Eastern equatorial Pacific bulk sediment properties and paleoceanography since the late Neogene

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Abstract

Reconstructing eastern equatorial Pacific (EEP) oceanography since the late Neogene (about 8 million years ago, Ma) is a central topic in current paleoceanographic investigations. The reason for this is two-fold. First, the EEP exerts a strong control on global climate because steep gradients in sea surface temperature (SST) and biological productivity linked to equatorial wind-driven upwelling affect global climate and carbon cycling, including the exchange of upwelled CO₂ to the atmosphere. Second, during the last 8 Ma global climate underwent major changes before arriving at its current state, evolving through the last period of widespread global warmth (the early Pliocene) to the colder ‘mean’ global climate state of the pre-industrial world. Deciphering the dynamics of the EEP system since the late Neogene is thus important for understanding how this ocean area works under changing climatic conditions.

Despite the large numbers of studies devoted to the EEP, its paleoceanographic evolution since 8 Ma is still debated and contrasting scenarios have often been proposed. This is in part because paleoceanographic reconstructions are challenging in the EEP due to the high environmental, and thus sedimentary, heterogeneity, as well as the extreme seafloor depth, which compromises the preservation of useful foraminiferal archives in many regions. Moreover, some existing legacy data sets are confounded by some basic issues with the way in which the data were collected. Yet, reconstructing properties of surface mixed-layer remains a crucial requirement for deciphering EEP paleoceanography. Fossil foraminifera tests are typically not available for tracing EEP surface ocean properties because of strong sea floor diagenetic alteration. However, calcareous nannofossil carbonate, also produced in the surface mixed layer and accessible in the form of the bulk sedimentary carbonate or sediment ‘fine fraction’, is available. The challenge is to understand what these bulk geochemical signals mean.

Bulk sediment comprises a mixture of different, mostly biogenic particles. The information carried by its properties, including physical and geochemical signals, comprises a mixed signal reflecting different ecological, metabolic and depositional processes associated with the formation and sedimentation of the various calcite particles. The purpose of this thesis is to understand what bulk sediment records represent in terms meaningful for deciphering the paleoceanographic history of the EEP. The results add to, and significantly improve the paleoceanographic “tool box” available for developing proxy records in this complex oceanic region. This thesis comprises a kappa, two published papers and a manuscript, in review as this is written (April 2019). Paper I examines the factors linking sediment composition and physical properties in the EEP through analysis of the relationship between sediment carbonate content and sediment density. Paper II and Paper III focus on improving the understanding of bulk carbonate carbon and oxygen stable isotope signals by disentangling the contribution of different carbonate components. In these studies, a multiproxy approach was adopted to reconstruct ocean evolution of the EEP since the late Miocene. A major conclusion is that bulk carbonate stable isotope reflect the isotopic composition of calcareous nannofossils, and therefore surface water conditions, despite complication by several factors. The ideas and findings of the latter two papers have been further tested in an unpublished inter-basin comparison presented in the Chapter 6 of this kappa. The findings of this doctoral thesis demonstrate that bulk sediment is more than just a correlation tool and can provide a reliable indicator of surface ocean conditions that can be used to decipher EEP oceanographic history since 8 Ma.

Keywords: Paleooceanography, late Neogene, eastern equatorial Pacific, deep sea sediments, bulk sediment, stable isotopes, surface mixed layer, sediment physical properties.
EASTERN EQUATORIAL PACIFIC BULK SEDIMENT PROPERTIES AND PALEOCEANOGRAPHY SINCE THE LATE NEogene

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Cover: Aqua MODIS image of anomalous algal bloom in the eastern equatorial Pacific. The algal bloom (green shaded) is centered at about 3°S latitude and the base of image is comprised between 129.0°W and 135.5°W longitude. Computed chlorophyll concentration exceeds 30 milligrams per cubic meter. The image was taken on November 7th 2007. Courtesy of NASA/GSFC OBPG.
To my family
“Learning is always rebellion. Every bit of new truth discovered is revolutionary to what was believed before.”

Margaret Lee Runbeck
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Abstract

Reconstructing eastern equatorial Pacific (EEP) oceanography since the late Neogene (about 8 million years ago, Ma) is a central topic in current paleoceanographic investigations. The reason for this is two-fold. First, the EEP exerts a strong control on global climate because steep gradients in sea surface temperature (SST) and biological productivity linked to equatorial wind-driven upwelling affect global climate and carbon cycling, including the exchange of upwelled CO₂ to the atmosphere. Second, during the last 8 Ma global climate underwent major changes before arriving at its current state, evolving through the last period of widespread global warmth (the early Pliocene) to the colder ‘mean’ global climate state of the pre-industrial world. Deciphering the dynamics of the EEP system since the late Neogene is thus important for understanding how this ocean area works under changing climatic conditions.

Despite the large numbers of studies devoted to the EEP, its paleoceanographic evolution since 8 Ma is still debated and contrasting scenarios have often been proposed. This is in part because paleoceanographic reconstructions are challenging in the EEP due to the high environmental, and thus sedimentary, heterogeneity, as well as the extreme seafloor depth, which compromises the preservation of useful foraminiferal archives in many regions. Moreover, some existing legacy data sets are confounded by some basic issues with the way in which the data were collected. Yet, reconstructing properties of surface mixed-layer remains a crucial requirement for deciphering EEP paleoceanography. Fossil foraminifera tests are typically not available for tracing EEP surface ocean properties because of strong sea floor diagenetic alteration. However, calcareous nanofossil carbonate, also produced in the surface mixed layer and accessible in the form of the bulk sedimentary carbonate or sediment ‘fine fraction’, is available. The challenge is to understand what these bulk geochemical signals mean.

Bulk sediment comprises a mixture of different, mostly biogenic particles. The information carried by its properties, including physical and geochemical signals, comprises a mixed signal reflecting different ecological, metabolic and depositional processes associated with the formation and sedimentation of the various calcite particles. The purpose of this thesis is to understand what bulk sediment records represent in terms meaningful for deciphering the paleoceanographic history of the EEP. The results add to, and significantly improve the paleoceanographic “tool box” available for developing proxy records in this complex oceanic region. This thesis comprises a kappa, two published papers and a manuscript, in review as this is written (April 2019). Paper I examines the factors linking sediment composition and physical properties in the EEP through analysis of the relationship between sediment carbonate content and sediment density. Paper II and Paper III focuses on improving the understanding of bulk carbonate carbon and oxygen
stable isotope signals by disentangling the contribution of different carbonate components. In these studies, a multiproxy approach was adopted to reconstruct ocean evolution of the EEP since the late Miocene. A major conclusion is that bulk carbonate stable isotopes reflect the isotopic composition of calcareous nannofossils, and therefore surface water conditions, despite complication by several factors. The ideas and findings of the latter two papers have been further tested in an unpublished inter-basin comparison presented in the Chapter 6 of this kappa. The findings of this doctoral thesis demonstrate that bulk sediment is more than just a correlation tool and can provide a reliable indicator of surface ocean conditions that can be used to decipher EEP oceanographic history since 8 Ma.
Svensk Sammanfattning

Rekonstruktion av östra ekvatoriella Pacifikens (EEP) oceanografi sedan sen-neogen tid (omkring 8 miljoner år före nu, Ma) är en centralt ämne i pågående paleoceanografiska undersökningar. Det finns två skäl till detta. För det första har EEP ett påtagligt inflytande på det globala klimatet eftersom starka gradienter i ytvattnets temperatur (SST) och biologisk produktivitet kopplad till vinddriven uppåtåsning påverkar det globala klimatet och kolykeln, som inkluderar utbytet av uppåtålta CO\textsubscript{2} till atmosfären. För det andra har det globala klimatet under de senaste 8 miljoner åren genomgått stora förändringar före det att nuvarande tillstånd nåddes, i en utveckling från den senaste större globala värmeperioden (under tidig-pliocen tid) till det kallare medeltillståndet som karakteriserade den pre-industriella världen. Att utvärdera dynamiken i EEP systemet sedan sen-neogen tid är därför viktigt för förståelsen om hur detta havsområde fungerar under olika och ändrade klimatförhållanden.

Trots det stora antalet studier som tillägnats EEP är dess paleoceanografiska utveckling sedan 8 Ma fortfaranande debatterad, där kontrasterande scenarier har föreslagits. Detta beror delvis på att paleoceanografiska rekonstruktioner är utmanande i EEP på grund av stora miljömässiga, och således sedimentära, heterogenitet, samt på grund av de extrema vattendeptheter, vilka försämrrar bevaringen av användbara foraminiferarkiv i många regioner. Därutöver, några befintliga dataset har problem med hur dessa data insamlades. Rekonstruktion av egenskaper hos ytvattnets blandlager kvarstår som ett viktigt krav för att kunna utvärdera EEPs paleoceanografi. Fossila foraminiferskal finns oftast inte tillgängliga för att spåra ytvattnesvenskungar i EEP på grund av starka diagenetiska förändringar vid havsbotten. Emellertid, kalknannofossilkarbonat, som också produceras i ytvattnets blandlager och som finns tillgängligt i form av bulk sedimentkarbonat eller i ‘finfraktionen’, är tillgängligt. Utmaningen består i att förstå vad dessa geokemiska signaler i bulk sedimentet betyder.

Bulksediment består av en blandning av olika, mestadels biogena, partiklar. Informationen som finns i bulksedimentets egenskaper inbegriper fysikaliska och kemiska signaler, som i sin tur representerar olika ekologiska, metaboliska och depositionsprocesser associerade med bildningen och sedimentationen av de olika kalcitpartiklarna. Syftet med denna avhandling är att förstå vad bulksedimenten representerar i term av meningsfull utvärdering av EEPs paleoceanografiska historia. Resultaten bidrar till och förbättrar signifikant den paleoceanografiska ”verktygslådan” som används för utveckla proxydata i denna komplexa havsregion. Avhandlingen består av en e, två publicerade artiklar och ett manuskript som för närvarande (april 2019) sakunniggranskas. Artikel I undersöker de faktorer som länkar ihop sedimentsammansättning och fysikaliska egenskaper i EEP genom analyser av förhållandet mellan sedimentets karbonatinnehåll och sedimentdensitet. Artikelerna II och III fokuserar på att förbättra
förståelsen av bulkcarbonatets kol- och syreisotopsignaler genom att reda ut de relativa bidragen från olika karbonatkomponenter. I dessa studier har multiproxymetoder använts för att rekonstruera utvecklingen i EEP sedan sen-miocen tid. En huvudsaklig slutsats är att stabila isotoper hos bulkcarbonatet reflekterar isotopsammansättningen hos kalknannofossil, och därför förhållanden i ytvattnets blandlager, trots komplikationer från olika faktorer. Idéer och rön i de två senare artiklarna har blivit ytterligare prövade i en opublicerad interbassängjämförelse presenterad i Kapitel 6 i denna kappa. Rönen framtagna i denna doktorsavhandling visar att bulksediment utgör mer än endast ett korrelationsverktyg och kan utgöra en pålitlig indikator för ytvattenförhållanden som i sin tur kan användas för att utvärdera EEPs oceanografiska historia sedan 8 Ma.
List of papers and author contributions

This thesis is composed of a ‘kappa’, which provides a general introduction to the thesis and a synthesis of the results, followed by three manuscripts. Paper I was published in Marine Geology in 2013 and is here printed with the permission of Elsevier. Paper II was published in Paleoceanography in 2015 and is here printed with permission of AGU Publications. Paper III was submitted to Paleoceanography and Paleoclimatology on 16th February 2019 and is currently in review at time of writing (April 2019).


*Publication status as of 20 April, 2019*

Daniele Reghellin was the lead author of the three manuscripts. He was responsible for the experimental design, carried out most of laboratory and micropaleontological analysis, created all figures and tables and led the writing. All authors have contributed ideas, commented and edited text of the manuscripts. In all the three papers Klara Hajnal, Carina Johansson and Laura Martinez performed coulometer analysis In Paper I Carl-Magnus Mörth contributed with statistical analysis. In Paper II, Marianne Ahlbom gave assistance with Environmental Scanning Electron Microscopy. In Paper III, Kajsa Markdahl performed samples sieving and Anna Nyberg helped with carbonate particles picking. In Paper II and Paper III, Heike Sigmund conducted mass spectrometry analyses. Martin Jakobsson created eastern equatorial Pacific bathymetry maps in the kappa.

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1. Introduction

The equatorial Pacific encompasses 50% of the global equatorial oceans and is an important driver of global climate [van Andel et al., 1975; Seki et al., 2012; Fielder and Lavin, 2017; Zhang et al., 2017]. It is characterized by strong zonal (east-west) and meridional (north-south) gradients in surface water temperature and marine biological productivity. The ocean area between 80°W and 150°W longitude and 15°N and 15°S latitude is here defined as the eastern equatorial Pacific (EEP; Figure 1). The EEP is of particular importance because of its high biological productivity and its role as i) primary source of carbon dioxide (CO₂) from the deep ocean to the atmosphere [Lyle et al., 2010; Lyle and Baldauf, 2015; Martinez-Boti et al., 2015a; Rippert et al., 2017] and ii) controller of ocean-atmosphere heat exchange under modern global warming conditions [Kosaka and Shang, 2013; Linsley et al., 2015]. The EEP is thus a sensitive area of the global ocean/climate system.

