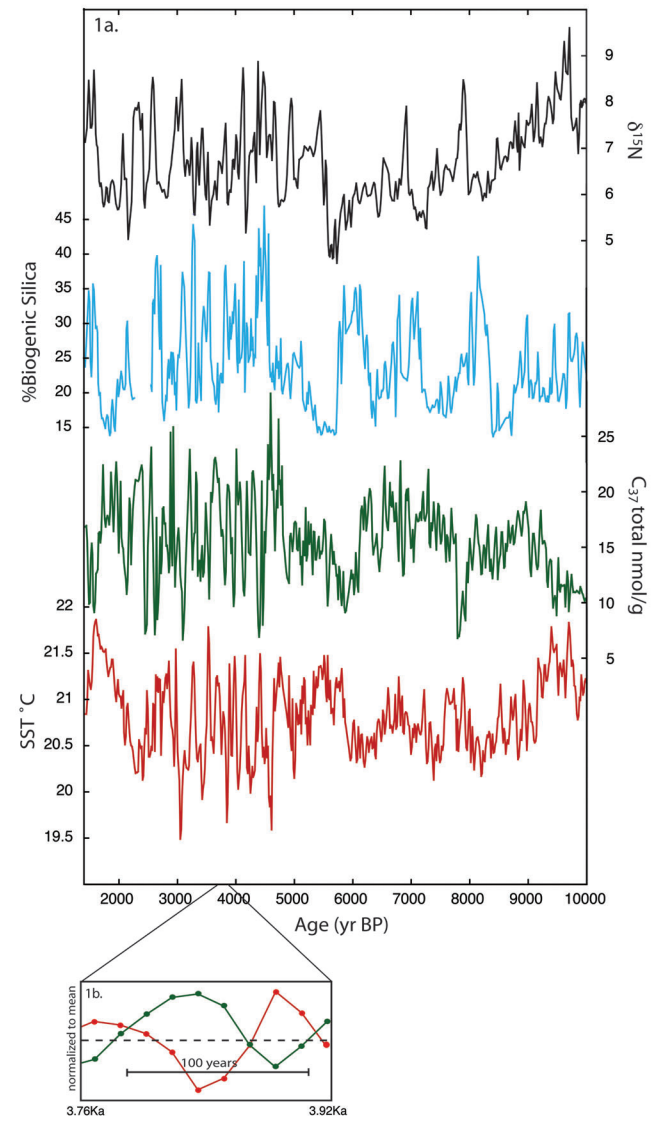


Figure 1.

Auxiliary Materials

1. Auxiliary Text

PC-2 Core Chronology

Previous studies along the Peruvian shelf have revealed frequent hiatuses in the sediment record, related to periods of low deposition or erosion [*De Vries and Schrader*, 1981; *Reinhardt et al.*, 2002]. Records of Holocene sedimentation along the Peruvian shelf are particularly sparse; among the possible Holocene records that we consulted, radiocarbon dating suggests that sedimentation is absent between ~9-3 ka [*Rein et al.*, 2003; *Skilbeck and Fink*, 2004]. This observation has been erroneously interpreted as evidence of sediment starvation brought on by persistent La Niña-like conditions (or a lack of El Niño events) during the early Holocene [*Moy et al.*, 2002; *Rein et al.*, 2003]. PC-2 is the first core from the Peru-Chile margin that has continuous, high-resolution, sedimentation through the Holocene (~10 kyr BP to 1.5 kyr BP). The nearly constant sedimentation rate (~70cm/kyr) provides the first evidence that sedimentation along the margin was not uniformly reduced during the early Holocene.

Age Model

Our age model was constructed from eight AMS ^{14}C age estimations from bulk organics, which were converted to calendar ages using the Fairbanks0107 radiocarbon calibration curve [*Fairbanks et al.*, 2005] and a reservoir correction of 450 yrs [*Bard et al.*, 1990]. A linear curve fit was used to obtain our age model, which shows a nearly constant sedimentation rate (~70cm/kyr) from approximately 10 kyr BP to 1.5 kyr BP. ($r^2 = 0.98$, Fig S2). The top section of the core was likely lost during deployment of the piston core.

Laminations

Annual couplets of sediment (Fig. S3) alternate between diatom rich (light) and diatom poor (dark) material. Laminations tend to occur when $\delta^{15}\text{N}$ is high, which is consistent with the expectation of diminished bioturbation in low oxygen conditions. A gradual increase in the frequency of laminated sections overprints this pattern, such that laminations are more common in the late Holocene than the early.

Auxiliary References

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2. Auxiliary Table

	Holocene	Late Holocene	Early Holocene	Expected ENSO Pattern
	1.5-10 ka	1.5-5 ka	5-10 ka	
C₃₇total-BSi	-0.24	-0.45	-0.13	N/A
*C₃₇total-BSi	0.12	-0.09	0.25	N/A
SST-C₃₇total	-0.28	-0.35	-0.21	(-)
SST-*C₃₇total	-0.31	-0.42	-0.27	(-)
SST-$\delta^{15}\text{N}$	0.14	-0.22	0.49	(-)
C₃₇total-$\delta^{15}\text{N}$	0.11	0.21	-0.25	(+)
*C₃₇total-$\delta^{15}\text{N}$	0.21	0.35	-0.15	(+)
BSi- $\delta^{15}\text{N}$	0.08	0.29	-0.10	(+)
* Indicates that C ₃₇ total is normalized to the biogenic silica-free fraction.				

Table S1. Correlation coefficient (r) table. The sign of the expected ENSO pattern, based on observations of the oceanographic response during ENSO events, is indicated in the column on the right-hand side of the table.

Supporting Figures

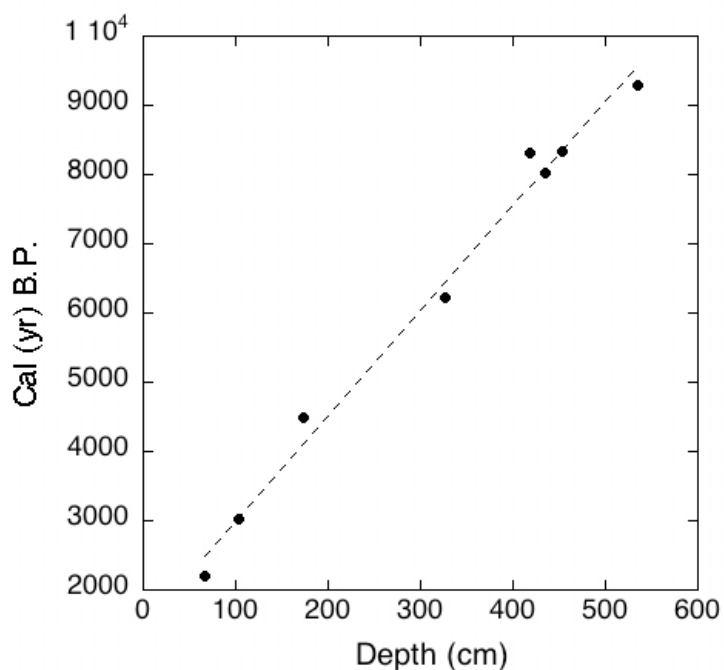


Figure S1. PC-2 age model. Circles indicate depths of bulk ^{14}C measurements, which were converted into calendar ages using the fairbanks0107 calibration curve. The age model was constructed using a linear curve fit (hatched line) ($r^2 = 0.98$).

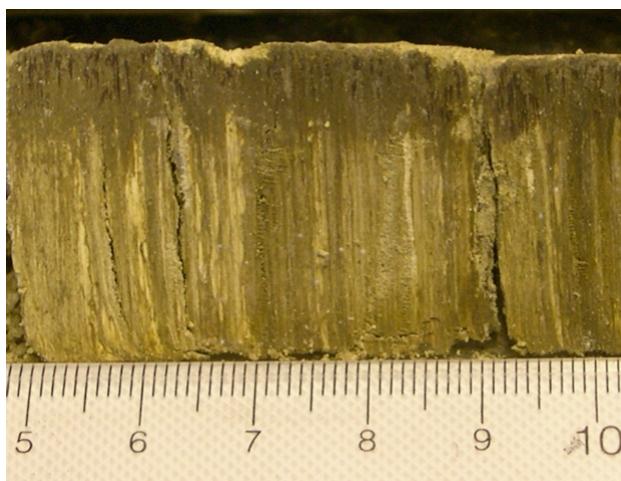


Figure S2. Annual laminations from the late Holocene section of PC-2. Annual couplets alternate between diatom rich and diatom poor sediments.

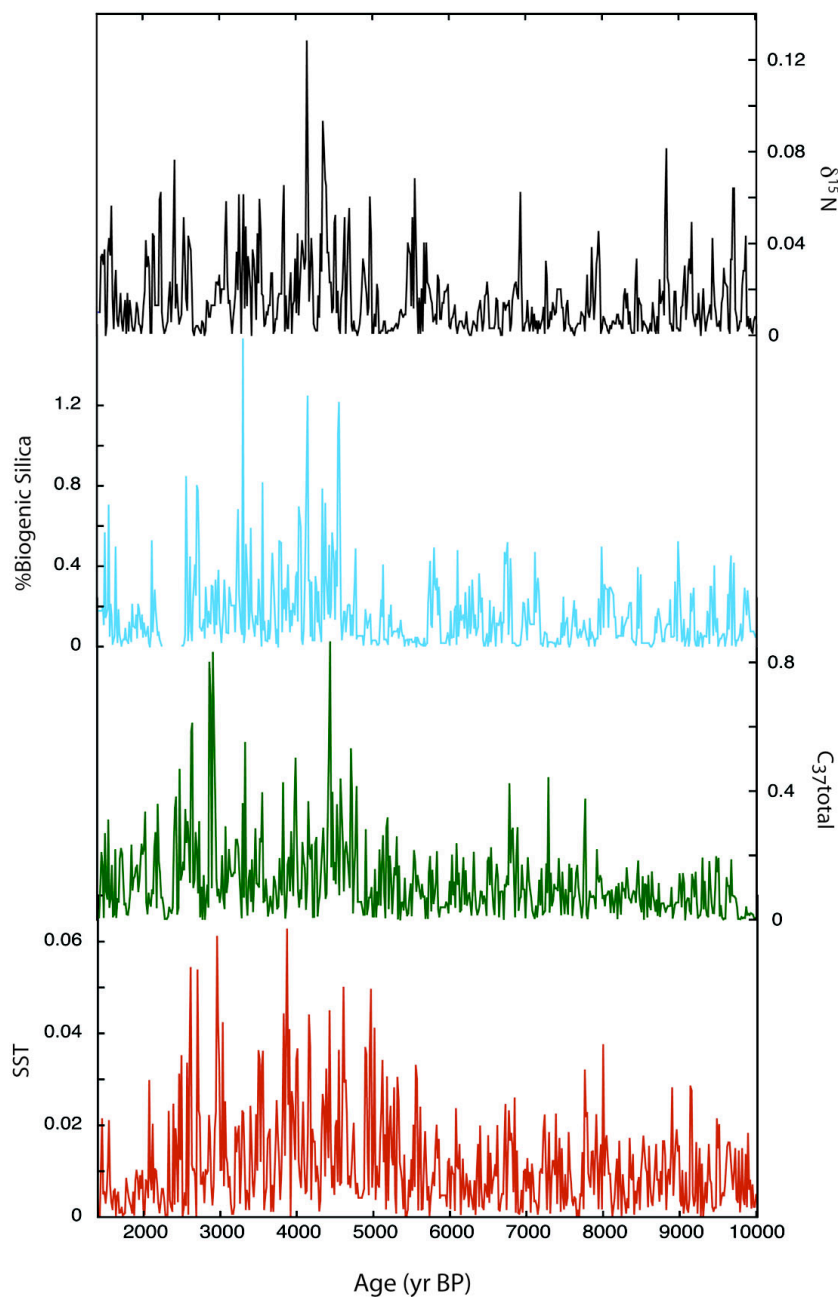


Figure S3. Prewhitened ($\Delta\text{proxy}/\Delta\text{time}$) time series. SST (red), $\text{C}_{37}\text{total}$ (green), biogenic silica (blue) and $\delta^{15}\text{N}$ (black). The largest change in each proxy record occurs between 5.7-4.6 ka. SST appears to lead the other proxies.

CHAPTER THREE

The Curious Case of the Peru Margin Benthos

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Abstract

Certain species of benthic foraminifera flourish in extremely oxygen-depleted environments. The population densities and species diversity of these select benthic foraminifera appear to respond to the dynamic environmental conditions of the Peru margin. Here, we present a multiproxy reconstruction of subsurface oxygen (inferred from $\delta^{15}\text{N}$ and the presence/absence of annual laminations) and surface productivity (inferred from $\text{C}_{37}\text{total}$ and biogenic silica) across the Holocene to understand what environmental factors affect these remarkable organisms. Using an annually laminated, high sedimentation-rate (70cm/kyr) core from the heart of the Eastern South Pacific Oxygen Minimum Zone we find remarkable similarities between decadal changes in benthic foraminiferal community structure, surface productivity and subsurface oxygenation. We identify eighteen distinct species of benthic foraminifera, whose diversity fluctuates across the Holocene. Along with fluctuations in species diversity, we see dramatic, sub-decadal oscillations in species abundance, ranging from < 20 individuals per gram to $> 20,000$ individuals per gram of sediment.

Subsurface oxygen and surface productivity (i.e. benthic food supply) appear to be the dominant controls on benthic foraminiferal abundance across the Holocene. When food supply is low, small changes in surface productivity are positively correlated with foraminiferal abundance. As food supply increases- the relationship between surface productivity and foraminiferal abundance breaks down and subsurface oxygen (inferred from $\delta^{15}\text{N}$) emerges as a more reliable indicator of foraminiferal abundance; higher $\delta^{15}\text{N}$ corresponds to greater foraminiferal abundance. The positive correlation between $\delta^{15}\text{N}$

and benthic foraminiferal abundance likely reflects the reduction in predators during extreme oxygen deficits. We also find a strong anti-correlation between foraminiferal abundance and diversity. Subsurface oxygen is the dominant control on species diversity; diversity is reduced when subsurface oxygen is low. Peru margin benthic foraminifera are remarkably responsive to small changes in subsurface oxygen and surface productivity. They may provide valuable information about past environmental changes in low oxygen environments.

1. Introduction

Benthic foraminifera are found in the fossil record as far back as the Cambrian [Glaessner, 1979] although hyaline varieties first appear in the Permian [Sen Gupta, 1999]. Over 200,000 extant species currently inhabit the world's oceans. This diverse group of protists thrive in a wide variety of physical, biological and chemical environments. While certain species appear to favor specific environmental conditions, global surveys indicate that no particular species of foraminifera is restricted to a single geographic region [Bernhard, 1989]. The occurrence and population density of benthic foraminifera has been linked to a wide variety of biotic (predation, ultracellular adaptations, food availability, etc.) and abiotic (dissolved oxygen, temperature, salinity, pH, etc.) marine conditions [Bernhard and Bowser, 1999]. Many studies have focused on spatial variations in benthic foraminiferal assemblages [e.g. Bernhard, 1989; Bernhard and Reimers, 1991; Moodley *et al.*, 1997; Bernhard and Bowser, 1999] but here we focus on temporal variations at one particular site in the Eastern South Pacific (see Figure 1). The goal of this study is to evaluate the primary environmental factors that influence benthic foraminiferal assemblages in the Peru margin over the course of the Holocene.

Previous work at the Peru margin has revealed a major shift in climate variance near the mid-Holocene, where the late Holocene is characterized by decadal-centennial-scale fluctuations in surface productivity (C_{37} total and biogenic silica) and subsurface ventilation ($\delta^{15}N$ and alternating sequences of bioturbated and laminated sediments) [Chazen *et al.*, 2009; Chazen *et al.*, 2010 (Chapter 1)]. In contrast the early Holocene is comparatively stable [Chazen *et al.*, 2009]. We approach this study with two related questions, 1) what are the dominant environmental factors that influence benthic foraminifera in the Peru margin and, 2) are the major decadal climate oscillations that characterize the oceanographic conditions of the Peru margin (during the late Holocene) expressed in benthic foraminiferal community structure and/or abundance. Each of these questions will help us understand the utility of benthic foraminiferal assemblages as a tool for paleoclimate reconstructions in low oxygen environments.

The Peru margin, situated in the heart of the eastern south Pacific oxygen minimum zone (OMZ), is ideally situated for this kind of study due to the high sedimentation rates (70cm/kyr). We also selected this particular site because of the dynamic climate history recorded in core PC-2 (see Figure 1, [Chazen *et al.*, 2009]) that enables us to directly compare our foraminifera records to several key indices of past oceanographic conditions at the Peru margin.

2. Background

2.1. Site Location

The Peru margin is situated at the interface between the poorly ventilated, poleward Peru Undercurrent (PUC, 50-500 m depth) and the equatorward Peru Coastal

Current (see Figure 2). Equatorward along-shore winds are deflected offshore by the Coriolis effect, forcing cold nutrient-rich waters to the surface. Peru margin upwelling represents the final stages of a ventilation process that begins in the southern high latitudes and extends to the western subtropics, before travelling across the Pacific basin as the eastern equatorial undercurrent (EUC) [Toggweiler *et al.*, 1991; Sarmiento *et al.*, 2004]. A portion of the EUC is deflected south, forming the Peru undercurrent [Lukas, 1967] which eventually upwells off Peru. This strong year-round upwelling is responsible for making the Peru Current the most productive of the world's eastern boundary currents [Berger *et al.*, 1987]. The poor ventilation of the subsurface waters along with high respiration rates creates a persistent oxygen deficit in the intermediate waters of the Peru margin, the largest of the world's three Oxygen Minimum Zones (OMZ). OMZs have major impacts on the ocean nitrogen cycle and Earth's biological pump [Stramma *et al.*, 2008]. In oxygen-depleted environments, microbial bacteria reduce NO_3^- into nitrogen gas N_2 . Microbial denitrification represents the major loss of nitrate from the global ocean [Wyrski, 1973; Codispoti and Christensen, 1985]. Thus, while OMZs occupy just over 1% of the global ocean [Kamykowski and Zentara, 1990] these regions account for the primary loss of nitrate from the ocean.

Along the Peruvian margin the OMZ intercepts shelf sediments (see Figure 2) imprinting the physical character of sediments (laminations) and the biota that inhabit those sediments. The benthic organisms that reside in these dynamic environments provide compelling clues to changes Margin climate over time. Organic carbon in Margin sediments ranges from 2-12 (wt%) but is highest in the southern Margin where core PC-2

was collected. The thick Holocene sequences recovered in core PC-2 reflect the long upwelling history of the Margin.

2.2 *Making a living on the Peruvian Shelf*

On first examination, finding a thriving group of aerobic fauna, with calcareous tests, in a low pH environment, nearly devoid of oxygen seems unlikely. However, for species that can survive oxygen minimum zones the ecological advantages are vast: high food supplies, little competition and reduced predation [Bernhard and Sen Gupta, 1999; Gooday *et al.*, 2000]. Here we examine the adaptations that allow certain benthic foraminifera species to flourish in such harsh environments and the ecological advantages to living in the Peru margin benthos. The principal genera that characterize oxygen-depleted environments include, *Bolivina*, *Epistominella*, *Uvigerina*, *Cassidulinoides*, *Buliminella* and *Nonionella*. These genera have been previously reported in low oxygen environments [Bernhard, 1987] including the Peru margin [Risgaard-Petersen *et al.*, 2006]. Several adaptations and morphological advantages may explain why these particular genera tend to dominate oxygen-depleted environments. The presence of symbiotic bacteria and the ability to sequester chloroplasts have been identified in several species of low oxygen foraminifera, including *Nonionella Stella* and *Buliminella sp.*, these adaptations may explain how aerobic organisms survive prolonged periods of oxygen depletion [Bernhard and Sen Gupta, 1999; Bernhard *et al.*, 2000; Risgaard-Petersen *et al.*, 2006]. Morphologic advantages may also play a role in low oxygen foraminiferal assemblages. Bernhard [1987] found that genera typical of low oxygen environments tend to have morphological commonalities; elongate and flattened morphologies (eg. *Bolivina* and *Stainforthia*) tend to dominate over upright varieties

possibility due to the increased surface area and thus enhanced oxygen exchange [Bernhard, 1987; Murray, 2001]. Benthics with perforated tests (eg. *Nonionella*) may also enhance oxygen exchange, giving porous foraminifera an ecological advantage [Leutenegger and Hansen, 1979] over taxa that lack pore walls. Oxygen concentrations also influence the macro-fauna, making subsurface O₂ an important contributor of the predator/prey dynamic of benthic environments [Thistle *et al.*, 1993]. Subsurface [O₂] can also affect benthic biota by altering the oxygen gradient in the sediments [Loubere *et al.*, 1993] and thus change the micro-environments of benthic foraminifera. Individual species of benthic foraminifera differ in their tolerance to anoxia, thus alterations in subsurface oxygen can lead to shifts in species assemblages [Bernhard, 1987; Denne and Sen Gupta, 1991] and abundance [Bernhard, 1993].

In addition to species-specific adaptations, several studies have noted increased species abundances and decreased species diversity in low oxygen foraminiferal assemblages compared to similar assemblages found in oxygenated environments [Boltovskoy and Lena, 1969; Phleger and Soutar, 1973; Bernard and Bowser, 1991]. The species capable of withstanding low oxygen conditions benefit from the enhanced food availability and reduced predation [Loubere, 1994; Gooday *et al.*, 2000]. Observations off the eastern north pacific minimum oxygen zone found peak species densities following seasonal inputs of organic matter [Rathburn, 1998]. The limiting factor for species capable of surviving low oxygen environments appears to be the availability of food; the greater the food availability the higher the species abundance [Gooday *et al.*, 2000]. The amount of ‘food’ that reaches the subsurface is a function of the surface

carbon flux and thus can be estimated using proxies for surface productivity [Loubere, 1994; Gooday *et al.*, 2000].

3. Materials and Methods

Core PC-2 is the only known Holocene sediment archive with uninterrupted sedimentation from the southern Peru margin [Chazen *et al.*, 2009]. The age model was constructed using 8 AMS ^{14}C age estimations from bulk organics. Sedimentation rates are nearly constant across the length of the core (70cm/kyr, 10ka-1.4ka). Based on our age model, laminations present in core PC-2 range from annual (Figure 3b) to multi-decadal (Figure 3c).

3.1 Indicators of Subsurface Oxygen

We use two independent proxies to reconstruct subsurface oxygen: nitrogen isotopes and the presence/absence of laminations. Nitrogen isotopes ($\delta^{15}\text{N}$) were measured on bulk sediments following the procedure established by Altabet and Francois [1994a]. Samples extracted for nitrogen isotope analysis were sampled at an estimated resolution of every 26 years. Particulate nitrogen is converted into N_2 using a CN analyzer attached to an isotope-ratio Mass Spectrometer, which uses He as the carrier gas. $\delta^{15}\text{N}$ values are referenced to atmospheric N_2 with an uncertainty of $\pm 0.2\%$.

In low oxygen environments [$\text{O}_2 < 0.5 \text{ mg/L}$] heterotrophic bacteria reduce NO_3^- to N_2 , which is termed denitrification. During denitrification, light nitrate ($\text{N}^{14}-\text{NO}_3^-$) is preferentially removed leaving the remaining nitrate pool enriched in heavy nitrate ($\text{N}^{15}-\text{NO}_3^-$). This heavy nitrate signal is transferred to the surface through upwelling where it is used by biota and eventually buried in the underlying sediments. $\delta^{15}\text{N}$ has been used as

an indicator of changing subsurface oxygen in a number of studies [*Codispoti et al.*, 1986, 2001; *Deutsch et al.*, 2001; *Brandes and Devol*, 2002]. However, we argue that interpreting the $\delta^{15}\text{N}$ signal must be done with caution as several other factors can contribute to the sedimentary $\delta^{15}\text{N}$ signal. These include: secondary fractionation during assimilation in the euphotic zone [*Altabet and Francois*, 1994a], incomplete nitrate utilization and preexisting nitrogen pools [*Altabet and Francois*, 1994b; *Sigman et al.*, 1999].

To validate the use of $\delta^{15}\text{N}$ as a proxy for subsurface oxygen we compare our records to the presence/absence of laminations (see Figure 3a). The preservation of laminations precludes disturbance by bioturbators and thus provides strong independent evidence of bottom water anoxia.

3.2 Surface Productivity

Only a minor fraction of the organic matter produced in the surface ocean ever reaches the sea floor. The vast majority of organic matter is recycled in the upper ocean; and ultimately only a small fraction of the material that does reach the sediments is ultimately buried and preserved in the sediment record. Paleoceanographers have the challenging task of reconstructing surface production based on the small environmental clues preserved in ocean sediments. Coastal upwelling regions provide the highest organic matter accumulation and burial rates of the global ocean [*Berger et al.*, 1989; *Berger and Wefer*, 2002]. Here, we present two independent productivity proxies, $\text{C}_{37}\text{total}$ and Biogenic Silica, each of which, record different aspects of phytoplankton production. We use the collective pattern of these two productivity proxies as an index for changes in

labile organic material transferred to the subsurface and thus we can use our productivity reconstructions to estimate changes in the food available to benthic foraminifera [Loubere, 1994; Gooday *et al.*, 2000].

Core PC-2 was sampled for alkenones and biogenic silica analysis at an estimated resolution of every 13 years. The concentration of alkenones (C_{37} di- and triunsaturated ketones) preserved in sediments is a function of surface haptophyte productivity, water column export and organic matter preservation. Alkenones have been widely used in paleoclimate temperature reconstructions [Brassell *et al.*, 1986; Muller *et al.*, 1998; Herbert *et al.*, 1998; Conte *et al.*, 2006] but their utility in paleoproductivity reconstructions has also proved robust [Bolton *et al.*, 2010]. Compared to other phytoplankton lipids, alkenones are highly refractory [Brassell *et al.*, 1993; Budziak *et al.*, 2000]. Degradation of alkenones has been noted in low sedimentation rate environments [Sun and Wakeham, 1994; Rontani *et al.*, 2009]. However, recent work from the eastern equatorial Pacific and Atlantic upwelling regions demonstrates that over orbital cycles alkenone accumulation rates are closely tied not only to alkenone-synthesizing haptophyte concentrations but also to total phytoplankton productivity [Bolton *et al.*, 2010].

Alkenone concentrations (C_{37} di- and triunsaturated ketone mass/grams of dry sediment = “ C_{37} total”) were calculated by normalizing to an internal standard (C_{37} total and C_{37} n-alkanes) following a modified method of Herbert *et al.* [1998]. Sample replicates (10% of samples were replicated) were used to estimate the relative error of +/- 10% for C_{37} total.

In addition to alkenones, we reconstruct biogenic silica (BSi), a widely used proxy for marine surface productivity. The primary source of BSi in this study comes from diatoms (and in smaller part radiolarians and sponges). In many highly productive regions, annual opal production is closely associated with organic carbon [Treguer *et al.*, 1995; Fischer and Wefer, 1999]. However, inconsistencies between BSi and other paleoproductivity proxies may reflect the availability of dissolved silica in the surface waters and the silicic acid saturation of the water column, both of which can effect opal preservation [Ragueneau *et al.*, 2000]. Hutchins and Bruland [1998] argue that iron availability can have major consequences on the export and preservation of opal by altering the thickness of tests. Thus, variations in down core opal may be more sensitive to changes in Fe than other productivity proxies.

Biogenic silica (BSi) was measured using a continuous flow analysis, using a Molybdate spectrometry method modified from Mortlock and Froelich [1989]. Approximately, 0.3g of sediment were extracted in a hot alkaline digestion at 85°C in 0.5 M NaOH for 2 hours. Sample duplicates (10% of samples were duplicates) were used to calculate the relative analytical error of +/- 10% for BSi.

3.3 Foraminifera Preservation

Dissolution/preservation of calcareous foraminifera in oxygen minimum zones varies with alkalinity and pH. In ocean margins, and oxygen minimum zones in particular, mineral oxidation and the breakdown of organic matter can lead to acidic conditions through the production of H_2CO_3 , HNO_3 and H_2SO_4 [Green *et al.*, 1993]. However, when conditions approach anoxia, sulfate reduction can lead to secondary

production of alkalinity, creating conditions that promote calcareous preservation. As a result dissolution of benthic foraminifera in the heart of oxygen minimum zones (OMZ) is rare [Berger and Soutar, 1970; Berelson *et al.*, 1996; Murray, 2006]. Unlike thin-shelled planktonic foraminifera, the test walls of benthics tend to be solid and robust, further enhancing preservation [Gooday *et al.*, 2000]. However, along the perimeter of oxygen minimum zones where oxygen levels are too high to produce secondary alkalinity, the preservation of calcareous benthic foraminifera is extremely poor. As a result major changes in the oxygenation of the Peru subsurface across the Holocene may affect the preservation of benthic foraminiferal assemblages.

3.4 Benthic Foraminifera Abundance and Diversity

Core PC-2 was sampled at an estimated resolution of every 30-40 years from ~10-1.4kyr. The sampling resolution was increased to a sample spacing of every ~6-7 years across intervals with high concentrations of benthics (i.e. >10 individuals/gram). Each sample was carefully homogenized, sieved and picked wet to prevent damage of thin-shelled foraminifera (following the method of Bernhard *et al.*, 1997). Benthic foraminifera identification to the species level was conducted using a portion (~0.1g-0.5g) of each homogenized sample under a dissection microscopy. The abundance (individuals per gram) and diversity (number of species per sample) was tabulated for each sediment sample.

4. Results

4.1 Laminations and $\delta^{15}\text{N}$: Proxies for Subsurface Oxygen

The thick Holocene sediment sequence recovered in core PC-2 reflects the long upwelling history of the Margin. Laminated sections vary from several millimeters to sub-millimeter scale (multi-decadal to annual) and fluctuated back and forth in narrow bands (see Figure 3). Individual lamina, alternate between, pale, porous layers of well-preserved diatom frustules and dark, tightly packed, clay rich diatomaceous mud layers (see Figure 3b). The non-laminated core sections are medium in color, crumbly and contain abundant diatom debris. These alternating facies reflect alterations in the strength of the Peru Oxygen Minimum Zone. As a result, there is a striking correlation between $\delta^{15}\text{N}$ and the presence of laminations (Figure 3a). Laminated core sections tend to occur when $\delta^{15}\text{N}$ is high ($> 7.5\text{‰}$). This observation is consistent with the expectation of reduced bioturbation during periods of low subsurface oxygen. Thus, despite other potential influences on sedimentary $\delta^{15}\text{N}$ (discussed in section 3.1) the strong association between elevated $\delta^{15}\text{N}$ values and the presence of annual laminations over centennial to millennial timescales gives us confidence in the use of nitrogen isotopes as indicators of fluctuating oxygenation in Peru sediments.

4.2 Surface productivity

Each productivity proxy reveals similar structures of production across the Holocene. All three productivity proxies reveal a major increase in variance near the mid-Holocene; centennial scale fluctuations in productivity characterize the late Holocene but are absent from the early Holocene part of the record (see Figure 4). Despite this major

change in variance, the mean productivity does not change significantly across the Holocene.

On centennial to subcentennial timescales BSi and C_{37}^{total} exhibited some notable differences; three significant peaks in BSi (which last between 300-500 years) punctuate the early Holocene section of the record (see Figure 4). These events may correspond to increases in diatom production relative to other phytoplankton or fluctuating Fe inputs during the early Holocene. Regardless, the general agreement between C_{37}^{total} and BSi gives us confidence in our productivity proxies.

4.3 Preservation of Foraminifera

A few planktonic foraminifera (<10 individuals per gram of sediment) were recovered from a limited number of PC-2 samples but preservation was extremely poor, showing signs of pitting and breakage. The majority of late Holocene (5.5-1.4ka) sediments surveyed contained measurable amounts of benthic foraminifera (>10 individuals per gram of sediment). During the early Holocene, benthic foraminifera are restricted to regions with extremely low subsurface oxygen (see Chazen et al., 2010 (Chapter 1) for a detailed summary of benthic foraminiferal presence/absence in core PC-2). The preservation of benthic foraminifera also varies between the early and late Holocene. Benthic foraminifera recovered during the late Holocene section (5.5-1.4ka) of PC-2 are extremely well preserved (see Figure 5a). The benthic preservation during the early Holocene section of PC-2 varies between excellent to moderate (etching on the outer shell creates a dull appearance, see Figure 5b) to poor (see Figure 5c). To avoid any possible aliasing caused by dissolution we only focus on foraminiferal species

assemblages during the late Holocene section of core PC-2, where foraminifera preservation is excellent. As a result, we feel confident that dissolution does not bias benthic species assemblages across the Holocene.

4.4. Linking Productivity and Subsurface Oxygen to Benthic Foraminifera

The benthic foraminifera assemblages identified in PC-2 are typical of ‘low oxygen’ genera [Bernhard, 1987]. The benthic assemblages consist entirely of *Rotaliina* taxa with a documented high tolerance to low oxygen conditions. The benthics found in PC-2 are also very small (< 250 microns) compared to identical species found in oxygenated environment. The occurrence of small benthic foraminifera has been linked to environments with prolonged oxygen depletion [Bernhard and Sen Gupta, 1999; Morales et al., 2006].

Surface productivity and subsurface [O₂] appear to be the dominant influences on the abundance of benthic foraminifera in Peru margin sediments. Surface productivity proxies (C₃₇total and BSi) are positively correlated with foraminiferal abundance (Figures 6a, b); higher foraminiferal abundances correspond with periods of inferred enhanced surface production. Interestingly, this relationship changes with increasing productivity; when surface productivity is low (BSi < 23%, C₃₇total < 12nmol/g) the correlation between productivity and foraminifera abundance is strong (BSi and C₃₇total R² = 0.48 and 0.5, respectively, see Figures 6a and b) but gradually weakens with increasing productivity. In addition to surface productivity, subsurface oxygen (inferred from δ¹⁵N) is also positively correlated with foraminiferal abundance (see Figure 6c). The samples that exhibit a linear relationship between productivity and abundance (see black circles in

Figure 6a) cluster at the lower end of our $\delta^{15}\text{N}$ reconstruction (i.e. $\delta^{15}\text{N} < 6\text{‰}$) (see Figure 6c).

While both surface productivity and inferred subsurface oxygen appear to affect foraminiferal abundance, subsurface oxygen alone stands out as the primary control on species diversity through time; periods of low subsurface oxygen (i.e. $\delta^{15}\text{N} > 7\text{‰}$) correspond with reduced species diversity (see Figure 6d). There is no significant correlation between surface productivity and species diversity (see Figures 6e and f).

The species assemblages and diversity repeatedly shift through time, alternating from low diversity high abundance assemblages, which are dominated by species possessing flattened or elongate morphologies (e.g. *Bolovina*, *Buliminella* and *Stainforthia*) and ultracellular adaptations that enhanced oxygen exchange (e.g. *Nonionella Stella*, *Buliminella Tenuata* and *Stainforthia sp.*, see yellow bars in Figure 7) [Leutenegger and Hansen, 1979; Risgaard-Petersen et al., 2006; Bernhard and Bowser, 2008] to assemblages with increased diversity but reduced abundance, dominated by species that tend to prefer better oxygenated environments (e.g. *Epistominella* and *Cassidulina* see blue bars in Figure 7) [Bernhard and Bowser, 1999].

These shifts in species diversity, abundance and assemblages occur in tandem with changing subsurface oxygen. Low diversity, high abundance assemblages tend to correspond with intervals with elevated $\delta^{15}\text{N}$ ($>7\text{‰}$), while the high diversity, low abundance assemblages correspond to periods when $\delta^{15}\text{N}$ is low ($<6\text{‰}$). This pattern is best illustrated during the late Holocene when foraminiferal assemblages reflect repeating shifts in $\delta^{15}\text{N}$ (see Figure 7).