Figure 1. Map of the modern eastern equatorial Pacific region showing bathymetry and location of Deep Sea Drilling Project (DSDP, black dots), Ocean Drilling Program (ODP, dark grey dots) and Integrated Ocean Drilling Program (IODP, light grey dots) drill sites. Dots with a white ring represent sites investigated in this study. White shaded ellipses identify the drilling transects of ODP Leg 138 and IODP expeditions 320/321. Bathymetric data and map are from GEBCO Compilation Group [2019].

The EEP has a long history of interest for the paleoceanography community. Since the Challenger expedition (1872-1876) [Thompson et al., 1885] sediments collected from the EEP were described to be sensitive to oceanographic changes. The pioneering Swedish Deep Sea Expedition (1947-1948), involving
the four-masted schooner *Albatross*, initiated scientific deep-sea coring in the region [Arrhenius, 1950, 1952; Pettersson, 1953]. Succeeded by Deep Sea Drilling Project (DSDP) Legs 5, 8, 9 and 16 (1969-1973), the EEP became a focus for paleoceanographic and paleoclimatic studies [van Andel *et al.*, 1975]. These early coring and drilling expeditions provided basic spatial coverage of the EEP and described large heterogeneity in sediment physical and chemical properties across the region involving major switches in carbonate, biosilica and abyssal clay dominance (Paper I) [Kominz *et al.*, 1977]. Already then, it was recognized that this was a consequence of complex interactions between plate tectonic motion, surface winds, biological productivity and ocean chemistry on millions to millennial times scales, and even decadal (El Niño/El Niña times scales).

EEP scientific drilling continued in 1995 with Ocean Drilling Program (ODP) Leg 138. This took the approach of drilling two north-south transects (centered at about 95°W and 110°W longitude; Figure 1) to study variability in sedimentation patterns across areas located under different productivity/upwelling intensities [Pisias *et al.*, 1995]. Using sediment collected at multiple sites during this expedition, *Shackleton and Hall* [1995] emphasized the potential of stable carbon and oxygen isotopes (δ13C and δ18O) measured on bulk carbonate for late Cenozoic paleoceanographic reconstructions. The study made two important findings, (i) there is striking spatial coherency in δ13C records since 15 Ma, while (ii) the complementary δ18O showed significant δ18O separations between records from sites located on and off the Equator during the late Miocene and the early Pliocene. The ca 1 ‰ higher δ18O values along the Equator, in comparison with those from off Equator sites, were interpreted as reflecting lower sea surface temperature (SST) and enhanced wind-driven circulation and upwelling and were suggested as providing a tool to monitor the variability of this system over time. Despite the potential of these data sets to improve the understanding of EEP paleoceanography the *Shackleton and Hall* [1995] ideas have been mostly ignored.

A third phase of EEP drilling took place in the 2000s with ODP Leg 199 in 2002 and Integrated Ocean Drilling Program (IODP) expeditions 320/321 in 2009. These expeditions comprised further water-depth and age transects, designed to record the evolution of the EEP through the Cenozoic and its interactions with global climate [Lyle and Wilson, 2006; Pälike *et al.*, 2010]. Technological advances in drilling methods, such as the use of Advanced Piston Corer (APC) and Extended Core Barrel (XCB) succeeded in reducing the sediment disturbance from coring. Multiple coring of holes at single sites contributed to the retrieval of complete recovery of the penetrated sediment column. The use of sediment chemical and physical properties in EEP sediment has permitted correlations of high-resolution changes over large distances across the EEP [Pälike *et al.*, 2010]. These sediments provide excellent archives to test and develop *Shackleton and Hall*‘s (1995) observations on bulk carbonate δ13C and δ18O and other properties (Paper II and Paper III).

EEP paleoceanography in the last 8 million years ago (Ma) is of key interest because it shows the development of the modern Pacific Ocean geographic configuration, i.e. spanning the eventual closing of
Central American Seaway (CAS) at about 3 Ma, and the evolution to the modern climate state with its characteristic patterns of variability, including the last period of sustained global warmth (5.3-3.5 Ma), the onset of the large scale Northern Hemisphere glacial cycles of the Quaternary, and the transition into our current interglacial (the Holocene) (section 3.3). Despite the number of scientific drilling campaigns and publications, much of this history remains uncertain and/or is still debated [Lea, 2014; Zhang et al., 2017]. Two factors make paleoceanographic reconstructions of the EEP challenging. The first is the extreme environmental heterogeneity. The complex ocean-atmosphere interactions generate steep gradients in water masses properties (temperature, salinity, pH, nutrients and dissolved ions) over relatively short intervals in space and time (chapter 3). The second factor is the water depth of the seafloor. Most of the EEP seafloor lies below 4000 mbsl, where carbonate dissolution is intense. The combination of these two factors results in major changes in sediment composition, chemical and physical properties over short increments of depth and time (chapter 4). Surprisingly, these changes display a high coherency once aligned in the time domain.

Currently the picture of EEP paleoceanography is incomplete because basic information on the important oceanic parameters are either missing or inconsistently recorded. First, some prominent studies on EEP paleoceanography have reconstructed SSTs without including information on changes in biological production and, vice versa, some other studies have reconstructed changes in biological production without including information on SSTs [Wara et al., 2005; Brierley et al., 2009; Fedorov et al., 2006]. For a comprehensive view of EEP oceanographic evolution studies need to include constraints on both SST and biological production given the close interplay between oceanography and biological productivity in modern EEP. Second, proxy records have been generated from a limited number of sites which do not account for the prominent environmental heterogeneity of EEP across latitude and longitude, and iii) proxy records of past SST span the 5-0 Ma time interval and thus lack to provide crucial information of late Miocene and earliest Pliocene [above references and Cannariato and Ravelo, 1997].

The EEP ocean system is governed by interactions between the surface and deep ocean, and the atmosphere. Thus, reconstructing surface mixed-layer water properties and dynamics is crucial to deciphering the history of EEP ocean/climate evolution. The “favorite” approach for tracing mixed layer variability in paleoceanography is to look at the chemistry of isolated foraminifera tests. This is problematic in the EEP because planktonic foraminifera are often affected by diagenetic alteration, or dissolved. This is evident in sediments deposited during the late Miocene and the early Pliocene, when the diagenetic alteration of fossil planktic foraminifera shells, involving recrystallization at the seafloor, was demonstrated to be more intense compared to modern times [Lyle, 2003; Pälike et al., 2012]. This limitation prompts a return to the palaeoceanographic archive that is persistent, i.e. bulk sedimentary carbonate. Bulk carbonate accumulating in the EEP seafloor is mostly biogenic in origin and is produced in the surface mixed layer. It thus, should preserve information on mixed layer dynamics and chemistry, as originally noted by Shackleton and Hall [1995]. Bulk sediment, however, is a mixture of different types of particles, dominantly coccoliths and whole and broken foraminifera shells, over printed to variable degrees by post depositional processes,
including dissolution, fragmentation, and potentially diagenetic alteration. The challenge is to isolate the important oceanographic signals.

This thesis was designed to answer to one basic question: **what do bulk sedimentary carbonate records from the EEP represent in terms of meaningful paleoceanographic signals?** This general question has been addressed in different parts resulting in 3 papers, 2 published and a third in review at time of writing. First, an in depth understanding of the factors controlling general sediment properties and composition and their analysis was carried out (Paper I). Next, multi-proxy data sets of sediment composition and isotope geochemistry were generated to reconstruct both surface water temperature and carbon cycling at multiple locations across the EEP, and extending back 8 million years (Myrs). This involved generating records of bulk sediment, ‘fine fraction sediment’ and foraminifera carbonate δ¹³C and δ¹⁸O to help disentangle the relative contributions of various contributing signals (Paper II and Paper III). Ultimately, new and published proxy records from multiple locations were compared and synthesized to produce a comprehensive picture of late Neogene EEP paleoceanography (Paper III).

Chapters 1-5 present the wider background and context for the thesis. After a broad introduction (Chapter 1), Chapter 2 presents the specific aims of the project. Background information on the EEP study area and a description of its evolution during the late Cenozoic is presented in Chapter 3. Chapter 4 introduces bulk sediment composition and properties in more detail, highlighting the importance of coccolith carbonate, i.e. the remains of calcareous phytoplankton, that turn out to be the dominant contributor to EEP sediment. Chapter 5 presents a summary of the analytical methods used. Chapter 6 provides an overview of the main findings of the research and a forward-looking perspective on the next steps. This includes an unpublished inter-basin comparison of stable isotope and grain size data from the tropical Atlantic Ocean and a set of unresolved questions. Following the kappa, two published papers and a manuscript in revision are presented.
2. Thesis aims

The overarching goal of this Ph.D. thesis is to better understand the history of EEP ocean circulation and climate interactions during the late Neogene (from 8 Ma to present day), a time during which the modern continental geography emerged, and Earth transitioned from times of elevated global temperatures (average global surface temperature was up to 2-3°C warmer during the early Pliocene) to the glacial cycles of the Pleistocene (average 2°C colder than today). Given challenges to reconstructing Pacific Ocean paleoceanography using foraminifera shells, other tools are needed. This thesis aims to develop the paleoceanography ‘tool box’ with a focus on optimizing information available from bulk sediments recovered in deep sea drill cores from the EEP. The approach taken has been to: (i) generate new and synthesize existing data in order to decipher the links between changes in sediment physical, chemical and compositional properties and EEP paleoceanographic evolution, and (ii) apply the findings to improve understanding of the ocean-climate evolution of this region from the late Miocene to modern times. This research resulted in three papers, two published and the third in review at the time of writing, and a summary ("kappa" in Swedish) that includes suggestions for future research.

Paper I


The first step towards developing the EEP paleoceanography tool box was to constrain the dominant factors linking sediment composition to sediment physical properties. An example of this linkage is the relationship between sediment density and calcium carbonate content. The density of deep-sea sediment varies with sediment porosity, decreasing with increasing burial depth and sediment compaction, and with type of sedimentary grains. The latter factor mainly subdivides carbonate particles with relatively high grain density (2.6-2.7 g/cm$^3$) and biosilica particles with relatively low grain density (2.1-2.3 g/cm$^3$). A third sedimentary component are clays. In ocean regions located thousands of kilometers from land masses such as most of the EEP, deep-sea clays are mainly composed by aeolian dust [Hovan, 1995]. Clays have grain densities similar to that of carbonate particles and are significant contributors to sediment in areas of low surface water production and where the seafloor depth exceeds the CCD depth [Dutkiewicz et al., 2015; 2016]. In contrast, clays show consistently lower relative contributions to sediments beneath the EEP area where wind-driven upwelling occurs (±2° latitude) close to the Equator (Chapter 3) [Dutkiewicz et al., 2016]. Thus, clays are considered to have less impact on bulk density variations in comparison to shifts in...
biogenic carbonate/silica deposition [Farrell et al., 1995; Pälike et al., 2010]. Thus, sediment bulk density, once accounted for sediment compaction, can be used as a proxy of carbonate/biosilica content.

Sediments deposited in the EEP show a clear relationship between wet bulk density (WBD) and carbonate content. This relationship was first described by Luz and Shackleton [1975] at multiple sites across the EEP. The interest to this originates from the fact that gamma ray attenuation porosity evaluator (GRAPE) measurements approximate WBD, and are routinely measured during deep sea drilling expeditions at <5 cm resolution. Taking advantage of this relationship, GRAPE measurements can thus be used to produce high-resolution carbonate content records [Mayer, 1991]. Carbonate content records are of primary importance for paleoceanographic reconstructions as they give insights on sediment composition, biological productivity, sediment diagenesis and ocean chemistry (section 5.2). To generate high-resolution CaCO$_3$ % records the WBD-CaCO$_3$ % relationship has been described empirically [Lyle and Dymond, 1976; Mayer, 1991], but the equations proposed do not fully describe the variance of data. In addition, the relationship has never been verified from first principles involving volume and mass and porosity of sediment components. In this study we measured CaCO$_3$ %, and coarse particles (>63 µm) content (CF %) of samples with known WBD from IODP Site U1338. Using new and published data we developed a mathematical model to describe numerically the WBD-CaCO$_3$ % relationship.

The specific aims of this paper are to:

- verify whether the relationship between WBD and CaCO$_3$ % in sediment is present also at IODP Site U1338;
- Examine the factors generating the WBD-CaCO$_3$ % relationship.
- Examine the causes of differences in the WBD-CaCO$_3$ % relationship at different sites within the EEP.
- Investigate whether WBD-CaCO$_3$ % relationship can be described by an empirical equation, as proposed by Lyle and Dymond [1976] and Mayer [1991]. Such an equation would be of great importance as it allows to quickly generate high-resolution CaCO$_3$ % estimates from WBD with a simple calculation.

**Paper II**

**Regnellin, D., H. K. Coxall, G. R. Dickens, and J. Backman (2015), Carbon and oxygen isotopes of bulk carbonate in sediment deposited beneath the eastern equatorial Pacific over the last 8 million years, Paleoceanography, 30. doi:10.1002/2015PA002825.**

In the second paper the EEP paleoceanography tool box was further developed by examining how changes in sediment properties are related to the oceanographic evolution of the EEP. This paper was designed to better understand to what extent bulk carbonate stable isotopes records contain information useful for paleoceanographic reconstructions. The paleoceanographic meaning of bulk sediment $\delta^{13}$C and $\delta^{18}$O is of
particular interest for scientists working on deep-time intervals, for which the use of bulk sediment stable isotopes is a common practice. In an inspiring study, Shackleton and Hall [1995] generated bulk carbonate $\delta^{13}$C and $\delta^{18}$O records from multiple locations across the EEP. They emphasized the potential of such records as proxies for mixed layer water properties and biological productivity in the EEP. The paleoceanographic meaning of bulk carbonate stable isotopes is largely unknown, mostly because bulk carbonate represents a mixture of different components each carrying a different stable isotope composition. In addition, the relative abundance of each component changes over time.

To improve the utility of bulk carbonate stable isotopes new EEP records were generated from IODP Site U1338 and ODP Site 573 over the 8-0 Ma time period, and compared to published bulk carbonate stable isotope records from ODP Leg 138 sites. To disentangle the contribution of different carbonate components to bulk carbonate $\delta^{13}$C and $\delta^{18}$O we measured the stable isotope composition of sieved-separated <63 $\mu$m and <38 $\mu$m sediment and compared the records. The basic assumption is that calcareous nanofossils content increases with decreasing sediment size, thereby progressively excluding foraminiferal carbonate (Chapter 4). CaCO$_3$ %, CF % and sedimentation rate records as well as scanning electron and light microscopy images were produced to provide a comprehensive understanding of stable isotope records and give new insights on EEP paleoceanographic evolution since the late Miocene.

The specific goals of the paper are to:

- Examine whether previously published bulk carbonate $\delta^{13}$C and $\delta^{18}$O records coherently vary over large distances (>2500 km) across the EEP.
- Verify if the absence of decimeter- to centimeter-scale variability in published bulk stable isotopes records is the result of larger-than-typical sampling practices (150 cm integrated intervals in Shackleton and Hall [1995] compared to 1-4 cm depth interval in this study, or not.
- Verify if bulk $\delta^{13}$C and $\delta^{18}$O signals reflect the isotopic composition of calcareous nanofossils or a mixed signal of variations in the proportion of calcareous nanofossils and foraminifera.

Paper III

Reghellin, D., H. K. Coxall, J. Backman and G. R. Dickens (manuscript), Comparison of stable isotope records across the Eastern Equatorial Pacific, from the Biogenic Bloom to Present-day, in review, Paleoceanography and Paleoclimatology.

The next step in the effort of understanding bulk carbonate $\delta^{13}$C and $\delta^{18}$O records was to further dissect the relative contributions of different calcareous particles to bulk carbonate. A key conclusion of Paper II was that bulk $\delta^{13}$C and $\delta^{18}$O reflects the stable isotope composition of coccoliths. However, the relative contribution of the various other contributing carbonate components (calcareous nanofossils, planktic and benthic foraminifera, and foraminifera fragments) to the bulk signal is still under debate and needed further
disentangling. Critically, it was still not well understood how the relative contribution of the different components vary with surface water oceanographic changes and thus might variably contribute to the bulk $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signal. Comparisons of how different carbonate components influence stable isotopes generated from the same sample remain poorly known. To fill this gap is an important step, given the remarkable short-term changes in sediment composition.

The approach taken was to generate a range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records (bulk, fine fractions, mixed foraminifera particles) measured on single samples from ODP Site 851 for the 7-0 Ma time period. As for Paper II, other proxies for mixed layer temperature and carbon cycling such as grain-size distribution, CaCO$_3$ % and biosilica content, and sedimentation rates were also generated. These records were compared to published single-species planktic foraminifera $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from the same site [Cannariato and Ravelo, 1997], and to published single-species benthic foraminifera $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from the neighboring Site 849 [Mix et al., 1995], which provide ‘clean’ and isolated surface mixed layer, thermocline and deep water signals respectively.

The specific aims of this study are to:

- Examine the relative contributions of different carbonate components in terms of useful paleoceanographic signals, e.g., mixed layer biological productivity, SST, nutrient availability.
- Investigate how bulk carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are generated in the first place, including the contributions of various biological isotopic fractionations by photosynthesizing calcifiers.
- Investigate how modifications in bulk carbonate composition due to ocean, climate, biological production and dissolution changes, are reflected in bulk carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signals.
3. The eastern equatorial Pacific Ocean

3.1 Bathymetry and hydrography

The eastern Pacific Ocean lies on three lithospheric plates, the Pacific, Nazca and Cocos plates [Van Andel et al., 1975; Mayer et al., 1992]. The Pacific plate is located west of the East Pacific Rise, which separates the plate from the Nazca and Cocos plates, located to the east. The Cocos and the Colon ridges separate the Cocos plate to the north and the Nazca plate to the south. The East Pacific Rise represents the most important bathymetric feature of the region and extends from northeast to southwest between about 100°W and 120°W longitude (Figure 2) [Mammerickx, 1989]. Given the orientation of the rise, depth and age of the Pacific plate seafloor increases roughly westward. Over the Cenozoic Era (the last 66 Ma), drilling sites located on the western flank of the East Pacific Rise (of interest to this thesis) have moved to the northwest because of plate tectonics [Mayer et al., 1985; Mayer et al., 1992; Pälike et al., 2010].

Figure 2 Map of the modern eastern equatorial Pacific region showing bathymetry, ocean currents and location of DSDP, ODP and IODP drill sites of interest for this thesis. Bathymetric data and map are from GEBCO Compilation Group [2019]. Black solid arrows represent surface water currents whereas black dashed arrows represent deep currents. White dots represent location of sites from which new sedimentary records were produced in this thesis work: IODP Site U1338 (Paper I and II), DSDP Site 573 (Paper II) and ODP Site 851 (Paper III). Grey dots represent other sites of interest to this thesis. EUC: Equatorial Under Current, NEC: North Equatorial Current, NECC: North Equatorial Counter Current, PC: Peruvian Current; SEC: South Equatorial Current.

In the modern EEP the water circulation is strongly bound to the trade winds system (Figure 3) [Hovan, 1995; Lyle et al., 2010; Beltran et al., 2014; Fiedler and Lavin, 2017]. South- and North-East Trade Winds, respectively SETW and NETW the surface branches of the Hadley cell, converge north of the Equator at...
the Inter-Tropical Convergence Zone (ITCZ). Converging SETW and NETW move surface water apart from the Equator because of the Coriolis effect, generating wind-driven upwelling. The upwelling rate at the Equator exceeds 1 m/day [Fiedler and Lavin, 2017]. The motion of surface water masses in the EEP is thus generated by the wind stress on ocean surface rather than by density gradients, which instead drive deep water circulation.

![Figure 3](image)

**Figure 3.** Three-dimensional sketch illustrating the ocean/atmosphere system operating in the modern EEP along a north-south transect located at about 110°W longitude [modified from Hovani, 1995; Cannariato and Ravelo, 1997]. The grey arrows represent surface wind direction and grey band represents the inter-tropical convergence zone (ITCZ) defined as the region where these winds converge. Black arrows represent water currents. EUC = Equatorial Under Current, EqPIW = Equatorial Pacific Intermediate Water, NEC = North Equatorial Current, NECC = North Equatorial Counter Current, NETW = North-East Trade Winds, SEC = South Equatorial Counter Current, SETW = South-East Trade Winds.

Trade winds also drive the South Equatorial Current (SEC) and the North Equatorial Current (NEC) to the west. The SEC is centered at about 3° N whereas the NEC is centered at about 10° N because trade winds converge north of the Equator (Figures 2 and 3). These two currents push water to the west of the equatorial Pacific where it stacks up, generating a pressure gradient that forms two east-flowing currents, the North Equatorial Counter Current (NECC) and the Equatorial Under Current (EUC).

The NECC flows at the surface in the ITCZ where opposing trade winds converge, weakening their strength. The EUC flows eastward below SEC and within the thermocline, the zone of abrupt temperature change from warm surface waters to cold deeper waters. This current also shoals from west to east following the thermocline and represents the main source of nutrients to upwelling waters in the EEP [Ford et al., 2015; Fiedler and Lavin, 2017]. The EUC receives nutrients by the underlying sub-thermocline equatorial Pacific Intermediate Water (EqPIW). The latter is mainly formed by Southern Ocean Intermediate Water (SOIW), which comprises Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW). These two intermediate water masses, including their physical and chemical characteristics (density, CO₂ and nutrient content) are transferred from the Southern Ocean to the EEP via the so called “oceanic tunnelling” [Martínez-Boti et al., 2015a]. The North Pacific Deep Water (NPDW) fills the EEP between ca
2500 and 4000 m depth whereas the main bottom water mass (>4000 m) is the Lower Circumpolar Water (LCPW) [Fiedler and Talley, 2006]. These deep and bottom water masses are formed in the North Atlantic and Southern oceans.

The EEP is generally referred to as an upwelling region. However, it is important to emphasize that wind-driven equatorial upwelling mostly occurs at ±2° latitude around the Equator and west of the Galapagos Islands (Figure 4) [Fielder and Lavin, 2017]. Just north and south of the ±2° latitude upwelling band, downwelling occurs. Due to the complexity of the atmospheric and oceanic system and its fluctuation over time (Section 3.2), water masses located very close in space can have significantly different properties, such as temperature, salinity, dissolved ions and nutrient content. To account for this extreme variability, paleoceanographic studies need to be based on records from multiple location scattered across the EEP (Paper II).

Figure 4. Annual surface water vertical velocity [cm/day] reflecting wind-driven upwelling and downwelling in the EEP averaged over the 1950-1997 period [modified after Fiedler and Lavin, 2017]. Data are from Xie and Hsieh [1995]. Land map is from Ocean Data View [Schlitzer, 2018]. Warm colors represent rising water (upwelling) whereas cold colors represent sinking water (downwelling). Note that equatorial upwelling almost exclusively occurs in the narrow ocean band comprised between ±2° latitude and west of the Galapagos Islands. Just north and south of the upwelling band, downwelling occurs.

3.2 EEP and global climate

The interaction between the lower atmospheric circulation and the upper water column generates, under normal conditions, steep SST gradients across the tropical Pacific Ocean. Today, the mean annual SST is 23°C in the EEP and 29°C in the Western Equatorial Pacific (WEP) [Locarnini et al., 2013]. These SST gradients are coupled to differences in atmospheric pressure (high in the EEP and low in the WEP) and in the thermocline depth [Fiedler and Lavin, 2017]. The latter deepens westward across the tropical Pacific Ocean, as depicted by an oceanographic transect along the Equator from the westernmost EEP (160°W) to
the coasts of South America (Figure 5). These ocean-atmosphere gradients drive atmospheric Walker circulation and the Hadley cell, regulating heat exchange, precipitation patterns and hence the climate within the tropics and globally [Lyle et al., 2010; Pälike et al., 2010; Fiedler and Lavin, 2017]. Trade wind strength and SST gradients sustain each other in a positive feedback loop (also known as Bjerknes feedback) that controls the state of EEP [Collins et al., 2010].

![Diagram of ocean-atmosphere gradients](image)

**Figure 5.** Modern annual mean sea surface temperature (SST) in the EEP (panel a) and modern distribution of water temperature with depth along an equatorial transect (0° latitude) from 160°W longitude to the coast of South America (panel b) [Schlitzer, 2018]. Dark grey areas depict terrestrial surfaces (panel a) and bathymetric features (panel b). Water temperature data are from the World Ocean Atlas 2013 version 2 and are averaged over the 1955-2012 time period [Locarnini et al., 2013]. Black lines represent SST isotherms and corresponding temperature numbers are expressed in °C whereas the white dashed segment represents the equatorial transect along which the water/depth profile was designed (panel a). Note that SST increases and thermocline deepens westward along the Equator. Cooler SST in the easternmost part of the EEP originates from wind-driven upwelling and influx of cool currents (e.g. the Peruvian Current). Also note that the subsurface Equatorial Under Current (EUC) flows within the thermocline and source upwelling waters. mbsl= meters below sea level, EqPIW= Equatorial Pacific Intermediate Water, NPDW= North Pacific Deep Water, LCPW= Lower Circumpolar Water.

The EEP is also one of Earth’s most important ocean areas for biological production and plays a central role in the global carbon cycling [Lyle et al., 2010; Pälike et al., 2012]. Upwelling brings sub-surface...
nutrient-rich water to the surface photic zone, where they are employed by phytoplankton during photosynthesis, supporting biological primary production in the region (Figure 6). In the modern EEP biological productivity is so intense that the region is responsible for approximately 20 to 60% of global new production [Chavez and Barber, 1987]. Primary producers (mainly diatom and coccolithophorid phytoplankton) fix dissolved inorganic carbon (DIC), the sum of all inorganic carbon species in solution with seawater (CO$_2$, HCO$_3^-$, and CO$_3^{2-}$), into organic matter by means of photosynthesis. When these organisms die and rain down to the ocean interior, the organic matter is decomposed within the first 1000 m of the water column adding dissolved CO$_2$ to subsurface waters [Harvey, 2012]. The latter is known as the “carbon pump” and is a key step of global carbon cycling [Honjo et al., 1995]. Equatorial upwelling eventually brings the CO$_2$-rich water from intermediate depths to the surface mixed layer, where the dissolved CO$_2$ is outgassed to the atmosphere. The EEP is considered the largest source of oceanic CO$_2$ to the atmosphere because about $10^9$ metric tons of carbon per year are released to the atmosphere, equivalent to two thirds of the global ocean-atmosphere CO$_2$ flux [McPhaden et al., 2006; Takahashi et al., 2009; Martinez-Boti et al., 2015a]. The CO$_2$ flux maintains the ocean-atmosphere CO$_2$ disequilibrium and thus controls the atmospheric CO$_2$ levels.