The correlations between proxies of surface productivity, inferred subsurface anoxia and benthic foraminiferal assemblages appear to be in-phase with one another. We cannot rule out short time lags since each sample integrates over 6-7 years of deposition but we see no evidence for time lags longer than 7 years between any of our climate proxies. The short life span of benthic foraminifera (< 1 year) allows for rapid changes in species assemblages. Thus, the settling rate of organic matter would be a more likely source of any significant lag between proxies. The absence of a time lag between our surface productivity proxies and benthic foraminifera indicates that the settling flux of organics is relatively fast in Margin sediments.

5. Discussion

Using a suite of surface and subsurface climate proxies from the Peru margin we searched for connections between benthic foraminiferal species assemblages and indices of Peru margin climate across the Holocene. We find a strong association between inferred subsurface oxygen and surface productivity on the community structure of foraminifera.

5.1. Food Supply and Oxygen: Maximizing Foraminiferal Population Density

Both food supply and subsurface oxygen influence the abundance of benthic foraminifera. The strong association between surface productivity and the delivery of labile organics to the subsurface [Loubere, 1991; Loubere *et al.*, 1994; Gooday *et al.*, 2000] enables us to relate major changes in surface productivity (inferred from C_{37}^{total} and BSi) to benthic food supply. The correlations between our productivity proxies and benthic foraminiferal abundance change as food supply increases (Figures 6a, b). When

the amount of labile organics reaching the subsurface is low, food supply appears to be the primary factor determining benthic foraminiferal abundance, thus, as food supply increases foraminiferal abundance increases. However, the correlation between surface productivity and foraminiferal abundance breakdown after surface productivity values exceed a certain value (23% for BSi and 12nmol/g for C_{37} total, see Figures 6a and b). Interestingly, when we track the samples that show a strong linear relationship between productivity and abundance (see black circles in Figure 6) we find that these samples tend to exhibit low $\delta^{15}N$ (Figure 6c) and high diversity (Figure 6f).

We argue that during periods of relatively high oxygenation, when the most diverse benthic assemblages are supported, food supply is the ultimate control on species abundance. When conditions approach anoxia, species assemblages shift and diversity decreases dramatically, since only select species possess low oxygen adaptations. During periods of extreme oxygen depletion, food supply is no longer the most important determinant of foraminiferal abundance. The increase in benthic foraminifera during extreme oxygen deficits may be the result of a reduction in macrobenthic predators, which have a lower tolerance for oxygen depletion than foraminifera [Douglas and Heitman, 1979; Bernhard, 1987].

5.2. Benthic Community Response to Anoxia

Subsurface oxygen (inferred from $\delta^{15}N$ and the presence/absence of laminations) appears to be the primary control on the diversity and community structure of benthic foraminifera across the Holocene (Figure 7). The increase in variance at the mid-Holocene and the large centennial scale fluctuations in $\delta^{15}N$ make the association

between subsurface oxygen and foraminiferal assemblages apparent (see Figure 7). The percentage of benthic foraminifera with flattened or elongated morphologies increase markedly when $\delta^{15}\text{N}$ rises above 7‰; as do species that possess ultracellular adaptations that enhance the exchange of oxygen [Bernhard and Sen Gupta, 1999; Bernhard *et al.*, 2000] making these particular species better equipped to survive anoxia (see yellow bar in Figure 7). The observation that only particular species of benthics have adaptations that enhance oxygen exchange may explain the associated reduction in species diversity during anoxic periods (Figure 6d). The inverse correlation between species diversity and abundance (see Figure 7) is the indirect result of the fact that only certain species can tolerate low oxygen conditions and the corresponding ecological advantages associated with low oxygen environments.

5.3. $\delta^{15}\text{N}$: a Proxy for Anoxia

The association between heavy nitrate (i.e. $\delta^{15}\text{N} > 7\text{‰}$) and the presence of annual laminations (see Figure 3) provided initial support for the use of $\delta^{15}\text{N}$ as a proxy for subsurface oxygen in Peru margin sediments. Laminations however do not provide any evidence about small modifications in subsurface oxygen; they simply are present or are not. Thus, comparing $\delta^{15}\text{N}$ values with our benthic foraminiferal assemblages, which shift progressively in response to changing subsurface oxygen provides the first independent confirmation of the use of $\delta^{15}\text{N}$ as a subsurface oxygen proxy in Peru margin sediments.

6. Conclusions

We evaluate changes in benthic foraminiferal abundance and diversity over periods of major change in surface productivity and subsurface oxygen. We find that subsurface oxygen and benthic food supply (inferred from surface production) are the dominant factors that contribute to fluctuations in foraminiferal abundance. Subsurface oxygen appears to be the dominant influence on benthic foraminiferal diversity. Paradoxically, these aerobic organisms not only survive low oxygen conditions but also appear to flourish when oxygen is the lowest, reflected in the inverse relationship between species abundance and species diversity. This unusual biological response indicates that there are ecological advantages during periods of oxygen depletion, possibly a response to a reduction in predation.

These findings suggest that benthic foraminifera are extremely sensitive to changes in oxygen and are capable of recolonizing and/or migrating on subdecadal timescales. These observations provide support for the use of benthic foraminifera species assemblages as indicators of subsurface oxygen levels in low oxygen environments.

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Figure Captions

Figure 1. Bathymetric map of the Peru Margin. The triangle indicates the position of the core PC-2. PC-2 age model. Circles indicate depths of bulk ^{14}C measurements, which were converted into calendar ages using the fairbanks0107 calibration curve. The age model was constructed using a linear curve fit (hatched line) ($r^2 = 0.98$).

Figure 2. Schematic water column profile of Peru margin oxygen minimum zone. The poorly ventilated Peru undercurrent (solid blue arrow) in combination with upwelling induced surface productivity (green arrows) leads to a persistent oxygen deficit at depth (dashed box). The low oxygen conditions inhibit bioturbation resulting in laminated sediments along parts of the Peruvian shelf (black lines).

Figure 3. (a) $\delta^{15}\text{N}$ record superimposed on a reversed X-ray image of core PC-2. Red dots indicate the location of ^{14}C AMS dates for core PC-2. Shaded bars indicate the presence or absence of laminations. Black bars mark annual laminations (pictured on upper left, panel b), grey bars represent the presence of centennial laminations (for example see panel c) and the white bars indicates the absence of laminations (see panel d for visual example). The $\delta^{15}\text{N}$ record correlates with the presence/absence of laminations; higher $\delta^{15}\text{N}$ corresponds with more annual laminations, while lower $\delta^{15}\text{N}$ is associated with an absence of laminations.

Figure 4. Paleoproductivity proxy time series. Biogenic silica is plotted in blue above $\text{C}_{37}\text{total}$ in green. Each proxy shows a major increase in variance near the mid-Holocene but high-resolution structure differs between proxies.

Figure 5. Individual foraminifera images (species *Nonionella Stella*) (a) Example of a pristine foraminifera without any signs of test dissolution from the late Holocene section of core PC-2. (b) Moderately well preserved example of *Nonionella Stella* from the early Holocene section of core PC-2. Notice the visible etching on the outer shell giving the foraminifera a dull finish. (c) Poorly preserved example of *Nonionella Stella* showing signs of dissolution.

Figure 6. Benthic foraminiferal assemblages vs Environmental Parameters. When foraminiferal abundance is low we see a clear linear correlation between C_{37} total (A), Biogenic Silica (B) and abundance. This relationship weakens as abundance increases. $\delta^{15}N$ has an exponential relationship with abundance (C) while $\delta^{15}N$ vs species diversity is linear and negative (D). Notice that the relationship between $\delta^{15}N$ and diversity is significantly better at high $\delta^{15}N$. The individual samples that exhibited a strong correlation between productivity and abundance (see black circles) have the weakest relationship between $\delta^{15}N$ and species diversity. Inferred productivity does not appear to influence species diversity (E, F).

Figure 7. Each horizontal bar indicates the presents of a species of benthic foraminifera. Yellow bars indicate species previously identified as ‘low oxygen tolerant’ and blue bars represent all other species. The total foraminiferal abundance (red) for each individual sample is plotted below the corresponding $\delta^{15}N$ (black). Notice the inverse relationship between species abundance and diversity.

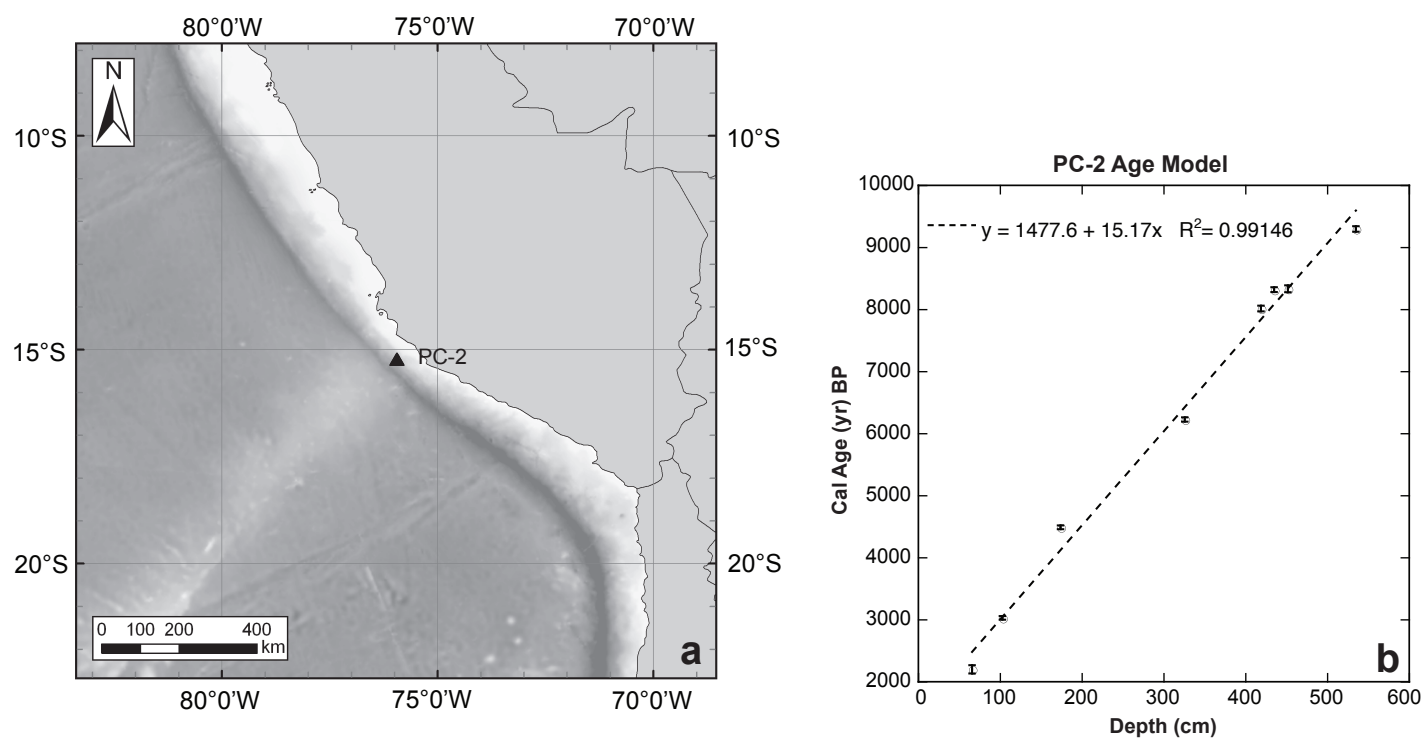


Figure 1.

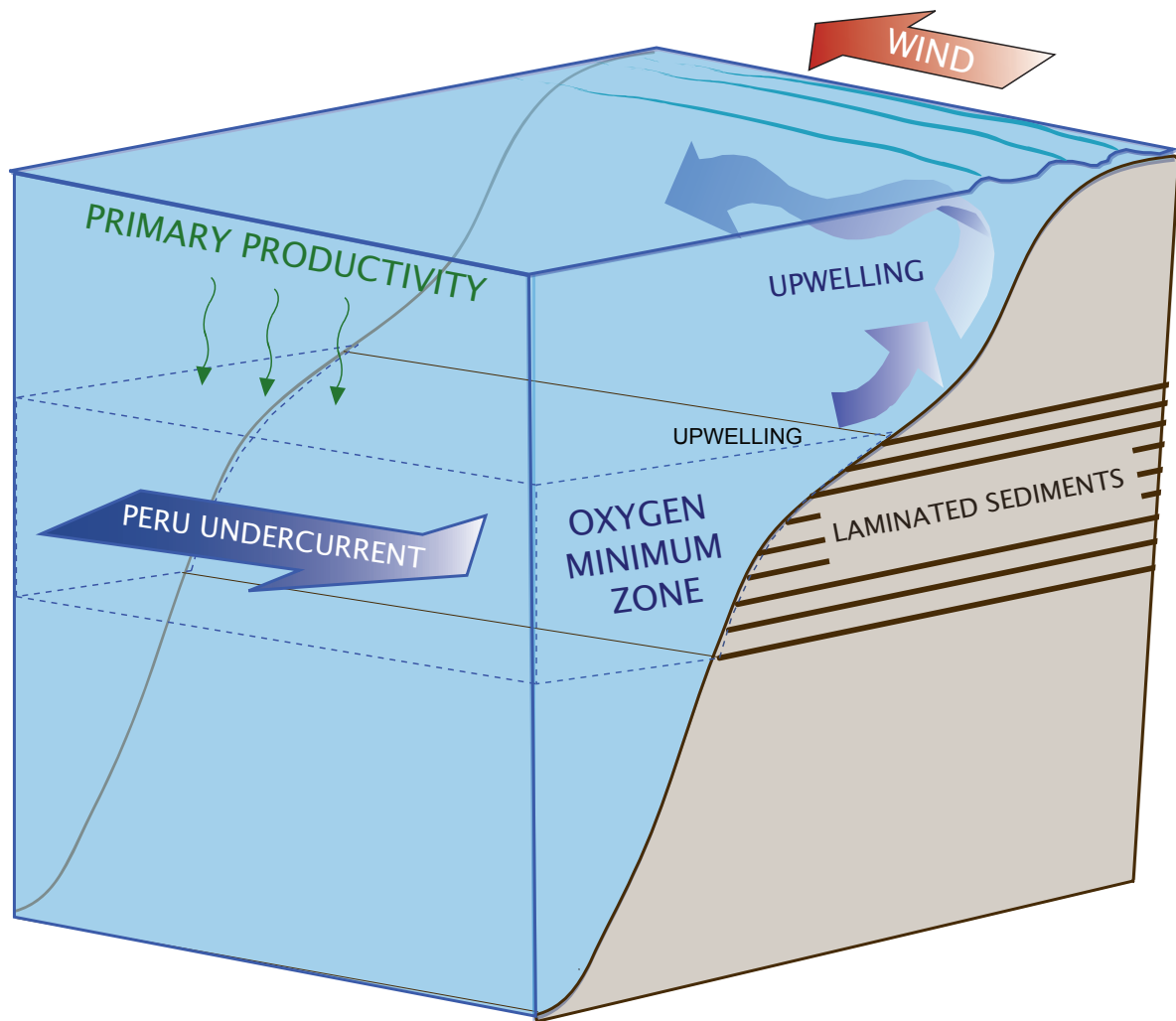


Figure 2.

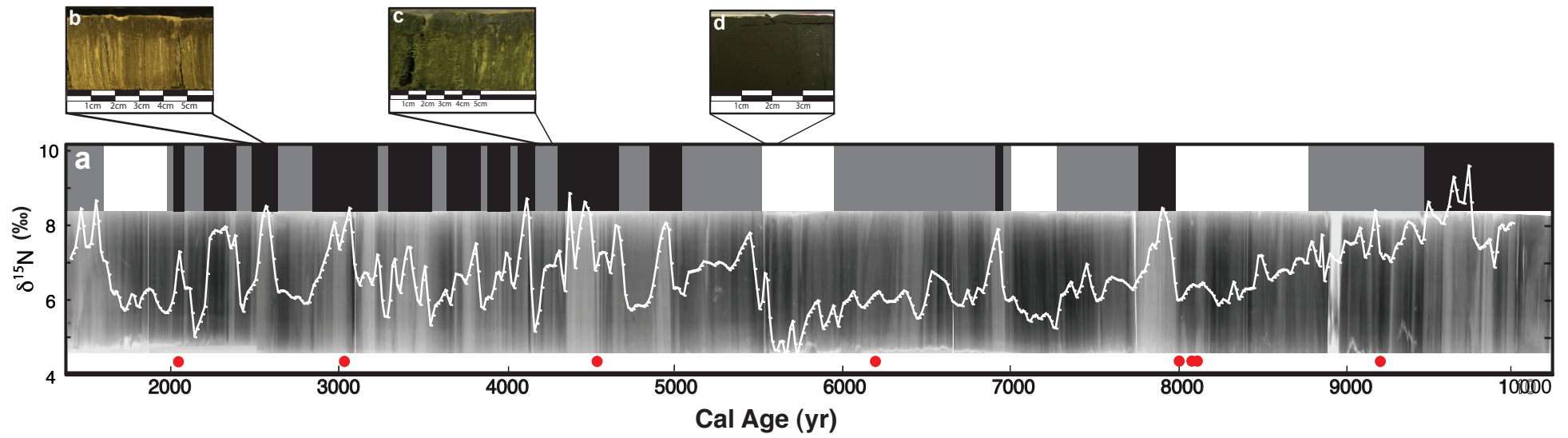


Figure 3.

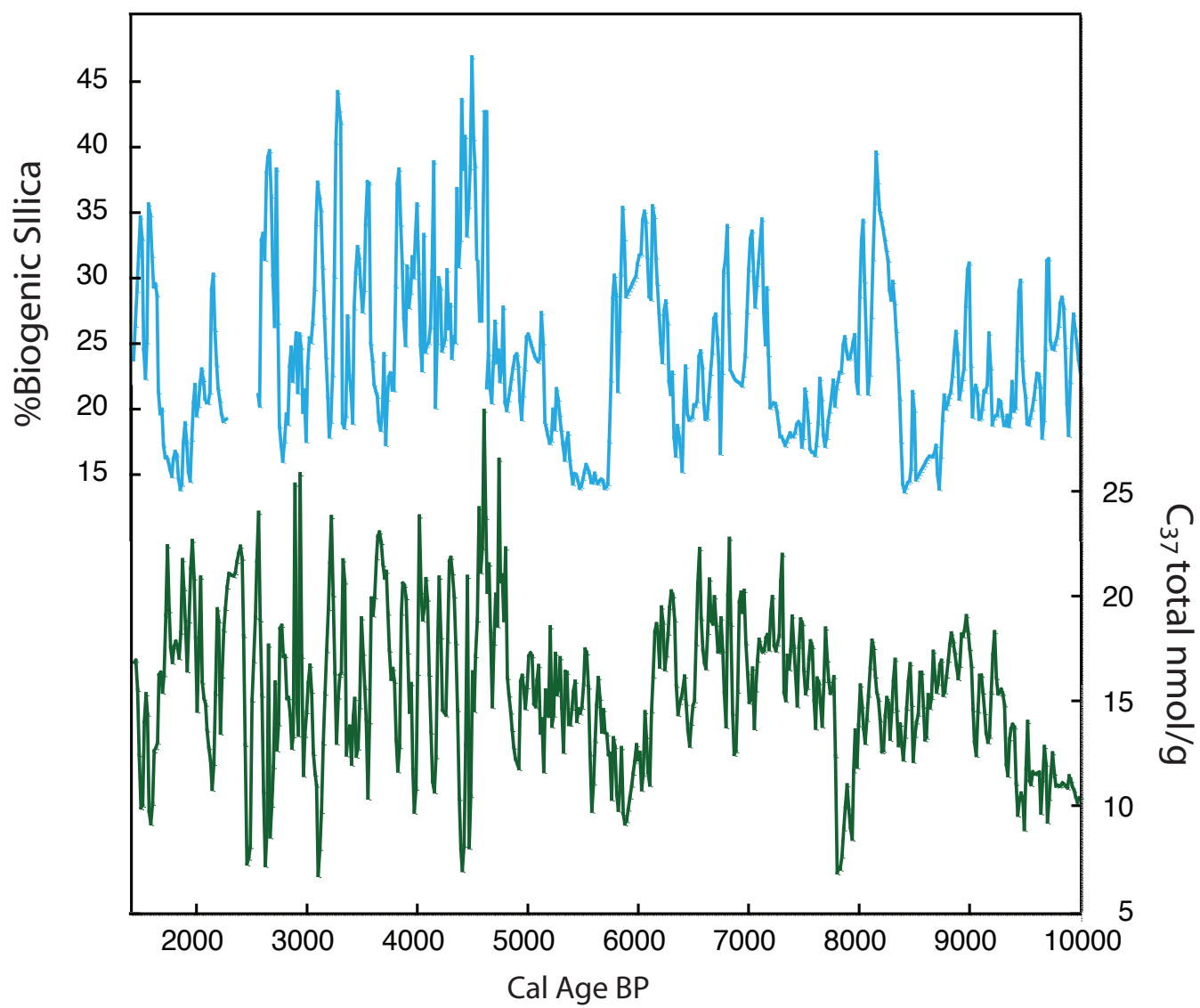
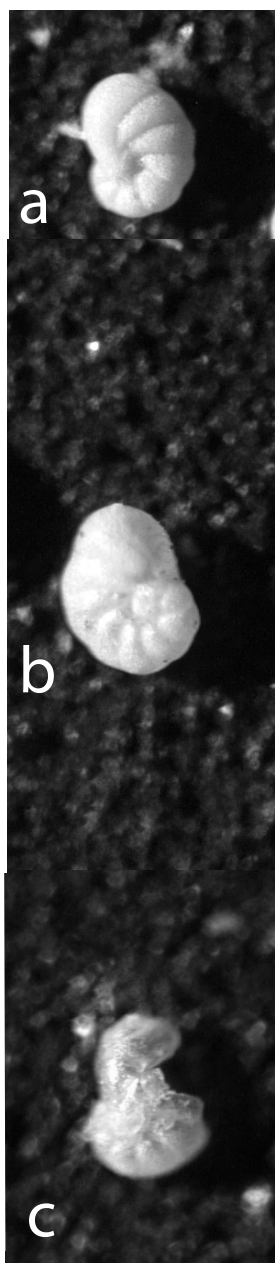


Figure 4.



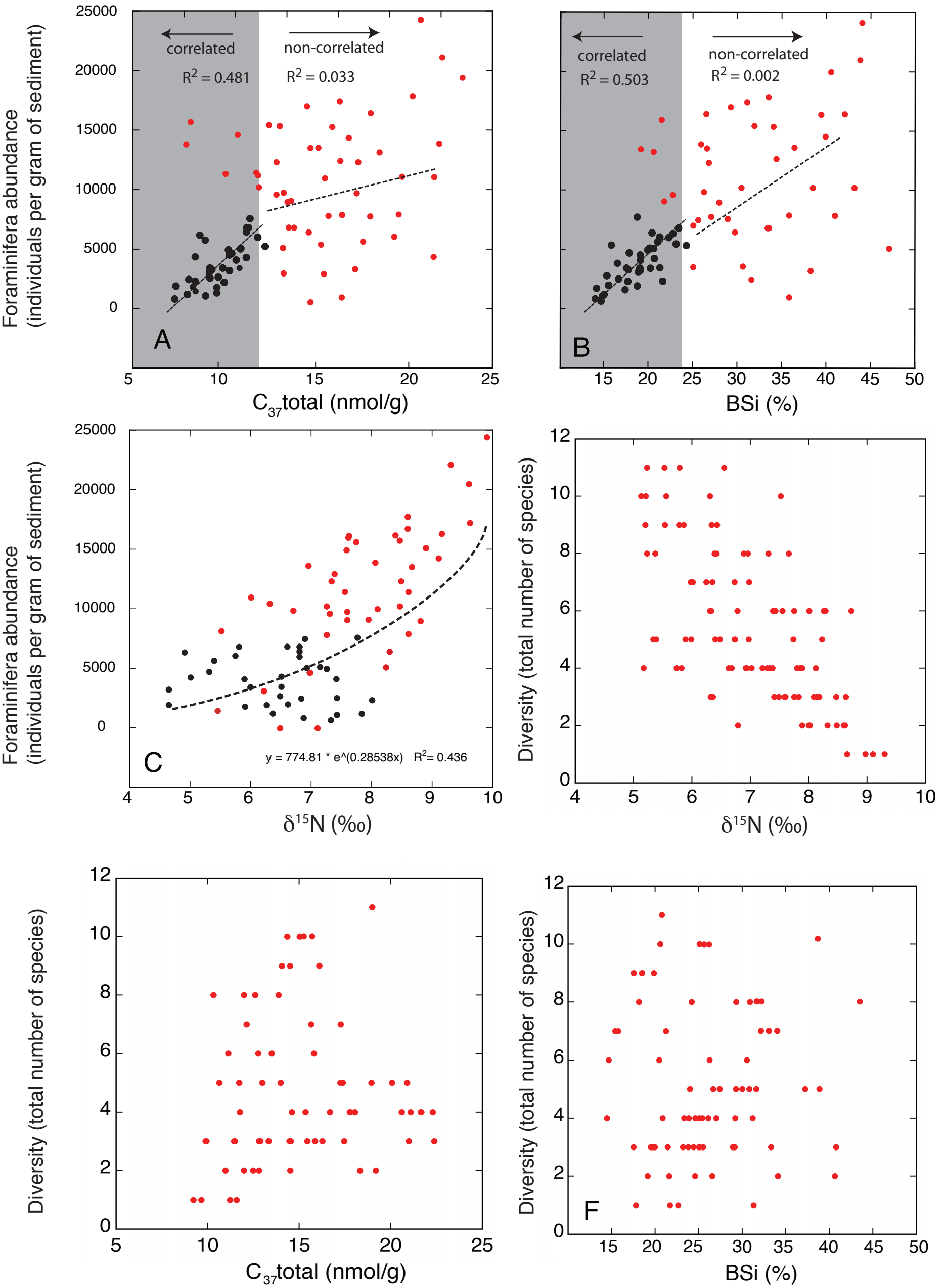
Well-preserved benthic foraminifera from the late Holocene section of PC-2

Moderately well-preserved benthic foraminifera from the early Holocene section of PC-2. Etching is visible on the outer shell.

Poorly preserved/ partially dissolved benthic foraminifera from the early Holocene section of PC-2.

Figure 5.

Figure 6. PC-2 Benthic Foraminifera vs. Environmental Parameters



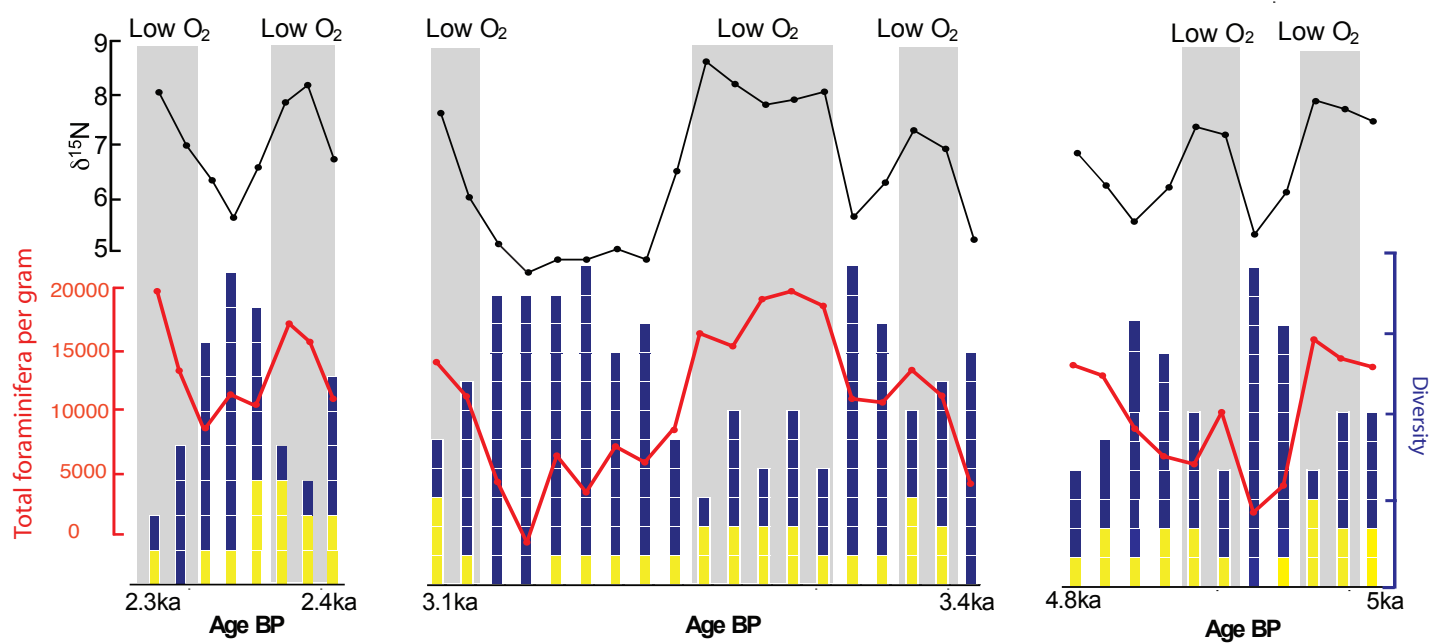


Figure 7.

CHAPTER FOUR

Temperature and productivity changes in the Eastern Tropical Pacific since the end of the last glacial maximum

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Abstract

Using a high-resolution sediment record from the boundary between the Peru margin and eastern equatorial Pacific upwelling regions we reconstruct sea surface temperature ($U_{37}^{K'}$) and surface productivity (C_{37}^{total}) since the end of the Last Glacial Maximum (LGM). The high sedimentation rates and high sampling resolution in our study allow us for the first time to compare this important region directly to reconstructions of the southward Peru margin and north eastward equatorial cold tongue. Our temperature records diverge markedly from Holocene temperature reconstructions from the central and southern Peru margin. Instead, our temperature and productivity records reveal similar trends found in lower resolution alkenone records from the equatorial cold tongue region with the exception of the late Holocene. Although other alkenone cold tongue records indicate a gradual warming in alkenone-derived temperatures we find evidence of regular millennial-scale temperature oscillations.

Sea surface temperatures (SST) fluctuate dramatically between ~15ka and 0.4ka. The coolest temperatures (~20.5°C) occur near the late glacial termination (~15ka). This period is followed by steadily increasing temperatures until ~7ka when temperatures reach values similar to modern conditions at the location of site CDH-23/GGC-14 (~23.3°C). From the early Holocene until the end of the record (0.4°C) temperatures undergo millennial-scale oscillations between (~23.5°C and 22.5°C). The temperature in the most recent section of the core is consistent with modern day temperature estimates at the location of CDH-23/GGC-14. Despite the expected anticorrelation between SST and productivity typical of upwelling regions our productivity reconstruction mirrors changes in SST throughout the length of the record.

Today the location of our study site is heavily influence by both the seasonal migration of the ITCZ and the interannual El Niño southern oscillation. However, the long-term temperature and productivity fluctuations in our record are at odds with Holocene reconstructions of the position of the intertropical convergence zone and with changes in ENSO strength. These results indicate that fluctuation in upwelling alone may not account for long term changes in productivity or temperature at the location of CDH-23/GGC-14.

1. Introduction

Influenced by both local and remote environmental properties, eastern tropical Pacific (ETP) sea surface temperatures (SSTs) and surface productivity provide a link between climates of the high and low latitudes. The cool, nutrient rich undercurrent of the eastern equatorial Pacific originates in the high southern latitudes. The environmental conditions of the southern ocean and sub Antarctic have a direct connection to the physical and biological properties of the tropical undercurrent and thus to the ETP upwelling regions [Wyrski, 1973; Toggweiler *et al.*, 1991]. Upon reaching the tropics the strength of the tropical trade winds in combination with the depth of the tropical thermocline dictate how much of these undercurrent waters reach the surface in the ETP [Enfield and Allen, 1980; Enfield and Mestas-Nuñez, 2000; Vargas *et al.*, 2007]. As a result we expect our SST and productivity reconstructions to reflect the dual influences of extra tropical and tropical climate dynamics.

The eastern tropical Pacific undercurrent represents the final stages of a ventilation process that originates in the southern high latitudes flows to the western sub Antarctic and is eventually entrained into the Equatorial Undercurrent (EUC)

[*Toggweiler et al.*, 1991]. A portion of the EUC surfaces in the eastern tropical cold tongue region- while the remainder is deflected south and joins the South Equatorial Undercurrent to form the Peru undercurrent [*Lukas*, 1986; *Wyrski*, 1966; *Kessler*, 2006]. As a result, the properties of each undercurrent are distinct. The Peru undercurrent is cool, nutrient rich and oxygen poor compared to the EUC [*Pennington et al.*, 2006]. The location of cores CDH-23 and GGC-14 are near the interface of these two undercurrents. Using reconstructions from the Peru margin and equatorial cold tongue as a guide we seek to understand which undercurrent is more influential in the location of cores CDH-23 and GGC-14.

Our cores were collected in a region of the ETP where the climate history has yet to be explored, at the boundary between the southward Peru margin and the northeastward tropical cold tongue (see Figure 1). On decadal timescales SSTs and local carbon flux in both the Peru margin and equatorial cold tongue regions are primarily influenced by tropical climate dynamics, including migrations in the position of the intertropical convergent zone (ITCZ) and the El Niño Southern Oscillation [*Barber and Smith*, 1981; *Barber and Chavez*, 1983; *Sanchez et al.*, 2000]. The ITCZ follows the region of maximum heating and therefore migrates in latitude seasonally; the ITCZ is positioned furthest north during boreal summer and furthest south during austral summer [*Chelton et al.*, 2001]. The position of the ITCZ has a strong impact on the tropical rain belt and wind fields. As a result precipitation and wind strength in the eastern tropical Pacific vary with the seasonal migration of the ITCZ [*Samelson et al.*, 2006; *Conroy et al.*, 2008]. Ekman transport off the South American continent controls upwelling at the location of CDH-23; Strong equatorward coastal winds are deflected offshore by the Coriolis effect, causing cool subsurface waters to upwell to the surface. The position of

the ITCZ is key to wind-induced upwelling since its position heavily influences the strength of the trade winds in the ETP [Grodsky and Carton, 1993]. The coolest SSTs in the ETP region occur during austral winter when the ITCZ is positioned furthest north and upwelling off of the Peru margin joins with equatorial upwelling to create a single tongue of cold water extending from the coast of central Peru out into the eastern equatorial Pacific [Toggweiler *et al.*, 1991]. On millennial timescale the average position of the ITCZ can shift by several degrees due to changes in orbital insolation [Samelson *et al.*, 2006]. Near the mid Holocene the position of the summer insolation maximum shifted from the northern to southern hemisphere [Kutzbach *et al.*, 1998; Wang *et al.*, 2006]. Using the seasonal migration of the ITCZ as an analogy we would expect long-term (i.e. millennial to orbital) changes in the position of the ITCZ to cause fluctuations in wind-induced upwelling and precipitation. This is supported by several paleoclimate reconstructions from locations sensitive to changes in summer insolation [Wang *et al.*, 2005] and ITCZ-related precipitation changes [Haug *et al.*, 2001; Conroy *et al.*, 2008].

The El Niño Southern Oscillation (ENSO) provides the primary source of interannual variability in the ETP region [Philander, 1983, Philander, 1990]. During El Niño events the trade winds weaken and the thermocline deepens leading to increases in SST and decreases in productivity throughout the ETP. The opposite trend is found during La Niña events although climate anomalies associated with La Niña events are significantly weaker than those associated with El Niño events [Enfield and Allen, 1980; Enfield and Mestas-Núñez, 2000; Vargas *et al.*, 2007]. Using today's climate as a guide we might expect long-term (millennial-orbital) changes in ENSO strength and/ or frequency to change ETP SSTs and surface productivity. Several records indicate that El Niño strength increased during the mid-Holocene possibility related to changes in

insolation and the position of the ITCZ [*Clement et al.*, 1999, 2000; *Koutavas et al.*, 2002; *Moy et al.*, 2002; *Conroy et al.*, 2008]. The ability to collapse Walker Circulation is critical to generate strong El Niño events [*Cane*, 2005]. It follows that until the ITCZ can be pulled off of the equator the strength of ETP trade winds precluded the development of strong El Niño events during the early Holocene.

Using high sedimentation rate (100 cm/kyr) marine cores we reconstruct two of the key climate parameters of ETP climate, alkenone derived sea surface temperature (U_{37}^K) and surface productivity ($C_{37total}$), since the late glacial termination (~15-0.4ka). This unique location and high resolution climate reconstruction will allow us to explore several important questions including, 1) Does the climate at the location of CDH-23 reflect changes seen in the equatorial cold tongue region or does it seem more closely tied to coastal wind dynamics seen in records from the Peru margin? 2) Can the millennial and orbital-scale temperature and productivity changes at this site be explained by modifications in the El Niño Southern Oscillation and/ or the position of the ITCZ or 3) Does the temperature pattern in this region point to extra tropical forcing mechanisms including modifications in the physical and biological properties of the southern high latitudes? We will address these questions by comparing climate reconstructions from the location of CDH-23 with previously constructed alkenone records from the central Peru margin and the equatorial cold tongue (see Figure 1 for each of the site locations consulted in this study). To better constrain the forcing mechanisms we can compare our temperature reconstructions to climate reconstructions of El Niño events and precipitation records sensitive to changes in the location of the ITCZ. If the temperature record from CDH-23 cannot be explained by these local upwelling dynamics then we need to explore extra tropical dynamics including the physical and biological properties of the source

waters to the eastern tropical Pacific- which could alter the temperature and/ or depth of the tropical thermocline independent of local wind dynamics.

1.1 Study Region

The sediment cores used in this study were collected at the boundary between the Peru margin and eastern equatorial upwelling regions (3°44' S, 81°08' W) (see Figure 1). The combination of coastal and equatorial divergence leads to a persistent tongue of cold water and high surface productivity, which extends from the western coast of South America into the central equatorial Pacific, termed the equatorial Pacific 'cold tongue' [Wyrski, 1981; Barber and Chavez, 1986; Fiedler and Talley, 2006]. Cores CDH-23 and GGC-14 are located several degrees north of the Peru upwelling region (located between 4°S-16°S along the coast of Peru) but south east of the central equatorial cold tongue (defined as the band of cool waters between 3°N to 3°S) (see Figure 1). Our site is situated just north of the Gulf of Guayaquil, which receives discharge from three major rivers: the Tumbes River of Peru, the Jubones River of Ecuador and the Zarumilla River, which marks the boarder between Peru and Ecuador all discharge into the Gulf of Guayaquil. During El Niño events the sediment transport in this region is so strong that it can move significant amounts of sediment into the ocean [Caviedes, 1975; Machii and Rodriguez, 1990; Junk and Piedade, 2010]. Thus, alterations in El Niño strength may have major consequences for the supply of sediment and micronutrients (principally Fe) in this region.

Modern SSTs fluctuate between ~19 and 24°C annually with the seasonal migration of the intertropical convergent zone (ITCZ). Although the annual average SST

at the location of core CDH-23/GGC-14 is similar is similar to that of the equatorial cold tongue region (see Figure 1) seasonality is stronger at the location of CDH-23/GGC-14 since it is situated off of the equator [*Chao et al.*, 2000; Aqua-MODIS SST climatology, 2003]. Upwelling peaks during austral winter when the ITCZ reaches its most northerly position coinciding the minimum SSTs. Peak chlorophyll concentrations are offset from maximum upwelling and peak in austral summer and fall [*Calienes et al.*, 1985; *Chavez*, 1995; *Pennington et al.*, 2006]. This offset may be linked to limited Fe availability during peak upwelling but its exact origin is uncertain [*Blackburn et al.*, 1970; *Thomas*, 1979]. Primary productivity at the location of core CDH-23 is higher on average than the cold tongue but slightly lower than total production off the central and southern Peru margin [*Behrenfeld and Falkowski*, 1977; *Chavez*, 1995]. Large radially symmetric diatoms comprise the majority of the phytoplankton biomass from the southern Peru margin up to the location of CDH-23 [*Chavez and Barber*, 1987; *Rojas de Mendiola*, 1981]. Diatom blooms have a significant impact on the seasonality of primary production since they appear to have a stronger seasonal signal than other phytoplankton [*Chavez and Barber*, 1987].

Despite the high surface productivity of the eastern tropical Pacific region, the ETP is classified as a high nitrate low chlorophyll (HNLC) region. Several factors may contribute to the eastern tropical Pacific's classification as a HNLC region including, light limitation when the mixed layer expands, over grazing or limited micro nutrients, primarily dissolved Fe [*Chavez et al.*, 1991; *Landry et al.*, 2007]. Incubation studies from the Peru Current and equatorial cold tongue regions indicate that the eastern tropical Pacific phytoplankton community is heavily Fe limited [*Hutchins et al.*, 2002]. In the cold tongue dissolved Fe is primarily supplied through aeolian transport. Along the broad

continental shelf of the northern and central Peru margin micronutrients are supplied through contact with the organic rich shelf sediments [*Strickland et al.*, 1969; *Bruland et al.*, 2004]. The extent of Fe limitation at the location of site CDH-23 is uncertain, but its proximity to several large river systems suggests that a significant proportion of dissolved micronutrients are likely supplied through river input.

Although the surface conditions of the Peru margin and cold tongue regions are coupled to seasonal and interannual changes in upwelling, the subsurface conditions of these two regions are very different. The cool waters and high macro-nutrients that fertilize the eastern equatorial cold tongue and the Peru current originate from an extension of the eastward flowing Equatorial Undercurrent (EUC) [*Gruber and Sarmiento*, 1997; *Kessler*, 2006]. The EUC is vertically partitioned between the cooler, oxygen depleted lower layer and the well oxygenated upper layer [*McCartney*, 1982; *Toggweiler et al.*, 1991; *Goodman et al.*, 2005]. After traveling east along the equator, a portion of the EUC surfaces near the Galapagos. The deeper portion of the EUC is deflected south where it merges with the South Equatorial Undercurrent (SEU) to form the Peru Undercurrent [*Lukas*, 1986; *Wyrski*, 1966; *Toggweiler et al.*, 1991; *Kessler*, 2006]. Because core CDH-23 and GGC-14 are situated between the influence of the EUC and the Peru undercurrent, our sediment cores provide novel information about the climate history of this particular region. The physical and biological properties of the undercurrent in combination with local upwelling dynamics controls both the temperature and nutrient properties of the waters upwelling in the eastern equatorial pacific. Therefore, if the undercurrent at the location of CDH-23 was more closely tied to the equatorial undercurrent rather than the Peru undercurrent we would expect temperature

and productivity records from CDH-23 to track more closely to records from the cold tongue than records from the Peru margin.

1.2 Background

The evolution of eastern tropical Pacific SSTs and the driving mechanisms of those climate changes during the late Quaternary are a subject of significant debate. The similarities between cold tongue SST records, derived from Mg/Ca of planktonic foraminifera and oxygen isotope records from Antarctic ice cores led researchers to speculate about possible mechanistic links between these two regions [Lea, 2004; Lea *et al.*, 2006; Pena *et al.*, 2008]. One possible connection may be global changes in CO₂, which would result in synchronous changes in global temperature. Another possible link, and one that would be relevant during periods when CO₂ is relatively stable is a direct ocean pathway. The waters that eventually provide the source of the Equatorial Undercurrent are thought to originate as subantarctic mode waters before being subducted into the lower layers of the EUC and transferred across the Pacific basin to the ETP where they eventually surface during upwelling [Wyrki, 1973; Toggweiler *et al.*, 1991]. Thus, this oceanic pathway ('tunnel') provides a direct connection by which high latitude climates can translate to the tropics on relatively short timescales.

Recently the importance of the ocean tunnel and its impact on tropical Pacific temperatures has been called into question. Koutavas and Sachs [2008] assembled a composite alkenone record based on several cores collected throughout the equatorial cold tongue (ECT). Unlike Mg/Ca records, the ECT alkenone index shows a deglacial rise in-phase with Northern Hemisphere ice records, nearly 5kyrs later than changes in

Southern Hemisphere ice records dictate [*Grootes and Stuiver, 1997; Blunier and Brook, 2001; Koutavas and Sachs, 2008*]. Although the precise connection between the North Atlantic and the eastern tropical Pacific remains unclear, Koutavas and Sachs [2008] speculate that this connection is attached to the El Niño Southern Oscillation and its teleconnections.

The connection between eastern tropical Pacific wind strength and the position of the ITCZ is key to understanding modern changes in ETP upwelling. Migrations in the position of the ITCZ are strongly coupled to changes in ETP wind strength and upwelling; northward displacement of the ITCZ leads to enhanced wind strength and southward displacement leads to reduced wind strength. Thus, long-term changes in the position of the ITCZ are closely associated with the mean state of the El Niño Southern Oscillation (ENSO) and its two modes: La Niña (enhanced wind strength) and El Niño (reduced wind strength) [*Barber and Chavez, 1986; Philander, 1990*].

2. Material and Methods

Sediment cores CDH-23 and GGC-14 were collected in April of 2009 during a coring cruise on the R/V Knorr. This was one of the first cruises to make use of Woods Holes' newly developed long-coring device, which allowed us to obtain piston cores of 17.5 and 26 m in length. This region was selected for coring due to its sensitivity to high frequency climate variability including anomalies associated with ENSO. The particular core site was chosen based on the thick sediment sequences visible from shipboard sonar surveys. When coring, the upper section of sediment is often lost due to the high penetration velocity needed to retrieve a core. As a result, we collected three separate types of cores, a long core (CDH-23) a gravity core (GGC-14) and multi-cores (MC-16).

Splicing together each of these cores will give us a complete sequence from 15ka to modern. The records presented here include 2 cores (GGC-14, ~2m length and CDH-23, ~17m length) from the eastern tropical Pacific (3°44' S, 81°18' W). All of the data presented in this manuscript (Chapter 4) are exclusively from the gravity core (GGC-14), long core (CDH-23) and one core top sample from a multi core (MC-16E).

Age controls for cores CDH-23 and GGC-14 are based on multiple AMS ^{14}C age estimations obtained from planktonic foraminifera (*N. dutertrei*). ^{14}C age estimations were calculated at the National Ocean Sciences Accelerator Mass Spectrometry Facility at the Woods Hole Oceanographic Institute. ^{14}C ages were converted into calendar ages using the IntCal4 calibration program [Reimer *et al.*, 2004] with a reservoir correction of 450 years [Bard *et al.*, 1993]. All ^{14}C age estimations and their corresponding errors are listed in Table 1. The age model for CDH-23 was constructed using 22 individual age estimations (see Figure 2a). Although CDH-23 has a nearly constant sedimentation rate between 15ka-2ka, a polynomial age model produced the best curve fit with an R^2 of 0.993. The number of individual age estimations in addition to the high R^2 value makes us very confident in the accuracy of the CDH-23 age model (see Figure 2a). The age model for GGC-14 is based on 3 ^{14}C age estimations and extends from 3ka to 0.4ka (see Figure 2b). The agreement in temperatures between GGC-14 and CDH-23 when each record is plotted on their respective age models (the overlapping section is between ~3-2ka) gives us confidence in the GGC-14 age model in addition to the age model used for CDH-23 (see Figures 3a,b).

Our paleotemperature records were obtained using the alkenone unsaturation ratio ($\text{U}^{\text{K}'}_{37}$ index) [Prah *et al.*, 1988; Müller *et al.*, 1998]. We also use the concentration of alkenones ($\text{C}_{37\text{total}}$) as an indicator of haptophyte productivity. The $\text{U}^{\text{K}'}_{37}$ index is a

robust and widely used tool for SST reconstructions. Compared to other phytoplankton lipids, alkenones are highly refractory [Brassell *et al.*, 1993; Budziak *et al.*, 2000] and thus are generally well preserved in ocean sediments. While degradation of alkenones has been observed in a variety of oceanographic settings [Prah *et al.*, 1998] particularly in regions with low sedimentation rates [Sun and Wakeham, 1994; Rontani *et al.*, 2006] their use has proven remarkably successful in paleoceanographic studies [see proxy reviews in Herbert *et al.*, 1998; Conte *et al.*, 2006 and Mix, 2006]. Initial $U_{37}^{K'}$ temperature measurements obtained from our companion multi-core (MC-16E) indicate that core top samples from this region correspond closely with mean annual SSTs (see red arrow in Figure 3b).

The use of C_{37}^{total} as a proxy for surface productivity is a qualitative approach to estimate haptophyte production, which is closely linked to total phytoplankton productivity [Brassell, 1993; Budziak *et al.*, 2000]. Recent work from the eastern equatorial Pacific and Atlantic upwelling regions demonstrates that on orbital cycles alkenone accumulation rates are closely tied to alkenone-synthesizing haptophyte concentrations and to other indices of phytoplankton productivity including the thermocline depth proxy based on the abundance of *F. profunda* [Bolton *et al.*, 2010].

Cores were sampled for alkenone analysis every 4cm, which according to the age models (see Figure 2) is approximately every 40 years. Each individual sample [of 0.5 cm thickness] integrates ~5 years of time. Alkenone analysis was conducted following the procedure modified from Herbert *et al.* [1998]. Wet samples were freeze-dried and homogenized. Approximately 0.8-0.9g of dry sediment was extracted using a Dionex 200 accelerated solvent extractor in 100% Dichloromethane within 2 weeks of freeze-drying. Sample extracts were evaporated under nitrogen gas and reconstituted in 200 μ L of

toluene containing a C_{37} and C_{36} alkane standard. Samples were analyzed by gas chromatography, using a 60m Agilent DB1 column. Lab analytical error, $\pm 0.2^{\circ}\text{C}$, is calculated based on a laboratory sediment standard, which is extracted and measured every few months. An additional analytical error is reported, $\pm 0.1^{\circ}\text{C}$ based on sample duplicates from this particular study ($\sim 10\%$ of samples were duplicated). Alkenone concentrations (C_{37} di- and triunsaturated ketone mass/grams of dry sediment = " $C_{37}\text{total}$ ") were calculated by normalizing to the internal standard (C_{37} and C_{36} n-alkanes). The relative error for $C_{37}\text{total}$ of $\pm 10\%$ is calculated based on 15% sample replication.

3. Results

3.1 Temperature Records

$U_{37}^{\text{K'}}$ temperature estimates are plotted in Figure 3b for the gravity core (dashed line) and long core (solid line). Core top measurements from the companion multi core (23.06°C), match closely with modern mean annual sea surface temperatures (23.12°C , see Figure 3b) [USGS SST program (Tcl/Tk version 1.3)]. Previous work from the ETP has indicated a possible bias in $U_{37}^{\text{K'}}$ towards warmer temperatures [Conte *et al.*, 2006; Leduc *et al.*, 2008; Koutavas and Sachs, 2008] possibly related to an ecological seasonal preference [Tyrrell and Merico, 2004]. However, results from this study (see Figure 3b) and those from a recent EEP core top reconstruction [Chazen *et al.*, 2010 (dissertation chapter 3)] indicate that alkenone sea surface temperatures closely match mean annual temperatures in the eastern tropical Pacific.

Down-core temperature records show significant ($\sim 0.5\text{--}1^{\circ}\text{C}$) oscillations in temperature on the order of several hundred years, which persist back to $\sim 8.5\text{ka}$ (see Figure 3b). Maximum temperatures occur between $\sim 6\text{--}8.5\text{ka}$, which corresponds to the

Holocene thermal maximum. The Holocene thermal maximum refers to a period of enhanced global temperatures near the beginning of the Holocene ~9-6ka. Heating is most exaggerated in the Northern Hemisphere as it corresponds to the NH perihelion and maximum axial tilt [Masson-Delmotte *et al.*, 2009] but evidence suggests that it is a global event accompanied by latitudinal displacement of vegetation zones [Ritchie *et al.*, 1983] a strengthening of monsoons [Gasse and Van Campo, 1994] and perhaps changes in precipitation related to the northerly migration of the ITCZ [Haug *et al.*, 2001].

Near 8.5ka, temperatures begin a sharp ~3°C decline until ~15ka (see Figure 3b) which is interrupted by several short-lived, high-amplitude increases in temperature. The highest variance occurs between 10-13ka during the period of decreasing temperatures.

3.2 Surface Productivity

C₃₇total values oscillate regularly over 100-500 year intervals across the Holocene (see Figure 3c). This pattern is interrupted by two prominent highs at ~4ka and 7ka which last for ~100 years. Near 8.5ka C₃₇total values gradual decrease until ~15ka. The C₃₇total record exhibits substantially more variance [(standard deviation)²] than SSTs but the records are otherwise remarkably similar in long-term trends (see Figure 3b, c). Figure 4. depicts the correspondence between these two proxies. The positive correlation between these proxies is contrary to what we would expect in a typical upwelling regime, where upwelling brings cool, nutrient rich waters to the surface and thus stimulates surface productivity [Calienes *et al.*, 1985; Chavez, 1995].

3.3 Comparison with records from the Peru margin

Figure 5 shows temperature records from CDH-23 and GGC-14 plotted with 3 alkenone derived temperature records from the Peru margin (11-15°S). Peru margin

temperature records exhibit a major increase in variance near the mid-Holocene, whereas the late Holocene is characterized by dramatic centennial scale fluctuations in temperature that are absent from the early Holocene section of the record [Chazen *et al.*, 2009]. There is also no change in mean annual sea surface temperatures between the early and late Holocene at the Peru margin. In contrast, CDH-23 exhibits significantly less high frequency variability but more millennial scale variability, and a major cooling event during the early Holocene. During the early Holocene, temperatures off Peru appear to be warmer than those in the EEP, which is difficult to envision with modern upwelling dynamics, where Peru upwelling feeds into the northward tropical Pacific cold tongue (see Figure 1 and 5). The differences between CDH-23 temperature records and those from the Peru margin suggest that the central and southern Peru margin may have been decoupled from the larger eastern tropical Pacific wind dynamics during the early Holocene. This is supported by modeling work from Liu and colleagues who demonstrate that a tongue of warm sea surface temperatures develops along the Peruvian coast during early Holocene simulations- possibly related to alterations in boreal summer wind structure [Liu, 1994; Liu *et al.*, 2000, 2003]. Liu *et al.* [2003] find that the SST field of the Peru margin is significantly more susceptible to local coastal wind dynamics than the greater eastern tropical Pacific.

3.4 Comparison with other records from the cold tongue region

The CDH-23 temperature record shows many similarities with other lower resolution alkenone records from the equatorial cold tongue (ECT) region, including the Koutavas and Sachs [2008] ECT temperature index which is itself a composite of 5 ECT alkenone records (see Figure 6). Generally, the trends between the CDH-23/GGC-14

temperature record and ECT alkenone derived temperature records are very similar but there are several intriguing differences. From ~15ka to 10ka CDH-23 temperature estimates display an increasing trend that is consistent in amplitude with the post glacial warming shown in several other alkenone reconstructions [*Kienast et al.*, 2006; *Pahnke et al.*, 2007; *Koutavas and Sachs*, 2008] (see Figure 6). However, we cannot determine the timing of the onset of warming at CDH-23 since the core only extends to 15ka. It is also important to note that both the age controls and sampling resolutions vary greatly between ECT cores. The temperature records from CDH-23 and GGC-14 were sampled at more than triple the sampling resolution of the other ECT records referenced in this study (see individual sample markers on Figure 6). Additionally, the CDH-23 temperature record has much better age constraints than other cold tongue records. The ME0005A-24JC core only contains 4 ^{14}C age estimations [see *Kienast et al.*, 2006, Figure 6c] compared to the 22 age estimations used to make the CDH-23 age model (see Figure 2a). The age controls for the Koutavas and Sachs [2008] ECT stack range from ^{14}C age estimations to $\delta^{18}\text{O}$. Koutavas and Sachs [2008] estimate the error to be ± 500 years on their composite record and slightly higher for core V19-30 (see Figure 6b,d).

During the mid-late Holocene several of the ECT temperature records exhibit a warming trend, this is most clearly visible in the alkenone derived temperature record from *Kienast et al.* [2006], where a gradual warming trend beginning near the mid-Holocene persists towards the present (see Figure 6c). Temperature reconstructions from CDH-23 and GGC-14 also show a modest (although muted) warming trend during the late Holocene but superimposed on this trend are prominent centennial to millennial-scale temperature oscillations, which are absent from other ECT alkenone derived temperature records (see Figure 6). On the whole, the reproducibility of the ECT alkenone records

(see Figure 6) and the close association between core top temperatures and mean annual SSTs at CDH-23 (see Figure 3b) gives us confidence that our temperature records accurately reflect mean annual sea surface temperatures.

4. Discussion

Here we explore several potential forcing mechanisms to explain the long-term pattern in CDH-23 surface temperatures including, migrations in the position of the ITCZ, changes in the strength of the El Niño Southern Oscillation and modifications in the physical properties of the Equatorial Undercurrent. It is important to note that none of these forcing mechanisms fully account for the positive correlation between sea surface temperature and surface productivity the significance of which is discussed in section 4.4.

4.1 Connecting SST with fluctuation in the position of the ITCZ

Implicit to the connection between eastern tropical Pacific SST and the position of the ITCZ is wind-induced upwelling; a northward migration of the ITCZ is thought to correspond to ETP cooling because of the associated enhancement in wind strength and upwelling. Thus, if the cooling during the early Holocene was forced by modifications in the position of the ITCZ we would expect to see a correlation between CDH-23 SSTs and changes in seasonal insolation. While, the ITCZ migrates between the northern and southern hemispheres seasonally, its average position is north of the equator due to the higher landmass area in the northern hemisphere. As a result, the long-term (i.e. orbital) migration of the ITCZ should be more sensitive to northern hemisphere warming than temperature changes in the southern hemisphere [Chelton *et al.*, 2001; Samelson *et al.*, 2006]. Northern hemisphere warming should result in a northward displacement of the

ITCZ leading to enhanced wind strength and reduced SSTs in the eastern tropical Pacific [Conroy *et al.*, 2008]. Orbital parameters indicate that the summer insolation maximum was situated in the northern hemisphere near 11ka and gradually shifted to the southern hemisphere near the mid-Holocene [Kutzbach *et al.*, 1998]. Several paleoclimate reconstructions support the theory that the position of the ITCZ followed the summer insolation maximum during the late Quaternary [Haug *et al.*, 2001; Wang *et al.*, 2006]. It then follows that wind-induced upwelling in the ETP should have been enhanced during the early Holocene and gradually reduced during the mid-late Holocene- if the relationship between the position of the ITCZ and wind-induced upwelling holds. This prediction is consistent with the general structure of orbital-scale temperature changes in CDH-23; the late termination and early Holocene are cooler than the mid-late Holocene. The timing however, is somewhat off- if the position of the ITCZ (forced through changes in seasonal insolation) was the ultimate control on long term (i.e. orbital) temperature changes in CDH-23 we would expect to see cool temperatures during the early Holocene with a gradual increases in SSTs near 6ka when orbital insolation shifted from the northern to southern hemispheres, instead maximum Holocene temperatures occur between 6.75ka and 7.5ka (see Figure 3) and gradually decrease towards 6ka. This indicates that either the position of the ITCZ was not the ultimate determinant on upwelling strength at the location of CDH-23, or that surface temperatures in CDH-23 are not controlled by wind induced upwelling alone on orbital timescale.

The position of the ITCZ also varies on millennial timescale. To understand these changes we can compare our temperature record from CDH-23 to the Haug *et al.* [2001] reconstruction of %Ti in the Cariaco Basin (see Figure 3). Using the relationship between the position of the ITCZ and precipitation over the Cariaco Basin, Haug *et al.* [2001]

demonstrate that %Ti can be used to reconstruct precipitation over the Cariaco Basin and thus, the relative position of the ITCZ. Haug et al. [2001] interpret increases in %Ti as periods when the ITCZ was situated near the Cariaco Basin, while reductions in %Ti reflect a southward displacement in the position of the ITCZ (see Figure 3). The northward displacement of the ITCZ between ~15-14ka (according to Haug et al., 2001) corresponds to a cooling in CDH-23 (see Figure 3). The timing of this cooling is similar in timing to the Antarctic Cold Reversal (ACR) (see Figure 3) when records from the Antarctic region indicate a growth in ice accompanied by a regression in sea level and a ~3°C cooling [Blunier et al., 1997; Blunier and Brook, 2001]. The ACR is associated with cooling in the Southern Hemisphere and warming in the Northern Hemisphere [Blunier and Brook, 2001]- both of which should lead to cooler SSTs at the location of CDH-23; a warming in the North should have accompanied a northward migration of the ITCZ and a cooling in ETP SSTs (due to enhanced wind-induced upwelling) while a cooling in the Southern Hemisphere could cool ETP SSTs through its connection (via the ocean tunnel) with the tropical undercurrent. This cooling is followed by a sharp increase in sea surface temperature consistent in timing with the younger Dryas (although opposite in temperature sign) (~13.75-11.5ka) when the ITCZ was displaced to the south (see Figure 3). The late Holocene (~1.5-0.5) SST warming is also consistent with a southward migration of the ITCZ according to Haug et al. 2001 (see Figure 3). Each of these temperature changes is consistent with modifications in wind strength predicted to accompany shifts in the position of the ITCZ. However, during the Holocene thermal maximum (~10-6ka), the warm CDH-23 SSTs are at odds with the northward migration of the ITCZ (Figure 3) predicted by both precipitation records from the Cariaco Basin [Haug et al., 2001] and modifications in seasonal insolation reconstructed from Dongge

Cave stalagmite records [Wang *et al.*, 2006]. A northward migration of the ITCZ should have accompanied cooler rather than warmer SSTs in the ETP if upwelling was the ultimate control of CDH-23 SSTs.

Despite the strong correlation today between the seasonal migration of the ITCZ and ETP SSTs- orbital and millennial scale changes in the position of the ITCZ do not appear to explain the temperature changes found in CDH-23. This is consistent with climate reconstructions from the tropical Atlantic where the expected northward migrations of the ITCZ during the Bølling Allerød and following the Younger Dryas [Peterson *et al.*, 2000; Haug *et al.*, 2001] failed to produce enhanced upwelling. Koutavas and Sachs [2008] point out that differences in the behavior of the ITCZ in the Atlantic and Pacific Ocean basins complicate our ability to directly correlated reconstructions in the position of the ITCZ with tropical sea surface temperatures. These apparent inconsistencies between long-term changes in the position of the ITCZ and tropical Pacific temperature records hint at the importance of considering other forcing mechanisms including the El Niño Southern Oscillation and the temperature of the tropical thermocline.

4.2 Sea surface temperatures and the El Niño Southern Oscillation

The connection between tropical Pacific wind strength and SST is fundamental to the underlying tendency to generate El Niño events and to maintain Pacific Walker Circulation [Bjerknes, 1969]. The strong eastern Pacific trade winds help to maintain the perched thermocline between the eastern and western tropical Pacific and the strong convection cell termed, Walker circulation. A breakdown in any part of this system, surface pressure or ocean temperatures and lead to the collapse of walker circulation and

the development of an El Niño event [*Bjerknes*, 1969; *Philander*, 1990; *Cane*, 1995]. As a result the strength of the tropical trade winds and the associated position of the ITCZ is related to the strength of the ENSO but not the only control on ENSO strength. Several paleoclimate reconstructions indicate that El Niño strength was reduced during the early Holocene and gradually increased toward the present [*Moy et al.*, 2002; *Koutavas et al.*, 2002; *Conroy et al.*, 2008]. Cane and colleagues argue that the northward displacement of the ITCZ during the early Holocene prevented the development of strong ENSO event during the early Holocene [*Clement et al.*, 1999, 2000; *Cane*, 1995]. Until the ITCZ can be pulled of the equator the strength of eastern tropical Pacific trade winds precludes the development of strong El Niño events during the early Holocene [*Cane*, 2005].

The location of CDH-23 is sensitive to temperature anomalies associated with El Niño and La Niña events today. During El Niño (La Niña) event the eastern tropical thermocline deepens (shoals). While upwelling may still persist this change in thermocline depth leads to increase in SST during El Niño events and slight decreases in SST during La Niña events [*Barber and Chavez*, 1986; *Philander*, 1990]. Although our climate reconstruction does not capture individual ENSO events we can make some predictions about the changes in temperature and variability we might expect if the frequency and/or strength of ENSO events changed during the course of our record based on modern observations. While ENSO has both a cold (La Niña) and warm (El Niño) end-member the temperature anomalies associated with each end-member are not equal; anomalies associated with the warm end-member are significantly larger than those associated with the cold end-member [*Barber and Chavez*, 1986; *Hoerling et al.*, 1997]. Therefore, we expect to see increases in temperature on multi-decadal and millennial time scales if the frequency and/or strength of ENSO increased during the Holocene.

Additionally, we would expect the variance [i.e. (standard deviation)²] in SST to increase with increasing ENSO strength since ENSO is the primary control on interannual variability in this region. The precise timing of the mid Holocene strengthening of El Niño varies between ~6ka and 3ka but generally points towards the late mid-late Holocene [Moy *et al.*, 2002; Koutavas *et al.*, 2002; Conroy *et al.*, 2008; Chazen *et al.*, 2009]. While CDH-23 temperature increase over the course of the Holocene (see Figure 2) the timing of this temperature change is not consistent with reconstructions, which indicate increased ENSO strength during the Holocene. Additionally, our record does not show increased variance as temperatures increase. In fact, the highest variance occurs between 12.5ka and 11ka long before paleoclimate reconstructions indicate an increase in ENSO strength. Neither changes in the position of the ITCZ or modification in El Niño appear to explain the SST changes recorded in CDH-23. Another possibility is that the temperature of the tropical undercurrent changed during the course of the Holocene. Changes in the physical character of the undercurrent could potentially modify SST independent of local upwelling strength.

4.3 The tropical undercurrent and CDH-23 Sea Surface Temperatures

The cool waters and high macro-nutrients that fertilize the eastern equatorial cold tongue and the Peru undercurrent originate from an extension of the eastward flowing Equatorial Undercurrent (EUC) [Gruber and Sarmiento, 1997; Kessler, 2006]. The EUC is vertically partitioned between the cooler, oxygen depleted lower layer and the comparatively well oxygenated upper layer [McCartney, 1982; Toggweiler *et al.*, 1991; Goodman *et al.*, 2005]. If the proportion of these two end members were to vary by volume or if the physical and biological properties of the source waters to the EUC

changed, the temperature and/ or nutrient concentration of the undercurrent may have been modified [Lukas, 1986; Liu *et al.*, 1999]. Modifications in the temperature of the undercurrent may alter the depth of the thermocline and the temperature of the waters upwelled in the eastern tropical Pacific [Toggweiler *et al.*, 1991; Liu *et al.*, 1999] both of which could affect SSTs at the location of CDH-23. Using a global coupled model Liu [2001] found that changes in orbital parameters during the Holocene might have altered the temperature of the waters subducted into the EUC and eventually upwelled in the eastern tropical Pacific. This model suggests that changes in the temperature of the southern high latitudes and the subantarctic mode waters can translate to changes in the temperatures of waters upwelling off of Peru. Unfortunately, the dearth of high resolution temperature records from the southern ocean and western Pacific limit our ability to compare temperatures directly in these two regions but we emphasize the importance of the ocean pathway as a potential contributor to surface temperatures in the eastern tropical Pacific.

4.4 Holocene changes in inferred surface productivity and surface temperature

A particularly surprising result in our study is the positive correlation between temperature and $C_{37}total$ in cores CDH-23 and GGC-14 (see Figures 3b,c and 4). A similar pattern is found in other records from the ETP where low early Holocene SSTs correspond to low $C_{37}total$ values, which gradually increased towards the late Holocene [Koutavas and Sachs, 2008]. The positive correlation between productivity and surface production is inconsistent with modification in upwelling related to changes in the position of the ITCZ or changes in the depth of the thermocline. If wind-induced upwelling was responsible for the pattern we find in CDH-23 SSTs and productivity we would expect these proxies to be anti-correlated. Similarly, if the temperature changes in

CDH-23 were forced by modifications in the physical or biological character of the EUC we would also expect temperature and productivity to be anti correlated; the ECU contains a cooler, nutrient rich layer and a warmer nutrient poor end member [McCartney, 1982; Toggweiler *et al.*, 1991; Goodman *et al.*, 2005]. To account for this correlation using changes in the undercurrent there would have had to be a consistent supply of both warm and nutrient rich water either through the southern ocean or sub Antarctic mode waters. However, this is inconsistent with our understanding of these two currents [Lukas, 1986; McCartney, 1982; Toggweiler *et al.*, 1991; Goodman *et al.*, 2005]. For all of these reasons it is difficult to fully account for the positive relationship between productivity and temperature. We have to consider the possibility that despite changes in temperature- possibly related to modifications in upwelling strength and/or changes in the temperature of the undercurrent- this upwelling failed to produce higher surface productivity.

Although $C_{37}total$ is not calibrated to export production it has been shown to correspond closely with other indicators of phytoplankton production [Budziak *et al.*, 2000; Chazen *et al.*, 2009; Bolton *et al.*, 2010; Chazen *et al.* 2010 (dissertation chapter 3)]. As a result we evaluate $C_{37}total$ as a reliable indicator of relative phytoplankton productivity across the Holocene. An alternative explanation is that the availability of micronutrients largely supplied through river input was the ultimate limiting factor of surface production. The location of CDH-23 is near the outlet of several large river systems, which bring micronutrients (principally Fe) to the surface [Junk and Piedade, 2010]. River discharge increases dramatically during El Niño events when precipitation increases over South America. If periods of enhanced SST at the location of CDH-23 correspond to periods dominated by El Niño like climate- either resulting from more

frequent El Niño events or a shift in the mean state towards a relaxation of walker circulation- warmer SSTs could correspond to increased river discharge and increased availability of micronutrients. This scenario may explain the positive correlation between SST and $C_{37}total$ but many uncertainties remain; if enhanced El Niño-like climate led to increased productivity in the past we would expect to see increased productivity during El Niño events today at the location of CDH-23. According to satellite *Chlorophyll a* reconstructions from SeaWiSE, surface production decreased slightly at the location of CDH-23 during the El Niño event of 1997/1998. This decrease in productivity is significantly smaller than corresponding changes seen off the central Peru margin and in the cold tongue but there is little evidence for an increase in productivity associated with El Niño events. Furthermore, the warmest temperatures and highest $C_{37}total$ values occur near 7.5ka (see Figure 3), nearly 2kyrs before changes in seasonal insolation could have caused the ITCZ to move off the equator [Haug *et al.*, 2001; Wang *et al.*, 2005; Cane, 2005] and nearly 3kyrs before climate reconstructions from Ecuador indicate enhanced El Niño strength [Moy *et al.*, 2002] (see Figure 3). Thus, the occurrence of strong El Niño events during this period is unlikely [Cane, 1998, 2005]. At present, we cannot fully account for this interesting pattern between SST and productivity in cores CDH-23 and GGC-14. The use of additional productivity proxies including biogenic silica and percent nitrogen may help to shed light on this intriguing problem.