![Figure 6. Modern annual mean sea surface chlorophyll-a concentration of the EEP. Data are monthly-composite averaged over the 2003-present time period (courtesy of NASA/GSFC OBPG). Land map is from Ocean Data View (Schlitzer, 2018). Black areas represent gaps in coverage, i.e. areas where no valid pixels were recorded over the entire compositing period. The primary causes of these gaps are persistent cloud cover, sun glint or heavy aerosol. Note that west of the Galapagos Islands, the chlorophyll-a concentration (and thus primary production) is higher within the ±2° latitude ocean band compared to higher latitudes.](image-url)

Upper ocean DIC is fixed into carbonate (CaCO$_3$), largely in the form of calcite, by means of calcification in organisms generating calcareous shells, mainly coccolithophorids and planktic foraminifera. The CaCO$_3$ remains of these organisms can either dissolve in deep waters below the lysocline, reverting the carbon to DIC, or can be stored in pelagic sediment. The amount of carbon stored by sediment burial in the EEP is
as much as 40% of the global carbonate production, significantly impacting global climate regulation [Lyle et al., 2008; Pälike et al., 2012].

The state of the dynamic EEP ocean/atmosphere system is not constant through time and may vary on orbital, decadal to interannual timescales, as happens in the modern ocean as part of the El Niño-Southern Oscillation (ENSO). The ENSO is a quasi-periodic fluctuation between anomalous warm SST and weakened upwelling (El Niño) conditions and anomalous cold SST and enhanced upwelling (La Niña) conditions in the EEP [Molnar and Cane, 2002; McPhaden et al., 2006]. During El Niño, the strength of trade winds and equatorial upwelling weakens and the thermocline deepens, suppressing SST and atmospheric gradients across the tropical Pacific Ocean. Under these conditions, the strengths and positions of the Walker and Hadley circulations are altered, affecting tropical precipitation patterns, extra-tropical heat transport, global atmospheric circulation and mean temperatures. El Niño events cause droughts in Africa, southwest Asia and Australia, extreme rainfall and floods in South America along the Andes mountain range, and alter marine ecosystems due to relative increases or decreases in nutrient supplies to the photic zone impacting primary production [McPhaden et al., 2006]. The weakening of equatorial upwelling in the EEP also causes a reduction of ocean-atmosphere CO₂ fluxes and biological production, altering atmospheric CO₂ concentrations and carbonate burial, thus impacting global carbon cycling.

3.3 Evolution of the global climate and EEP since the late Neogene

The Earth’s climate evolution during the Cenozoic Era is characterised by a long term trend and transition from warm-greenhouse climates of the Paleocene and Eocene to cold-icehouse climates of the Oligocene through the Pleistocene were one or more pole was ice covered (Figure 7) [Zachos et al., 2008]. The time interval on which this thesis focuses, the last 8 Myr, begins in the late Miocene and includes the transition from the last period of widespread climate warming, the early Pliocene, to the colder pre-industrial climate of the late Neogene, with extended glaciations in both the Southern and Northern Hemispheres. Numerous studies have reported dramatic changes in the ocean/climate system in the tropical Pacific over this time interval. In parallel the Earth underwent some major tectonic changes since 8 Ma, which have played an important role in regulating global water circulation, heat transport and hence climate [Zachos et al., 2001; Haug et al., 2001; Brierley and Fedorov, 2010; De Schepper et al., 2013; Burls et al., 2017]. The study of EEP paleoceanographic changes is essential to understand how the climate system developed towards modern conditions.

During the late Miocene (11.6-5.3 Ma) global climate, temperature, and ecosystems changed significantly [Herbert et al., 2016]. Multi-proxy studies have shown large-scale SST cooling and increased pole-to-Equator temperature gradients between 7.0 and 5.4 Ma [Seki et al., 2012; Herbert et al., 2016]. Over the same time period, global atmospheric CO₂ concentrations declined below 500 ppm (Figure 7) [Bolton et al., 2012; Bolton and Stoll, 2013; Haywood et al., 2016]. Aeolian sediments in cores from ODP Sites 848 and 849 located near the Equator in the EEP indicate strongest trade-winds between about 8 to 5 Ma.
During this time interval, the CAS was open and shallow currents flowed between the EEP and the Caribbean Sea [O’Dea et al., 2016]. Recent climate modelling studies have shown that an open CAS is coherent with enhanced wind-driven circulation in the EEP during the late Miocene [Brierley and Fedorov, 2016; Sentman et al., 2018]. These changes, combined with reduced atmospheric CO₂ resulted in large-scale terrestrial aridification and favoured the expansion of C₄ plants (tropical grasses adapted to arid climates) relative to the C₃ plants (trees and bushes adapted to temperate climates) in low and mid latitudes [Bolton and Stoll, 2013; Herbert et al., 2016].

Figure 7. Tectonic, climatic and biotic events, global benthic foraminifera δ¹⁸O stack and alkenone- and boron-derived pCO₂ estimations representing climate evolution over the Cenozoic era [Zachos et al., 2001; 2008]. Benthic foraminifera δ¹⁸O data (grey dots) are from Cramer et al. [2009] and are Cibicidoides adjusted. Black dots represent 21 points smoothed data. pCO₂ estimation
data are from Pagani et al. [2005; 2010; 2011], Honisch et al. [2009], Seki et al. [2010], Bartoli et al. [2012], Badger et al. [2013a; 2013b], Foster et al. [2012], Zhang et al. [2013], Greenop et al. [2014], Martinez-Bori et al. [2015b] and Anagnostou et al. [2016].

Dark and light blue dots respectively represent alkene- and boron-derived pCO\textsubscript{2} estimations. Note that the larger error bars associated with these estimates are not shown. The dashed box represents the time interval of interest to this thesis (8-0 Ma). Solid and dashed black bars represent permanent and ephemeral events respectively. Note the overall cooling trend and the transition from greenhouse to icehouse conditions. Permanent Antarctic ice sheets appeared at the Eocene/Oligocene transition [Zachos et al., 2008], while permanent Arctic ice sheets are present since the Plio-Pleistocene transition [Lawrence et al., 2006]. The Bering Strait opened during the early Pliocene, between 4.8 and 3.1 Ma [Marincovich and Gladenkov, 1999; Brierley and Fedorov, 2016]. The Indonesian Throughflow started to close during the middle Miocene and became shallow during the Pliocene [Brierley and Fedorov, 2016]. The Panama seaway started to close at about 30 Ma, with deep water passages open until about 9 Ma, and becoming permanently closed at about 3 Ma [Brierley and Fedorov, 2016; O’Dea et al., 2016]. Large-scale vital effects on coccolith stable isotopes emerged at about 7.5 Ma when pCO\textsubscript{2} went below the critical threshold of 500 ppm [Bolton and Stoll, 2013]. Also note that the early Pliocene was the latest time interval of sustained global warmth. EECO= Early Eocene Climatic Optimum, MECO= Middle Eocene Climatic Optimum, MMCO= Middle Miocene Climatic Optimum, NADW= North Atlantic Deep Water, PETM= Paleocene Eocene Thermal Maximum.

In addition, the low atmospheric CO\textsubscript{2} levels of the late Miocene might have induced coccolithophorids to adopt new carbon concentration mechanisms (vital effects, see sections 4.1.1 and 6.3) for the first time [Bolton and Stoll, 2013]. The climate cooling, terrestrial aridification and the C\textsubscript{4} plants expansion has been hypothesized and evidenced with proxies to be associated with increased nutrient supply to the oceans, specifically because of i) greater soil erosion and ii) larger dust fluxes to the ocean, forcing a rapid increase of biological productivity in the upwelling areas of the Atlantic, Indian and Pacific Oceans, including the EEP [van Andel et al., 1975; Dickens and Owen, 1999; Hovan, 1995; Farrell et al., 1995; Grant and Dickens, 2002; Diester-Haas, 2006; Lyle and Baldauf, 2015; Zhang et al., 2017]. This is evidenced by a widespread increase in primary production, recognized in marine sediment sequences across the EEP, and termed the “biogenic bloom”. The biogenic bloom, lasted into the early Pliocene (ca 4.6 Ma, Paper III) and resulted in distinctly increased biogenic sedimentation rates. This event is of primary importance in current debates within the paleoceanography community on how the EEP, and other low latitude upwelling areas, function under changing ocean/climate conditions (Paper II and Paper III). The major ~1‰ negative shift in global deep marine carbonate δ\textsuperscript{13}C records during the late Miocene at the peak of the biogenic bloom (ca 7.6-6.6 Ma), provides important support for the biogenic bloom idea, and the conclusions that its principal cause was higher biological productivity due to increased erosion of δ\textsuperscript{13}C-depleted terrestrial organic matter [Diester-Haas, 2006; Herbert et al., 2016].

In the early Pliocene (5.3-3.5 Ma) global climate warmed. Climate reconstruction both based on observational and modelling data show evidence that the early Pliocene was the last time period of sustained global warmth [Haywood et al., 2016]. During this time period mean global surface temperatures were about 3°C warmer than pre-industrial times and atmospheric CO\textsubscript{2} concentration was similar to today (350-450 ppm) [Haywood and Valdes, 2004; Lawrence et al., 2006; Foster et al., 2009; Brierley and Fedorov., 2010; Seki et al., 2012; Haywood et al., 2016]. Between 4.8 and 3.1 Ma the Bering Strait opened and deep channels of the Indonesian Throughflow started to close [Marincovich and Gladenkov, 1999; Hall, 2002; Brierley and Fedorov 2016]. The understanding of how the EEP behaved in the transition from the cool climate of the late Miocene to the warm climate of the early Pliocene is of primary interest for the paleoceanographic community because it gives information on how this important ocean region operated in the most recent major greenhouse warming episode. One of the most widely supported hypotheses is that
During the early Pliocene, SST was higher and equatorial upwelling was weaker along the EEP Equator compared to today [Wara et al., 2005; Ravelo et al., 2014; Ford et al., 2015]. This scenario is often referred to as “permanent El Niño” or as to “El Padre” because it invokes similar conditions of a modern El Niño event over almost 2 Myr, implying that temperature gradients across the tropical Pacific were extinguished and SSTs in the EEP and WEP were similar. The problem with this scenario is that it proposes opposite ocean-climate conditions to that implied by the biogenic bloom. In the modern EEP, enhanced primary productivity (typical of the biogenic bloom) is bound to i) enhanced wind-driven circulation, ii) cool SST along the Equator, and iii) steep regional and meridional SST gradients [Farrell et al., 1995; Dickens and Owen, 1999; Grant and Dickens, 2002; Lyle and Baldauf, 2015; Zhang et al., 2017]. These two scenarios cannot co-exist because they invoke opposite ocean conditions.

After the early Pliocene warm period global, climate cooled to pre-industrial conditions. In the EEP, modern ocean-climate conditions started to develop during the late Pliocene [Lawrence et al., 2006]. SST cooled establishing the modern east-west SST gradient across the tropical Pacific Ocean. During the Plio-Pleistocene transition, extensive glaciations began in the Northern Hemisphere as documented by a global enrichment of benthic foraminifera δ¹⁸O and by the appearance of ice-rafted detritus in cores from the North Atlantic and the Nordic Seas [Shackleton et al., 1984; Zachos et al., 2001; Kleiven et al., 2002], as well as multiple other sources of proxy evidence from the terrestrial realm [Hovan et al., 1989; Head and Gibbard, 2015]. At about the same time, climate began to show high variability as reflected in the higher amplitude of the 41 kyr-long climate cycles of benthic δ¹⁸O records [Lisiecki and Raymo, 2005]. These events coincide with the end of surface water exchange between the Caribbean Sea and the EEP, which represents evidence of the final closure of the CAS at ca 2.8 Ma [Brierley and Fedorov, 2016; O’Dea et al., 2016]. The climate variability further increased before the middle Pleistocene transition (ca 900 ka), when the benthic δ¹⁸O began to display 100 thousand years (kyrs)-long climate cycles with even higher amplitude variability [Willeit et al., 2019].
4. Eastern equatorial Pacific sediments

4.1 Sediment composition

The composition of sediment from the EEP is directly related to the high rates of production of shell-forming marine phytoplankton in the surface ocean, which is in turn linked to the wind-driven equatorial upwelling system. Given the great distance from land the sediments deposited within the upwelling band are predominantly of biogenic origin (Figure 8). Primary sediment components are i) biogenic carbonate (CaCO$_3$; about 75% of the sediment), mostly composed of calcareous nannofossils and foraminiferal tests, and ii) biogenic silica (opal, SiO$_2$ · nH$_2$O; about 20% of the sediment), mostly composed of diatom frustules and radiolarian tests [Farrell et al., 1995; Pälike et al., 2010; Dutkiewicz et al., 2015; 2016]. Terrigenous material, mostly fine-grained wind-blown terrestrial clays, constitute a minor component (about 5%) in the EEP, especially in areas close to the Equator where biological production is most intensive. These terrestrial wind-blown clays can themselves be used as palaeoclimatological tracers both of atmospheric processes, including wind patterns and sources of terrestrial dust. Dust particles are also a source of biologically important minerals to the surface ocean that play a further role ocean fertilization [Hovan et al., 1989; Hovan, 1995]. These processes, however, are not considered in this thesis.