4.5 Cold Tongue and Peru margin Alkenone-based Temperature Records

Multiple alkenone records from the equatorial Pacific exhibit a warming trend during the late Holocene [Kienast *et al.*, 2001; Kienast *et al.*, 2006; Koutavas and Lynch-Stieglitz, 2003; Koutavas *et al.*, 2004; Leduc *et al.*, 2007; Pahnke *et al.*, 2007; Koutavas and Sachs, 2008]. This warming is enigmatic since it occurs on both sides of the equator

(see Figure 1). Because precession modifies the seasonal heat balance between the hemispheres, it is unlikely that warming on both sides of the equator is forced solely by changes in seasonal insolation. This warming trend is also absent from Mg/Ca records from the same region which show a decreasing temperature trend during the late Holocene [Lea *et al.*, 2006; Leduc *et al.*, 2007]. Despite mounting evidence indicating that alkenone temperature estimates from marine sediments most closely approximate mean annual SSTs [Muller *et al.*, 1998; Conte *et al.*, 2006; Chazen *et al.*, 2010 (dissertation chapter 5)] researchers have speculated that the late Holocene warming trend inferred from alkenone paleothermometry results from a seasonal bias in the alkenone proxy [Leduc *et al.*, 2007].

Direct comparison between the CDH-23/GGC-14 record and other alkenone records from the ETP may shed new light on this apparent late Holocene warming. Although several alkenone records (see Figures 6c and d) display a late Holocene warming trend, the amplitude and slope of this warming varies between cores. Additionally, apart from the Kienast *et al.* [2006] record (see Figure 6d) each record shows some degree of late Holocene structure rather than the monotonous warming trend described by others [e.g. Leduc *et al.*, 2007]. Finally, when comparing these lower resolution records to the CDH-23/GGC14 record the differences in resolution allows for the possibility that the apparent lack of late Holocene structure (i.e. oscillating temperatures) in other ECT records results from under sampling. The Kienast *et al.* [2006] record for example uses an age model that contains only four ^{14}C age estimations and the sampling resolution is a third of the resolution of CDH-23. This allows for the possibility that with higher resolution sampling and better age constraints these other alkenone records may reveal more structure.

Proxy uncertainties for the $U_{37}^{K'}$ index and the Mg/Ca of planktonic foraminifera [see *Mix*, 2006] may also contribute to discrepancies between Mg/Ca and alkenone temperature reconstructions from the ETP. $U_{37}^{K'}$ temperatures may be influenced by nutrient and light stress in addition to potential seasonal biases [*Prahl et al.*, 2006, 2010]. We also note that significant biases in $U_{37}^{K'}$ may result from laboratory error. Samples exposed to oxygen or prolonged room temperatures prior to analysis may impart preferential degradation of the $C_{37:3}$ alkenone resulting in a warm temperature bias [*Herbert and Chazen*, unpublished]. Additionally, overuse of GC-FID columns and differences in peak area quantification may bias temperatures. Temperatures derived from Mg/Ca of planktonic foraminifera may be more sensitive to salinity changes than previously thought [*Ferguson et al.*, 2008; *deMenocal et al.*, 2007] and significant temperature artifacts may be related to dissolution of foraminiferal calcite [*Mix*, 2006]. Furthermore, some of the variability in Mg/Ca derived temperature records may be an artifact of the small sampling sets used (~30-40 individual forams) rather than true temperature variability. Many gaps in our ability to interpret tropical temperature records (including those derived from alkenones) remain, but until the mechanisms that govern tropical Pacific climate and their teleconnections are better understood these apparent gaps in understanding cannot be used to argue against the fidelity of the proxy.

The differences in temperatures records from CDH-23 (3°S) and the Peru margin (11-15°S) (see Figure 5) indicate a fundamental divide between the climates of these two regions between 15ka and present. Instead, the similarities between the CDH-23 temperature reconstruction and alkenone records from the equatorial cold tongue region indicate that the location of CDH-23 is more closely tied to cold tongue dynamics rather than the Peru margin upwelling system. A number of reasons may explain this

discrepancy involving both the tropical undercurrent and surface wind dynamics. The location of CDH-23 is just south of the Peru undercurrent [Pennington *et al.*, 2006]. This, in combination with our results suggests that the location of CDH-23 is more sensitive to changes in the EUC than the Peru undercurrent. Discrepancies between these two sites may also be related to local upwelling dynamics. The Peru Current is more sensitive to changes in seasonality than equatorial upwelling; while temperatures in both regions fluctuate with the seasonal migration of the ITCZ, seasonal changes are stronger at the Peru margin than the cold tongue region due to its distance from the equator [Strub *et al.*, 1998]. Using a coupled ocean-atmosphere general circulation model Liu *et al.* [2000] demonstrated that fluctuations in the strength of the South Pacific subtropical high led to a reduction in wind strength (and an associated increase in SSTs) along the Peru coast during the early Holocene. This localized band of reduced wind never reached the equatorial cold tongue region in the model simulation. Liu *et al.* [2000] argue that these local wind dynamics along with changes in the tropical undercurrent created a disconnect between the climates of the Peru margin and the equatorial cold tongue regions [Liu, 1994; Liu *et al.*, 2000]. We speculate that both local wind dynamics and the differences in their respective undercurrents make records from the location of CDH-23 diverge from those along the Peru margin. Despite its position along the Peru/Ecuador coast, records from the location of CDH-23 seem closely tied to climate dynamics of the eastern equatorial cold tongue region.

5. Conclusions

Alkenone records from the boundary between the Peru margin and equatorial upwelling regions (3°44' S, 81°08' W) reveal a significant cooling relative to modern temperatures (2.5-3°C) between 8.5 and ~15ka followed by 1°C millennial-scale temperature oscillations, which persist until present day (~0.4ka). Maximum temperatures occur at 7.5ka, 2kyrs before climate records indicate the southward migration of the ITCZ [based on *Haug et al.*, 2001] The positive correlation between $C_{37}total$ and surface temperatures is inconsistent with the expected enhancement in surface productivity associated with upwelling. This pattern is not easily explained by our current understanding of the source waters to the EUC or changes in upwelling strength. It is possible that the input of micronutrients was the limiting factor for productivity at the location of CDH-23 but more information is needed to understand this unexpected pattern.

The long term trend (i.e. multi-millennial) captured in our high resolution SST reconstruction is consistent with other alkenone records from the ECT including the ECT alkenone index [*Koutavas and Sachs*, 2008] with the exception of the late Holocene warming. This apparent warming has been used as evidence for a possible warm season bias in alkenone temperatures [*Leduc et al.*, 2007]. However, alkenone derived temperatures from surface sediments at the location of CDH-23/GGC-14 (Figure 3b) match mean annual sea surface temperature estimates. We argue that the apparent late Holocene warming may result from the undersampling of millennial scale climate oscillations rather than a gradual increase in alkenone derived temperatures. Regardless of its origin, we caution against using an anomalous temperature trend as evidence for proxy deficiencies until we reach a greater understanding of the forcing mechanisms that

govern eastern tropical Pacific climate.

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Table 1. ^{14}C Age estimations

Depth (cm)	^{14}C Age (yr)	Error (+/- yr)	*Median Prob Calibrated Age (yr)	Depth (cm)	^{14}C Age (yr)	Error (+/- yr)	*Median Prob Calibrated Age (yr)
30.00	1680	40	1588	7.25	890	30	809
160.00	3420	35	3671	100.25	1860	45	1796
260.50	3980	35	4467	200.25	2860	35	2979
350.50	4540	40	5162	* ^{14}C age estimations, which were converted into calendar ages using the IntCal4 calibration program [Reimer et al., 2004] with a reservoir correction of 450 years [Bard et al., 1997].			
400	4800	35	4918				
460.50	5290	50	6077				
500	5752	30	6059				
550	6230	35	6583				
600	6510	45	6916				
660.50	6900	40	7731				
781	7950	40	8331				
850.25	8640	45	9596				
900	8600	45	9090				
1000.25	9220	60	10386				
1100	9920	40	10713				
1230	10750	45	12091				
1285	10900	50	12371				
1360.50	11650	55	13499				
1440	12000	55	13388				
1500.00	12200	70	14056				
1600	12600	55	13995				
1700.00	12800	95	15240				

Figure Captions

Figure 1. (a) Mean annual sea surface temperature, estimated mean wind stress and major surface currents of the tropical Pacific. Major currents are denoted with thick black lines. Thin black line with arrows denotes wind strength and direction. The locations of CDH-23/GGC-14 along with three other cores from the Peru margin are indicated with black circles. Colors are a six year Aqua-MODIS SST reconstruction while wind data is from 1999-2003 FSU/COAPS Tropical Pacific pseudostress [modified from Pennington et al., 2006]. **(b)** Inset of mean annual sea surface temperatures in the eastern tropical Pacific. Black circles mark the location of alkenone records referenced in this study (see Figure 6) [Figure modified from *Koutavas and Sachs, 2008*].

Figure 2. Age models for cores CDH-23 and GGC-14 are based on multiple AMS ^{14}C age estimations, which were converted into calendar ages using the IntCal4 calibration program [Reimer et al., 2004] with a reservoir correction of 450 years [Bard et al., 1997]. The age model for CDH-23 was constructed using a polynomial fit. The age model for GGC-14 is constructed using a linear fit, while there are only 3 age estimation for core GGC-14 the overlap in temperatures is excellent.

Figure 3. (a) Red color intensity from Laguna Pallcacocha, southern Ecuador. Plotted as counts per 100 years in non-overlapping windows. Moy et al. [2002] interpret enhanced late Holocene red color as a response to increased ENSO related rain fall events. **(b)** The $\text{U}^{\text{K}'}_{37}$ temperature and **(c)** $\text{C}_{37}\text{total}$ productivity reconstructions for CDH-23 (solid line) and GGC-14 (dashed line). **(d)** Percent titanium from the Cariaco Basin [Haug et al., 2001]. Haug et al. [2001] interpret high %Ti as an indicator of enhanced precipitation related to a northward displacement of the ITCZ. Reduced %Ti is thought to indicate a southward migration in the position of the ITCZ.

Figure 4. CDH-23 $\text{U}^{\text{K}'}_{37}$ vs $\text{C}_{37}\text{total}$. Contrary to the expected anti-correlation of an ‘upwelling’ model (e.g. enhanced upwelling leads to cool SSTs and enhanced macronutrients) proxies for temperature and productivity are positively correlated in core CDH-23.

Figure 5. Comparison between $U_{37}^{K'}$ temperature reconstructions from CDH-23/ GGC-14 (red) and temperature reconstructions from the Peru margin. Cores PC-2 (black) is from 15°S [Chazen et al., 2009] core W7706-40K (maroon) is from 11°4'S and core 1228D (blue) is from 11°S [see Chazen et al., 2010 (dissertation chapter 1)].

Figure 6. Comparison of $U_{37}^{K'}$ temperature reconstructions of the equatorial Pacific. **(a)** SSTs from cores KNR195-5 CDH-23 and GGC-14, red arrow indicates the mean annual sea surface temperatures for the core location; **(b)** SSTs from core V19-30 [Koutavas and Sachs, 2008]; **(c)** SSTs from core ME0005A-24JC [Kienast et al., 2006]; **(d)** Composite alkenone SST index (standard deviation units) based on the five records from the equatorial pacific (V19-30, V19-27, V19-28, V21-30 and RC11-238) [Koutavas and Sachs, 2008].

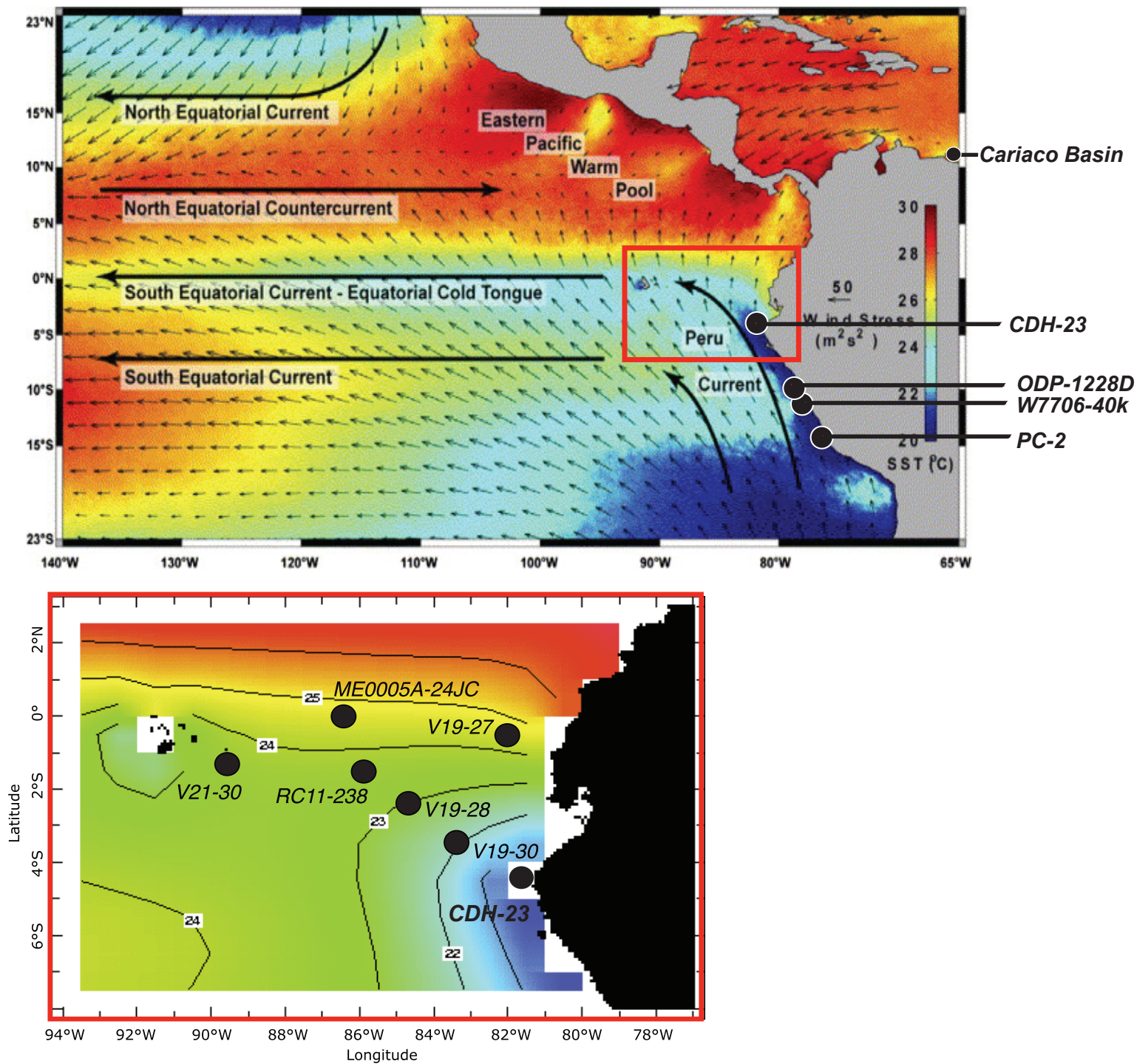


Figure 1.

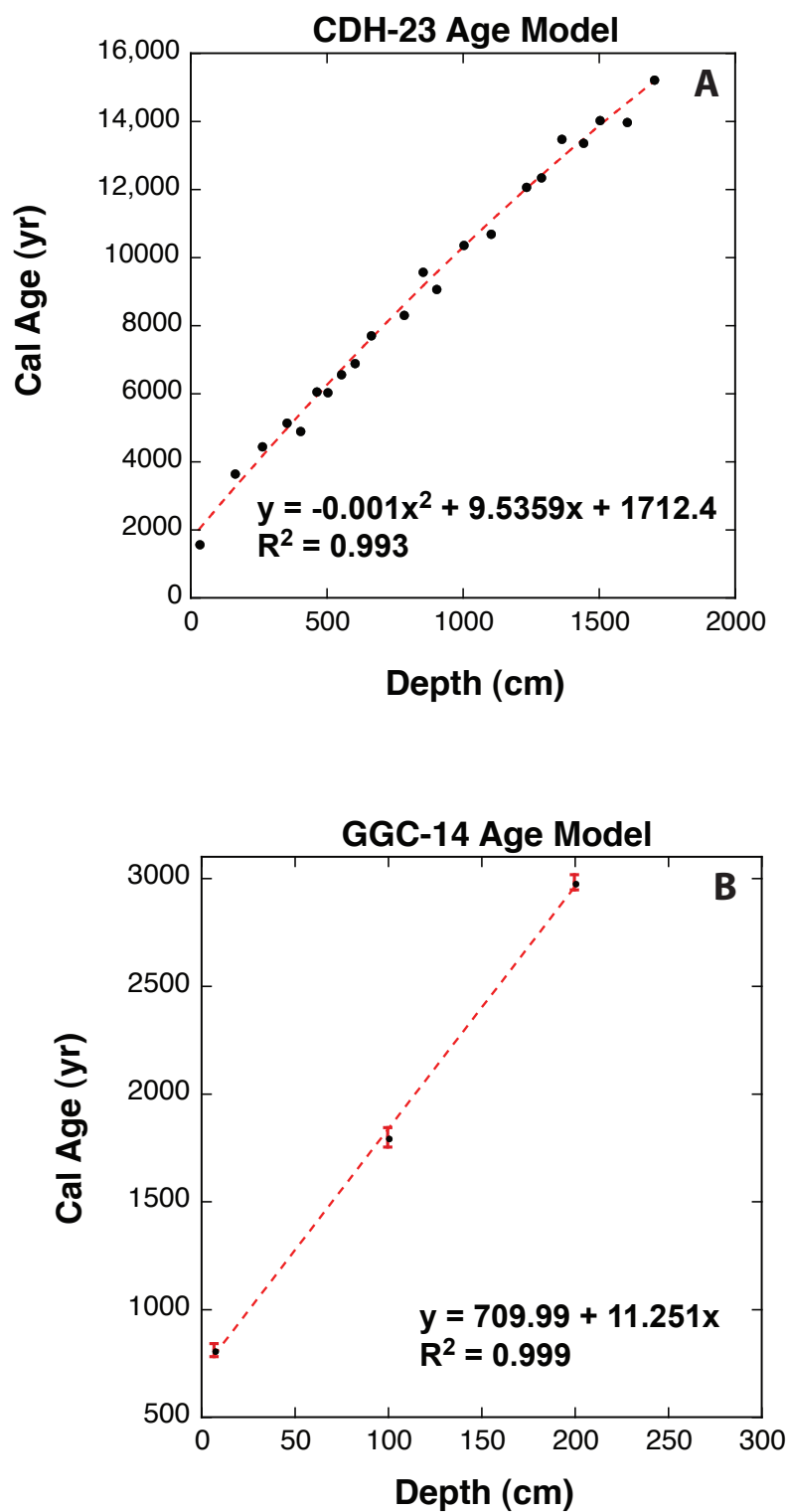


Figure 2.

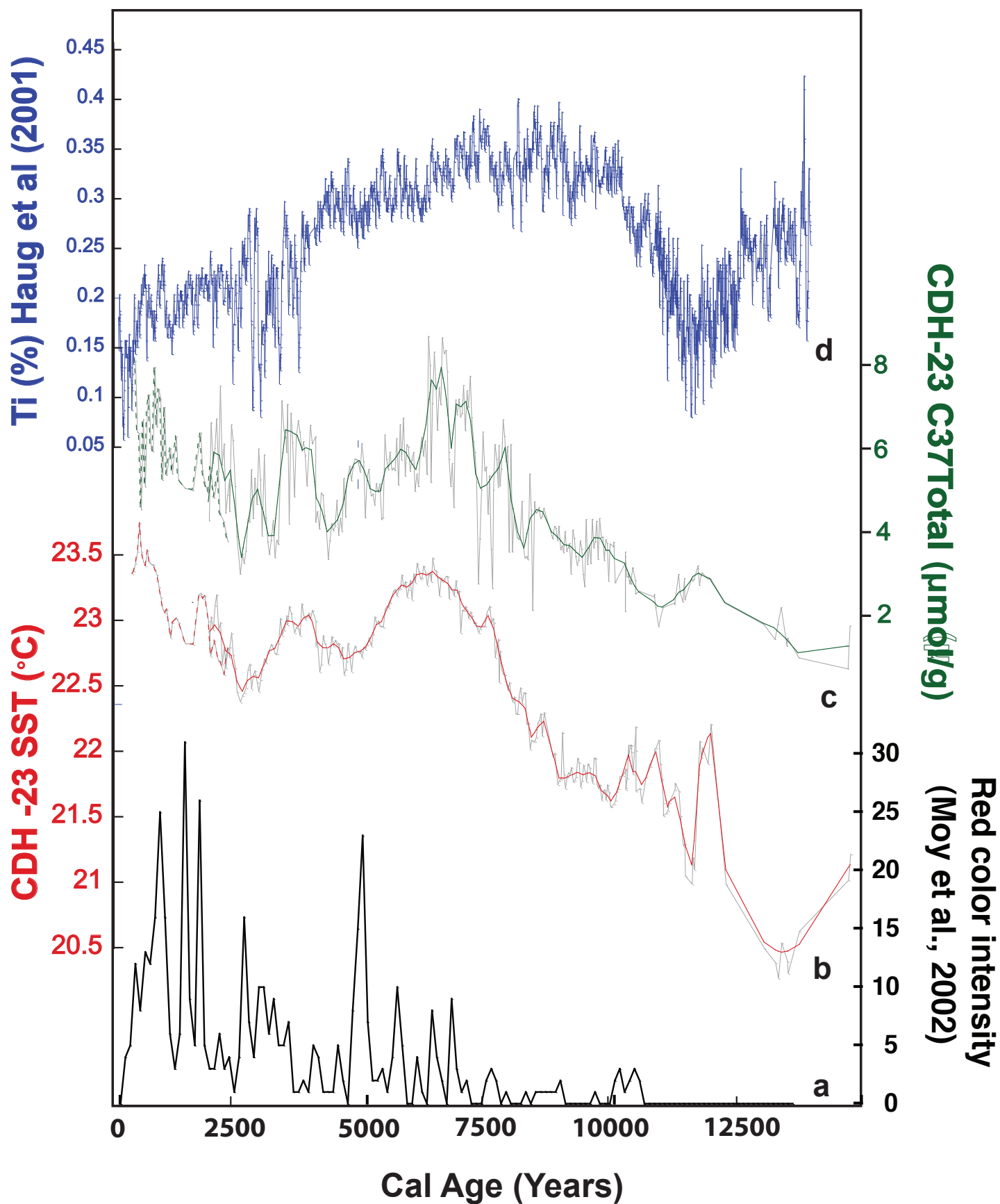
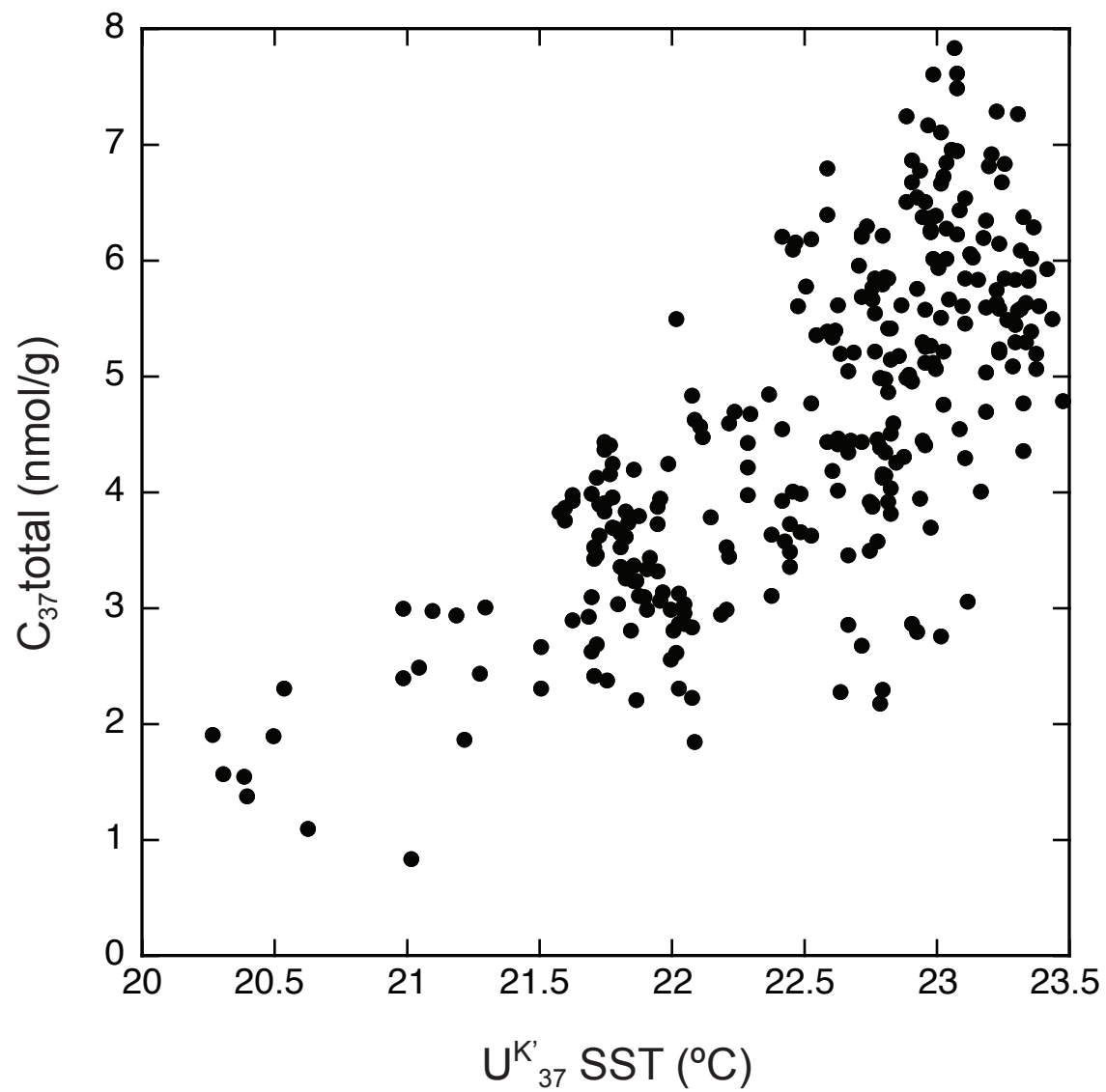


Figure 3.

**Figure. 4**

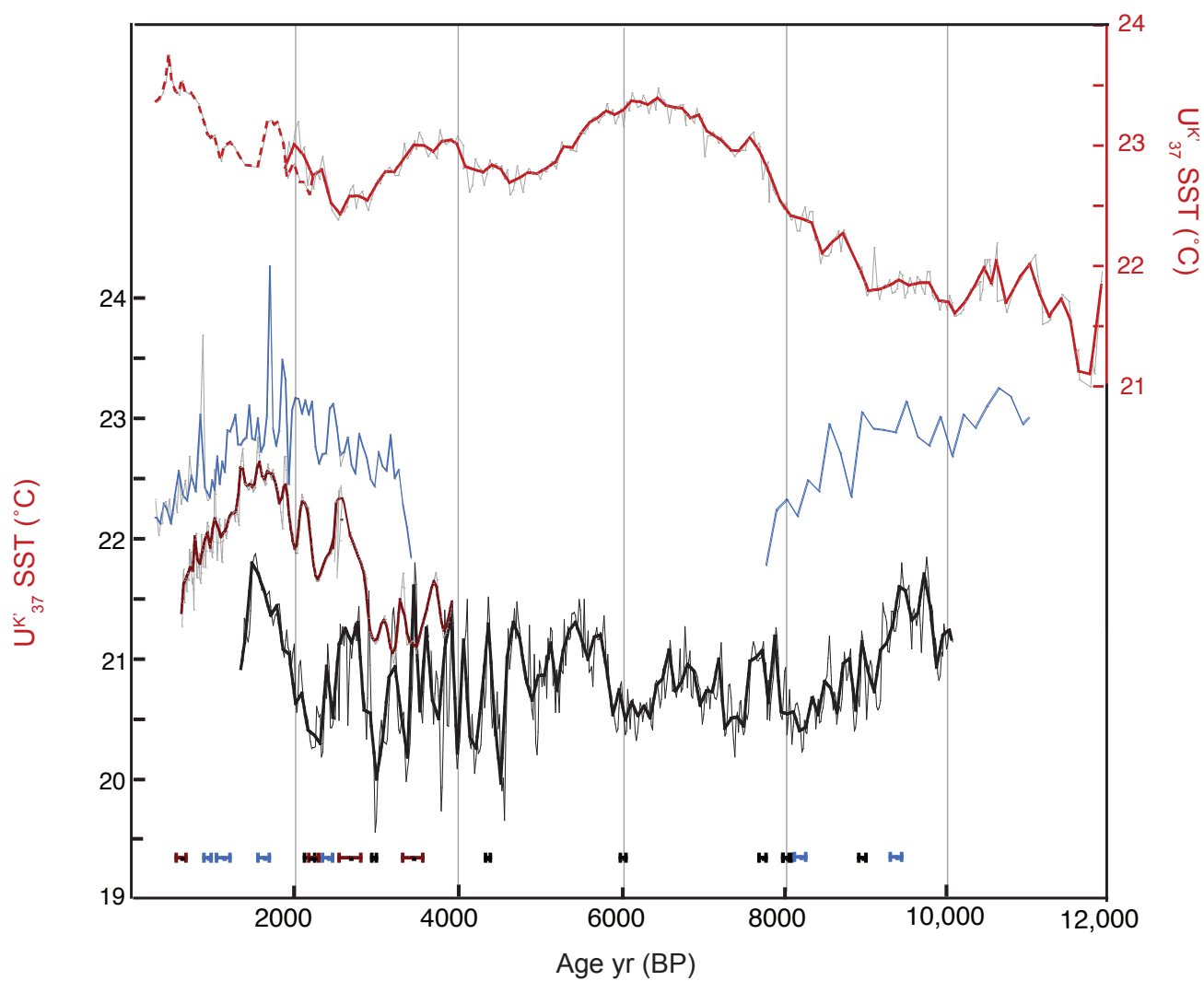


Figure 5.

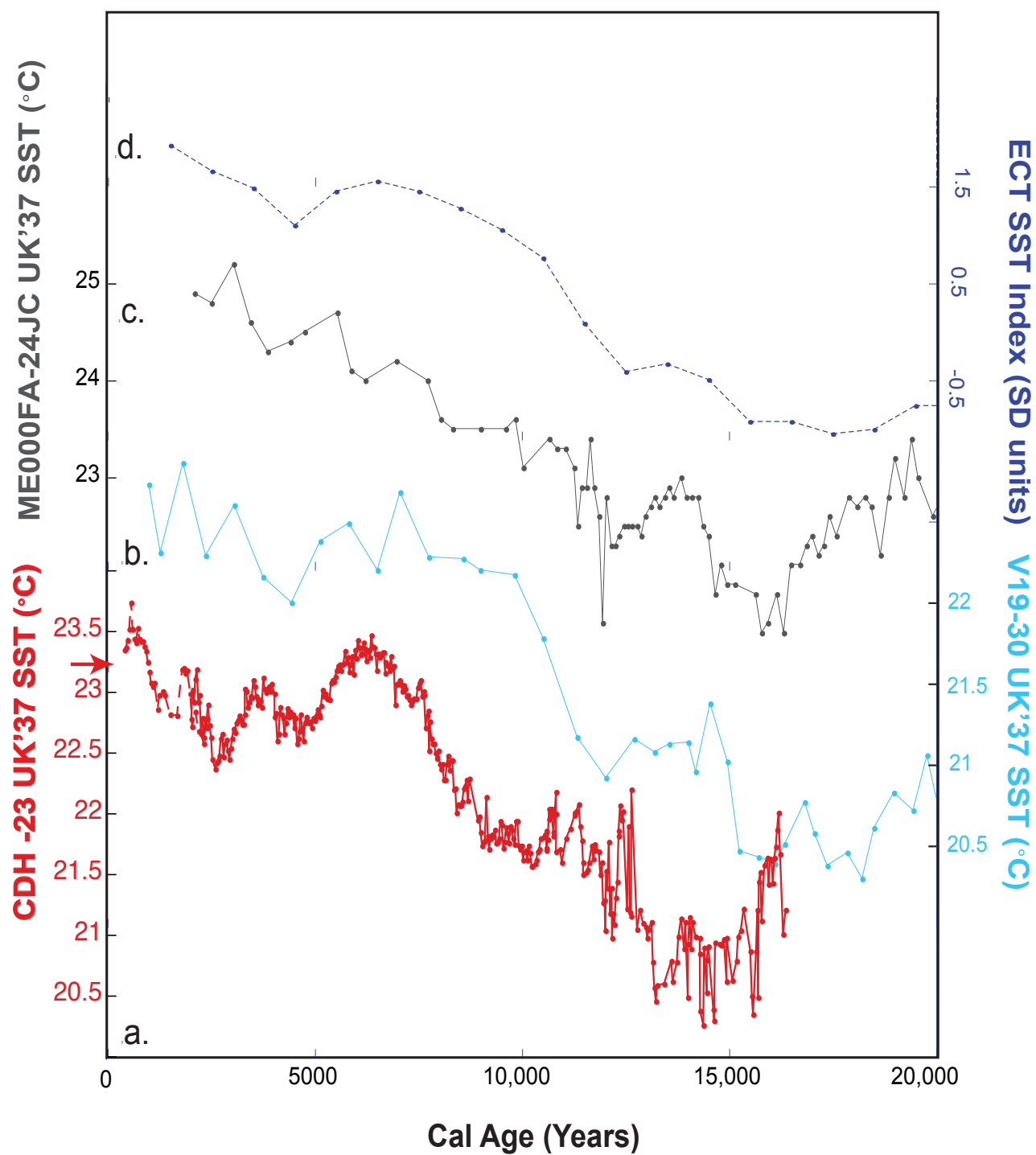


Figure 6.

CHAPTER FIVE

Who's on Top: TEX₈₆ and U^k₃₇ proxy comparison from the Peru Margin Upwelling System

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Abstract

Using a high deposition rate Holocene sediment core from the southern Peru margin we compare the widely used $U^{K'}_{37}$ sea surface temperature index with the novel TEX_{86} temperature proxy. The $U^{K'}_{37}$ index is based on the unsaturation ratio of alkenone producing haptophytes, while TEX_{86} is based on the number of cyclopentane moieties in the glycerol dialkyl glycerol tetraethers (GDGTs) synthesized by Crenarchaeota. Because haptophytes and Crenarchaeota possess different ecological niches we anticipate potential offsets between these two temperature proxies. We compare these proxies over two time intervals during the Holocene; A high-resolution interval (every ~ 7 -8 years) between 3-2.7 ka and a lower resolution interval (every ~ 220 years) between ~ 10 -1.4 ka. Using an alkenone-derived proxy for surface productivity ($C_{37total}$) we also compare changes in our temperature proxies with inferred productivity. TEX_{86} derived temperature estimates are consistently cooler and less variable than our $U^{K'}_{37}$ derived temperature estimations. This is particularly evident during the late Holocene when alkenone-derived temperatures reveal dramatic centennial scale oscillations. TEX_{86} values appear to be anti-correlated with $U^{K'}_{37}$ temperature estimates during the late Holocene.