![Digital map of main deep-sea sediment lithologies and seafloor topography of the EEP](image)

Figure 8. Digital map of main deep-sea sediment lithologies and seafloor topography of the EEP [modified from Dutkiewicz et al., 2015]. Sediment distribution depends mostly on surface water properties and ocean bathymetry. Data are from Dutkiewicz et al., [2015] whereas land map is from Ocean Data View [Schlitzer, 2018].
In general, EEP bulk sediments can be considered as a two-component system given that clays become significant components only in areas i) close to the land where the supply of terrigenous material is high, ii) where the surface ocean biological production is low, and iii) where the seafloor is located below the CCD. Traditional marine seafloor sediment maps depicted a clear tongue of silica beneath the upwelling belt, carbonate above 4000 m and abyssal (red) clay below 4000 m [Berger, 1974; Lyle, 1992]. However, the picture seems to be more complex in reality as depicted by a recent map of seafloor sediments which implies more of a mosaic pattern of surface lithology (Figure 8). This map is based on locations and descriptions of 14399 surface or near-surface samples, extracted from expedition cruise reports since the 1950s and the Index of Marine and Lacustrine Geological Samples [Curators of Marine and Lacustrine Geological Samples Consortium, 2015]. The map was created using a Support Vector Machine (SVM) nonparametric model [Dutkiewicz et al., 2015]. The following sections provide further details on the calcareous and siliceous biogenic components.

4.1.1 Coccolithophores

Calcareous nannofossils are the most abundant carbonate components in EEP sediments. They were first recognized and described as important biogenic particles in a pioneering study by Ehrenberg (1836) and since then have been of primary interdisciplinary interest as they are one of the major ocean primary producers [Giraudeau and Beaufort, 2007]. The dominant component of modern calcareous nannofossils are coccoliths, minute (on average <10 \( \mu \)m in length) plate-like remains of coccolithophore cells [Bown, 1998]. Coccolithophores are single-celled marine haptophyte algae. Their cell is covered by a calcareous (calcite) spherical external cell-wall, called coccosphere, which on average have a diameter of 20 \( \mu \)m [Giraudeau and Beaufort, 2007]. The coccoliths are the individual plate like elements that make up the coccosphere. Because coccolithophores are photosynthetic organisms, they calcify within the photic zone, mostly in the uppermost 100 m of the water column [Honjo and Okada, 1974; Hagino et al., 2000]. Thus, their calcite shells carry information on mixed layer water properties. Once the organism dies the coccospheres or, more frequently the disaggregated coccoliths are preserved in the sedimentary record. Calcareous nannofossils commonly contribute 40-60 % of calcareous deep-sea oozes and thus play a central role in carbon cycling and global climate [Broecker and Clark, 2009].

Coccolithophores contribute to the global climate system regulation over sub-millennial time scales by impacting the organic carbon and carbonate pumps [Westbroek et al., 1993]. Coccolithophore algal blooms are also considered to impact global climate through their emission of gaseous dimethyl sulphide (DMS), an important metabolic product that oxidizes in the atmosphere to produce aerosols and fosters the formation of highly reflective clouds, which in turn has large-scale albedo effects [Westbroek et al., 1993]. Species compositions of coccolithophore assemblages vary spatially, reflecting different water currents, temperature, salinity and nutrient availability [Okada and Honjo, 1973; Okada and McIntyre, 1979; Brand, 1984; Giraudeau and Beaufort, 2007; Dutkiewicz et al., 2016]. In the modern EEP the coccolithophore assemblage is dominated by the opportunistic species *Emiliania huxleyi* across the equatorial upwelling.
The divergence zone (±2° latitude) of the EEP, which is characterized by high nutrient concentration in surface waters [Okada and Honjo, 1973; Giraudeau and Beaufort, 2007]. In the oligotrophic conditions characterizing the EEP areas located north and south of the equatorial divergence, assemblages are dominated by *Gephyrocapsa oceanica*. The calcareous nannofossil assemblages preserved in the sedimentary records since the late Neogene, however, are significantly different compared to the modern. Late Neogene assemblages are composed of ancestors of *E. huxleyi* and *G. oceanica* within the phylomorphogenetic reticulofenestrid lineage [Marlowe et al., 1990; Young et al., 1992]. The fossil assemblages are dominated by smaller (<3 μm) and larger (>3 μm) reticulofenestrids and *F. profunda* [Bolton et al., 2010]. The coccolithophores assemblages are similar in the Caribbean Sea (Section 6.2), where reticulofenestrids and *F. profunda* are the dominant components [Anderson and Steinmetz, 1981; Kameo et al., 2004].

![Figure 9. Schematic illustrating a simplified model of the calcification-photosynthesis mechanisms in a modern coccolithophores](modified from Anning et al., 1996; Buitenhuis et al., 1999; Paasche, 2001; Rickaby et al., 2010; Bolton and Stoll, 2013]. Solid arrows represent active fluxes whereas dashed arrows represent passive fluxes. The Rubisco is the principal enzyme responsible for the fixation of CO$_2$ into organic matter. The production of coccolith (calcification) has been described as a mechanism for concentrating CO$_2$ within the cell to support photosynthesis [Buitenhuis et al., 1999]. Despite the understanding of intracellular carbon fluxes is at present controversial and different pathways likely operate in species with different cell size, there is a general consensus on the idea that protons (H$^+$) are transferred out of the coccolith vesicle to elevate the concentration of CO$_2$ at the photosynthesis site. This mechanism seems to be adopted preferentially by larger species, such as *Coccolithus* spp., while smaller species, such as *Gephyrocapsa oceanica*, seem to mostly rely on diffusive supply of CO$_2$.

The calcification mechanisms adopted by coccolithophores are central to understanding the discussion on bulk carbonate stable isotopes presented in Paper II, Paper III and in Chapter 6 of this thesis. Thus, the
mechanisms are briefly introduced in the following paragraphs. Calcification in coccolithophores involves complex biogeochemical interactions believed to represent a mechanism adopted by the cell to increase the intracellular concentration of CO₂ for photosynthesis [Buitenhuis et al., 1999]. Coccolithophores fix inorganic carbon to make the calcite needed to build coccoliths in an intracellular structure called coccolith vesicle (Figure 9) [Anning et al., 1996; Buitenhuis et al., 1999; Paasche, 2001; Rickaby et al., 2010; Bolton and Stoll, 2013].

Although an univocal view on the mechanisms regulating the calcification in coccolithophores is still missing, several studies suggest that DIC is transported within the cell either by active transport of HCO₃⁻ in larger species such as Coccolithus spp., or by passive transport (diffusion) of CO₂ in smaller species such as Gephyrocapsa spp. [above references]. In large species, protons (H⁺) are transferred from the coccolith vesicle to the cell main internal space, the cytosol [Rickaby et al., 2010]. This has the effect of increasing the pH (>8) within the vesicle so that coccolith calcite is precipitated in an alkaline environment and using dissolved carbonate ions, i.e. CO₃²⁻ [Anning et al., 1996; Buitenhuis et al., 1999; Paasche, 2001]. In addition, the higher concentration of H⁺ in the cytosol increases the [CO₂], which is then fixed into organic matter by the enzyme Rubisco. In smaller species such as Gephyrocapsa oceanica, and small reticulofenestrids, the mechanism linking calcification to photosynthesis seems to be rather different [Rickaby et al., 2010]. These species preferentially uptake bicarbonate ions, HCO₃⁻, for calcification and mostly rely on the diffusive supply of CO₂ from the extracellular environment. These biochemical processes alter the carbon and oxygen isotopic composition of the coccolith calcite, which is secreted out of thermodynamic equilibrium with seawater [Paasche, 2001; Rickaby et al., 2010; Bolton and Stoll, 2013]. These alterations of calcite isotopic composition are called vital effects and are much stronger than those found in planktonic foraminifera. Understanding the mechanisms and strength of these vital effects is pivotal for the paleoceanographic interpretation of bulk carbonate stable isotope records (Sections 6.2 and 6.3).

4.1.2 Other relevant EEP sediment components

Other important carbonate components of EEP sediments are shells (tests) of foraminifera. Foraminifera [d’Orbigny, 1826] are single-celled protists that range between 10 µm and 1 mm in size, but that mostly in the EEP, as adults fall in the size range 63 - 500 µm [Ravelo and Hillaire-Marcel, 2007]. Foraminifera produce a calcareous test which is preserved in the sediment record above the CCD. There are benthic varieties, living within the upper few centimeters of sediments (infaunal) or on the seafloor (epifaunal), and planktic varieties, which live at different depth habitats over the upper ca 200 m of the water column. In deep ocean settings like the EEP, where only a tiny fraction surface food reaches the seafloor (<6 %) [Billett et al., 1983], benthic foraminifera are rare (<5 %) whereas planktic foraminifera can contribute up to 25 % of the total carbonate weight. As for coccolithophores, foraminifera calcify their calcite from C and O contained in ions dissolved in seawater. Their calcareous remains preserve information of the seawater chemical composition in which they calcify at the time of shell formation. Fossil foraminifera are widely
used as proxies for many different ocean-climate processes and parameters, including for reconstructing
global ice volume [Shackleton, 1967], and estimating past seawater chemistry and temperature at the
specific water depths in which the organism calcified [e.g. Emiliani, 1955; Lear et al., 2000].

The second most abundant sediment component in the EEP is biogenic silica, which here is mainly
composed of the separated frustules of diatoms, single-celled members of the phytoplankton. Diatoms range
between 1 µm and 1 mm, thus are a little larger than coccoliths, but most species are smaller than 63 µm.
Diatoms are responsible for 40 % of the total marine organic carbon production [Nelson et al., 1995;
Pichevin et al., 2014; Dutkiewicz et al., 2015]. The second most abundant biosilica sediment component in
the EEP are skeletons of radiolaria. These are single-celled protists ranging from 30 µm to 2 mm but are
mostly greater than 63 µm in size. Both diatoms and radiolaria are eutrophic species and thus occur in large
numbers in upwelling areas [above references]. These four main EEP biogenic sediment groups can be
roughly separated into two size fractions, where calcareous nannofossils and diatoms fall into the fine
fraction (<63 µm), and foraminifera and radiolaria fall into the coarse fraction (>63 µm).

4.2 Sediment supply and preservation

The global distribution of open ocean biogenic sediments primarily reflects changes in surface water
oceanographic parameters, including water temperature, salinity and nutrient concentration, and dissolution
at depth [Dutkiewicz et al., 2016]. The ratio of carbonate to opal produced in the EEP photic zone depends
on primary productivity of mainly coccolithophores and diatoms. The relative production of these two
phytoplankton groups is a function of nutrient availability (the most important nutrients are nitrate,
phosphate, silicate and iron), which in turn is linked to the intensity of equatorial upwelling. Under present
day conditions the production of CaCO₃ varies with latitude mimicking different upwelling intensity
(Figure 10) [Dutkiewicz et al., 2015; 2016; Lyle et al., in revision]. Under strong upwelling conditions the
production of biosilica shows a larger relative increase compared to coccolithophore production because of
the greater efficiency of diatoms under eutrophic conditions [Kemp and Baldauf, 1993; Kemp et al., 1995;
Pisias and Moore, 1995; Dickens and Barron, 1997; Pichevin et al., 2014; Lyle and Baldauf, 2015]. In
contrast, the production of biosilica particles decreases under weak upwelling conditions, like during modern El Niño events [Pichevin et al., 2014].

The second factor influencing carbonate and biosilica content in EEP sediment is the differential dissolution
of these two sediment groups [Edmond, 1974; Dutkiewicz et al., 2016]. Sediment accumulation occurs only
when the rate of sediment supply is greater than the rate of sediment removal [van Andel et al., 1975]. As
carbonate particles rain down to the seafloor the rate of CaCO₃ solution increases because water masses
become progressively more undersaturated with respect to calcium carbonate with increasing depth.
Calcium carbonate is strongly dissolved below the lysocline and is totally dissolved below CCD. Ocean
bathymetry hence needs to be added to the oceanographic parameters influencing calcareous sediment
distribution together with surface water parameters. Importantly, most of the EEP seafloor lies below the
lysocline, which in the modern EEP occurs at a depth of ca 3500-4000 mbsl (meters below sea level) [Berger, 1973; Archer, 1991].

**Figure 10.** Digital map of main deep-sea sediment lithologies and seafloor topography (panel a) and modern annual mean sea surface chlorophyll-a concentration of the EEP (panel b). The digital map is modified from Dutkiewicz et al. [2015] whereas sediment lithology data are from Dutkiewicz et al., [2015]. Land map and bathymetric profiles are from Ocean Data View [Schlitzer, 2018]. Rectangular at the top and on the left of the map (panel a) depicts a bathymetric profile respectively along the Equator between 80°W and 160°W longitude and along 110°W longitude between 20°N and 20°S latitude. Chlorophyll-a concentration data are monthly-composites averaged over the 2003-present time period [courtesy of NASA/GSFC OBPG]. Black areas in panel b represent gaps in coverage. Sediment distribution depends mostly on surface water properties and ocean bathymetry. Note that west of ca 110°W longitude, the seafloor depth generally increases westward. The seafloor depth also generally increases southward. Calcareous ooze and mixed calcareous/siliceous ooze are the predominant lithologies beneath the area where the equatorial upwelling is focused. Biogenic sediment generally decreases with latitude moving away from the equator because of decreasing biological production. In the area west of ~110°W calcareous sediment decreases westward because of enhanced dissolution associated to increasing seafloor depth. In the area west of the Galapagos Islands calcareous sediment increases
southward because of increasing seafloor depth. In areas of deepest seafloor and in areas located far from surface water production zones and close to the land, clay is the main lithology. mbasl= meters below sea level.

In addition, the EEP lysocline changed through time and was shallower during the late Neogene [Archer, 1991; van Andel, 1975; Broecker and Clark, 2009; Pälike et al., 2012; Lyle and Wilson, 2006]. In the EEP carbonate dissolution varies with longitude (Figure 10). It is stronger at sites located to the west where the seafloor is deeper (Section 3.1) and where productivity is lower compared to sites located to the east [Lyle et al., in revision]. Carbonate dissolution also varies with latitude depending on carbonate production and seafloor depth. High carbonate production increases the water CaCO$_3$ saturation state and hence limits carbonate solution. Thus, higher carbonate production limits carbonate dissolution at the Equator compared to higher latitudes. West of the Galapagos Islands, the seafloor depth increases southward, hence decreasing carbonate dissolution (Figure 10). Lastly, different carbonate particles are susceptible to dissolution to different extents depending on their shape and construction. In general, thin, globular and porous calcite tests of surface dwelling planktic foraminifera are more prone to dissolution compared to tests of calcareous nannofossils and benthic foraminifera, that are more resistant to carbonate dissolution [Broecker, 2008]. Moreover, thermocline or subthermocline-living planktic and benthic foraminifera are more resistant to dissolution compared to surface dwellers that construct their shells in the carbonate-oversaturated mixed layer [Kucera, 2007].

Unlike carbonate, ocean bathymetry does not discriminate the distribution of opal sediments because oceanic waters are undersaturated with respect to opal at all depths [Ragueneau et al., 2000; Pichevin et al., 2014; Dutkiewicz et al., 2016]. Therefore, there is no correlation between opal dissolution and water depth and opal preservation is solely influenced by surface water parameters. In present day oceans, only a small fraction (ca 3 %) of biosilica particles produced in the surface ocean are preserved as seafloor sediments [above references]. Despite this, massive opal burial events occur in the EEP during intervals of high primary productivity. These intervals are associated with low carbonate content because of the dilution of carbonate particles by biosilica particles [Lyle and Baldauf, 2015; Lyle et al., in revision]. Laminated diatom ooze in cores from multiple locations across the EEP, also known as diatoms mats, are sediment layers composed almost exclusively by near monospecific assemblages of the pennate diatom genera Thalassiothrix and Thalassionema and are indicative of this high-opal/low-carbonate sediment intervals [Kemp and Baldauf, 1993; Pearce et al., 1995; Dickens and Barron, 1997]. For this reason, the presence of diatom laminations in EEP sediments is a widely used indicator of enhanced upwelling conditions [Kemp et al., 1995].

In summary, differential dissolution changes the amount and the type of sediment preserved in the sedimentary record by selectively removing part of the carbonate and opal material produced in surface waters. The microfossil assemblages in sediment cores are only partly reflecting the actual living assemblages. The carbonate/opal content in sediment is thus different from the relative amount of carbonate/opal produced in surface waters.
4.3 Bulk sediment properties

As discussed in Chapter 3, the EEP is characterized by strong environmental variability, both in time and in space. This heterogeneity impacts sediment burial in multiple ways. First, the upwelling intensity controls the amount of nutrients transferred to the photic zone and surface water properties, regulating the relative production of carbonate versus biosilica particles as well as the overall volume of biogenic remains. Second, the amount of settling organic matter regulates the amount of CO$_2$ released by its oxidation in the water column and thus carbonate preservation. Third, changes of chemical parameters, for example DIC and silica content of water masses, alter the preservation of carbonate and opal particles both in the water column and at the seafloor.

EEP paleoceanographic variability is, thus, reflected in changes in seafloor sediment composition. In cores collected from the EEP, sediment properties change significantly over short depth intervals, from a few centimeters to a few decimeters. For example, lighter sediment color is associated with higher GRAPE measurements (approximating sediment wet bulk density) and higher carbonate content (Figure 11). In parallel darker sediment color is associated with generally lower GRAPE and lower carbonate content. Changes in sediment composition, indicated by carbonate content, are paralleled by changes in sediment...
properties, such as color and density. The relationship between wet bulk density and carbonate content represents a striking characteristic of EEP sediments and has been examined by means of new and published observational data and an empirical model in Paper I. The relationship between sediment properties and composition rely on the fact that sediment production at the sea surface and preservation at the seafloor are linked to EEP oceanography. These considerations lead to the perhaps most striking feature of EEP sediment properties. Despite the strong environmental heterogeneity over >3000 km, changes in physical properties and composition of sediments are highly coherent at multiple locations across the equatorial Pacific. This is not as might be expected considering the large changes in surface water conditions and biological productivity (Paper II and Paper III).
5. Methods background

A variety of different methods were applied during this Ph.D. involving measuring the physical and chemical properties of bulk sediment and the chemistry of carbonate constituents of the bulk. A novel aspect was to deconstruct the bulk stable isotope signals by making measurements on separated sub-sieved fractions and isolated foraminifera tests and fragments. Imaging of biogenic material was also carried out to explore carbonate preservation quality. These methods and the background theory are described in more detail below.

5.1 Grain size analyses and foraminiferal carbonate extraction

Given that various biogenic sediment particles fall into predictable size classes, it is possible to roughly separate different carbonate components by sieving samples at certain mesh sizes. The most common grain-size analysis is to determine the weight of coarse fraction particles (CF %), also known as the sand fraction, relative to the total sediment sample weight by separating out particles smaller than 63 µm by dry or wet sieving. The CF % indicates the relative proportion of fine particles (mostly coccoliths and diatoms) and coarse fraction particles (mostly foraminifera and radiolaria) (Paper I). In addition, the CF % is used as a proxy of carbonate dissolution at lysocline depths (Paper II and Paper III) [Broecker and Clark, 1999; Hancock and Dickens, 2005]. The theory behind this is that increased carbonate dissolution related to shallowing of the lysocline commonly leads to lowered CF % and increased fragmentation of foraminifera tests, which generally are more susceptible to carbonate dissolution compared to calcareous nanofossils [Berger, 1973; Broecker, 2008, Blaj et al., 2009].

In Paper II and Paper III, the contribution of foraminiferal material to bulk carbonate $\delta^{18}$O and $\delta^{13}$C was measured on bulk carbonate and on different fine fractions. The basic assumption is that the proportion of coccoliths increases as particle size fraction decreases. In both papers stable isotopes were measured on the <63 µm fine fraction, which includes coccoliths, juvenile foraminifera and foraminifera fragments. In paper II, stable isotopes were analyzed from the <38 µm fine fraction, which includes lower amounts of foraminiferal carbonate compared to the <63 µm fraction. In Paper III, to further isolate/concentrate coccoliths from foraminifera particles, the <20 µm fine fraction was used instead of the <38 µm fraction. Foraminifera fragments are generally >20 µm and thus the <20 µm sediment fraction is mostly composed of calcareous nanofossils [Chiu and Broecker, 2008; Broecker and Clark, 2009].

Samples were rinsed twice to remove constituent salts (Paper I and II). All samples sieved for this thesis work were then dried in an oven and weighed on a Sartorius LP220S balance having a readability of 1 µg.
The sieving of sediment samples at 63 µm, 38 µm and 20 µm requires the use of de-ionized water and thus it is called wet-sieving. For each sample a clean sieve of the appropriate mesh size was put on top a clean 1000 ml beaker. Sediment was put on the mesh surface and de-ionized water was sprayed on the sediment to let it disaggregate and let grains finer than the mesh size to fall into the beaker. Sediment grains coarser than the mesh size was collected on the mesh surface whereas sediment grains finer that the mesh size was collected in the beaker. All sediment fraction was then dried and stored in labelled vials. Dry >63 µm sediments were weighed on the Sartorius LP220S balance.

In Paper III, to further understand what the bulk carbonate stable isotope signal actually represents in terms useful for EEP paleoeceanography, stable isotopes were also measured on mixed planktic foraminifera, mixed benthic foraminifera and foraminifera fragments greater than 63 µm in size. To extract mixed foraminifera particles each coarse fraction sample was split into two aliquots (each half of the original sample) using an ASC Scientific micro-splitter following the procedure shown in Figure 12. From the first aliquot all benthic foraminifera specimens were hand-picked using a soft paintbrush. The second aliquot was split again into two sub-aliquots, each a quarter of the original sample. All planktic and benthic foraminifera specimens and foraminifera fragments were picked from one sub-aliquot, while the sediment material of the other sub-aliquot, was stored in a labeled glass tube for non-destructive analyses, such as coarse fraction composition estimates (Section 5.4). To get enough specimens for stable isotope analyses, benthic foraminifera were picked from two sample splits given that benthic foraminifera are rare in EEP sediments. Here, a foraminifera fragment was defined as any broken portion of a foraminiferal test less than two thirds of the original test size [Berger et al., 1982; Hancock and Dickens, 2005].

![Figure 12](image-url)

**Figure 12.** Schematic showing an example of the splitting method for foraminiferal and foraminifera fragment extraction from a coarse fraction (>63 µm) sediment sample. Note that benthic foraminifera were hand-picked from two different sample splits to have enough material for stable isotopes analyses. This procedure preserves part of the sample for non-destructive analyses, such as determination of coarse fraction sediment composition (Section 5.4).
5.2 Carbonate content

The bulk CaCO$_3$ % of deep-sea sediments indicates the relative abundance of carbonate particles (mostly coccoliths and foraminifers) compared to opal particles (mostly diatoms and radiolarians) and clays. CaCO$_3$ % is a key proxy of biogenic carbonate flux to the seafloor and of CCD depth changes over time [Broecker and Clark, 1999; Broecker, 2008; Lyle et al., in revision]. Importantly, the combination of CaCO$_3$ %, coarse fraction content, coarse and fine carbonate preservation analyses (see sections below) provides indication about biological production of the different sediment components, differential carbonate dissolution and carbonate dilution by biosilica particles [Hancock and Dickens, 2005]. Shipboard CaCO$_3$ % measurements have been routinely performed since the first scientific drilling expeditions. During DSDP expeditions, CaCO$_3$ % was determined using the carbonate bomb technique [Müller and Gastner, 1971]. This technique was substituted by the coulometric titration technique, or coulometry, in 1985 with ODP Leg 107 and it is still the method used for shipboard CaCO$_3$ analyses by the IODP [Kastens and Mascle, 1990].

All CaCO$_3$ % measurements presented in this thesis was analyzed on bulk sediment samples and determined using an UIC Inc. Coulometer Model 5012, following the methodology presented by Mörth and Backman [2011]. A portion of dried sediment samples was homogenized to fine powder using an agate mortar. A dry and clean Teflon cup with an inner diameter of 8 mm and a height of 12 mm was put on a Sartorius MC5 microbalance, which was tared to 0.000 mg. Sediment was added into the Teflon cup to reach a mass of 30-35 mg. This sample mass resulted in a precision of ±0.8 % down to 20 % calcite in the sample. The Teflon cup partially filled with sediment was put in a coulometer sample tube with an outer diameter of 18 mm. The measurement of CaCO$_3$ % was obtained by the reaction of sediment with 2 ml of 2M HCl, injected in the sample tube.

5.3 Oxygen and carbon stable isotopes

The term isotope, from the Greek isos “equal” and topos “place”, defines an atom having the same number of protons but a different number of neutrons of a given element. The study of oxygen and carbon stable, non-radioactive, isotopes is one of the most important tools in paleoceanographic and paleoclimate research. The most abundant naturally occurring carbon stable isotopes are $^{12}$C, that forms ca 98.9 % of the total carbon, and $^{13}$C that form the remaining ca 1.1 % [Faure, 1977]. Oxygen has three naturally occurring stable isotopes, $^{16}$O which comprises the 99.8 % of the total oxygen and $^{18}$O which comprises the remaining 0.2 %, whereas $^{17}$O is too small (0.04 %) to be of practical use. Analyses of the stable carbon and oxygen isotope composition of a given sample measure the small variation in the ratio (R) $^{13}$C/$^{12}$C for carbon and $^{18}$O/$^{16}$O for oxygen. These ratios are compared to a standard with a known isotopic composition. Results are expressed as a delta ($\delta$) value in the per mil (‰) notation according to the equations:

$$\delta^{13}C (‰) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 10^3$$  

(1)
\[ \delta^{18}O \ (\%) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 10^3 \]  

The basis of stable isotope geochemistry dates back to 1947 when Harold Urey first described the thermodynamic properties and the discrimination (also known as fractionation) between isotopes of light elements [Urey, 1947]. With the simultaneous development of mass spectrometry techniques [Nier, 1947], Urey discovered that the oxygen stable isotope composition of calcite could serve as a paleothermometer. Cesare Emiliani was a student at Urey’s laboratory and measured oxygen stable isotopes on shells of planktic foraminifera from deep-sea sediments of the Caribbean Sea, Atlantic and eastern equatorial Pacific Oceans. He first noted that relatively higher \( \delta^{18}O \) values are linked to lower calcification temperatures and vice versa. Thus, he used \( \delta^{18}O \) records to describe late Pleistocene glacial-interglacial climate fluctuations [Emiliani, 1954; 1955]. In parallel, other studies focused on describing how the \( \delta^{13}C \) varied in different natural material, such as marine and terrestrial organism tissues, sediments, rocks, water and atmospheric CO\(_2\). Clearly different natural materials show a wide range of \( \delta^{13}C \) [Craig, 1953]. Later studies revealed that the significant difference in the carbon isotopic composition between inorganic and organic compounds was generated by a strong fractionation between carbon isotopes during the photosynthesis, which preferentially fixes \( ^{12}CO_2 \) into organic matter [Park and Epstein, 1960].