We also see evidence for a gradual cooling ($\sim 1^\circ\text{C}$) in TEX_{86} derived temperature estimates from the early to late Holocene. We speculate that the GDGT producers live deeper in the water column, below the mixed layer. During periods of strong upwelling, the thermocline shoals and TEX_{86} derived temperatures converge with $U^{K'}_{37}$ derived temperatures. When upwelling is reduced, thermal stratification is enhanced and TEX_{86} temperatures record a deeper (cooler) temperature than $U^{K'}_{37}$ temperature estimates. The gradual cooling in TEX_{86} derived temperature estimates across the Holocene suggests that

either TEX₈₆ producers lived deeper in the water column during the late Holocene compared to the early Holocene or that subsurface temperatures were warmer during the early Holocene.

1. Introduction

1.1 Merging old and new proxies

The alkenone unsaturation index ($U^{K'}_{37}$) is a widely used and well-established paleoceanographic sea surface temperature proxy [Brassell *et al.*, 1986; Muller *et al.*, 1998; Herbert *et al.*, 1993, 1998; Conte *et al.*, 2006]. The observation that the structure of long chain ketones inside the cell of certain species of haptophyte algae varies with growth temperature provides the basis for alkenone paleothermometry [Volkman *et al.*, 1980; Marlowe *et al.*, 1984]. During warmer conditions these haptophytes (principally *Emiliania huxleyi* and *Gephyrocapsa oceanica*) synthesize a larger proportion of the di C₃₇ methyl ketone while more tri C₃₇ methyl ketone is produced during cooler conditions. Prahl and Wakeman [1987] demonstrated that the unsaturation ratio of *Emiliania huxleyi* grown in batch culture could be calibrated linearly to growth temperatures [Prahl *et al.*, 1988]. Since the development of this initial calibration [Prahl *et al.*, 1988] several global statistically- based core top calibrations have shown that the $U^{K'}_{37}$ index of alkenones preserved in ocean sediments provide a faithful record of mean annual sea surface temperatures at a wide range of latitudes and environmental conditions [Muller *et al.*, 1998; Conte *et al.*, 2006].

The $U_{37}^{K'}$ index introduced several advantages lacking in other temperatures proxies. Compared to other paleotemperature proxies, including $\delta^{18}\text{O}$ and Mg/Ca ratios of planktonic foraminifera, the $U_{37}^{K'}$ index is not subject to uncertainties attributed to the depth habitats of foraminifera since alkenone production is restricted to the photic zone [Marlowe *et al.*, 1984; Brassell *et al.*, 1993; Budziak *et al.*, 2000]. Alkenones are remarkably refractory lipids and not the unsaturatuon ratio is subject to changes in ocean carbonate saturation or the preservation of carbonate [Mix, 2006] which makes them useful in a variety of environmental conditions and time scales [Herbert *et al.*, 2003; Lesley *et al.*, 1996; Budziak *et al.*, 2000].

The most recent, and by far the largest in sample number, core top calibration by Conte *et al.* [2006] showed remarkable agreement with the 1988 culture calibration produced by Prahl *et al.* [1988]. Using over 600 core top samples, the Conte *et al.* [2006] calibration lends support to the use of $U_{37}^{K'}$ to approximate mean annual sea surface temperatures. This study also reveals outliers that cluster away from mean annual SSTs. The discrepancies between $U_{37}^{K'}$ and mean annual sea surface temperatures are largely attributed to seasonal production biases [Volkman, 2000; Conte *et al.*, 2006; Popp *et al.*, 2006] preferential degradation of the $\text{C}_{37:3}$ alkenone [Sun and Wakeman, 1994; Kim *et al.*, 2009; Rontani *et al.*, 2009], light and nutrient stress [Mix, 2006; Prahl *et al.*, 2006, 2010] and variations in species compositions [Conte *et al.*, 2006]. The $U_{37}^{K'}$ index has proven to be a remarkably reliable indicator of mean annual SST but like all proxies it is not without complicating factors.

In the last five years a number of studies have emerged focusing on the use of glycerol dialkyl glycerol tetraethers (GDGTs) as potential indicators of surface temperature. GDGT cell membrane lipids synthesized by a select group of archaea have been shown to respond to lake and ocean temperatures in a number of environmental conditions [Schouten *et al.*, 2002; Wuchter *et al.*, 2005; Kim *et al.*, 2008, 2010]. GDGTs are particularly abundant in marine environments and thought to be produced by both non- hyperthermophilic crenarcheota and euryarchaeota [Karner *et al.*, 2001; Powers *et al.*, 2004; Leider *et al.*, 2010]. The TetraEther indeX of tetraethers consisting of 86 carbons (TEX₈₆) describes the best linear equation relating the relative distribution of GDGTs to growth temperatures [Schouten *et al.*, 2002; Wuchter *et al.*, 2005; Kim *et al.*, 2008, 2010]. The advent of this novel temperature proxy has many advantages compared to other paleoclimate proxies. Unlike the U^{K'}₃₇ index, GDGTs do not saturate outside the 4-28°C temperature range, they also appear long before alkenones are present in the geologic record [Bard *et al.*, 2001]. Additionally, GDGTs appear unaffected by changes in redox conditions [Schouten *et al.*, 2004] or by fluctuations in nutrients or salinity [Wuchter *et al.*, 2004].

Nevertheless, many unsolved issues remain in interpreting TEX₈₆ derived temperatures [Pearson *et al.*, 2007]. Variations in the ecological niche and depth habitat of Crenarchaeota introduce a major source of uncertainty into TEX₈₆ interpretation [Wuchter *et al.*, 2005; Lee *et al.*, 2008]. Although some TEX₈₆ reconstructions in modern ocean sediments have yielded temperature estimates close to mean annual SSTs [Schouten *et al.*, 2002; Kim *et al.*, 2008] an increasing number of studies have found that TEX₈₆ derived temperatures are skewed from mean annual SSTs. Studies from the

Mediterranean region indicate that TEX₈₆ derived temperatures over estimate mean annual SSTs by several degrees [Menzel *et al.*, 2006; Leider *et al.*, 2010; Castaneda *et al.*, 2010] possibly related to increased GDGT production during the warm season. It has also been suggested that GDGTs produced by non- Crenarchaeol organisms (including euryarchaeota) may result in a warm season bias [Schouten *et al.*, 2008; Turich *et al.*, 2008]. Despite this warm bias found at Mediterranean sites, TEX₈₆ reconstructions from upwelling regions consistently underestimate surface temperatures [Huguet *et al.*, 2007; Lee *et al.*, 2008; Lopes dos Santos *et al.*, 2010], which may indicate that GDGT producers live too deep in the water column to record surface temperatures. This is supported by observational studies indicating that GDGT production is concentrated below the mixed layer in upwelling regions [Pearson *et al.*, 2001; Huguet *et al.*, 2007; Lee *et al.*, 2008]. The reason for Crenarchaeota to live deeper in the water column (i.e below the mixed layer) in upwelling regions compared to other ocean environments is not entirely clear. While relatively little is known about the biochemical role of isoprenoidal GDGT producers, empirical evidence suggests that they are ammonium oxidizers and thus require both ammonium and a small amount of oxygen [Konneke *et al.*, 2005; Wuchter *et al.*, 2006; Kim *et al.*, 2008]. This, in combination with the observation that Crenarchaeota are outcompeted by phytoplankton may limit their success in the surface ocean [Wuchter *et al.*, 2004]. It is possible that the high rates of surface production in upwelling regions force TEX₈₆ producers to move deeper in the water column.

Our results indicate that TEX₈₆ estimates a deeper water column temperature than the U^K₃₇ sea surface temperature proxy in Peru margin sediments. The ability to record temperatures below the mixed layer is invaluable to future climate reconstructions from

the Peru margin. Fluctuations in thermocline depth, changes in surface winds and modifications in the temperature of the Peru undercurrent all have the potential of altering the surface to subsurface gradient making comparisons between these two proxies extremely valuable.

1.2. Oceanographic Setting

The Peru margin is situated at the interface between the poleward Peru Undercurrent (PUC, 50-500 m depth) and the equatorward Peru Coastal current. Equatorward, along-shore winds are deflected offshore by the Coriolis effect, which forces cold nutrient-rich, thermocline waters to the surface. Sea surface temperatures from the Peru margin are highly sensitive to changes in the position of the intertropical convergence zone (ITCZ), the strength of Walker circulation [Strub *et al.*, 1998; Lavin *et al.*, 2006] and the El Niño Southern Oscillation [Chavez, 1995], making it an ideal location to compare surface temperature proxies. While wind induced upwelling persists year-round, seasonal fluctuations in the position of the ITCZ modify the upwelling strength and surface temperatures of the Peru margin. The coldest sea surface temperatures ($\sim 17^{\circ}\text{C}$) occur during austral winter when wind-induced upwelling is strongest and the thermocline shoals [Strub *et al.*, 1998; Lam *et al.*, 2009]. Peak SSTs ($\sim 24^{\circ}\text{C}$) occur during austral summer when wind strength is reduced and the waters become more stratified [Wyrtki, 1973; Strub *et al.*, 1998, USGS SST program (Tcl/Tk version 1.3)]. The depth of the nutricline is closely associated with the thermocline and appears to track the annual changes in thermocline depth [Chavez, 1995; Pennington *et al.*, 2006]. The thermocline resides < 40 m below the surface during most of the year but

nearly reaches the surface during periods of enhanced upwelling [*Fiedler and Talley, 2006; Pennington et al., 2006*]. The thermocline marks the bottom of the mixed layer, above which temperatures are uniform. Figure 3 depicts annual climatologies of mixed layer depth and thermocline depth (20°C isotherm) from 1960-1990 bathythermograph data from the tropical Pacific [*Fiedler, 1992*]. Annual ETP temperature estimates from below the mixed layer (~40-50m) are shown in Figure 3. Thermocline depth and sea surface temperatures also oscillate with the El Niño Southern Oscillation; El Niño events correspond to a deepening of the thermocline and increases in sea surface temperatures, while La Niña events correspond to shoaling of the thermocline and decreases in sea surface temperatures [*Chavez and Barber, 1987; Chavez, 1995*].

2. Methods and Results

2.1. Sediment Core PC-2

Core PC-2 was collected from the upper Peruvian shelf (15°S) in the heart of the Peru oxygen minimum zone (OMZ) (see Figure 1). This region exhibits particularly high sedimentation rates (70cm/kyr), which in combination with the persistent oxygen deficit creates excellent conditions for the preservation of organic matter. PC-2 is the only known sediment archive from the southern Peru margin with continuous sedimentation across the Holocene (10-1.4ka) [*Chazen et al., 2009*].

The age model for core PC-2 was constructed using 8 AMS ^{14}C age estimations from bulk organics. Each ^{14}C age estimation was converted into calendar ages using the Fairbanks calibration curve [*Fairbanks et al., 2005*] and a uniform reservoir correction of 450 years [*Bard et al., 1993*]. A linear curve fit between calendar ages and depth was

used to construct our age model (see Figure 1b). Based on this age model, PC-2 exhibits a nearly constant sedimentation rate (70cm/kyr) between ~10ka and ~1.4ka.

Annual laminations, consisting of alternating couplets of light and dark sediment correspond to diatom rich and diatom poor layers. These laminations occur periodically throughout the sediment core but are particularly common during the late Holocene [see Chazen et al., 2010 (dissertation chapter 1) for more information about core PC-2 laminations].

2.2. Alkenone and TEX_{86} Analysis

Core PC-2 was sampled for alkenone analysis at an estimated resolution of every 13 years for the full length of the core (10ka-1.4ka) [Chazen et al., 2009, see Figure 5]. High resolution sampling for both $U^{K'}_{37}$ and TEX_{86} was conducted at an estimated spacing of every ~7-8 years between 3ka and 2.7ka (Figure 2a). Samples for TEX_{86} were also sampled at lower resolution spacing across the Holocene, approximately every 220 years (see Figure 5). Each sample integrates over 6-7 years of deposition.

Wet samples were freeze-dried and homogenized. Samples were extracted using 0.8-1.2g of sediment in a Dionex 200 Accelerated Solvent Extractor with a DCM/methanol solution (9:1, v/v). Sample extracts were evaporated under nitrogen gas and reconstituted in 200 μ L of toluene containing a C_{37} and C_{36} alkane standard. Extracts were separated with an Al_2O_3 stationary phase column. The DCM fraction was collected for alkenone analysis with a Gas Chromatograph Flame Ionization Detector, using a modified method of Herbert et al. [1998]. Alkenone concentrations (C_{37} di- and triunsaturated ketone mass/grams of dry sediment = " C_{37} total") were calculated by

normalizing to the internal standard (C_{37} and C_{36} n-alkanes). The polar fraction was blown down under N_2 gas and reconstituted in a hexane/propanol (99:1, v/v) solution, which was filtered through a PTFE 0.45 μm filter. Analysis by high performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry (HPLC/APCI-MS) followed a method modified from Schouten et al. [2002]. TEX_{86} values were corrected using an interlab comparison with the Royal Netherlands NIOS laboratory [Tierney et al., 2008]. Corrected TEX_{86} values were converted into temperature using the Kim et al., [2008] calibration. Alkenone analytical 2σ standard error, ± 0.1 $^{\circ}C$, was calculated based on sample replicates (10% of alkenone samples were duplicated). Analytical 2σ standard error, on the basis of duplicate measurements, was ± 0.3 $^{\circ}C$ for TEX_{86} (20% of TEX_{86} samples were replicated).

The use of C_{37}^{total} as a proxy for surface productivity is a qualitative approach to estimate haptophyte production, which is closely linked to total phytoplankton productivity [Brassell, 1993; Budziak et al., 2000]. Recent work from the eastern equatorial Pacific and Atlantic upwelling regions demonstrates that on orbital cycles alkenone accumulation rates are closely tied to alkenone-synthesizing haptophyte concentrations and to other indices of phytoplankton productivity including the thermocline depth proxy based on the abundance of *F. profunda* [Bolton et al., 2010].

2.3 Eastern Equatorial Pacific Core top survey

While we are unable to confirm $U_{37}^{K'}$ values from surface sediments at the location of core PC-2 (core PC-2 is missing the most recent 1.4kyrs of sediment) our core top transect from the Eastern Equatorial Pacific (EEP) allows us to compare surface $U_{37}^{K'}$

and TEX₈₆ derived temperature estimates with mean annual sea surface temperature in the Eastern Tropical Pacific region (see supplemental information). This core-top transect extends from the Galapagos Islands (01°15' S, 89°41' W) to the northern Peru margin (03°44'S, 81°18'W) (see supplemental information, Table S1). U^{K'}₃₇ temperature estimates are very close (within 0.5°C) to mean annual sea surface temperatures while TEX₈₆ temperature estimates are significantly cooler (see supplemental information, Figure S1) and are consistent with temperatures below the mixed layer (40-50m, see Figures 2, 3). The differences between U^{K'}₃₇ and TEX₈₆ derived temperature estimates are reduced moving towards the Margin away from the Galapagos; the difference between U^{K'}₃₇ and TEX₈₆ off the Galapagos is ~3°C while the difference is only ~0.5°C off Peru. There is also significantly less range in the TEX₈₆ temperature estimates compared to U^{K'}₃₇ derived temperatures (see supplemental information for further information about the Eastern Equatorial Pacific core top transect).

2.4 Peru margin comparison between alkenone and TEX₈₆ temperature estimates

We compare alkenone and TEX₈₆-derived temperature estimates on two separate timescales. The decadal-scale comparison was conducted during the late Holocene between 3ka and 2.7ka (see Figure 2a). This specific interval was chosen due to the high variability in U^{K'}₃₇; there are three major temperature oscillations during this interval ranging from ~20.1-19.6°C. Each oscillation lasts between 80-100 years (see Figure 2a). U^{K'}₃₇ derived temperatures range between ~22-19.4°C across this interval. By contrast, TEX₈₆ temperatures are consistently cooler and show little variation (see Figure 2a). While TEX₈₆ temperature estimates are relatively stable compared to U^{K'}₃₇ temperature estimates, the proxies appear to be anti-correlated (see Figure 2b); TEX₈₆ temperatures

increase slightly when $U_{37}^{K'}$ temperatures decrease. C_{37}^{total} is highly variable over this high-resolution interval (see Figure 4a) while it appears to be weakly anticorrelated with alkenone-derived SST and is thus weakly correlated with TEX_{86} derived temperatures (see Figure 4) a longer interval is needed to make a definitive conclusion. What we can say is that surface productivity (inferred through changes in C_{37}^{total}) does not appear to be the primary control on changes in TEX_{86} derived temperatures over our high-resolution interval.

We also compare $U_{37}^{K'}$ and TEX_{86} temperatures at lower resolution sampling across the Holocene (see Figure 3). The $U_{37}^{K'}$ temperatures exhibit a dramatic change in variance from the early to late Holocene, where the late Holocene is characterized by high amplitude, centennial scale fluctuations in temperature that are absent from the early Holocene section of the record. Despite this dramatic change in variance there is no substantial change in mean $U_{37}^{K'}$ temperatures between the early and late Holocene [Chazen *et al.*, 2009]. During the late Holocene (5.7-1.4ka) the $U_{37}^{K'}$ - TEX_{86} relationship is similar to what we observed over the high-resolution interval (i.e. Figure 4a); TEX_{86} derived temperatures are cooler and less variable than $U_{37}^{K'}$ derived temperatures. However TEX_{86} derived temperatures during the early Holocene (~10-5.7ka) are nearly a degree warmer than late Holocene values. Thus, TEX_{86} derived temperatures are only slightly warmer than mean $U_{37}^{K'}$ derived temperatures during the early Holocene section of the record. C_{37}^{total} increases in variance near the mid-Holocene (not shown). However it is important to note that the mean C_{37}^{total} values between the early and late Holocene do not change [see Chazen *et al.*, 2009]. Thus, it is unlikely that the long-term changes in TEX_{86} across the Holocene are the result of changes in surface production.

3. Discussion

3.1. $U_{37}^{K'}$ and TEX_{86} proxies in the Peru margin

The connection between mean annual sea surface temperature and the alkenone unsaturation index ($U_{37}^{K'}$) has proven remarkably reliable in both modern and paleoceanographic studies [Brassell *et al.*, 1986; Muller *et al.*, 1998; Herbert *et al.*, 1998; Conte *et al.*, 2006]. As the global survey of core top $U_{37}^{K'}$ expands certain areas have emerged as regional outliers from the alkenone calibration [see Conte *et al.*, 2006]. The North Atlantic and the Pacific subarctic for example, diverge from the global calibration with a strong warm bias. Prah1 *et al.* [2010] speculate that this offset may be the result of light stress. Anomalous $U_{37}^{K'}$ values have been linked to both light and nutrient stress in laboratory batch culture experiments using *Emiliania huxleyi* [Prah1 *et al.*, 2003, 2006].

Surprisingly, core top $U_{37}^{K'}$ values from the Peru margin, which is neither light nor macronutrient limited, also show anomalously warm temperatures according to a recent global survey [McCaffrey *et al.*, 1990; Prah1 *et al.*, 2006, 2010]. Prah1 *et al.* [2010] speculate that these anomalously warm temperatures are the result of increased alkenone production during the warm season. If this were the case we might expect to see similar biases in sites adjacent to the Peru margin, where the seasonal range is similar or greater than Peru. But sites directly south of the Peru margin are reported as having a slight cold bias in the same global survey [Prah1 *et al.*, 2010]. Core PC-2 is missing the upper ~1.4 kyrs of sediment so we are unable to compare core-top $U_{37}^{K'}$ values directly with modern mean annual sea surface temperatures at the location of core PC-2. However, the mean SSTs during the late Holocene section of core PC-2 are approximately 0.7°C warmer than modern mean annual sea surface temperatures at the location of PC-2 [see Chazen *et al.*,

2010 (dissertation chapter 1)]. This offset is significantly smaller than the $\sim 3^{\circ}\text{C}$ offset reported by Prahl et al. [2010]. We also note that in our EEP core top transect (see supplemental materials, Figure S1) $U^{K'}_{37}$ derived temperature estimates are within 0.5°C of mean annual sea surface temperatures.

The anomalously warm Peru margin core tops presented in Prahl et al. [2010] come from an earlier study by McCaffrey et al., [1990]. During sample preparation these particular core tops were dried using a low temperature oven rather than a freeze dryer, as is customary today. Herbert and Chazen [unpublished] have demonstrated that prolonged exposure to room temperatures and/or oven drying can result in a several degree warming in alkenone temperatures related to preferential degradation of the $C_{37:3}$ alkenone. Without more core top data directly from the Peru margin we cannot say with certainty whether Peru margin temperature estimates based on alkenone unsaturation are biased or not but we caution against assuming a warm bias without more information.

This is the first study to evaluate TEX_{86} in sediments from the Peru margin. Other TEX_{86} reconstructions from upwelling regions have found that TEX_{86} derived temperatures consistently underestimate surface temperatures compared to instrumental measurements and $U^{K'}_{37}$ derived temperature reconstructions [Lee et al., 2008; Lopes dos Santos et al., 2010]. These low TEX_{86} derived temperatures may be related to GDGT producers living deeper in the water column (i.e. below the mixed layer) [Huguet et al., 2007; Lee et al., 2008; Lopes dos Santos et al., 2010]. Our preliminary work from the eastern equatorial Pacific (see supplemental information) reconstructs TEX_{86} derived temperatures that correspond to temperatures below the mixed layer ($\sim 45\text{mbs}$) (see Figures 2 and 3).

3.2. $U_{37}^{K'}$ -TEX₈₆ comparison at the Peru Margin

The high-resolution comparison between TEX₈₆ and $U_{37}^{K'}$ derived temperatures suggests that each proxy records fundamentally different temperature signals. $U_{37}^{K'}$ derived temperatures are consistent with mean annual SSTs at the location of core PC-2 while, TEX₈₆ derived temperatures are cooler and less variable than surface temperatures in this region (see Figure S1 in supplemental information). While we caution against over interpreting absolute TEX₈₆ derived temperatures (since the calibration is still in its infancy) our TEX₈₆ derived temperatures are consistent with temperature estimates at ~40-50m below the surface at the location of PC-2- this depth is consistent with a depth below the thermocline (see Figure 2 and 3). These observations are consistent with other TEX₈₆ reconstructions from ocean margins [Lee *et al.*, 2008; Lopes dos Santos *et al.*, 2010] where TEX₈₆ temperature estimations were significantly cooler and less variable than surface temperatures. Sediment trap work from the Santa Barbara Basin and Arabian Sea also found evidence of TEX₈₆ producing living below the surface mixed layer [Kramer *et al.*, 2001; Huguet *et al.*, 2007]. A number of biological and ecological factors may help explain why TEX₈₆ producers appear to inhabit waters below the mixed layer. TEX₈₆ producers are readily out-competed by phytoplankton and thus benefit from an environment with reduced competition [Huguet *et al.*, 2006; Kim *et al.*, 2008]. Additionally, ammonium concentrations increase rapidly below the mixed layer due to the decay of zooplankton and phytoplankton [Huguet *et al.*, 2007; Lam *et al.*, 2009]. The combination of high ammonium, available oxygen and reduced competition make the depth directly below the mixed layer favorable for Crenarchaeota [Huguet *et al.*, 2007; Lee *et al.*, 2008].

The centennial-scale fluctuations in $U_{37}^{K'}$ derived temperatures indicate that the Peru surface waters oscillated between prolonged (50-100 years) cooling and warming events, which likely correspond to periods of enhanced and reduced upwelling [Strub *et al.*, 1998]. Across the high-resolution interval (see Figure 4a) the highest $SST_{UK'37}$ values correspond to the lowest inferred productivity values, the opposite is also true, this pattern is consistent with modifications in upwelling strength. We speculate that during periods of reduced upwelling, thermal stratification is enhanced and the temperature gradient between the surface dwelling alkenone producers and the sub-mixed layer dwelling TEX_{86} producers diverge (see Figure 4a). When upwelling increases the thermocline shoals along with the mixed layer, causing the $U_{37}^{K'}$ and the deeper dwelling TEX_{86} producers to converge in temperature (see Figure 4a). The fact that TEX_{86} temperatures increase slightly when surface temperatures decrease (see Figure 4b) suggests that TEX_{86} producers are not fixed at a specific depth but rather shift their position based on environmental conditions. Since the nutricline shoals along with the thermocline [Lam *et al.*, 2009] we speculate that TEX_{86} producers shift upward in the water column during periods of enhanced upwelling. Thus, as surface temperatures decrease, TEX_{86} derived temperatures increase slightly. It is also possibly that GDGT producers modify their position in the waters column in response to changes in surface production. Studies from the Santa Barbara Basin show that GDGTs shift their position in the water column during El Niño events in response to changes in surface production [Black *et al.*, 2001; Huguet *et al.*, 2007]. However, without a clear correspondence between C_{37}^{total} and TEX_{86} derived temperatures (see Figure 4) it is difficult to evaluate the effect of surface production at this time.

3.3. $U_{37}^{K'}$ - TEX_{86} comparison across the Holocene

From the early to late Holocene, TEX_{86} derived temperatures exhibit a gradual (1°C) cooling. This shift in TEX_{86} coincides with an increase in $U_{37}^{K'}$ derived temperature variability (see Figure 5). This pattern suggests that either TEX_{86} producers lived higher in the water column during the early Holocene (possibly related to changes in the position of the nutricline) or that the temperatures of the Peru subsurface were warmer during the early Holocene than they are today. Enhanced upwelling during the early Holocene is supported by climate models [Clement *et al.*, 1999, 2000] and EEP paleoclimate reconstructions [Koutavas *et al.*, 2002; Conroy *et al.*, 2008] that attribute enhanced early Holocene upwelling to a northerly shift in the position of the ITCZ [Haug *et al.*, 2001]. Alternatively, modeling results predict an early-mid Holocene deepening of the Peru margin thermocline related to changes in the physical properties of the equatorial undercurrent [Liu *et al.*, 1994; Liu *et al.*, 2000; Chazen *et al.*, 2010 (dissertation chapter 1)]. Either of these scenarios could cause TEX_{86} producers to record slightly warmer temperatures during the early Holocene.

4. Conclusions

Our comparison of TEX_{86} and $U_{37}^{K'}$ temperatures suggests that $U_{37}^{K'}$ faithfully estimates mean annual sea surface temperatures while TEX_{86} values are more closely related to temperatures below the mixed layer (near 45m), where waters are cooler and temperature variations are small. The dramatic late Holocene centennial-scale fluctuations in sea surface temperature recorded by $U_{37}^{K'}$, likely reflect modifications in upwelling strength. The corresponding increase in TEX_{86} derived temperatures during

periods of enhanced upwelling may reflect modifications in the depth habitat of Crenarchaeota possibly related to ammonium concentrations in the water column. These results are supported by our Eastern Equatorial Pacific core top transect where, alkenone derived temperatures closely estimate mean annual sea surface temperatures and TEX₈₆ derived temperature estimates are consistent with temperatures below the mixed layer. The ~1°C cooling in TEX₈₆ temperatures between the early and late Holocene may reflect changes in the depth of the nutricline/ thermocline or subsurface temperatures changes.

While TEX₈₆ does not appear to record mean annual sea surface temperatures in Peru margin sediments we stress the importance of a proxy that can potentially record subsurface temperatures. The combination of U^{K'}₃₇ and TEX₈₆ derived temperature estimates may provide important information about changes in ocean stratification through time. But to fully understand the potential of the TEX₈₆ proxy more work is needed to understand the depth habitat of TEX₈₆ producers.

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Figure Captions

Figure 1. (a) Bathymetric map of the Peru Margin. The triangle indicates the position of the core PC-2. (b) PC-2 age model. Circles indicate depths of bulk ^{14}C measurements, which were converted into calendar ages using the fairbanks0107 calibration curve. The age model was constructed using a linear curve fit (hatched line) ($r^2 = 0.98$).

Figure 2. Annual climatologies of (a) mixed layer depth (m) and (b) thermocline depth (20°C isotherm depth, m), from 1960- 1990 bathythermograph data. The location of core site PC-2 and our EEP core top transect are indicated with triangles [Fiedler, 1992].

Figure 3. Estimated mean annual temperatures (NOAA NODC WOAOF, 1×1 grid) in the eastern tropical Pacific below the depth of the mixed layer (40m). The location of PC-2 is indicated with a diamond (World Ocean Atlas 2005, temperature data) [Locarnini *et al.*, 2006].

Figure 4. (a) High resolution time series of TEX_{86} (blue) and $U_{37}^{K'}$ (red) temperatures plotted on a single axis. Analytical error for each proxy is indicated with error bars. Alkenone-derived temperatures show large centennial scale fluctuations while TEX_{86} temperatures are less variable. TEX_{86} temperatures overlap with alkenone temperatures when alkenones temperatures are low. (b) TEX_{86} (blue) and $U_{37}^{K'}$ (red) temperatures across the same time interval plotted on separate y-axis. TEX_{86} is inversely correlated to $U_{37}^{K'}$.

Figure 5. $U_{37}^{K'}$ derived temperatures (red line) from 10-1.4ka from core PC-2. Low resolution (every ~ 220 years) TEX_{86} temperatures (blue dots) show a gradual cooling ($\sim 1^\circ\text{C}$) between the early and late Holocene.

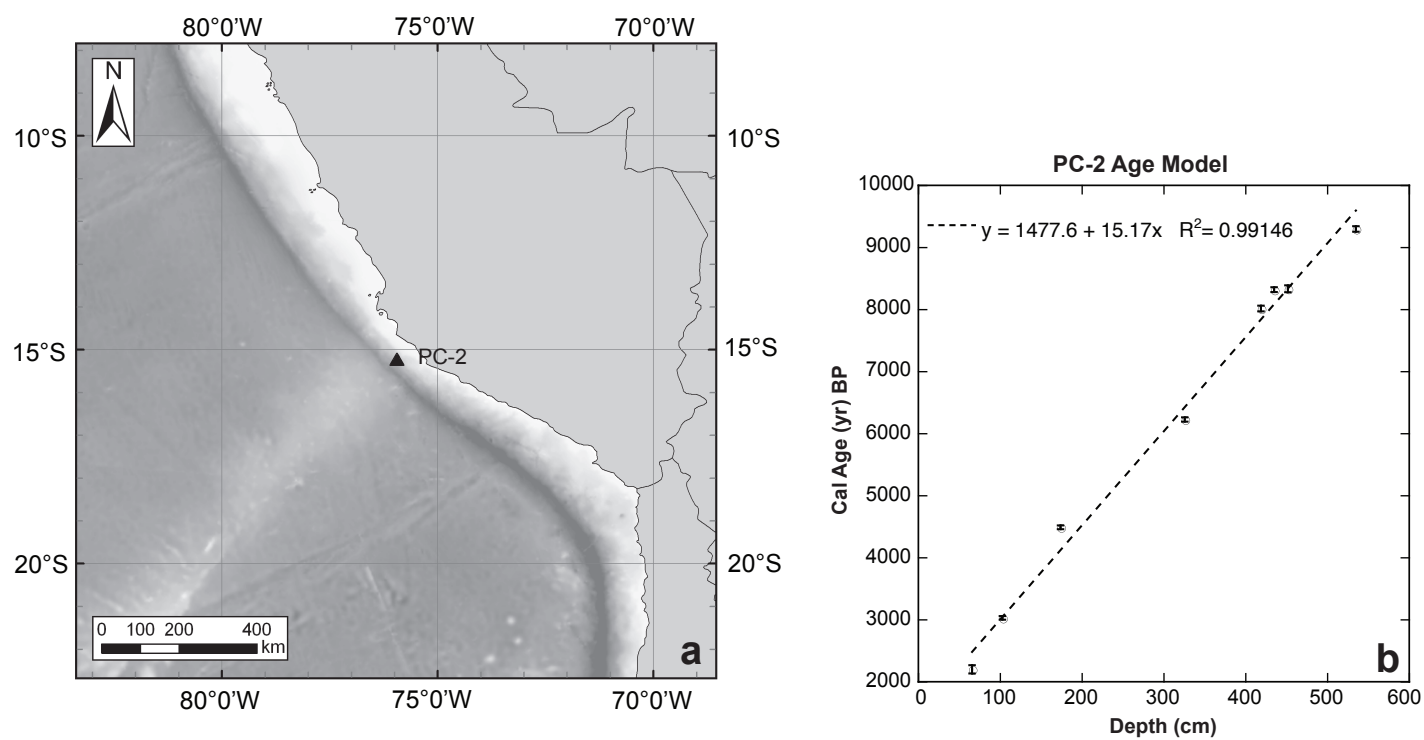


Figure 1.

Figure 1.

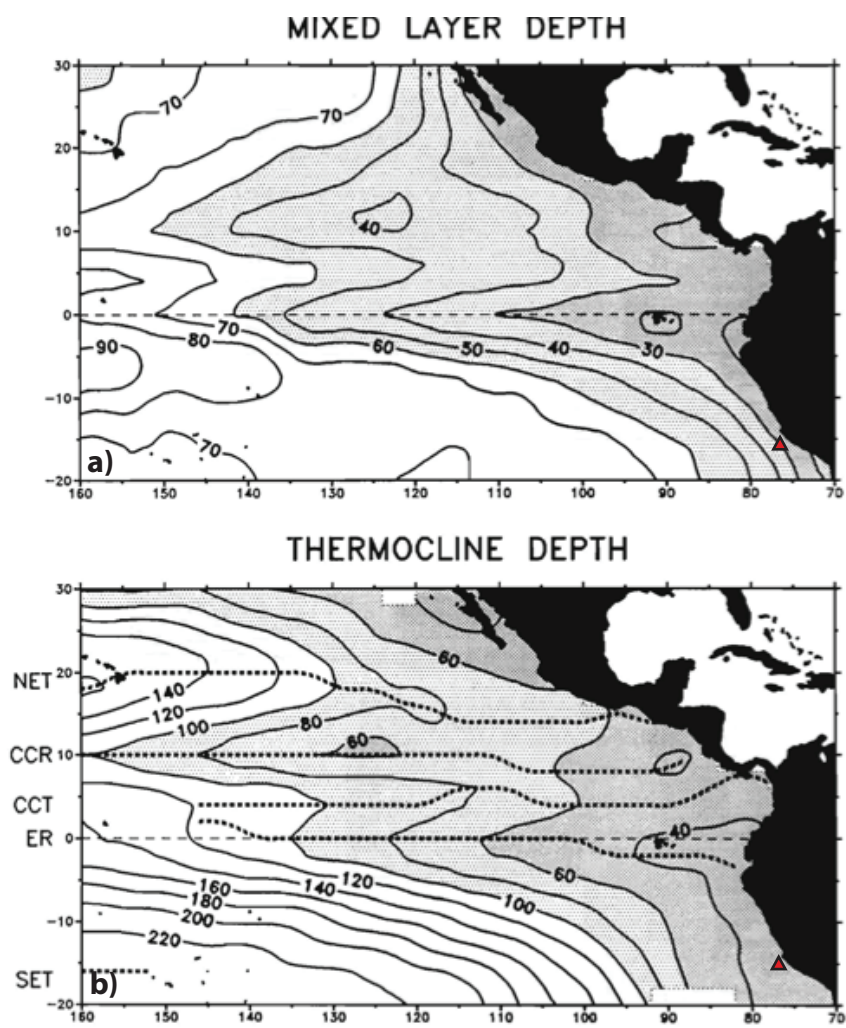


Figure 2

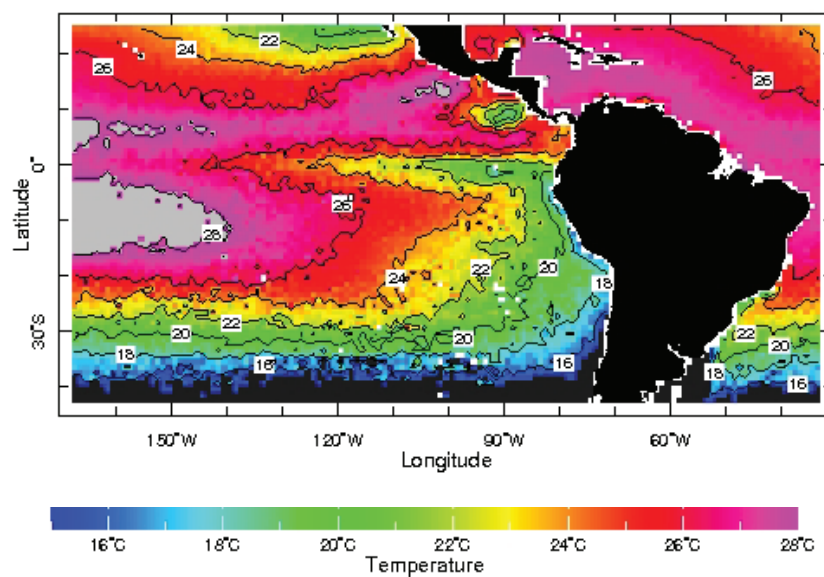
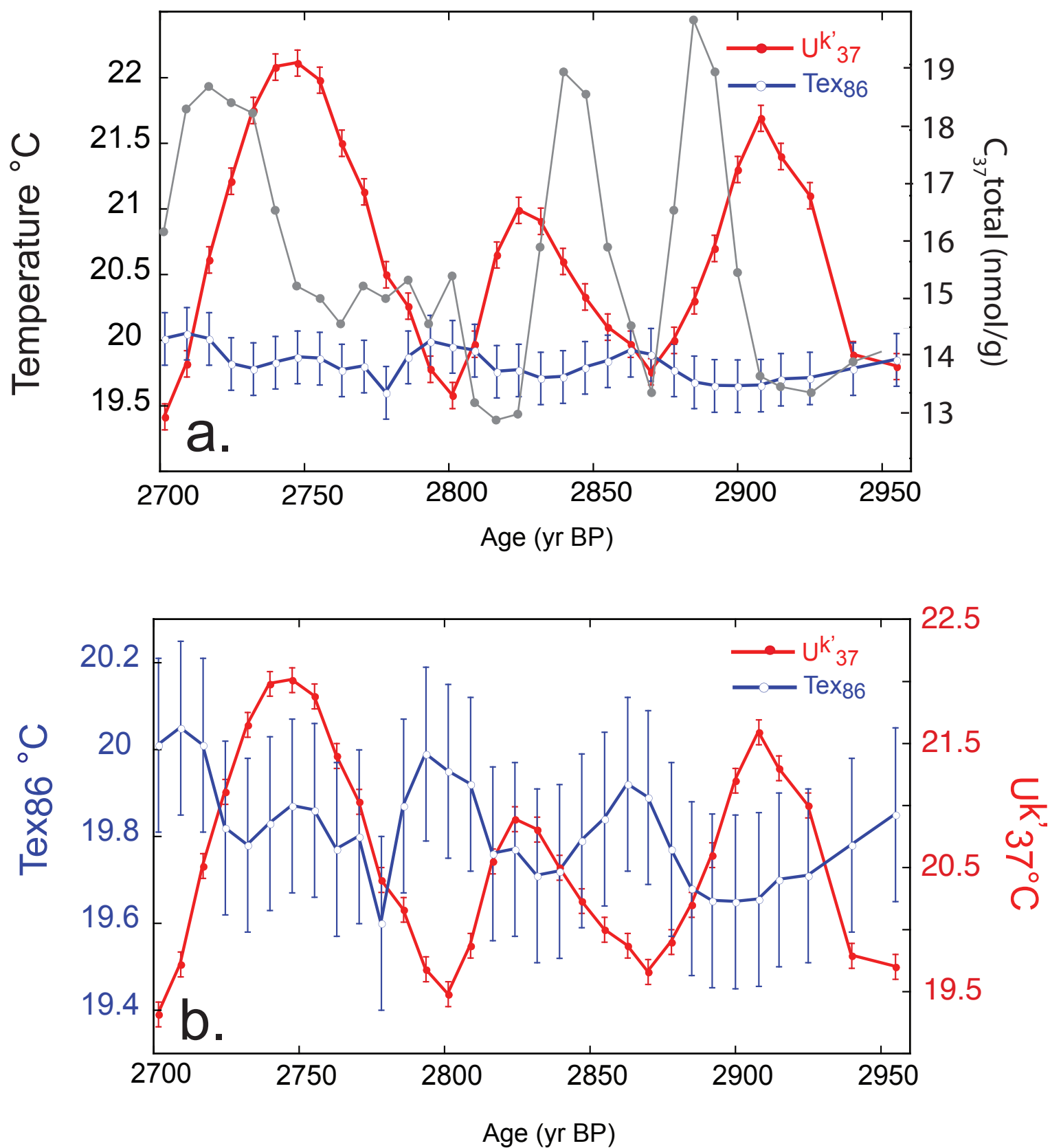
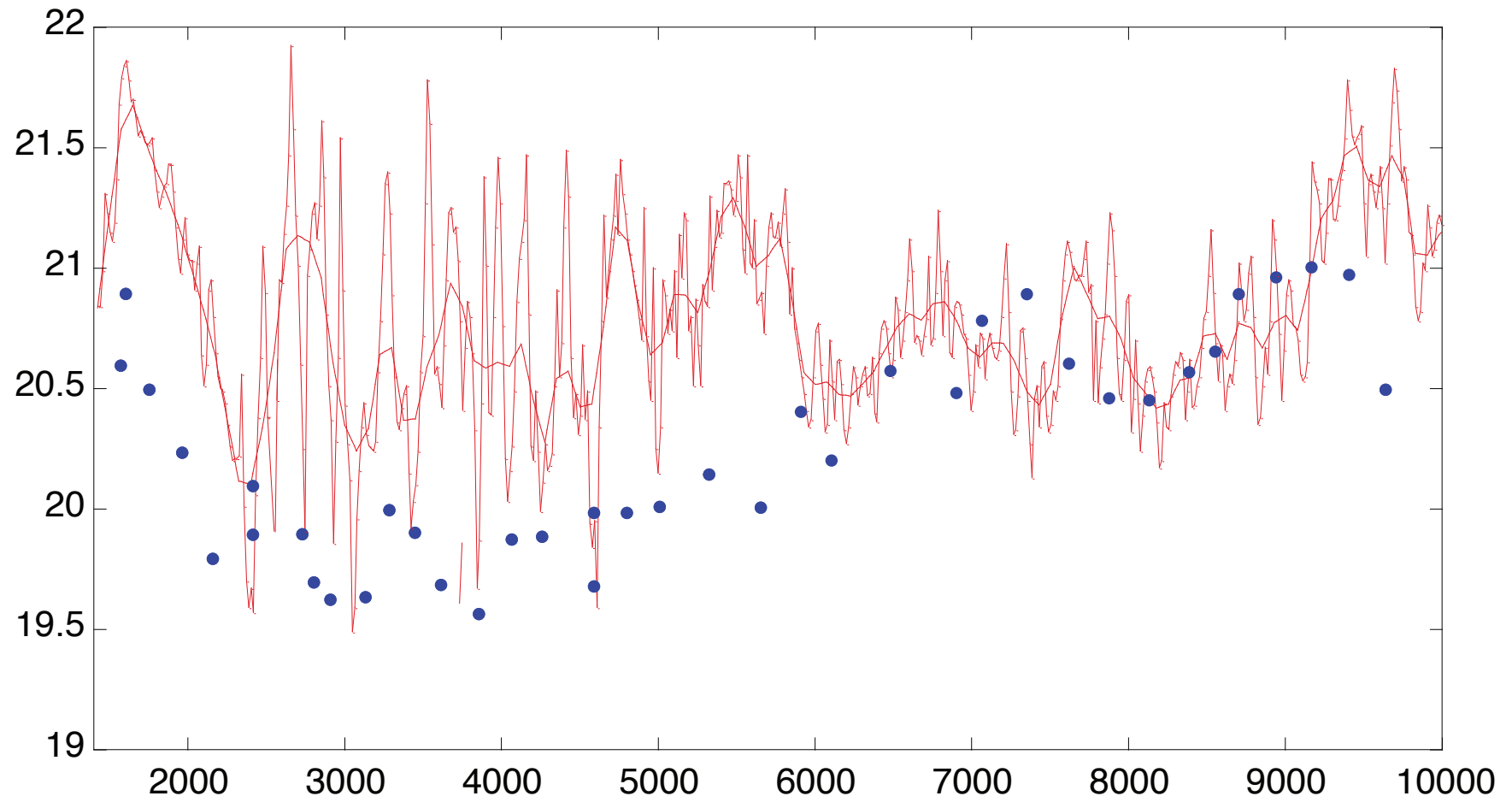


Figure 3

**Figure 4**

**Figure 5**

Supplementary information for Chapter 4: Who's on Top: TEX₈₆ and U^{K'}₃₇ proxy comparison from the Peru Margin Upwelling System

Core top number	Lat	Lon	U ^{K'} ₃₇	SST (Prah et al., 1988)	Mean annual SST (Tcl/Tk version 1.3)	TEX ₈₆	SST (Kim et al., 2008)*
1	00 49.56 S	87 54.49 W	0.849	23.82	23.48	0.569	21.2
2	01 31.96 S	86 47.11 W	0.84	23.56	23.15	0.570	21.2
3	03 42.63 S	81 06.92 W	0.82	22.97	23.12	0.570	21.2
4	03 45.01 S	81 08.15 W	0.823	23.06	23.12	0.572	21.4
5	03 59.20 S	81 18.60 W	0.818	22.91	22.3	0.568	21.1
6	03 51.02 S	81 15.00 W	0.823	23.06	22.4	0.567	21.1
7	03 13.42 S	82 54.85 W	0.781	21.82	21.45	0.572	21.4
8	03 35.85 S	83 57.79 W	0.795	22.24	21.9	0.571	21.3
9	01 15.94 S	89 41.96 W	0.829	23.24	23.4	0.567	21.1
10	01 15.18 S	89 41.13 W	0.862	24.21	23.4	0.563	20.9

* Tex86 values are normalized to NIOS to account for differences between Brown and NIOS Laboratories

Table S1.

Eastern Equatorial Pacific Core Top Transect

Ten core top samples were collected in a transect from the Galapagos Islands (01°15' S, 89°41' W) to the northern Peru margin (03°45' S, 81°08' W) during the 2009 Eastern Equatorial Pacific R/V Knorr cruise (KNR195-5). Core top samples were analyzed for U^{K'}₃₇ and TEX₈₆. These results, along with the corresponding core locations and mean annual sea surface temperatures [USGS SST program (Tcl/Tk version 1.3)] are listed in Table S1 and plotted in Figure S1. The U^{K'}₃₇ temperatures appear to faithfully estimate mean annual sea surface temperatures. U^{K'}₃₇ derived temperatures are consistently warmer and more variable than TEX₈₆ temperatures. Several factors may explain the discrepancies between U^{K'}₃₇ and TEX₈₆ temperatures, including differences in growth seasons between haptophytes algae and Crenarchaeota [Hueget *et al.*, 2006]

lateral transport of GDGTs from colder environments and degradation of $U^{K'}_{37}$ and/or GDGTs [Kim *et al.*, 2008]. However, we argue that the differences between $U^{K'}_{37}$ and TEX_{86} temperatures are related to the different water depths where haptophyte algae and Crenarchaeota reside. Unlike haptophyte algae, Crenarchaeota can reside below the photic zone and thus, may reflect subsurface temperatures [Karner *et al.*, 2001; Huguet *et al.*, 2007]. Two recent studies from the Benguela upwelling zone [Lee *et al.*, 2008] and the Guinea Plateau Margin [Lopes dos Santos *et al.*, 2010] demonstrate that TEX_{86} temperatures correspond to temperatures below the mixed layer where temperatures are cooler and less variable than the surface.

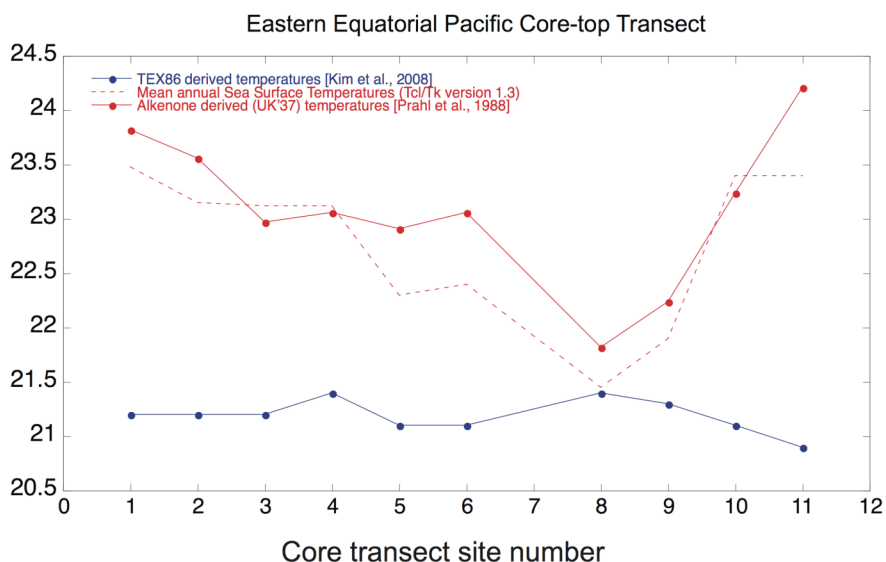


Figure S1. Eastern Equatorial Pacific core top transect. $U^{K'}_{37}$ temperatures (red solid line) are plotted along with TEX_{86} temperature (solid blue line) and corresponding mean annual sea surface temperatures (hatched red line) for each site. The site numbers correspond to site location in Table S1.

Data table for core PC-2

Data used in Chapters 1-4.

Age (yrs)*	Depth (cm)	Age (yrs)**	UK'37	SST (°C)	C ₃₇ total (nmol/g)	BSi (%)	δ ¹⁵ N (‰)
-5	0	1476	0.76354	21.31	12.42	31.72	7.94
30	1	1491	0.76082	21.23	9.88	34.65	8.46
64	2	1506	0.7581	21.15	10	33	8
98	3	1521	0.75674	21.11	13.99	24.52	7.44
132	4	1536	0.75946	21.19	15.32	22.35	7.44
165	5	1551	0.76558	21.37	14.35	25.13	7.52
199	6	1566	0.77612	21.68	9.72	35.64	8.05
232	7	1581	0.77986	21.79	9.13	34.83	8.68
266	8	1596	0.78156	21.84	10.1	31.7	8.14
299	9	1611	0.78224	21.86	12.6	29.32	7.31
332	10	1626	0.77952	21.78	12.76	29.55	7.07
365	11	1641	0.77646	21.69	13	28.73	7.02
398	12	1656	0.7768	21.7	16.24	21.3	6.71
431	13	1671	0.77442	21.63	16.36	19.63	6.28
463	14	1686	0.7717	21.55	15.41	19.97	6.18
496	15	1701	0.77238	21.57	16.24	17.23	6.24
528	16	1716	0.7717	21.55	19.07	16.28	6.1
561	17	1731	0.77068	21.52	22.38	16.32	5.83
593	18	1746	0.77034	21.51	19.3	15.88	5.74
625	19	1761	0.77068	21.52	17.54	15.36	5.78
657	20	1776	0.77136	21.54	16.83	14.85	5.92
689	21	1791	0.76694	21.41	17.57	16.21	6.15
720	22	1806	0.76388	21.32	17.82	16.75	6.13
752	23	1821	0.7615	21.25	17.59	16.48	5.86
783	24	1836	0.7632	21.3	17.03	14.68	5.83
815	25	1851	0.76456	21.34	18.27	13.85	6.05
846	26	1866	0.7649	21.35	21.73	14.24	6.21
878	27	1881	0.76762	21.43	20.34	17.37	6.27
909	28	1896	0.76762	21.43	18.43	18.92	6.3
940	29	1911	0.76388	21.32	16.42	17.52	6.27
970	30	1926	0.75878	21.17	18.8	15.16	6.18

1001	31	1941	0.75436	21.04	21.32	14.5	5.97
1032	32	1956	0.75232	20.98	22.65	17.67	5.8
1062	33	1971	0.75708	21.12	20.85	20.49	5.73
1093	34	1986	0.76014	21.21	18	21.86	5.67
1123	34	2001	0.75504	21.06	14.51	19.49	5.68
1153	35	2016	0.75402	21.03	17.59	20.25	5.74
1183	36	2031	0.75402	21.03	20.9	21.97	5.94
1213	37	2046	0.74994	20.91	15.9	23.03	6.22
1243	38	2061	0.75368	21.02	15.11	22.23	6.84
1273	39	2076	0.75606	21.09	14.82	20.74	7.3
1302	40	2091	0.74076	20.64	13.6	20.47	6.79
1332	41	2106	0.73634	20.51	12.77	20.48	6.33
1361	42	2121	0.7394	20.6	12.13	21.27	6.35
1391	43	2136	0.74994	20.91	10.77	29.12	6.33
1420	44	2151	0.7513	20.95	12	30.27	5.67
1449	45	2166	0.7462	20.8	15.35	26.06	5.03
1478	46	2181	0.7411	20.65	19.38	23.37	5.24
1507	47	2196	0.7377	20.55	18.81	21.56	5.44
1536	48	2211	0.736	20.5	13.45	20.66	5.64
1564	49	2226	0.73566	20.49	16.17	19.62	5.84
1593	50	2241	0.73396	20.44	18.37	19.06	6.72
1621	51	2256	0.7309	20.35	19.4	19.15	7.65
1650	52	2271	0.72784	20.26	20.42	19.24	7.8
1678	53	2286	0.7258	20.2	21.06	19.33	7.87
1706	54	2301	0.72614	20.21	21.02	19.42	7.86
1734	55	2316	0.72614	20.21	20.98	19.51	7.83
1762	56	2331	0.72648	20.22	20.95	19.6	7.9
1790	57	2346	0.73804	20.56	21.1	19.69	7.98
1818	58	2361	0.71934	20.01	21.66	19.78	7.74
1845	59	2376	0.7088	19.7	22.06	19.87	7.4
1873	60	2391	0.70506	19.59	22.37	19.96	7.49
1901	61	2406	0.70778	19.67	21.8	20.05	7.74
1928	62	2421	0.70438	19.57	18.11	20.14	7.02
1955	63	2436	0.72104	20.06	12.91	20.23	5.89
1982	64	2451	0.73192	20.38	7.21	20.32	5.71
2009	65	2466	0.74042	20.63	7.48	20.41	6.05
2036	66	2481	0.75606	21.09	8.04	20.5	6.23
2063	67	2496	0.7496	20.9	15.03	20.59	6.31

2090	68	2511	0.73192	20.38	16.89	20.68	6.42
2116	69	2526	0.73192	20.38	18.99	20.77	6.55
2143	70	2541	0.73294	20.41	21.64	20.87	7.02
2170	71	2556	0.73566	20.49	23.98	21.11	7.78
2196	72	2571	0.7343	20.45	18.86	20.23	8.28
2222	73	2586	0.7513	20.95	15.25	32.91	8.52
2248	74	2601	0.75096	20.94	10.69	33.38	8.36
2274	75	2616	0.75776	21.14	7.13	31.41	7.72
2300	76	2631	0.76184	21.26	8.89	38.06	7.12
2326	77	2646	0.76898	21.47	17.65	39.23	6.57
2352	78	2661	0.78428	21.92	8.5	39.71	6.23
2378	79	2676	0.77272	21.58	10.01	36.23	6.26
2403	80	2691	0.76048	21.22	11.85	30.18	6.26
2429	81	2706	0.75334	21.01	15.89	26.31	6.22
2454	82	2721	0.7394	20.6	12.64	38.3	6.16
2479	83	2736	0.7275	20.25	13.9	26.6	6.1
2505	84	2751	0.71594	19.91	18.45	18.68	6.06
2530	85	2766	0.75198	20.97	18.59	17.2	6.09
2555	86	2781	0.75572	21.08	17.11	16	6.1
2579	87	2796	0.76082	21.23	17.15	17.55	6.01
2604	88	2811	0.76218	21.27	15.11	19.58	5.93
2629	89	2826	0.75708	21.12	15.14	18.86	5.93
2654	90	2841	0.76184	21.26	14.32	23.26	5.96
2678	91	2856	0.77374	21.61	12.73	24.73	6.18
2703	92	2871	0.76592	21.38	13.32	22.13	6.4
2727	93	2886	0.74654	20.81	25.32	24.04	6.52
2751	94	2902	0.73634	20.51	14.86	25.78	6.63
2775	95	2917	0.73158	20.37	13.36	21.25	6.83
2799	96	2932	0.71424	19.86	25.83	25.72	7.02
2823	97	2947	0.72852	20.28	17.12	24.7	7.22
2847	98	2962	0.74042	20.63	11.44	19.75	7.41
2871	99	2977	0.77136	21.54	13.34	21.44	7.75
2895	100	2992	0.74994	20.91	14.47	17.54	8.09
2918	101	3007	0.73362	20.43	15.86	23.2	7.76
2942	102	3022	0.72818	20.27	16.69	25.42	7.38
2965	103	3037	0.72308	20.12	15.44	25.11	7.59
2989	104	3052	0.70166	19.49	12.49	26.56	7.89
3012	105	3067	0.70506	19.59	11.49	29.16	8.18

3035	106	3082	0.71764	19.96	10.97	34.12	8.48
3058	107	3097	0.72444	20.16	6.66	37.31	7.84
3081	108	3112	0.73056	20.34	7.94	36.22	6.97
3104	109	3127	0.73396	20.44	9.71	35.2	6.61
3127	110	3142	0.72954	20.31	12.98	30.82	6.4
3150	111	3157	0.72784	20.26	15.35	27.04	6.63
3172	112	3172	0.7275	20.25	17.38	23.99	6.74
3195	113	3187	0.72716	20.24	19.4	20.94	6.72
3217	114	3202	0.72852	20.28	21.59	17.88	6.6
3240	115	3217	0.73838	20.57	23.78	19.05	6.42
3262	116	3232	0.74552	20.78	20.05	22.58	6.68
3284	117	3247	0.75504	21.06	16.33	30.12	7.22
3307	118	3262	0.7649	21.35	12.98	40.34	6.92
3329	119	3277	0.7666	21.4	15.17	44.21	6
3351	120	3292	0.76082	21.23	16.22	42.81	5.57
3372	121	3307	0.74926	20.89	16.33	41.87	5.56
3394	122	3322	0.7377	20.55	21.72	18.89	6.01
3416	123	3337	0.73124	20.36	20.66	18.57	6.93
3438	124	3352	0.73022	20.33	12.41	19.49	7.11
3459	125	3367	0.73328	20.42	13.56	27.11	6.41
3481	126	3382	0.73532	20.48	13.78	22.74	6.21
3502	127	3397	0.73634	20.51	11.97	21.41	6.71
3523	128	3412	0.7241	20.15	14.25	18.93	7.13
3545	128	3427	0.71628	19.92	15.11	27.72	7.42
3566	129	3442	0.72002	20.03	12.35	30.41	7.42
3587	130	3457	0.7224	20.1	12.74	32.38	6.87
3608	131	3472	0.72716	20.24	14.72	31.59	6.36
3629	132	3487	0.73838	20.57	18.95	29.29	5.99
3649	133	3502	0.74348	20.72	17.25	27.41	5.89
3670	134	3517	0.76218	21.27	15.63	29.09	6.55
3691	135	3532	0.77952	21.78	14.1	34.1	6.9
3711	136	3547	0.7734	21.6	10.35	37.34	6.02
3732	137	3562	0.7564	21.1	13.99	37.23	5.34
3752	138	3577	0.73804	20.56	19.9	25	5.61
3773	139	3592	0.74926	20.89	19.07	23.73	5.86
3793	140	3607	0.74756	20.84	19.95	21.85	5.93
3813	141	3622	0.74484	20.76	21.81	21.35	6
3833	142	3637	0.74008	20.62	22.86	20.95	6.15

3853	143	3652	0.72988	20.32	23.05	19.04	6.28
3873	144	3667	0.73566	20.49	22.55	18.4	6.08
3893	145	3682	0.7479	20.85	21.29	19.74	5.89
3913	146	3697	0.75334	21.01	20.16	24.21	6.3
3932	147	3712	0.76218	21.27	18.7	17.28	6.71
3952	148	3727	0.75742	21.13	20.08	20.76	6.7
3972	149	3742	0.74552	20.78	21.21	22.46	6.67
3991	150	3757	0.73294	20.41	16.02	22.74	6.57
4011	151	3772	0.74178	20.67	16.54	21.46	6.46
4030	152	3787	0.74824	20.86	15.92	21.46	6.7
4049	153	3802	0.7462	20.8	13.1	29.38	6.97
4068	154	3817	0.7411	20.65	11.65	37.16	7.25
4087	155	3832	0.73022	20.33	12.81	38.3	7.53
4107	156	3847	0.70778	19.67	19.18	34.09	6.79
4125	157	3862	0.71458	19.87	20.6	31.2	5.82
4144	158	3877	0.76796	21.44	20.51	26.87	5.78
4163	159	3892	0.76592	21.38	19.91	24.86	6.04
4182	160	3907	0.75334	21.01	17.33	30.91	6.09
4201	161	3922	0.7292	20.3	14.45	27.76	6.05
4219	162	3937	0.71288	19.82	12.81	28.92	6.32
4238	163	3952	0.7071	19.65	11.72	31.61	6.73
4256	164	3967	0.70132	19.48	11.29	30.03	6.75
4275	165	3982	0.70744	19.66	12.82	33.22	6.55
4293	166	3997	0.71458	19.87	15.3	35.63	6.78
4311	167	4012	0.74484	20.76	17.81	30.43	7.28
4329	168	4027	0.7666	21.4	20.2	24.86	7.13
4347	169	4042	0.76286	21.29	18.86	22.93	6.48
4366	170	4057	0.7496	20.9	17.46	33.31	6.34
4383	171	4072	0.72784	20.26	20.83	24.35	6.68
4401	172	4087	0.73566	20.49	19.84	24.86	7.14
4419	173	4102	0.74824	20.86	16.26	25.05	7.76
4437	174	4117	0.75436	21.04	13.51	26.26	8.29
4455	175	4132	0.75674	21.11	11.13	30.53	8.73
4472	176	4147	0.7598	21.2	10.64	38.85	8.23
4490	177	4162	0.76898	21.47	12.33	20.13	6.32
4507	178	4177	0.74654	20.81	17.8	25.07	5.17
4525	179	4192	0.72784	20.26	20.89	30.01	5.39
4542	180	4207	0.7258	20.2	18.04	29.21	5.74

4559	181	4222	0.73566	20.49	14.55	24.43	6.36
4577	182	4237	0.72716	20.24	14.43	24.91	6.83
4594	183	4252	0.71866	19.99	14.31	25.39	6.9
4611	184	4267	0.72274	20.11	17.86	30.61	6.95
4628	185	4282	0.72818	20.27	21.67	26.12	6.92
4645	186	4297	0.72444	20.16	21.84	27.97	6.95
4662	187	4312	0.72512	20.18	21.09	23.87	7.21
4679	188	4327	0.72682	20.23	19.99	25.5	7.33
4695	189	4342	0.73634	20.51	17.77	25.07	6.68
4712	190	4357	0.74994	20.91	14.58	36.82	6.26
4729	191	4372	0.7377	20.55	10.32	30.88	7.66
4745	192	4387	0.74246	20.69	7.89	32.95	8.87
4762	193	4402	0.75878	21.17	6.89	43.61	7.85
4778	194	4417	0.76966	21.49	8.1	38.31	6.87
4795	195	4432	0.7632	21.3	12.88	40.78	7.41
4811	196	4447	0.74042	20.63	20.92	33.23	7.95
4827	197	4462	0.73192	20.38	7.99	35.45	8.29
4844	198	4477	0.73532	20.48	10.47	38.41	8.64
4860	199	4492	0.72954	20.31	16.37	46.87	8.49
4876	200	4507	0.73226	20.39	14.52	40.64	8.32
4892	201	4522	0.74212	20.68	17.15	38.59	7.59
4908	202	4537	0.73158	20.37	18.85	31.44	6.81
4924	203	4552	0.73566	20.49	24.2	26.88	6.96
4940	204	4567	0.71696	19.94	21.13	42.85	7.25
4955	205	4582	0.71356	19.84	22.3	24.61	7.29
4971	206	4597	0.7173	19.95	28.85	22.29	7.28
4987	207	4612	0.70506	19.59	23.73	22.86	7.04
5002	208	4628	0.73056	20.34	20.17	21.62	6.74
5018	209	4643	0.74552	20.78	21.52	24.21	7.23
5033	210	4658	0.76048	21.22	18.32	21.61	8
5049	211	4673	0.74892	20.88	14.72	20.48	7.98
5064	212	4688	0.75266	20.99	17.74	23.54	7.63
5079	213	4703	0.75708	21.12	20.08	26.68	6.97
5095	214	4718	0.76048	21.22	18.56	23.57	6.15
5110	215	4733	0.76626	21.39	26.52	24.47	5.8
5125	216	4748	0.75776	21.14	20.67	22.09	5.74
5140	217	4763	0.7683	21.45	21	22.98	5.77
5155	218	4778	0.76354	21.31	18.83	27.77	5.86

5170	219	4793	0.76082	21.23	22.29	20.48	5.88
5185	220	4808	0.75708	21.12	16.1	19.87	5.86
5200	221	4823	0.75504	21.06	15.27	20.7	5.85
5215	221	4838	0.75266	20.99	14.45	21.53	5.88
5230	222	4853	0.75062	20.93	13.62	22.36	5.96
5244	223	4868	0.74858	20.87	12.79	23.19	6.11
5259	224	4883	0.74586	20.79	12.21	24.02	6.41
5274	225	4898	0.7428	20.7	11.99	24.19	6.89
5288	226	4913	0.7615	21.25	11.76	23.35	7.33
5303	227	4928	0.74348	20.72	15.94	20.59	7.67
5317	228	4943	0.73702	20.53	16.2	19.22	7.94
5331	229	4958	0.7343	20.45	15.65	21.05	8.07
5346	230	4973	0.753	21	14.63	23.06	7.9
5360	231	4988	0.7275	20.25	15.66	25.49	7
5374	232	5003	0.7241	20.15	17.13	25.7	6.33
5389	233	5018	0.73056	20.34	17.28	25.25	6.35
5403	234	5033	0.7513	20.95	17.15	24.81	6.33
5417	235	5048	0.74926	20.89	14.84	24.36	6.19
5431	236	5063	0.74382	20.73	14.71	23.96	6.14
5445	237	5078	0.74722	20.83	15.98	23.79	6.47
5459	238	5093	0.74416	20.74	16.68	23.62	6.75
5473	239	5108	0.75266	20.99	13.45	23.87	6.77
5486	240	5123	0.74042	20.63	14.13	27.34	6.79
5500	241	5138	0.75776	21.14	11.62	25.06	6.81
5514	242	5153	0.75164	20.96	15.5	18.99	6.84
5528	243	5168	0.76082	21.23	14.36	18.46	6.94
5541	244	5183	0.7598	21.2	14.26	17.93	7.04
5555	245	5198	0.74416	20.74	18.52	17.4	7.02
5568	246	5213	0.7462	20.8	13.79	17.61	7
5582	247	5228	0.73634	20.51	14.31	19.96	6.97
5595	248	5243	0.74858	20.87	17.25	18.44	6.95
5609	249	5258	0.74212	20.68	15.29	21.55	6.99
5622	250	5273	0.73634	20.51	15.59	20.75	7.03
5635	251	5288	0.75062	20.93	17.05	19.59	7
5649	252	5303	0.74824	20.86	14.65	18.43	6.96
5662	253	5318	0.74756	20.84	12.55	17.27	6.89
5675	254	5333	0.7632	21.3	16.39	16.11	6.83
5688	255	5348	0.74994	20.91	16.35	17.42	6.88

5701	256	5363	0.75606	21.09	13.87	18.14	6.96
5714	257	5378	0.76116	21.24	13.87	16.2	7.1
5727	258	5393	0.75742	21.13	14.65	15.09	7.27
5740	259	5408	0.7581	21.15	15.45	14.27	7.41
5753	260	5423	0.7649	21.35	15.92	15.06	7.53
5766	261	5438	0.7649	21.35	14.01	14.97	7.67
5779	262	5453	0.76524	21.36	14.6	14.49	7.8
5792	263	5468	0.76422	21.33	14.41	13.95	7.46
5805	264	5483	0.76048	21.22	14.69	14.1	6.86
5817	265	5498	0.76252	21.28	15.81	14.67	6.31
5830	266	5513	0.76898	21.47	17.47	15.24	5.78
5842	267	5528	0.76592	21.38	17.27	15.75	5.98
5855	268	5543	0.75572	21.08	15.65	15.41	6.73
5868	269	5558	0.75232	20.98	12.46	15.06	6.56
5880	270	5573	0.76898	21.47	9.73	14.4	5.54
5893	271	5588	0.75368	21.02	11.06	14.4	4.91
5905	272	5603	0.753	21	13.09	15.08	4.68
5917	273	5618	0.7598	21.2	14.79	14.56	4.65
5930	274	5633	0.7479	20.85	16.1	14.3	4.89
5942	275	5648	0.74858	20.87	15.12	14.47	4.91
5954	276	5663	0.7496	20.9	13.5	14.64	4.61
5966	277	5678	0.74382	20.73	14.57	14.53	4.64
5979	278	5693	0.75334	21.01	13.49	13.94	5.24
5991	279	5708	0.75878	21.17	13.41	14.04	5.45
6003	280	5723	0.76082	21.23	12.42	14.28	4.85
6015	281	5738	0.75742	21.13	12.49	17.53	4.51
6027	282	5753	0.75742	21.13	10.3	22.18	4.84
6039	283	5768	0.75946	21.19	13.23	28.51	5.14
6051	284	5783	0.75606	21.09	12.81	30.19	5.38
6063	285	5798	0.76082	21.23	10.53	28.7	5.59
6075	286	5813	0.76422	21.33	9.77	21.35	5.69
6087	287	5828	0.75674	21.11	10.93	26.02	5.79
6099	288	5843	0.74654	20.81	12.75	30.29	5.92
6110	289	5858	0.753	21	9.6	35.36	5.99
6122	290	5873	0.7445	20.75	9.12	32.98	5.59
6134	291	5888	0.74246	20.69	9.27	28.57	5.24
6145	292	5903	0.74008	20.62	9.83	28.83	5.34
6157	293	5918	0.7377	20.55	10.4	29.09	5.45