In the 1960s and in the 1970s Nicholas J. Shackleton demonstrated that the \( \delta^{18}O \) composition of foraminifera shells primarily reflects changes in oxygen isotope composition of seawater, which in turn is mainly affected by the global ice sheet volumes rather than water temperature as first proposed by Emiliani [Shackleton, 1967; Shackleton and Opdyke, 1973]. Subsequently, Shackleton demonstrated the potential of foraminifera \( \delta^{13}C \) as an indicator of biological paleoproductivity in surface water and global carbon cycling [Shackleton and Kennett, 1974; Shackleton and Vincent, 1978]. All these pioneering studies gave birth to modern paleoceanography and established foraminifera stable isotopes as one of the most common techniques for reconstructing past climate and environment conditions.

For reconstructing surface ocean processes, \( \delta^{13}C \) and \( \delta^{18}O \) measured on planktic foraminifera is the preferred approach. The reason for this is that different plankton types and species live and calcify at different depths in the water column and, thus have slightly different ecologies that influence the shell chemistry. In order to obtain a consistent environmental signature for palaeoclimate studies, it is thus desirable to isolate and analyze a single species. From a practical perspective this is easy to do with planktic foraminifera, which are large enough (generally \( \geq 63 \) \( \mu \)m) to be hand-picked under conventional light microscopes using a fine paintbrush. Thus, stable isotope records can be generated from a single foraminifera species. In addition, any biologically-controlled deviation from ambient seawater stable isotope compositions can also be identified and accounted for (Birch et al., 2013). Planktic foraminifera stable isotope records generated from late Cenozoic EEP sediment have been largely used as a proxy of past surface water temperatures [e.g. Cannariato and Ravelo, 1997; Wara et al., 2005; Drury et al., 2018].
An important consideration is preservation quality of the fossil tests. The paleoecological information they carry can be significantly biased by diagenetic alteration of foraminiferal calcite such as recrystallization, given that most of the seafloor of the region have remained below the lysocline. Thus, the information carried by planktic foraminifera stable isotope records potentially contain deep water biases generated by diagenetic changes of foraminifera calcite [Sexton et al., 2006]. This is especially true over some time intervals when the lysocline was shallower compared to today, such as the late Miocene and the early Pliocene [Pälike et al., 2012]. The latter is a crucial period for paleoceanographic studies of the region and the understanding of the paleoceanographic state of the EEP during this time period is a main focus of this thesis (Paper II and Paper III). In addition, published planktic foraminifera $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records generally spans 5-0 Ma given that planktic foraminifera are rare in sediment older than 5 Ma because of enhanced dissolution and dilution by biosilica particles. Several paleoceanographic reconstructions based on this proxy are thus lacking information for the late Miocene.

Analyzing stable isotopes in bulk carbonate is an alternative to typical foraminifera-based analyses. This technique has so far mainly been used in the early years of palaeoceanography and in old, semi-lithified sediments and in sedimentary rocks from which foraminifera tests are difficult to extract [Scholle and Arthur, 1980; Slotnick et al., 2012]. The motivation to use bulk carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ as a proxy for EEP surface water conditions is two-fold: i) coccoliths, which, this thesis argues, is the dominant component of bulk carbonate, are less prone to dissolution compared to planktic foraminifera [Killingley, 1983; Chiu and Broecker, 2008], and, thus more likely to be preserved in the EEP, and ii) bulk carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses are easier to obtain in the EEP compared to planktic foraminifera, which can also be rather rare and or diluted by biosilica. Thus, records with high spatial and temporal resolution can be generated from areas where the sedimentation rates are typically low, such as the EEP.

Interpretation of bulk carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ as a proxy of surface water conditions, however, is far more complicated than single-species planktic foraminifera $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. In large part this is because bulk carbonate is a mixture of multiple carbonate components, including multi-species coccoliths and multi-species planktic foraminifera. Each of these components carry different $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions reflecting the calcification, metabolic and ecological conditions of each species. In addition, the relative abundance of the various components can vary over time depending on ocean condition and carbonate preservation. Deciphering what kind of ocean signal is carried by bulk carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is the main focus of Paper II and Paper III.

All the stable isotopes values presented in this thesis are given in ‰ relative to the Vienna Pee Dee Belemnite (VPBD) international standard. Stable isotopes measurements were performed using a Finnigan Mat 252 IRMS mass spectrometer coupled with a Finnigan Gasbench II device. During stable isotope measurements the in-house standards Carm-I and CaCO$_3$ Merck and the international standards IAEA-CO-1 and NBS19 were analyzed together with the samples to estimate the accuracy and precision of stable
isotope analyses [Révész and Landwehr, 2002]. The amount of each bulk carbonate (and fine fraction) sample to be analyzed for stable isotopes was calculated following the equation:

\[
\text{Sample weight (µg)} = \frac{\text{CaCO}_3 \% \times 200}{100}
\]

where \(\text{CaCO}_3 \%\) is the carbonate content of the sample measured following the procedure described in section 5.1. In equation 3 sample weight is calculated in order to obtain 200 µg of CaCO\(_3\) for each sample, which allows the best measurement precision. Mixed planktic and benthic foraminifera and foraminifera fragments samples were assumed to be composed of 100 % calcium carbonate and therefore the optimal weight for these samples was 200 µg. Each sample was flushed with gaseous helium in a septum-seal glass vial before reaction with 100 µl of 99 % phosphoric acid (H\(_3\)PO\(_4\)) to obtain CO\(_2\) following the reaction:

\[
3\text{CaCO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + \text{Ca}_3(\text{PO}_4)_2
\]

5.4 Evaluation of sediment composition and preservation

Evaluating the composition of bulk sediment and different size fractions is crucial for understanding bulk sediment physical and chemical properties. Moreover, assessing the preservation state of carbonate particles is essential for a correct interpretation of geochemical proxy signals. Two instruments housed at the Department of Geological Sciences of Stockholm University were used to investigate and document composition and preservation of sediments.

The first instrument is the Fei Quanta Feg 650 Environmental Scanning Electron Microscope (ESEM). This was used to determine the composition and preservation state of bulk and fine fraction sediment (Paper II). The ESEM provides images with a sub-micrometer resolution, and thus is suitable to depict fine sediment particles such as coccoliths [Echlin et al., 2013]. Moreover, ESEM investigations allow evaluations of the preservation quality of carbonate particles including revealing signs of diagenetic alteration (such as etching, overgrowths or infillings of secondary calcite) on coccoliths, foraminifera tests and foraminifera fragments. The second instrument is the Leica M250C stereomicroscope equipped with a Leica DFC295 digital microscope camera. The stereomicroscope is the most commonly used tool to investigate the composition and preservation state of particles >40 µm, such as foraminifera and radiolaria. This instrument was used to examine the composition of coarse fractions sediments (Paper II and Section 6.4) and for carbonate particles picking (Paper III).

5.5 Dating eastern equatorial Pacific sediments

Sediment age estimations stay at the base of every paleoceanographic reconstruction. When sedimentary records from different drilling sites are compared, these records need to be aligned in the time domain and thus a common age model is required. The age modelling for late Cenozoic EEP sediments is generally
challenging because low carbonate content at the seafloor can reduced the availability of calcareous biostratigraphic time markers, especially planktic foraminifera. However, age models are available and involve combinations of biostratigraphy, using calcareous and siliceous microfossils, and magnetic reversal stratigraphy.

\[
\text{LSR (m/Myr)} = \frac{\text{Depth}_2 - \text{Depth}_1}{\text{Age}_2 - \text{Age}_1} \tag{1}
\]

\[
\text{Age}_{\text{sample}} (\text{Ma}) = \text{Age}_1 + \frac{\text{Depth}_{\text{sample}} - \text{Depth}_1}{\text{LSR}} \tag{2}
\]

**Figure 13.** Image of a sediment core from the eastern equatorial Pacific and equations used to calculate age of samples in Paper II. The vertical black arrows indicate increasing depth and age of sediments downwards. The black rectangle represents a sediment sample. Age indicators used in this study are first or last occurrence of key nannofossils and diatoms species and geomagnetic reversal boundaries. Age; and Depth; are respectively the age and depth of the age indicator with lower depth respect to the sample. Age; and Depth; are respectively the age and depth of the age indicator with greater depth respect to the sample. Age; and Depth; are respectively the age and depth of the sample to be dated. The basic assumption in equation 5 is that the sedimentation rate between age Indicator 1 and age Indicator 2 is constant or linear. LSR = linear sedimentation rate.

In Paper II a new age model was constructed using biostratigraphic and magnetostratigraphic data. Abundant bio- and magneto-stratigraphic age indicators, including first and last occurrences of key calcareous nannofossils and diatoms species and geomagnetic reversal boundaries, have been identified in sediment cores from Sites U1338, 573 and 850. For sediment deposited at these three sites since 8 Ma the most significant bio- and magneto-stratigraphic data sets and reference frameworks used are Pälike et al. [2010], Backman et al. [2013], Baldauf, [2013] for Site U1338; Baldauf [1985], Barron [1985], Gartner and Chow [1985], Pujos [1985a, 1985b], Weinreich and Theyer [1985] and J. Backman [unpublished, 2012] for Site 573; and Mayer et al. [1992], Baldauf and Iwai [1995], Pisias et al. [1995] and Raffi and Flores [1995] for Site 850. In order to correlate between these three sites, biomagnostratigraphic data were placed onto a common time scale. In this study the GTS2004 time scale was used, which for the late Cenozoic is constructed using the orbital tuning method [Gradstein and Ogg, 2004; Lourens et al., 2004]. To assign ages of individual sediment samples, linear sedimentation rates were calculated between midpoint depth of biomagnostratigraphic indicators (equation 5 in Figure 13). Age of samples where then calculated using equation 6 in Figure 13. This age modelling method assumes that the rate of sedimentation between age indicators is constant or linear. This is a weak point of the method because, in reality, the sedimentation is unlikely constant trough time. Any discrepancies in calculated ages, however, are likely less than 100 kyr for most of the samples in Paper II, as indicated by age differences between bulk carbonate \(\delta^{13}C\) peaks, and do not represent a major problem for the aims of the study.
In Paper III, two strategies were followed for comparison of records from ODP Sites 851 and 849. For the 5-0 Ma time period we used the age model of Cannariato and Ravelo [1997]. The reason for this is that our new study integrates the 1997 study with new data from the same site. The Cannariato and Ravelo [1997] age model is a refined version of the Site 851 age model [Shackleton et al., 1995], and includes a more detailed correlation between the Site 851 G. sacculifer / G. tumida δ18O record and the Site 849 benthic δ18O record [Mix et al., 1995]. For the 7-5 Ma time interval (not covered by the Cannariato and Ravelo [1997] age model), the original Site 851 age model was used [Shackleton et al., 1995]. The latter is based on the late Neogene time scale [Shackleton et al., 1995] and was originally constructed on the basis of biomagnetostratigraphic data and on the Berggren et al. [1995] time scale, and refined using shipboard GRAPE measurements. The 0-6 Myr time period was further calibrated using orbital tuning. The weak point of this age model strategy is that LSRs display extremely low and high values (i.e. <2 and >100 m/Myr) over some short time intervals, which most likely represents artifacts of the dating technique.

Data presented in Paper II and Paper III are hence based on different time scales, the Lourens et al. [2004] and the Shackleton et al. [1995] respectively. In the introduction and background section for Paper III, and in Section 6.2 of this kappa, data based on these two time scales are compared. Comparing time series on different time scales will lead to imprecise correlations. This is because chronological frameworks have changed over the years (i.e. as revisions to the calibration of biostratigraphic evolutionary events, magnetic reversal boundaries are published, and even with addition of astronomical tuning constraints), resulting in changes in the absolute ages of intervals of geological time in the various iterations of the geological time scales [e.g. Berggren et al., 1995; Shackleton et al., 1995; Lourens et al., 2004]. Despite this, correlations between different data sets is still fairly good, and certainly adequate for the purpose of this thesis. This is especially true for Chapter 6, where EEP and Caribbean Sea δ13C and δ18O records are compared (Figure 15). Here records from the EEP are based on the Paper III age model, planktic foraminifera and calcareous nanofossils records from the Caribbean Sea are based on the late Pleistocene ODP Site 999 age model and on the “LR04” benthic δ18O stack [Lisiecki and Raymo, 2005; Schmidt et al., 2006], and benthic foraminifera records from the Caribbean Sea are based on Site 502 age model [deMenocal et al., 1992] and on the “TP607” time scale [Ruddiman et al., 1989]. Pleistocene glacial-interglacial δ18O peaks from the two ocean basins compare very well in the time domain with discrepancies less than 20 Kyr, which is adequate for the purposes of this study.
6. Discussion

In this final chapter of the kappa I present summaries of the key findings, paper by paper, and reflect on the wider implications of the findings by exploring some outstanding questions. A key part of this wider reflection is a comparison of the EEP data with published similar data sets in the tropical Atlantic (Section 6.2).

6.1 Summary of key results

Broad descriptions of the aims of each paper are presented in Chapter 2 and outlined below.

Paper I


This paper explores the relationship between sediment wet bulk density (WBD) and carbonate content using material from Site U1338. A mathematical model involving volume, mass and density, is used to describe the relationship between these parameters. Broad descriptions of the aims for this paper are presented in Chapter 2. The key goals and findings of Paper 1 are summarized here.

Overarching questions:

- Is the relationship, proposed previously, between WBD and CaCO₃ % also present in sediment at Site U1338?
- What are the main factors generating the WBD and CaCO₃ % relationship in EEP sediments?
- How can differences in the WBD - CaCO₃ % relationship between different EEP sites be explained?
- Can the WBD - CaCO₃ % relationship be described by an empirical equation?