6169	294	5933	0.73532	20.48	10.97	29.35	5.66
6180	295	5948	0.73294	20.41	11.53	29.61	5.86
6192	296	5963	0.73056	20.34	12.1	29.87	5.58
6203	297	5978	0.73158	20.37	12.89	30.13	5.3
6215	298	5993	0.7377	20.55	12.18	31.1	5.6
6226	299	6008	0.74416	20.74	12.52	31.73	5.92
6238	300	6023	0.74518	20.77	10.76	31.84	5.98
6249	301	6038	0.7394	20.6	11.48	34.43	6.02
6260	302	6053	0.73464	20.46	14.46	35.07	6.12
6272	303	6068	0.72988	20.32	13.3	34.34	6.24
6283	304	6083	0.7309	20.35	11.57	31.59	6.09
6294	305	6098	0.7428	20.7	10.98	28.57	5.89
6306	306	6113	0.73702	20.53	14.5	28.36	5.83
6317	307	6128	0.73158	20.37	16.16	35.5	5.81
6328	308	6143	0.73974	20.61	18.3	34.67	5.87
6339	309	6158	0.74008	20.62	18.68	31.58	5.96
6350	310	6173	0.73668	20.52	18.22	29.56	6.05
6361	311	6188	0.73022	20.33	16.6	27.31	6.14
6372	312	6203	0.72818	20.27	19.47	24.97	6.2
6383	313	6218	0.73056	20.34	18.74	23.55	6.24
6394	314	6233	0.73532	20.48	16.48	27.55	6.16
6405	314	6248	0.73906	20.59	17.18	28.23	6.01
6416	315	6263	0.7377	20.55	18.21	26.57	5.96
6427	316	6278	0.73362	20.43	19.45	22.1	5.97
6438	317	6293	0.73634	20.51	20.23	21.09	5.98
6449	318	6308	0.73804	20.56	20	22.78	5.98
6460	319	6323	0.73906	20.59	18.86	17.81	6.02
6471	320	6339	0.73498	20.47	15.73	16.41	6.11
6482	321	6354	0.73532	20.48	14.34	18.73	6.19
6492	322	6369	0.74042	20.63	14.91	17.88	6.25
6503	323	6384	0.7326	20.4	15.15	16.69	6.22
6514	324	6399	0.73124	20.36	15.54	15.24	6.07
6525	325	6414	0.7411	20.65	16.17	20.66	5.88
6535	326	6429	0.7445	20.75	14.87	23.26	5.66
6546	327	6444	0.74552	20.78	13.58	19.64	5.52
6557	328	6459	0.7445	20.75	12.84	19.14	5.54
6567	329	6474	0.7411	20.65	13.91	19.25	5.64
6578	330	6489	0.7377	20.55	14.77	19.36	5.89

6588	331	6504	0.74008	20.62	14.99	20.29	6.16
6599	332	6519	0.74892	20.88	17.71	20.23	6.52
6609	333	6534	0.74722	20.83	20.59	20.63	6.78
6620	334	6549	0.74042	20.63	22.25	24	6.72
6630	335	6564	0.7428	20.7	18.92	24.44	6.67
6641	336	6579	0.74688	20.82	17.39	23.23	6.62
6651	337	6594	0.7513	20.95	16.79	20.31	6.57
6662	338	6609	0.75708	21.12	16.54	19.2	6.52
6672	339	6624	0.75266	20.99	18.25	19.32	6.44
6682	340	6639	0.74246	20.69	20.8	21.04	6.2
6693	341	6654	0.74348	20.72	18.81	22.69	5.98
6703	342	6669	0.7428	20.7	18.66	24.32	5.92
6713	343	6684	0.74076	20.64	19.95	26.89	5.87
6724	344	6699	0.74348	20.72	18.64	27.23	5.87
6734	345	6714	0.74586	20.79	17.32	25.42	5.86
6744	346	6729	0.7547	21.05	17.35	23.61	6.06
6755	347	6744	0.74212	20.68	18.95	16.59	6.27
6765	348	6759	0.74314	20.71	17.39	22.79	6.1
6775	349	6774	0.7496	20.9	15.38	30.51	5.91
6785	350	6789	0.76116	21.24	13.75	31.47	6.1
6795	351	6804	0.75266	20.99	20.06	33.98	6.33
6806	352	6819	0.74348	20.72	22.74	27.41	6.29
6816	353	6834	0.7513	20.95	18.64	22.97	6.21
6826	354	6849	0.75402	21.03	14.39	22.7	6.43
6836	355	6864	0.7411	20.65	12.44	22.43	6.72
6846	356	6879	0.74042	20.63	12.59	22.2	7.05
6856	357	6894	0.74756	20.84	15.45	22.1	7.39
6866	358	6909	0.74824	20.86	19.72	22	7.66
6876	359	6924	0.7479	20.85	20.17	21.9	7.9
6886	360	6939	0.74654	20.81	19.21	21.77	7.31
6896	361	6954	0.74382	20.73	20.26	22.57	6.38
6906	362	6969	0.74314	20.71	17.75	24.11	6.03
6916	363	6984	0.73804	20.56	16.32	27.42	5.99
6926	364	6999	0.73294	20.41	14.93	30.64	6.03
6936	365	7014	0.73566	20.49	15.03	33	6.1
6946	366	7029	0.74212	20.68	16.55	33.57	6
6956	367	7044	0.73906	20.59	13.68	30.06	5.78
6966	368	7059	0.74382	20.73	15.51	27.8	5.69

6976	369	7074	0.74314	20.71	16.92	29.52	5.72
6986	370	7089	0.73736	20.54	17.93	31.18	5.65
6996	371	7104	0.74212	20.68	17.53	32.83	5.47
7006	372	7119	0.74382	20.73	17.33	34.48	5.44
7016	373	7134	0.74178	20.67	17.4	27.51	5.57
7026	374	7149	0.74042	20.63	18.02	24.9	5.61
7035	375	7164	0.74008	20.62	18.14	29.23	5.53
7045	376	7179	0.74144	20.66	17.44	24.15	5.51
7055	377	7194	0.7462	20.8	19.26	20.1	5.6
7065	378	7209	0.75164	20.96	19.97	20.28	5.64
7075	379	7224	0.7564	21.1	17.62	20.46	5.57
7085	380	7239	0.74688	20.82	17.38	20.42	5.46
7094	381	7254	0.73566	20.49	17.71	19.84	5.28
7104	382	7269	0.72954	20.31	18.11	18.79	5.26
7114	383	7284	0.73022	20.33	20.7	17.87	5.75
7124	384	7299	0.73498	20.47	21.98	17.88	6.14
7134	385	7314	0.74416	20.74	15.37	17.54	6.18
7143	386	7329	0.7445	20.75	15.01	17.2	6.24
7153	387	7344	0.74042	20.63	17.16	17.52	6.39
7163	388	7359	0.7343	20.45	16.5	17.87	6.49
7173	389	7374	0.72818	20.27	17.42	18.17	6.28
7183	390	7389	0.72342	20.13	19.04	17.9	6.1
7192	391	7404	0.73464	20.46	17.59	17.93	6.24
7202	392	7419	0.73634	20.51	16.13	18.19	6.39
7212	393	7434	0.73056	20.34	14.76	18.81	6.68
7222	394	7449	0.73906	20.59	17.59	19.02	6.98
7231	395	7464	0.73974	20.61	18.9	18.82	6.67
7241	396	7479	0.73226	20.39	18.67	17.1	6.37
7251	397	7494	0.72988	20.32	16.47	17.82	6.18
7260	398	7509	0.7309	20.35	15.33	21.5	5.99
7270	399	7524	0.73566	20.49	15.63	20.64	6.03
7280	400	7539	0.7343	20.45	17.02	19.06	6.08
7290	401	7554	0.73634	20.51	17.86	16.94	6.28
7299	402	7569	0.74586	20.79	17.58	16.7	6.5
7309	403	7584	0.7513	20.95	15.01	16.67	6.58
7319	404	7599	0.75504	21.06	13.69	16.46	6.63
7329	405	7614	0.75674	21.11	16.07	17.26	6.6
7338	406	7629	0.75538	21.07	15.86	18.95	6.55

7348	406	7644	0.75334	21.01	14.88	22.32	6.54
7358	407	7659	0.7513	20.95	13.79	20.78	6.54
7367	408	7674	0.7513	20.95	15.96	18.01	6.49
7377	409	7689	0.75198	20.97	18.46	17.15	6.43
7387	410	7704	0.75198	20.97	16.94	17.82	6.36
7397	411	7719	0.75436	21.04	15.96	19.1	6.29
7406	412	7734	0.75674	21.11	15.35	19.84	6.36
7416	413	7749	0.7496	20.9	15.47	20.91	6.51
7426	414	7764	0.75062	20.93	16.15	22.18	6.64
7435	415	7779	0.7343	20.45	12.37	20.24	6.76
7445	416	7794	0.74552	20.78	6.78	21.62	6.79
7455	417	7809	0.73396	20.44	7.03	22.16	6.98
7465	418	7824	0.73906	20.59	6.96	22.78	7.37
7474	419	7839	0.74314	20.71	7.58	22.83	7.51
7484	420	7854	0.74654	20.81	8.88	24.87	7.4
7494	421	7869	0.75368	21.02	9.93	25.5	7.6
7504	422	7884	0.76082	21.23	10.98	24.42	8.17
7513	423	7899	0.75844	21.16	9.89	23.82	8.47
7523	424	7914	0.75198	20.97	8.92	23.91	8.36
7533	425	7929	0.74042	20.63	8.39	24.45	8.13
7543	426	7944	0.73532	20.48	11.64	25.05	7.67
7553	427	7959	0.7343	20.45	13.61	25.65	7.14
7562	428	7974	0.74008	20.62	11.83	22.12	6.47
7572	429	7989	0.74824	20.86	13.86	21.19	6
7582	430	8004	0.74926	20.89	15.74	28.6	6.03
7592	431	8019	0.72988	20.32	14.74	32.91	6.07
7601	432	8034	0.73464	20.46	13.64	34.38	6.19
7611	433	8049	0.7428	20.7	12.98	29.76	6.3
7621	434	8065	0.73396	20.44	14.1	25.4	6.37
7631	435	8080	0.72716	20.24	15.26	21.15	6.43
7641	436	8095	0.73226	20.39	16.57	22.65	6.39
7651	437	8110	0.73702	20.53	17.88	27.06	6.37
7661	438	8125	0.73872	20.58	17.54	31.45	6.43
7670	439	8140	0.73906	20.59	16.17	35.74	6.48
7680	440	8155	0.7377	20.55	15.4	39.58	6.38
7690	441	8170	0.73566	20.49	15.06	37.35	6.29
7700	442	8185	0.73124	20.36	14.08	35.16	6.22
7710	443	8200	0.72478	20.17	12.56	34.49	6.14

7720	444	8215	0.7258	20.2	12.62	33.81	6
7730	445	8230	0.73396	20.44	14.28	32.99	5.87
7740	446	8245	0.73056	20.34	15.15	32.16	5.94
7750	447	8260	0.73022	20.33	14.87	31.34	6.02
7760	448	8275	0.73498	20.47	13.16	29.11	5.99
7770	449	8290	0.73804	20.56	14.52	28.29	5.94
7780	450	8305	0.73974	20.61	15.95	29.73	6.19
7790	451	8320	0.73906	20.59	16.97	28.09	6.49
7800	452	8335	0.7411	20.65	14.59	25.97	6.31
7810	453	8350	0.74008	20.62	12.86	23.85	6.04
7820	454	8365	0.73158	20.37	13.88	20.8	6.11
7830	455	8380	0.73566	20.49	12.97	17.53	6.26
7840	456	8395	0.74008	20.62	12.18	14.27	6.3
7850	457	8410	0.73328	20.42	13.3	13.68	6.31
7860	458	8425	0.73362	20.43	14.63	14.03	6.32
7870	459	8440	0.73634	20.51	15.92	14.37	6.34
7880	460	8455	0.7377	20.55	16.75	14.51	6.69
7891	461	8470	0.74178	20.67	14.81	15.45	7.19
7901	462	8485	0.74586	20.79	12.1	21.32	7.21
7911	463	8500	0.74688	20.82	13.34	19.9	6.97
7921	464	8515	0.75198	20.97	13.98	14.59	6.76
7931	465	8530	0.75844	21.16	14.36	14.82	6.57
7942	466	8545	0.7496	20.9	16.34	15.05	6.54
7952	467	8560	0.74246	20.69	16.36	15.29	6.63
7962	468	8575	0.73702	20.53	14.73	15.52	6.7
7972	469	8590	0.74212	20.68	13.13	15.75	6.77
7983	470	8605	0.74076	20.64	13.26	15.99	6.81
7993	471	8620	0.73294	20.41	15.29	16.22	6.82
8003	472	8635	0.73634	20.51	14.66	16.36	6.8
8014	473	8650	0.73804	20.56	15.14	16.37	6.72
8024	474	8665	0.73668	20.52	17.35	16.39	6.76
8034	475	8680	0.74008	20.62	16.24	16.62	6.97
8045	476	8695	0.74552	20.78	15.41	17.22	7.11
8055	477	8710	0.75368	21.02	15.82	14.98	7.13
8066	478	8725	0.7496	20.9	16.72	13.89	7.11
8076	479	8740	0.74552	20.78	16.93	16.4	7
8087	480	8755	0.74722	20.83	15.26	19.2	7.01
8097	481	8770	0.75232	20.98	15.43	21.06	7.37

8108	482	8785	0.7547	21.05	16.17	20.01	7.58
8118	483	8800	0.7462	20.8	16.92	20.39	7.34
8129	484	8815	0.7377	20.55	17.67	20.93	7.06
8140	485	8830	0.7309	20.35	18.23	21.31	6.92
8150	486	8845	0.73192	20.38	17.86	22.56	7.75
8161	487	8860	0.73634	20.51	17.32	24.24	6.53
8172	488	8875	0.74178	20.67	16.68	25.91	6.91
8182	489	8890	0.73804	20.56	16.05	24.26	7.24
8193	490	8905	0.74552	20.78	16.69	20.77	7.16
8204	491	8920	0.7598	21.2	18.17	21.53	7.09
8215	492	8935	0.75708	21.12	18.07	22.3	7.05
8225	493	8950	0.75198	20.97	18.38	23.11	7.02
8236	494	8965	0.74382	20.73	19.05	27.9	7.3
8247	495	8980	0.7343	20.45	18.27	30.63	7.59
8258	496	8995	0.74144	20.66	17.48	31.12	7.55
8269	497	9010	0.74926	20.89	16.68	23.32	7.5
8280	498	9025	0.7513	20.95	14.57	19.4	7.53
8291	499	9040	0.74994	20.91	13	21.4	7.56
8302	499	9055	0.74484	20.76	12.38	21.79	7.74
8313	500	9070	0.7445	20.75	14.51	21.2	7.94
8324	501	9085	0.7428	20.7	16.2	19.21	7.59
8335	502	9100	0.73804	20.56	16.21	19.3	7.15
8346	503	9115	0.73702	20.53	15.41	20.06	7.25
8357	504	9130	0.7377	20.55	14.42	21.39	7.47
8368	505	9145	0.73974	20.61	13.45	21.32	7.91
8380	506	9160	0.75402	21.03	13.02	21.88	8.41
8391	507	9175	0.76796	21.44	13.3	25.79	8.01
8402	508	9190	0.76524	21.36	15.39	23.13	7.27
8413	509	9205	0.76422	21.33	17.2	18.78	7.12
8425	510	9220	0.76218	21.27	18.29	19.33	7.23
8436	511	9235	0.75402	21.03	16.1	19.48	7.18
8447	512	9250	0.75368	21.02	15.32	19.54	7.04
8459	513	9265	0.7581	21.15	15.4	20.67	7.14
8470	514	9280	0.76558	21.37	15.55	20.57	7.41
8482	515	9295	0.76558	21.37	15.34	19.59	7.53
8493	516	9310	0.7598	21.2	14.8	18.74	7.53
8505	517	9325	0.7598	21.2	11.95	18.74	7.68
8516	518	9340	0.76184	21.26	11.43	19.49	7.98

8528	519	9355	0.76558	21.37	13.19	18.67	8.11
8539	520	9370	0.76694	21.41	13.68	19.44	8.07
8551	521	9385	0.77136	21.54	13.87	22.08	8
8563	522	9400	0.77952	21.78	13.74	19.83	7.88
8574	523	9415	0.77544	21.66	11.05	20.07	7.73
8586	524	9430	0.7717	21.55	9.53	24.52	7.54
8598	525	9445	0.77034	21.51	10.28	28.97	7.64
8610	526	9460	0.77136	21.54	10.59	29.81	8.27
8622	527	9475	0.77204	21.56	10.29	23.8	8.64
8634	528	9490	0.77306	21.59	8.85	22.07	8.44
8646	529	9505	0.76218	21.27	11.76	20.96	8.29
8658	530	9520	0.7547	21.05	14.01	18.88	8.23
8670	531	9535	0.7649	21.35	11.17	18.8	8.17
8682	532	9550	0.76626	21.39	10.99	19.39	8.08
8694	533	9565	0.76388	21.32	11.61	19.99	8.05
8706	534	9580	0.7615	21.25	11.51	20.82	8.27
8718	535	9595	0.76388	21.32	11.51	21.75	8.52
8730	536	9610	0.76728	21.42	11.55	22.69	8.95
8742	537	9625	0.7615	21.25	11.59	22.64	9.3
8755	538	9640	0.75368	21.02	9.65	21.7	8.97
8767	539	9655	0.76218	21.27	11.23	17.8	8.66
8779	540	9670	0.77034	21.51	12.81	19.16	8.62
8792	541	9685	0.77646	21.69	11.98	24.59	8.6
8804	542	9700	0.78122	21.83	9.22	31.32	9.1
8817	543	9715	0.77816	21.74	10.34	31.46	9.6
8829	544	9730	0.77272	21.58	11.44	25.23	8.64
8842	545	9745	0.76524	21.36	12.51	24.61	7.67
8854	546	9760	0.76728	21.42	11.54	24.55	7.51
8867	547	9776	0.76558	21.37	10.93	25.02	7.39
8880	548	9791	0.7581	21.15	10.97	25.48	7.42
8892	549	9806	0.75776	21.14	10.93	26.4	7.46
8905	550	9821	0.75504	21.06	10.95	28.05	7.54
8918	551	9836	0.74756	20.84	11.07	28.53	7.64
8931	552	9851	0.74552	20.78	11	27.76	7.31
8944	553	9866	0.74688	20.82	10.91	24.77	6.89
8956	554	9881	0.75368	21.02	10.84	20.4	7.31
8969	555	9896	0.75266	20.99	11.41	17.98	7.95
8982	556	9911	0.76184	21.26	11.19	22.08	8.02

8995	557	9926	0.75878	21.17	10.91	25.24	7.89
9009	558	9941	0.7547	21.05	10.71	27.24	7.93
9022	559	9956	0.75572	21.08	10.41	26.08	8.04
9035	560	9971	0.75946	21.19	10.14	24.92	8.07
9048	561	9986	0.76048	21.22	10.35	23.76	8.06
9062	562	10001	0.75912	21.18	10.41	22.82	7.97
9075	563	10016	0.75674	21.11	10.34	23.54	7.85
9089	564	10031	0.7547	21.05	9.74	26.57	7.41

Data Table for Core ODP 1228D

Data used in Chapter 1.

Depth (m)	Depth (cm)	Age (yrs)*	Age (yrs)**	UK'37	SST (C)	C ₃₇ total (nmol/g)	δ ¹⁵ N (‰)
0.1	10	-252.85	430	0.79074	22.11	53.94	5.28
0.12	12	-204.83	430	0.79618	22.27	46.73	5.21
0.14	14	-155.95	431	0.79074	22.11	48.8	5.43
0.16	16	-106.21	432	0.78598	21.97	54.64	5.28
0.18	18	-55.6	434	0.78904	22.06	53.08	5.33
0.2	20	-4.13	437	0.78938	22.07	54.85	5.35
0.22	22	48.2	440	0.79482	22.23	61.37	5.6
0.24	24	101.39	444	0.7955	22.25	50.17	5.6
0.26	26	155.45	448	0.79278	22.17	38.93	5.46
0.28	28	210.37	453	0.79618	22.27	46.36	5.21
0.3	30	266.15	458	0.78904	22.06	48.92	5.07
0.32	32	322.79	464	0.7921	22.15	53.44	5.22
0.34	34	380.3	470	0.79686	22.29	56.73	5.3
0.36	36	438.67	477	0.79244	22.16	53.4	5.33
0.38	38	497.9	485	0.804	22.5	60.36	5.81
0.4	40	557.99	493	0.79482	22.23	52.6	5.21
0.42	42	618.95	501	0.7972	22.3	52.05	5.25
0.44	44	680.76	510	0.80162	22.43	48.66	5.5
0.46	46	743.44	520	0.7955	22.25	41.45	5.68
0.48	48	806.99	530	0.80842	22.63	47.71	5.28
0.5	50	871.39	541	0.80264	22.46	42.73	5.44
0.52	52	936.66	552	0.79992	22.38	37.38	5.91
0.54	54	1002.79	564	0.79822	22.33	32.39	6.13
0.56	56	1069.78	576	0.80604	22.56	29.52	6.21
0.58	58	1137.63	589	0.81998	22.97	22.62	6.49
0.6	60	1206.35	603	0.84276	23.64	16.2	6.03
0.62	62	1275.93	616	0.79924	22.36	32.29	5.74

0.64	64	1346.37	631	0.79584	22.26	36.17	5.8
0.66	66	1417.67	646	0.79652	22.28	37.06	5.63
0.68	68	1489.84	662	0.80128	22.42	37.02	5.66
0.7	70	1562.87	678	0.79856	22.34	33.04	5.99
0.72	72	1636.76	694	0.80808	22.62	46.63	6
0.74	74	1711.51	712	0.80026	22.39	27.17	5.37
0.76	76	1787.13	729	0.80672	22.58	54.73	5.5
0.78	78	1863.61	748	0.80366	22.49	49.51	5.53
0.8	80	1940.95	767	0.81556	22.84	49.93	5.14
0.82	82	2019.15	786	0.81522	22.83	54.79	5.18
0.84	84	2098.22	806	0.81726	22.89	58.91	5.66
0.86	86	2178.15	827	0.81998	22.97	65.48	6.18
0.88	88	2258.94	848	0.81148	22.72	57.72	5.62
0.9	90	2340.59	869	0.81148	22.72	66.52	5.71
0.92	92	2423.11	891	0.81284	22.76		5.84
0.94	94	2506.48	914	0.81352	22.78	76.83	6.31
0.96	96	2590.72	937	0.8227	23.05	62.29	5.89
0.98	98	2675.83	961	0.81318	22.77	66.15	6.07
1	100	2761.79	985	0.81284	22.76	73.05	5.98
1.02	102	2848.62	1010	0.81896	22.94	71.89	5.9
1.04	104	2936.31	1035	0.80944	22.66	81.2	5.64
1.06	106	3024.86	1061	0.81148	22.72	80.64	5.56
1.08	108	3114.27	1088	0.81964	22.96	66.19	5.69
1.1	110	3204.55	1115	0.86214	24.21	41.96	5.79
1.12	112	3295.69	1142	0.8159	22.85	73.15	6.1
1.14	114	3387.69	1170	0.81114	22.71	76.35	5.99
1.16	116	3480.55	1199	0.81556	22.84	73.59	6.19
1.18	118	3574.28	1228	0.83562	23.43	50.06	6.33
1.2	120	3668.87	1258	0.82984	23.26	55.22	5.8
1.22	122	3764.32	1288	0.80026	22.39	54.78	6.54
1.24	124	3860.63	1319	0.82134	23.01	65.07	5.48
1.26	126	3957.81	1350	0.82474	23.11	80.28	5.63
1.28	128	4055.85	1382	0.8244	23.1	77.66	5.92

1.3	130	4154.75	1415	0.82032	22.98	85.88	5.9
1.32	132	4254.51	1448	0.82406	23.09	59.98	6.46
1.34	134	4355.14	1481	0.81998	22.97	51.62	5.51
1.36	136	4456.63	1515	0.82372	23.08	41.04	6.39
1.38	138	4558.98	1550	0.8108	22.7		5.39
1.4	140	4662.19	1585	0.80604	22.56	74.02	5.52
1.42	142	4766.27	1621	0.80876	22.64	78.06	5.7
1.44	144	4871.2	1657	0.8091	22.65	48.17	6.52
1.46	146	4977	1694	0.82168	23.02	30.83	6.8
1.48	148	5083.67	1731	0.82304	23.06	42.85	6.27
1.5	150	5191.19	1769	0.81658	22.87	58.22	5.36
1.52	152	5299.58	1807	0.80842	22.63	66.43	5.66
1.54	154	5408.83	1846	0.80944	22.66	93.53	5.82
1.56	156	5518.94	1886	0.81352	22.78	59.24	5.38
1.58	158	5629.91	1926	0.8057	22.55	74.92	5.19
1.6	160	5741.75	1966	0.80332	22.48	69.8	5.56
1.62	162	5854.45	2007	0.81454	22.81	38.92	6.1
1.64	164	5968.01	2049	0.8108	22.7		6
1.66	166	6082.43	2091	0.80774	22.61	48.47	5.46
1.68	168	6197.72	2134	0.80162	22.43	68.63	4.74
1.7	170	6313.87	2177	0.79958	22.37	80.43	4.8
1.72	172	6430.88	2221	0.80944	22.66	68.9	5.08
1.74	174	6548.75	2266	0.80536	22.54	87.96	4.67
1.76	176	6667.49	2311	0.804	22.5	90.2	4.4
1.78	178	6787.09	2356	0.8142	22.8	79.63	4.76
1.8	180	6907.55	2402	0.80196	22.44	69.72	5.23
1.82	182	7028.87	2449	0.80434	22.51	26.34	5.03
1.84	184	7151.06	2496	0.79448	22.22	32.55	4.38
1.86	186	7274.11	2543	0.78802	22.03	31.79	5.08
1.88	188	7398.02	2590	0.77952	21.78	19.93	4.98
1.9	190	7522.79	2638	0.79516	22.24	22.54	4.88
1.92	192	7648.43	2686	0.78156	21.84	20.14	
1.94	194	7774.92	2733	0.77952	21.78	17.98	5.51

				0.79516			
1.96	196	7902.28	2781		22.24	7.39	5.44
				0.79822			
1.98	198	8030.51	2830 ?		22.33	5.82	5.85
				0.79346			
2	200	8159.59	?		22.19	9.05	5.01
				0.80366			
2.02	202	8289.54	?		22.49	11.03	5.22
				0.8006			
2.04	204	8420.35	8256 ?		22.4	2.45	
2.06	206	8552.02	8363	0.81964	22.96	7.22	5.02
2.08	208	8684.55	8471	0.81148	22.72	5.65	5.43
2.1	210	8817.95	8578	0.7989	22.35	3.81	5.24
2.12	212	8952.21	8686	0.82304	23.06	5.03	5.19
2.14	214	9087.33	8793	0.81828	22.92	9.6	5.69
2.16	216	9223.31	8901	0.81794	22.91	15.54	6.39
2.18	218	9360.16	9008	0.81726	22.89	13.55	6.12
2.2	220	9497.87	9115	0.8261	23.15	14.3	6.09
2.22	222	9636.44	9223	0.8159	22.85	16.08	
2.24	224	9775.87	9330	0.81352	22.78	16.36	6.01
2.26	226	9916.17	9438	0.82168	23.02	13.26	6.05
2.28	228	10057.33	9545	0.81046	22.69	14	5.73
2.3	230	10199.35	9652	0.82236	23.04	14.57	6.21
2.32	232	10342.23	9760	0.81862	22.93	14.29	6.77
2.34	234	10485.98	9867	0.82474	23.11	17.17	6.68
2.36	236	10630.59	9975	0.82984	23.26	13.17	7.36
2.38	238	10776.06	10082	0.82746	23.19	17.06	7.05
2.4	240	10922.39	10190	0.81964	22.96	12.78	7.66
2.42	242	11069.59	10297	0.82304	23.06	10.34	6.69
2.44	244	11217.64	10404	0.81182	22.73	10.34	7.58
2.46	246	11366.56	10512	0.83018	23.27	9.49	7.02
2.48	248	11516.35	10619	0.80264	22.46	10.46	7.38
2.5	250	11666.99	10727	0.81828	22.92	16.09	6.7
2.52	252	11818.5	10834	0.80196	22.44	12.92	7.53
2.54	254	11970.87	10941	0.8023	22.45	15.54	7.51
2.56	256	12124.1	11049	0.77578	21.67	12.09	7.1
2.58	258	12278.19	11156	0.78394	21.91	9.1	7.05
2.6	260	12433.15	11264	0.82236	23.04	6.68	7.7

2.62	262	12588.97	11371	0.79924	22.36	7.52	6.89
2.64	264	12745.65	11479	0.82372	23.08	3.44	6.84
2.66	266	12903.19	11586	0.81488	22.82	4.01	8
2.68	268	13061.6	11693	0.80774	22.61	4.79	7.84
2.7	270	13220.87	11801	0.81046	22.69	8.47	7.42
2.72	272	13381	11908	0.82644	23.16	4.1	9.25
2.74	274	13541.99	12016	0.77884	21.76	8.94	8.47
2.76	276	13703.85	12123	0.78428	21.92	4.3	8.45
2.78	278	13866.57	12230	0.82372	23.08	2.48	8.81
2.8	280	14030.15	12338	0.76524	21.36	0.36	7.98

*Altabet age model **Chazen age model

Data Table for W7706-40K

Data used in Chapter 1.

Depth (cm)	Age (yrs)*	Age (yrs)**	%N	d ¹⁵ N (‰)	UK'37	SST (°C) [Prah et al., 1988]	C ₃₇ total (nmol/g)	BSi (%)
					0.7666			
3	481	252.01	0.0097	6.8307		21.4	33.82	45.01
					0.77204			
4	490	262.05	0.0108	8.0446		21.56	42.4	
					0.77306			
5	498	267.09	0.0083	7.6858		21.59	35.64	20.01
					0.76898			
6	507	267.09	0.0083	7.6858		21.47	34.78	
					0.7836			
7	516	277.24	0.0113	7.4915		21.9	35.69	
					0.77612			
8	524	282.36	0.0124	7.3773		21.68	44.09	47.78
					0.7768			
10	542	282.36	0.0124	7.3773		21.7	42.58	
					0.77986			
12	560	292.72	0.01	6.0201		21.79	30.31	
					0.76796			
13	569	308.63	0.0079	5.5142		21.44	28.29	
					0.76796			
14	578	314.04	0.008	5.6188		21.44	27.34	18.01
					0.77			
15	588	325.12	0.0088	5.6624		21.5	27.18	
					0.77578			
16	597	330.75	0.0078	5.512		21.67	30.38	
					0.77238			
17	606	342.31	0.009	5.7777		21.57	31.97	31.45
					0.77476			
18	616	348.24	0.0085	5.8528		21.64	34.07	
					0.77442			
19	625	360.36	0.0086	5.5378		21.63	26.68	
					0.77272			
20	635	366.64	0.0081	5.3908		21.58	27.96	50.08
					0.77068			
21	644	379.46	0.0074	5.1983		21.52	29	
					0.77714			
22	654	386.09	0.0079	5.2894		21.71	19.91	
					0.77544			
23	664	399.7	0.0072	6.0881		21.66	25.99	
					0.77476			
24	673	399.7	0.0072	6.0881		21.64	24.1	
					0.77476			
25	683	406.73	0.0084	5.0216		21.64	25.49	42.43
					0.77442			
26	693	421.24	0.0088	5.8038		21.63	31.32	
					0.78666			
27	703	428.71	0.0086	5.5626		21.99	25.08	
					0.78258			
28	713	436.36	0.0079	5.953		21.87	29.76	
					0.7785			
29	723	468.75	0.0105	5.9059		21.75	32.09	
					0.7836			
30	733	477.28	0.0106	6.0433		21.9	36.62	48.88
					0.77714			
31	743	495.01	0.0083	6.4079		21.71	34.89	
					0.77306			
32	753	504.2	0.0087	5.7674		21.59	33.88	

					0.77952			
33	764	523.13	0.0089	5.4384		21.78	39.68	
					0.77476			
34	774	523.13	0.0089	5.4384		21.64	36.09	29.09
					0.77612			
36	795	533.02	0.0087	5.7793		21.68	34.74	
					0.76388			
37	805	553.33	0.0105	5.4543		21.32	30.85	
					0.77816			
38	816	563.89	0.0112	5.2553		21.74	30.9	
					0.78632			
39	827	585.63	0.0089	6.6677		21.98	29.1	51.34
					0.77952			
40	837					21.78	27.96	
					0.78802			
41	848	620.07	0.0101	5.7335		22.03	22.75	
					0.77272			
42	859	631.99	0.0089	5.5797		21.58	22.25	
					0.77748			
43	870	656.67	0.0092	6.1634		21.72	30.33	26.23
					0.78054			
53	982	669.29	0.0089	5.9003		21.81	35.67	
					0.78258			
54	993	695.45	0.0098	5.783		21.87	32.44	
					0.77408			
55	1005	708.85	0.0091	6.0598		21.62	37.9	39.56
					0.7717			
56	1017	708.85	0.0091	6.0598		21.55	34.8	
					0.7768			
57	1028	736.45	0.0093	5.919		21.7	35.09	
					0.78802			
58	1040	750.65	0.0076	5.9748		22.03	30.25	
					0.77816			
59	1052	779.7	0.0071	5.4676		21.74	30.1	
					0.78156			
60	1064	794.71	0.0072	5.3664		21.84	31.44	35.27
					0.78734			
61	1076	825.3	0.0066	5.9845		22.01	21.43	
					0.77748			
62	1088	841.04	0.0089	6.6131		21.72	26.45	
					0.78972			
63	1100	873.19	0.0088	6.5066		22.08	28.69	
					0.79142			
64	1112	889.67	0.0091	6.0983		22.13	33.47	
					0.78632			
65	1124	923.4	0.0109	5.4752		21.98	34.25	43.78
					0.78258			
66	1136	940.62	0.0099	5.9104		21.87	43.8	
					0.78394			
67	1149	975.96	0.0096	5.98		21.91	37.84	
					0.78156			
68	1161	975.96	0.0096	5.98		21.84	39.33	
					0.7802			
69	1173	993.93	0.0099	6.618		21.8	31.66	
					0.78768			
70	1186	1030.9	0.0099	5.9316		22.02	38.88	52.67
					0.80604			
71	1198	1049.7	0.0095	6.9672		22.56	22.24	
					0.78836			
72	1211	1088.2	0.0088	6.9336		22.04	27.15	
					0.77952			
73	1224	1107.9	0.0063	8.1656		21.78	14.61	
					0.79278			
74	1236	1148	0.0075	7.3692		22.17	40.93	
					0.7904			
75	1249	1168.5	0.0093	5.8672		22.1	42.23	28.99

					0.77782			
76	1262	1210.3	0.0077	6.994		21.73	21.11	
					0.78632			
77	1275	1231.6	0.0068	7.2245		21.98	35.95	
					0.79176			
78	1288	1275	0.0082	5.0703		22.14	35.91	
					0.7853			
79	1301	1297.2	0.0086	4.7555		21.95	32.72	
					0.79142			
80	1314	1342.3	0.0083	4.9528		22.13	25.68	46.56
					0.78904			
81	1327					22.06	34	
					0.79414			
82	1340	1460.1	0.0085	5.2296		22.21	33.47	
					0.79108			
83	1354	1484.5	0.0086	5.3059		22.12	32.77	
					0.79584			
84	1367	1509.2	0.0085	5.5009		22.26	29.82	
					0.78972			
85	1380	1559.4	0.0085	5.5684		22.08	31.52	35.67
					0.80604			
86	1394	1585	0.0082	5.2472		22.56	36.47	
					0.81216			
87	1407	1637	0.0095	6.3539		22.74	37.32	
					0.80196			
88	1421	1663.5	0.009	6.4311		22.44	37.19	
					0.80162			
89	1434	1717.3	0.0085	6.3967		22.43	36.78	
					0.79992			
90	1448	1744.7	0.0088	5.9946		22.38	33.41	41.98
					0.80298			
91	1462	1800.2	0.009	5.6035		22.47	29.51	
					0.80026			
92	1476	1800.2	0.009	5.6035		22.39	29.52	
					0.79958			
93	1489	1828.5	0.008	5.761		22.37	32.33	
					0.80128			
94	1503	1885.9	0.0079	5.6292		22.42	41.29	
					0.8159			
95	1517	1915	0.0098	6.301		22.85	27.01	36.85
					0.80604			
96	1531	1974.2	0.0081	6.8378		22.56	18.53	
					0.804			
97	1545	2004.2	0.0076	6.6375		22.5	21.73	
					0.80094			
98	1560	2065.3	0.0075	7.6322		22.41	21.23	
					0.80774			
99	1574	2096.3	0.0078	6.1996		22.61	37.56	
					0.80298			
100	1588	2159.2	0.0086	6.2571		22.47	37.38	38.77
					0.80604			
101	1602	2191.1	0.0096	6.1183		22.56	31.79	
					0.8006			
102	1617	2255.8	0.0094	6.0257		22.4	37.51	
					0.79958			
103	1631	2288.8	0.0091	6.1619		22.37	24.51	22
					0.78904			
104	1646	2355.4	0.0085	6.0404		22.06	28.61	
					0.8125			
108	1704	2389.3	0.0094	5.8957		22.75	26.32	30.56
					0.79482			
109	1719	2457.9	0.0084	5.6317		22.23	34.6	
					0.79006			
110	1734	2492.6	0.0084	5.938		22.09	37.47	
					0.78224			
111	1749	2563.1	0.007	5.5841		21.86	38	34.34

					0.78224			
112	1764	2598.8	0.0078	5.7082		21.86	40.11	
					0.79924			
113	1779	2671.3	0.007	7.1402		22.36	27.43	36.87
					0.79618			
114	1794	2708	0.0066	7.0134		22.27	33.77	
					0.79482			
115	1809	2782.4	0.0067	5.7331		22.23	33.41	23.01
					0.78462			
116	1824	2820.1	0.0067	6.177		21.93	23.3	
					0.77918			
117	1840	2896.3	0.0053	5.918		21.77	3.48	
					0.77408			
118	1855	2896.3	0.0053	5.918		21.62	3.65	14.99
					0.77442			
119	1870	2934.9	0.002	5.4939		21.63	5.17	
					0.78224			
120	1886	2934.9	0.002	5.4939		21.86	5.46	18.33
					0.77442			
121	1901	2934.9	0.002	5.4939		21.63	5.14	
					0.76354			
122	1917		0.0023	5.5416		21.31	2.99	
					0.78088			
123	1932		0.0023	5.5416		21.82	3.48	
					0.78088			
124	1948	3051.9	0.0016	5.7214		21.82	29.67	
					0.78258			
125	1964	3130.8	0.0062	5.094		21.87	33.53	30.01
					0.78836			
126	1980	3170.6	0.0068	5.2699		22.04	25.49	
					0.78904			
127	1996	3250.5	0.0067	5.2638		22.06	28.38	
					0.78496			
128	2012	3290.6	0.0067	5.5016		21.94	27.77	32.03
					0.78836			
129	2028	3371.2	0.0067	5.2965		22.04	26.14	
					0.78666			
130	2044	3411.6	0.0075	5.6087		21.99	14.47	19.01
					0.77544			
131	2060	3614	0.0041	5.414		21.66	14.91	
					0.76014			
132	2076	3654.5	0.0037	5.248		21.21	12.51	
					0.7564			
134	2108	3735.4	0.0053	5.6546		21.1	18.37	20.9
					0.75776			
135	2125	3775.9	0.0051	5.3945		21.14	16.39	
					0.76048			
136	2141	3856.9	0.0071	5.6846		21.22	16.59	
					0.76456			
137	2158	3856.9	0.0071	5.6846		21.34	16.23	
					0.76116			
138	2174	3897.4	0.0071	5.7698		21.24	22.02	
					0.75062			
139	2191	3978.4	0.0055	7.2508		20.93	19.53	
					0.75674			
140	2207	4018.9	0.0058	6.4752		21.11	14.56	28.01
					0.77782			
141	2224	4099.8	0.0073	5.6632		21.73	17.25	
					0.75606			
142	2241	4140.3	0.0069	5.5996		21.09	27.01	
					0.75742			
143	2258	4221.3	0.0027	4.9949		21.13	20.49	
					0.75368			
144	2274	4261.8	0.003	5.4517		21.02	11.99	
					0.7615			
145	2291	4342.8	0.0055	5.3323		21.25	15.25	24.67

PC-2 Benthic foraminifera presence/absence data

Data used in Chapter 1.

Depth (cm)	Presence/Absence	Number value assignment
5	P	1
9	P	1
20	A	0
30	A	0
40	A	0
41	P	1
42	P	1
55.5	P	1
60	P	1
65.5	P	1
67	P	1
69.5	P	1
71	A	0
83	A	0
86	A	0
89	A	0
92	A	0
95.5	A	0
98	P	1
99	P	1
100	P	1
101	P	1
102	P	1
102.5	P	1
103.5	P	1
104.5	P	1
105.5	P	1
106.5	P	1
107.5	P	1
108.5	P	1
110.5	P	1
112	P	1
127	A	0
128	P	1
130	P	1
131	P	1
131.5	P	1
132.5	P	1
133	P	1
134.5	P	1
135.5	P	1
137	P	1
138	P	1
139	P	1

140	A	0
141	A	0
142	A	0
143	A	0
144	A	0
145	A	0
146	A	0
147	A	0
148	A	0
149	A	0
150	A	0
151	P	1
152	P	1
153	P	1
154	P	1
155	P	1
156	P	1
157	P	1
158	A	0
159	A	0
160.5	A	0
162	P	1
163	P	1
165	?	
168.5	A	0
169.5	A	0
170.5	P	1
171.5	A	0
172.5	A	0
173.5	P	1
174.5	P	1
175.5	P	1
176.5	P	1
177	P	1
177.5	P	1
178.5		
179	P	1
179.5		
180	P	1
180.5	P	1
181	P	1
181.5		
182		
184.5		
185	P	1
185.5		
186		
186.5		
187	P	1

187.5		
188		
188.5		
189	P	1
189.5		
190		
190.5		
191	P	1
191.5		
192		
193	P	1
193.5		
194		
195	P	1
200.5	P	1
205	P	1
210	P	1
213.5	P	1
220.5	P	1
225.5	P	1
229.5	A	0
235	A	0
239.5	A	0
224	A	0
248	A	0
251	A	0
257	A	1
258	A	0
261	A	0
262.5	A	1
265	A	1
267	A	1
267.5	A	1
270.27	P	0
272	A	0
273	P	0
274	A	0
274.5	A	0
275.5	P	0
276.5	P	0
277.5	P	0
278	P	0
278.5	P	0
280	A	0
281.5	A	0
282	A	0
283	A	0
350	A	0
355	A	0

360	A	0
362	A	0
363	A	0
364	A	0
365.5	A	0
366.5	A	0
368	A	0
369	A	0
370.5	A	0
371	A	0
372.5	A	0
374	A	0
375.5	A	0
377	A	0
378.5	A	0
418	A	0
421	P	1
423	P	1
424	A	0
442.5	A	0
443	A	0
443.5	A	0
444	?	
444.5	A	0
445	A	0
445.5	A	0
446	A	0
447	A	0
448.5	A	0
450	A	0
451.5	A	0
453	A	0
454.5	A	0
457.5	A	0
537	P	1
537.5	P	1
538	P	1
538.5	P	1
539.5	P	1
539.5	P	1
540	P	1
540.5	P	1
541	P	1
541.5	P	1
542	P	1
542.5	P	1
543.5	A	0

Benthic Foraminifera Data from core PC-2

Data used in Chapter 3

Depth (cm)	Foram Abundance (# of individual/ gram of sediments)	Foram Diversity	Globobulimina Pacifica	Cassidulina	Nonionella stella	Nonionella aurcula	Bolovina Pacifica	Bolovina Striatula	Buliminella elegantissima	Buliminella sp.	Buliminella Tenuata	Virgulilla fragile	Stainforthia sp.	Epistominella sp.	Epistominella Rugosa
5	6356	10	x	x		x	x	x	x	x		x		x	x
9	5263	8		x		x		x	x	x		x		x	x
41	4830	6		x		x		x	x					x	x
42	4722	7		x		x		x	x	x		x		x	
55.5	6854	3			x		x			x					
60	17486	3			x		x				x				
60.5	19865	2			x		x								
61	13899	4		x	x	x	x	x	x					x	
61.5	8593	7	x	x	x	x	x	x	x	x				x	
62	11034	9			x	x	x	x	x					x	
62.5	10474	8			x	x	x	x	x		x		x	x	
63	17234	4			x		x				x		x		
63.5	15089	3			x	x	x	x			x			x	
64	11078	6		x	x	x	x	x	x	x			x	x	x
67	6895	10	x	x	x	x	x	x	x	x		x		x	x
69.5	7548	11			x	x	x						x		
71	9654	4				x	x							x	
98	2924	3				x	x							x	
99	5642	3				x	x					x			
100	4265	3			x		x					x			
101	8745	3			x		x					x		x	
102	9456	4			x		x							x	
102.5	9253	3			x		x							x	

421	13264	3	x	x	x
423	14532	3	x	x	x
537	20552	1		x	

Benthic foraminifera data from core PC-2 (high resolution intervals)

Data used in Chapter 3.

Depth (cm)	$\delta^{15}\text{N}$	Foraminifera Abundance (# of individuals per gram of dry sediment)	Foraminifera diversity (number of species present)
60.5	8.02	19865	2
61	6.94	13899	4
61.5	6.245	8593	7
62	5.54	11034	9
62.5	6.39	10474	8
63	7.89	17234	4
63.5	8.14	15089	3
64	6.78	11078	6
116	7.74	14056	5
116.5	6.012	11023	7
117	5.56	4956	10
117.5	5.13	432	10
118	5.21	7432	10
118.5	5.23	3984	11
119	5.37	8644	8
119.5	5.2	6023	9
120	6.73	9077	5
120.5	8.64	16223	3
121	8.26	15897	6
121.5	7.88	18996	4
122	8.01	19653	6
122.5	8.12	18856	4
123	5.79	12033	11
123.5	6.43	11886	9
124	7.39	13452	6
124.5	6.98	11132	7
125	5.23	5063	8
214.5	7.02	14889	4
215	6.48	14702	5
215.5	5.78	10022	9
216	6.42	6744	8
216.5	7.55	6507	6
217	7.33	11523	4
217.5	5.53	4066	11
218	6.34	4277	9
218.5	These samples were obtained from the third round of sampling on core PC-2 and some of the depths may be slightly off from original sampling due to core shrinkage		
219			
219.5	7.43	15030	6

Data tables for core GGC-14

Data used in Chapter 4.

Depth (cm)	Age (yrs) *	UK'37	SST (°C) [Prah et al., 1988]	C ₃₇ total
0.5	394.70	0.833	23.35	10.14
4	429.55	0.834	23.37	8.78
8	469.38	0.836	23.43	8.21
12	509.21	0.839	23.52	6.51
16	549.04	0.846	23.74	6.47
20	588.87	0.839	23.52	4.66
24	628.70	0.836	23.44	6.81
28	668.53	0.835	23.41	5.20
32	708.36	0.839	23.53	6.99
36	748.19	0.836	23.44	7.40
40	788.02	0.835	23.42	6.12
44	827.85	0.835	23.42	6.04
48	867.68	0.834	23.38	8.06
52	907.51	0.833	23.34	6.63
56	947.34	0.830	23.25	7.53
60	987.16	0.827	23.17	7.29
64	1027.00	0.824	23.08	5.36
68	1066.80	0.823	23.05	7.10
72	1106.70	0.824	23.08	5.49
80	1186.30	0.816	22.86	6.12
84	1226.10	0.820	22.98	5.51
92	1305.80	0.821	23.01	6.40
96	1345.60	0.820	22.98	5.37
110	1485.00	0.815	22.82	5.17
126	1644.40	0.815	22.81	5.11
138	1763.80	0.827	23.19	6.18
142	1803.70	0.828	23.20	6.50
146	1843.50	0.826	23.16	5.59
150	1883.30	0.827	23.18	5.32
158	1963.00	0.821	22.99	5.04
162	2002.80	0.811	22.72	5.66
170	2082.50	0.816	22.84	4.94
178	2162.10	0.810	22.68	5.57
182	2202.00	0.810	22.68	4.58
190	2281.60	0.807	22.58	4.36
194	2321.50	0.812	22.73	4.09
198	2361.30	0.814	22.78	3.89

*Chazen age model

Data table for core CDH-23

Data used in Chapter 4.

Depth (cm)	Age* (yrs)	UK'37	SST (°C) [Prah et al., 1988]	C₃₇total
28	1982.41	0.814	22.78	2.19
32	2016.03	0.822	23.02	6.74
36	2049.65	0.818	22.92	5.77
40	2083.26	0.825	23.11	3.07
44	2116.88	0.828	23.19	6.83
48	2150.50	0.818	22.92	2.81
52	2184.11	0.820	22.98	7.62
56	2217.73	0.809	22.66	2.87
60	2251.35	0.814	22.79	6.23
64	2284.96	0.809	22.63	2.29
68	2318.58	0.814	22.78	5.00
72	2352.20	0.811	22.71	2.69
72	2352.20	0.814	22.79	2.31
76	2385.81	0.818	22.90	6.69
80	2419.43	0.812	22.73	6.31
84	2453.04	0.808	22.63	5.21
88	2486.66	0.802	22.45	4.02
96	2553.89	0.800	22.37	3.12
100	2587.51	0.801	22.42	3.59
104	2621.13	0.802	22.44	3.37
108	2654.74	0.803	22.48	3.67
112	2688.36	0.808	22.62	4.43
116	2721.98	0.809	22.66	4.36
120	2755.59	0.803	22.47	5.62
124	2789.21	0.807	22.58	4.45
128	2822.82	0.808	22.61	5.41
132	2856.44	0.805	22.52	4.78
136	2890.06	0.802	22.45	6.11
140	2923.67	0.805	22.54	5.37
144	2957.29	0.808	22.62	4.03

148	2990.91	0.811	22.70	5.97
152	3024.52	0.810	22.67	4.46
156	3058.14	0.813	22.75	3.89
160	3091.76	0.813	22.77	3.59
164	3125.37	0.814	22.81	3.93
168	3158.99	0.813	22.78	4.40
172	3192.61	0.812	22.74	3.51
176	3226.22	0.812	22.74	3.93
180	3259.84	0.815	22.82	3.83
180	3259.84	0.822	23.03	6.03
184	3293.45	0.821	23.01	5.52
188	3327.07	0.817	22.88	7.26
192	3360.69	0.818	22.92	6.56
196	3394.30	0.820	22.97	6.38
200	3427.92	0.820	22.96	7.18
204	3461.54	0.824	23.10	4.31
208	3495.15	0.823	23.05	6.97
212	3528.77	0.820	22.97	6.26
216	3562.39	0.818	22.90	4.97
220	3596.00	0.819	22.94	6.39
224	3629.62	0.819	22.93	6.79
228	3663.23	0.817	22.88	6.52
232	3696.85	0.825	23.12	6.07
236	3730.47	0.822	23.03	6.29
240	3764.08	0.821	23.00	5.95
244	3797.70	0.822	23.02	5.23
248	3831.32	0.823	23.05	
252	3864.93	0.821	23.01	6.68
256	3898.55	0.824	23.07	6.24
264	3965.78	0.821	22.99	6.40
264	3965.78	0.814	22.80	4.36
268	3999.40	0.815	22.83	4.61
272	4033.02	0.807	22.60	4.20

276	4066.63	0.810	22.66	5.06
280	4100.25	0.817	22.88	5.00
284	4133.86	0.815	22.82	4.52
288	4167.48	0.814	22.79	4.17
292	4201.10	0.809	22.66	3.47
296	4234.71	0.812	22.75	3.91
300	4268.33	0.817	22.87	4.32
304	4301.95	0.814	22.80	4.16
308	4335.56	0.816	22.84	4.27
312	4369.18	0.815	22.81	4.88
316	4402.80	0.815	22.82	4.05
320	4436.41	0.811	22.71	4.45
324	4470.03	0.814	22.79	4.14
328	4503.64	0.807	22.58	5.40
332	4537.26	0.808	22.62	4.48
334	4554.07	0.810	22.68	5.22
338	4587.69	0.815	22.82	5.43
342	4621.30	0.811	22.71	5.70
346	4654.92	0.808	22.60	5.35
350	4688.54	0.813	22.75	5.68
354	4722.15	0.814	22.80	5.87
358	4755.77	0.813	22.76	5.86
362	4789.38	0.813	22.75	5.78
366	4823.00	0.813	22.76	5.56
370	4856.62	0.811	22.71	6.24
374	4890.23	0.814	22.79	5.81
378	4923.85	0.813	22.77	4.47
382	4957.47	0.815	22.81	5.43
386	4991.08	0.816	22.86	5.63
390	5024.70	0.815	22.82	5.16
392	5041.51	0.814	22.80	4.99
396	5075.12	0.817	22.89	5.03
400	5108.74	0.822	23.02	4.77

404	5142.36	0.820	22.97	5.28
408	5175.97	0.821	22.99	5.08
412	5209.59	0.819	22.95	5.27
416	5243.21	0.819	22.95	4.42
420	5276.82	0.819	22.94	4.46
424	5310.44	0.824	23.08	6.45
428	5344.05	0.825	23.10	5.86
432	5377.67	0.824	23.09	5.62
436	5411.29	0.825	23.13	6.04
440	5444.90	0.827	23.18	5.61
444	5478.52	0.829	23.22	5.65
448	5512.14	0.829	23.23	5.60
452	5545.75	0.827	23.18	6.36
456	5579.37	0.829	23.23	5.25
460	5612.99	0.829	23.24	6.69
464	5646.60	0.833	23.34	5.84
468	5680.22	0.830	23.25	6.85
472	5713.84	0.831	23.29	5.46
476	5747.45	0.827	23.17	6.21
480	5781.07	0.829	23.23	6.16
484	5814.68	0.831	23.30	5.58
488	5848.30	0.826	23.15	5.85
492	5881.92	0.833	23.35	6.03
496	5915.53	0.831	23.28	5.10
500	5949.15	0.836	23.43	5.51
504	5982.77	0.833	23.37	5.21
508	6016.38	0.832	23.31	6.10
512	6050.00	0.832	23.32	6.39
516	6083.62	0.835	23.41	5.94
520	6117.23	0.833	23.36	6.30
524	6150.85	0.830	23.26	5.50
528	6184.46	0.833	23.34	5.87
532	6218.08	0.833	23.35	5.40

534	6234.89	0.831	23.29	5.31
538	6268.51	0.837	23.47	4.80
542	6302.12	0.834	23.38	5.62
546	6335.74	0.834	23.37	5.08
550	6369.36	0.832	23.32	4.37
554	6402.97	0.827	23.18	5.05
558	6436.59	0.832	23.32	4.78
562	6470.20	0.831	23.29	5.85
566	6503.82	0.832	23.31	5.60
570	6537.44	0.832	23.33	5.65
574	6571.05	0.832	23.33	5.31
578	6604.67	0.826	23.16	4.02
578	6604.67	0.830	23.25	5.86
582	6638.29	0.829	23.23	5.22
586	6671.90	0.829	23.22	5.76
590	6705.52	0.827	23.18	4.71
594	6739.14	0.831	23.30	7.28
594	6739.14	0.831	23.30	7.28
598	6772.75	0.828	23.20	6.93
602	6806.37	0.828	23.22	7.30
606	6839.98	0.818	22.90	6.88
610	6873.60	0.823	23.07	6.96
614	6907.22	0.823	23.07	7.63
618	6940.83	0.824	23.10	6.55
622	6974.45	0.823	23.07	7.50
626	7008.07	0.821	23.01	7.12
630	7041.68	0.823	23.06	7.85
634	7075.30	0.822	23.03	6.86
638	7108.92	0.820	22.97	6.28
642	7142.53	0.820	22.98	6.03
646	7176.15	0.819	22.94	5.31
650	7209.77	0.818	22.90	2.88
654	7243.38	0.819	22.93	3.96

658	7277.00	0.819	22.95	5.13
662	7310.61	0.819	22.95	6.52
666	7344.23	0.819	22.95	5.59
670	7377.85	0.822	23.04	5.68
674	7411.46	0.824	23.08	4.56
678	7445.08	0.824	23.10	5.47
682	7478.70	0.820	22.97	3.71
686	7512.31	0.821	23.01	2.77
688	7529.12	0.820	22.98	5.13
692	7562.74	0.811	22.71	6.22
696	7596.35	0.815	22.81	5.86
700	7629.97	0.816	22.85	5.19
702	7646.78	0.805	22.52	6.20
704	7663.59	0.813	22.76	5.23
708	7697.20	0.808	22.62	5.63
712	7730.82	0.807	22.58	6.81
716	7764.44	0.807	22.58	6.41
720	7798.05	0.804	22.50	5.79
724	7831.67	0.803	22.46	6.17
728	7865.28	0.805	22.52	3.64
732	7898.90	0.801	22.41	6.22
736	7932.52	0.800	22.37	3.65
740	7966.13	0.801	22.41	4.56
744	7999.75	0.797	22.28	4.23
748	8033.37	0.797	22.28	3.99
752	8066.98	0.801	22.41	3.94
756	8100.60	0.803	22.48	4.00
760	8134.22	0.799	22.36	4.86
764	8167.83	0.802	22.44	3.74
768	8201.45	0.802	22.44	3.50
772	8235.07	0.794	22.20	3.54
776	8268.68	0.794	22.21	3.46
780	8302.30	0.787	22.01	5.51

784	8335.91	0.790	22.08	4.64
788	8369.53	0.790	22.07	2.24
792	8403.15	0.789	22.07	4.85
796	8436.76	0.790	22.10	4.58
800	8470.38	0.794	22.21	4.61
804	8504.00	0.795	22.23	4.71
808	8537.61	0.796	22.28	4.44
812	8571.23	0.791	22.11	4.49
816	8604.85	0.797	22.29	4.69
840	8806.54	0.785	21.95	3.96
844	8840.16	0.786	21.98	4.26
848	8873.78	0.782	21.85	4.21
852	8907.39	0.778	21.74	3.92
856	8941.01	0.779	21.77	4.26
860	8974.63	0.780	21.78	3.70
864	9008.24	0.792	22.14	3.80
868	9041.86	0.781	21.82	3.63
872	9075.48	0.777	21.71	4.14
876	9109.09	0.780	21.80	3.66
880	9142.71	0.781	21.83	3.75
884	9176.32	0.781	21.82	3.85
888	9209.94	0.782	21.87	3.12
892	9243.56	0.779	21.76	4.17
896	9277.17	0.779	21.77	3.97
900	9310.79	0.780	21.80	3.54
904	9344.41	0.785	21.94	3.33
908	9378.02	0.784	21.91	3.45
912	9411.64	0.778	21.72	3.91
916	9445.26	0.779	21.77	3.71
920	9478.87	0.783	21.89	3.11
924	9512.49	0.782	21.84	2.82
928	9546.10	0.779	21.76	4.42
932	9579.72	0.784	21.90	3.35

936	9613.34	0.782	21.87	3.81
940	9646.95	0.780	21.80	3.37
944	9680.57	0.778	21.75	4.43
948	9714.19	0.785	21.94	3.74
952	9747.80	0.785	21.94	3.89
956	9781.42	0.778	21.74	4.38
960	9815.04	0.777	21.71	3.47
964	9848.65	0.778	21.74	4.45
968	9882.27	0.774	21.62	3.99
972	9915.89	0.777	21.69	4.00
976	9949.50	0.777	21.70	3.44
980	9983.12	0.774	21.62	3.94
984	10016.73	0.778	21.74	3.85
988	10050.35	0.776	21.68	2.94
992	10083.97	0.772	21.57	3.84
994	10100.7754	0.772	21.57	
1002	10168.0082	0.773	21.59	3.77
1002	10168.0082	0.773	21.59	3.88
1006	10201.62	0.774	21.62	2.91
1010	10235.241	0.776	21.69	
1014	10268.8574	0.777	21.71	
1018	10302.4738	0.780	21.8	
1026	10369.7066	0.781	21.81	
1030	10403.323	0.781	21.83	
1034	10436.9394	0.782	21.85	3.38
1034	10436.9394	0.782	21.86	2.22
1034	10436.9394	0.777	21.72	3.64
1034	10436.9394	0.777	21.7	3.54
1038	10470.5558	0.780	21.79	3.05
1042	10504.1722	0.788	22.04	3.05
1042	10504.1722	0.786	21.96	3.15
1046	10537.7886	0.788	22.02	2.88
1046	10537.7886	0.788	22.04	2.97

1050	10571.405	0.788	22.04	2.88
1050	10571.405	0.787	21.99	3
1054	10605.0214	0.782	21.85	3.25
1054	10605.0214	0.781	21.82	3.27
1062	10672.2542	0.793	22.18	2.96
1062	10672.2542	0.787	22	2.82
1062	10672.25	0.776	21.69	2.64
1073	10764.70	0.777	21.71	2.70
1078	10806.7198	0.773	21.60	
1090	10907.569	0.780	21.8	
1102	11008.4182	0.783	21.88	
1114	11109.2674	0.787	21.99	2.57
1114	11109.2674	0.787	22.01	2.63
1118	11142.8838	0.788	22.02	2.32
1126	11210.1166	0.790	22.08	1.86
1130	11243.733	0.784	21.9	
1135	11285.7535	0.780	21.78	
1138	11310.9658	0.773	21.6	
1138	11310.97	0.770	21.50	2.32
1147	11386.6027	0.771	21.52	
1151	11420.2191	0.771	21.54	
1155	11453.8355	0.773	21.6	
1163	11521.07	0.778	21.74	2.89
1167	11554.68	0.774	21.63	2.99
1171	11588.3011	0.777	21.7	2.43
1171	11588.3011	0.779	21.75	2.39
1183	11689.1503	0.776	21.69	3.11
1187	11722.7667	0.770	21.5	2.68
1191	11756.38	0.773	21.60	2.87
1195	11789.9995	0.762	21.27	2.45
1199	11823.6159	0.763	21.29	3.02
1201	11840.42	0.755	21.04	2.50
1203	11857.23	0.771	21.53	3.06

1207	11890.85	0.766	21.39	1.78
1211	11924.47	0.779	21.77	3.17
1215	11958.08	0.759	21.18	3.52
1219	11991.70	0.766	21.39	3.14
1220	12000.10	0.752	20.98	3.01
1223	12025.3143	0.759	21.18	2.95
1227	12058.9307	0.756	21.09	2.99
1231	12092.55	0.764	21.31	3.53
1235	12126.16	0.768	21.44	2.98
1239	12159.7799	0.781	21.82	3.32
1239	12159.7799	0.782	21.86	3.25
1243	12193.3963	0.789	22.07	2.85
1247	12227.0127	0.785	21.95	3.08
1251	12260.6291	0.788	22.02	3.14
1263	12361.48	0.761	21.22	2.75
1267	12395.0947	0.784	21.9	3
1271	12428.71	0.759	21.19	2.76
1274	12453.92	0.758	21.16	1.84
1275	12462.3275	0.794	22.2	3
1291	12596.79	0.755	21.05	2.64
1299	12664.03	0.760	21.21	3.93
1308	12739.66	0.756	21.10	3.40
1316	12806.90	0.755	21.07	3.06
1320	12840.51	0.752	20.98	2.41
1324	12874.13	0.755	21.05	3.36
1332	12941.36	0.757	21.11	3.25
1336	12974.98	0.746	20.78	2.62
1340	13008.59	0.738	20.57	2.88
1344	13042.21	0.735	20.46	3.46
1348	13075.83	0.739	20.59	3.05
1368	13243.91	0.739	20.60	2.85
1388	13411.99	0.746	20.79	3.11
1392	13445.61	0.740	20.62	3.22

1404	13546.46	0.746	20.78	2.58
1408	13580.07	0.753	20.99	3.01
1416	13647.31	0.758	21.14	1.14
1424	13714.54	0.749	20.89	1.65
1428	13748.15	0.757	21.11	2.28
1435	13806.98	0.736	20.49	1.91
1436	13815.39	0.750	20.93	1.77
1440	13849.00	0.758	21.15	2.37
1444	13882.62	0.749	20.89	2.09
1448	13916.24	0.757	21.11	2.29
1457	13991.87	0.753	20.99	2.68
1469	14092.72	0.752	20.98	2.20
1469	14092.72	0.748	20.85	1.49
1470	14101.13	0.732	20.38	1.56
1479	14176.76	0.728	20.26	1.92
1481	14193.57	0.750	20.90	1.98
1489	14260.80	0.737	20.53	2.32
1489	14260.80	0.746	20.80	1.58
1493	14294.42	0.750	20.91	3.08
1507	14412.08	0.732	20.39	1.39
1509	14428.89	0.729	20.30	1.58
1512	14454.10	0.751	20.94	2.65
1525	14563.35	0.751	20.93	2.35
1529	14596.97	0.750	20.92	1.14
1537	14664.20	0.752	20.97	2.28
1545	14731.43	0.740	20.62	1.11
1545	14731.43	0.752	20.98	1.91
1561	14865.90	0.741	20.63	3.12
1573	14966.75	0.746	20.79	2.45
1577	15000.37	0.753	20.99	2.12
1585	15067.60	0.754	21.04	1.91
1593	15134.83	0.760	21.22	1.97
1612	15294.51	0.749	20.87	1.76

1616	15328.13	0.736	20.50	2.58
1620	15361.74	0.731	20.35	3.02
1628	15428.97	0.749	20.87	2.14
1632	15462.59	0.760	21.21	1.56
1634	15479.40	0.736	20.49	2.45
1636	15496.21	0.768	21.44	1.75
1640	15529.82	0.771	21.52	1.53
1644	15563.44	0.757	21.12	1.99
1652	15630.67	0.773	21.58	1.81
1660	15697.91	0.775	21.64	1.64
1664	15731.52	0.767	21.42	1.81
1668	15765.14	0.774	21.63	1.82
1672	15798.76	0.774	21.62	1.62
1676	15832.37	0.768	21.43	1.94
1680	15865.99	0.775	21.64	1.63
1684	15899.60	0.778	21.73	1.54
1688	15933.22	0.783	21.87	1.37
1692	15966.84	0.787	22.01	1.33
1696	16000.45	0.776	21.67	1.36
1705	16076.09	0.753	21.01	0.85
1712	16134.92	0.760	21.21	1.88
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*Chazen age model

TEX₈₆ and U^{K'}₃₇ Comparison for core PC-2 (high resolution interval)

Data used in Chapter 5

Depth (cm)	U ^{K'} ₃₇	SST (°C) [Prah et al, 1988]	C37total (nmol/g)	TEX ₈₆	SST-TEX ₈₆ (°C) [Kim et al., 2008]	TEX ₈₆ correction	SST-TEX ₈₆ (°C) (corrected)
83.5	0.696	19.32	16.2	0.571	21.3	0.548	20.01
84	0.709	19.72	18.32	0.572	21.3	0.549	20.05
84.5	0.736	20.51	18.73	0.571	21.3	0.548	20.02
85	0.757	21.11	18.42	0.567	21.1	0.544	19.81
85.5	0.775	21.65	18.23	0.567	21.1	0.544	19.78
86	0.786	21.98	16.59	0.568	21.1	0.545	19.84
86.5	0.787	22.01	15.23	0.568	21.2	0.545	19.87
87	0.783	21.88	15.02	0.568	21.2	0.545	19.86
87.5	0.767	21.42	14.59	0.566	21.1	0.543	19.76
88	0.754	21.03	15.23	0.567	21.1	0.544	19.80
88.5	0.733	20.40	15.01	0.564	20.9	0.541	19.61
89	0.724	20.16	15.36	0.578	21.7	0.555	20.42
89.5	0.708	19.68	14.57	0.570	21.3	0.547	19.99
90.5	0.701	19.48	15.42	0.570	21.2	0.547	19.94
91	0.715	19.87	13.21	0.569	21.2	0.546	19.92
91.5	0.738	20.55	12.89	0.566	21.0	0.543	19.75
92	0.749	20.89	13.01	0.564	20.9	0.541	19.61
92.5	0.746	20.81	15.89	0.566	21.0	0.543	19.71
93	0.736	20.50	18.98	0.566	21.0	0.543	19.72
93.5	0.727	20.23	18.56	0.567	21.1	0.544	19.78
94	0.719	20.04	15.89	0.568	21.1	0.545	19.84
94.5	0.715	19.87	14.53	0.569	21.2	0.546	19.90
95	0.707	19.66	13.39	0.569	21.2	0.546	19.90
95.5	0.716	19.90	16.56	0.567	21.1	0.544	19.77
96	0.726	20.24	19.86	0.565	21.0	0.542	19.67
96.5	0.739	20.61	18.98	0.565	20.9	0.542	19.65
97.5	0.760	21.20	15.42	0.564	20.9	0.541	19.65
98	0.773	21.59	13.65	0.564	20.9	0.541	19.65
98.5	0.763	21.30	13.48	0.565	21.0	0.542	19.68
99	0.753	21.22	13.34	0.565	21.0	0.542	19.71
99.5	0.712	19.79	13.89	0.567	21.1	0.544	19.79
100	0.709	19.70	14.17	0.568	21.1	0.545	19.84

TEX₈₆ for core PC-2 (low resolution interval)**Data used in Chapter 5**

Depth (cm)	TEX ₈₆	SST-TEX ₈₆ (°C) [Kim et al., 2008]	TEX ₈₆ _ correction	SST-TEX ₈₆ (°C) (corrected)
5.5	0.572	21.4	0.549	20.06
8	0.572	21.4	0.549	20.09
17.5	0.572	21.3	0.549	20.05
32.5	0.575	21.5	0.552	20.25
44	0.567	21.1	0.544	19.78
55.5	0.569	21.2	0.546	19.90
55.5	0.573	21.4	0.550	20.12
82	0.569	21.2	0.546	19.88
87.5	0.566	21.0	0.543	19.71
94	0.564	20.9	0.541	19.63
108.5	0.564	20.9	0.541	19.64
118.5	0.571	21.3	0.548	20.03
128.5	0.569	21.2	0.546	19.91
140.5	0.565	21.0	0.542	19.69
156	0.563	20.9	0.540	19.56
170	0.569	21.2	0.546	19.88
183	0.569	21.2	0.546	19.89
205.5	0.565	21.0	0.542	19.68
205.5	0.571	21.3	0.548	19.99
218.5	0.571	21.3	0.548	20.02
231.5	0.571	21.3	0.548	20.02
252.5	0.574	21.5	0.551	20.16
275	0.571	21.3	0.548	20.01
292	0.579	21.8	0.556	20.46
305	0.575	21.5	0.552	20.25
329.5	0.583	22.0	0.560	20.67
356.5	0.581	21.9	0.558	20.59
368	0.586	22.2	0.563	20.88
387	0.588	22.3	0.565	20.99
405	0.584	22.0	0.561	20.73
421.5	0.581	21.8	0.558	20.56
437.5	0.580	21.8	0.557	20.54
455	0.583	22.0	0.560	20.67
465.5	0.584	22.0	0.561	20.75
475.5	0.588	22.3	0.565	20.98
492	0.588	22.3	0.565	21.00
506	0.590	22.4	0.567	21.10
522	0.590	22.4	0.567	21.07