Results showed that:

- Sediment samples from Site U1338 display a similar relationship between WBD and CaCO₃ % described at other EEP sites.
- The WBD and CaCO₃ % relationship is controlled by three main factors:
  - Differences in grain density; EEP sediments almost exclusively consist of two components, biogenic carbonate and biogenic silica. These two components have different
grain densities. Biogenic carbonate has a higher grain density (2.6-2.7 g/cm³) compared with biogenic silica (2.1-2.3 g/cm³).

(ii) Differences in porosity; the porosity of sediments varies with stratigraphic depth because of sediment compaction with burial and/or changes in grain size.

(iii) Differences in biogenic minerals; the range in porosity is much greater for biogenic carbonate particles compared to biogenic silica particles. The reason for this is that the porosity of the biogenic carbonate component changes significantly with grain size. Fine carbonate particles (<63 µm in size) are predominantly composed by coccoliths whereas coarse carbonate particles (>63 µm in size) mostly consists of tests of fossil planktic foraminifera. The latter typically have large-open tests with empty spaces within the test thus having a higher porosity compared to coccoliths. Sediment samples with high biogenic silica content have low carbonate content and low WBD but samples with high carbonate content can display a wide range of WBD depending on the relative amount of fine and coarse particles. A given sample with a higher number of foraminifera may have a WBD lower by up to 10 % of another sample with the exact same carbonate content but with a lower number of foraminifera.

- The inter-site difference in WBD - CaCO₃ % relationship depends on the relative proportion of biogenic carbonate and biogenic silica particles, and within the biogenic carbonate fraction, on the relative proportion of fine and coarse particles.
- The empirical equations offered in several previously published studies do not account for the variance in sedimentary components described above, especially when large numbers of samples are examined over wider depth intervals. Instead, to fully describe the range in WDB and CaCO₃ % requires an infinite series of curves accounting for different proportions of sediment component with different grain densities and porosities.

The results of Paper I have helped improve the application of bulk sediment WBD as part of the paleoceanographic tool box by: i) adding knowledge that it is not possible to generate accurate high-resolution carbonate content records from WBD measured by Gamma Ray Attenuation and Porosity Estimator (GRAPE) measurements as it has been proposed in several published studies and ii) rinsing samples prior to carbonate content analyses have demonstrated that salt precipitated in pore spaces dilute sediment grains. Measuring carbonate content of sediment samples at Site U1338 without previously rinsing the samples to remove interstitial salts results in an underestimation of the actual carbonate content by 4.2 % on average.

Paper II

Here the investigations of bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ were began by generating new data from Site U1338 and Site 573 to be compared with legacy *Shackleton and Hall* [1995] data sets. The key goals and findings of Paper II are summarized here.

Overarching questions:

- Does bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ vary coherently over large distances across the EEP?
- Can the absence of decimeter- to centimeter-scale variability in published bulk stable isotopes records be explained by larger-than-typical sampling practices?
- Do bulk $\delta^{13}C$ and $\delta^{18}O$ signals reflect the isotopic composition of calcareous nanofossils or a mixed signal of variations in the proportion of calcareous nanofossils and foraminifera?

Results showed that:

- Using published and new data from sites covering a wide area across the EEP (IODP Site U1338, ODP Site 573 and ODP Leg 138 sites) it is shown that bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ displays correlative changes, including changes $>1$ ‰ within 10-100 kyr time intervals, over long distances ($>2500$ km). These findings extend the original *Shackleton and Hall* [1995] observations of coherency in bulk records at Leg 138 Sites. Bulk carbonate $\delta^{13}C$ records are coherent regardless of whether they are from sites located near or far from the equatorial band where wind-driven upwelling occurs. $\delta^{18}O$ records show coherence with other records from on-equator sites and show significantly lower values during the late Miocene-earliest Pliocene (ca 8.4 Ma).
- Comparison of published records with the new records generated in this study, based on samples covering depth intervals from 1 to 4 cm, demonstrates that the sampling method used by *Shackleton and Hall* [1995] homogenized the short-term variability (10-100 kyr).
- **Results showed that bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ primarily reflects the stable isotope composition of calcareous nanofossils.** This is inferred by the absence of major differences between the $\delta^{13}C$ and $\delta^{18}O$ of bulk sediment and of the two fine fractions: $<63 \mu m$ and $<38 \mu m$ sediment. This is a primary conclusion that is carried forward in all subsequent work.

Other key findings are that:

- Variations in bulk stable isotopes are coupled to changes in sediment composition and physical properties as indicated by correlative changes in sediment color, carbonate content and coarse fraction content.
- The absolute values of bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ deviate from values expected from equilibrium calcite, most likely because of strong vital effects related to the intra-cellular pH regulation among coccolithophores.
- The excellent correlation potential of bulk carbonate $\delta^{13}C$ across most of the EEP suggests covarying changes in $\delta^{13}C$ of DIC within the EEP during most of the past 8 Ma.
Improvements from Paper II to the application of bulk sediment stable isotope measurements as part of the paleoceanographic tool box are that i) bulk carbonate stable isotopes reflect the stable isotope composition of calcareous nanofossils and thus can be used as a proxy of surface water properties including biological productivity and temperature, and ii) absolute δ^{13}C and δ^{18}O values should be used with caution because bulk carbonate stable isotopes measured in EEP sediments carry strong (>1 ‰) modifications (i.e. vital effects) related to intracellular processes among coccolithophores that fractionate isotopes from seawater as they become incorporated into calcite.

**Paper III**


The interrogation of bulk carbonate stable isotopes is continued in Paper III. By measuring the stable isotope composition on different biogenic carbonate materials and comparing the results with published δ^{13}C and δ^{18}O data from Site 851 we were able to address a series of further goals and arrive at some strong conclusions.

**Overarching questions:**

- What oceanic environment and therefore water mass does bulk carbonate trace?
- How are EEP bulk carbonate δ^{13}C and δ^{18}O generated in the first place, including the contributions of various biological isotopic fractionations by photosynthesizing calcifiers?
- How are modifications in bulk carbonate composition, due to ocean, climate, biological production and dissolution changes, reflected in bulk carbonate δ^{13}C and δ^{18}O signals?

**Results showed that:**

- New records from Site 851 support previous observations (Paper II) that bulk carbonate δ^{13}C and δ^{18}O mainly reflect the stable isotope composition of coccolith calcite. This is supported by the observations at Site 851 that there are no major offsets between the δ^{13}C and δ^{18}O of bulk carbonate and the <63 µm and <20 µm sediment fractions, which should increasingly exclude foraminiferal calcite. Moreover, the comparison between bulk carbonate stable isotopes to single-species planktic foraminifera, mixed planktic and benthic foraminifera and foraminifera fragments indicate that bulk carbonate stable isotopes reflect water conditions at a shallower depth of surface dwelling planktic foraminifera species, such as *G. sacculifer*. This likely reflects the shallower depth habitat of coccolithophores (about 50-100 mbsl) compared to *G. sacculifer* (about 120 mbsl).
- Bulk carbonate δ^{13}C and δ^{18}O records are affected by coccolithophore vital effects which lower δ^{13}C and increase δ^{18}O compared to calcite precipitated at equilibrium with surface water DIC.
Vital effects might originate from pH regulation within the coccolithophorid vesicle and are greater during intervals of lower atmospheric CO$_2$ concentration, such us during late Pleistocene glacial intervals. At Site 851 the greater vital effects during glacial intervals would generate greater amplitude of bulk carbonate $\delta^{13}$C compared to planktic foraminifera $\delta^{13}$C over glacial/interglacial transitions.

- Data from Site 851 support the idea that bulk carbonate $\delta^{13}$C reflects biological productivity changes in the upper mixed layer. Potentially, bulk carbonate $\delta^{13}$C is a more sensitive proxy of biological productivity in surface waters than the $\delta^{13}$C of the planktic foraminifera $G.\ sacculifer$. Bulk carbonate $\delta^{18}$O mainly reflects upper mixed layer water temperature. New data from Site 851 support previous observations of very coherent bulk carbonate $\delta^{13}$C and carbonate content records across most the EEP supporting speculations of correlative changes in DIC $\delta^{13}$C across the EEP since the late Miocene.

The results of Paper III brought us to the final conclusions regarding the use of bulk sediment as an ocean tracer in the EEP:

i) Bulk carbonate stable isotopes can be used as a tracer of ocean upper mixed layer properties, including temperature and biological production. This is despite biases to bulk isotopic signature due to coccolith vital effects, which seem strongest during Pleistocene glacial periods.

ii) Bulk carbonate $\delta^{13}$C is potentially a better proxy for primary production in the EEP than $G.\ sacculifer$ $\delta^{13}$C because of shallower depth habitat of most coccolithophores compared to $G.\ sacculifer$.

6.2 Testing the bulk carbonate stable isotope tracer outside of the EEP: Comparison of Pleistocene stable isotope records from the Caribbean Sea, Atlantic Ocean

Paper II and Paper III have focused exclusively on exploring bulk $\delta^{13}$C and $\delta^{18}$O in the EEP. An important question is: to what extent can these findings and ideas be extended to other tropical ocean settings, or does the bulk isotopic signature reflect different ocean processes in each basin? Here I investigate this by extending the comparison of late Pleistocene (0.56-0 Ma) bulk carbonate and planktic foraminifera $\delta^{13}$C and $\delta^{18}$O records from Paper III, to include equivalent published data sets from the Caribbean Sea (Figure 14).

There are several motivations for comparing records from the EEP and the Caribbean Sea. First, as the EEP, the Caribbean Sea is a tropical ocean basin that plays an important role in regulating global climate and that has a long history of interest [Emiliani, 1955; 1972; Shackleton, 1967; Anderson and Steinmetz, 1981; Kameo et al., 2004; Schmidt et al., 2006; Hermoso, 2016; Zhuravleva and Bauch, 2018]. Located in the western Atlantic Ocean, it plays a central role in regulating the heat, salt and water transport to the high
latitudes [Sepulcre et al., 2011]. Surface equatorial currents flow through the Caribbean Sea, becoming modified, i.e. salinified, due to the high evaporation rates before entering into the north flowing upper branch of the Atlantic Meridional Overturning Circulation system (AMOC), i.e. the Gulf stream [Kameo et al., 2004; Schmidt et al., 2006]. A notable difference however is that, unlike the EEP, the Caribbean Sea is not a wind-driven equatorial upwelling region [above references]. Second, published Caribbean Sea stable isotope records measured on similar carbonate material, i.e. fine fraction carbonate extracted from bulk sediment, the surface dwelling planktic foraminifera G. sacculifer and epibenthic foraminifera P. wuellerstorfi, already exist [Emiliani, 1972; Anderson and Steinmetz, 1981; deMenocal et al., 1992], allowing a direct comparison to the records produced for this thesis from EEP Site 851 (Paper III). Moreover, in a recent study the Caribbean Sea coccolith-planktic foraminifera δ¹³C and δ¹⁸O records were compared to estimate the magnitude of coccolith vital effects and potential changes in these effects over Pleistocene glacial-interglacial transitions [Hermoso, 2016], something also considered in Paper III for the EEP. Finally, despite the different surface water oceanography, i.e. the lack of strong wind-driven upwelling, the late Quaternary calcareous nannofossil assemblages of the EEP and Caribbean Sea are similar [Okada and Honjo, 1973; Kameo et al., 2004]. This is important for the interpretation of stable isotope records because it allows us to exclude differences in calcareous nannofossil assemblage composition as a cause for potential differences in coccolith δ¹³C and δ¹⁸O between the two basins.

The aim of this inter-basin stable isotope comparison is to answer some questions that arose while pursuing the Paper III goals:

1. Are abrupt calcareous nannofossil δ¹³C shifts (recorded by both bulk and fine fraction carbonate) at Site 851, which are not paralleled by correlative shifts in G. sacculifer δ¹³C, also displayed by Caribbean Sea coccolith δ¹³C?
2. Do calcareous nannofossil stable isotopes provide information on upper mixed layer conditions also in the Caribbean Sea? Or are these $\delta^{13}C$ shifts instead better traced by shallower dwelling foraminifera species such as G. ruber?

3. Does calcareous nannofossil $\delta^{13}C$ and $\delta^{18}O$ from the two ocean areas display similar amplitude fluctuations over glacial/interglacial cycles during the last 0.56 Ma?

4. Are absolute values of calcareous nannofossil $\delta^{13}C$ and $\delta^{18}O$ comparable between the two ocean basins?

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**Figure 15.** Comparison between carbon and oxygen stable isotope records of bulk carbonate, $<$20 $\mu$m carbonate and G. sacculifer from Site 851 and of P. wuellerstorfi from Site 849 over 7 Ma (modified from Paper III). Bulk carbonate and $<$20 $\mu$m sediment data are from Paper III. G. sacculifer data are from Cannariato and Ravelo [1997]. P. wuellerstorfi data are from Mix et al. [1995]. Site 849 benthic data are here included to represent EEP deep water properties because no benthic foraminifera data are available at Site 851. The thick color blue and red lines represent 21 point-average smoothed curves of corresponding color data. Light green shades represent intervals characterized by enhanced biological productivity. Note that differences between bulk and $<$20 $\mu$m carbonate stable isotope data are minimal, implying that bulk carbonate is composed largely of calcareous nannofossils (see papers II and III for details). Planktic and benthic foraminifera data are missing from the published records prior to 5 Ma, presumably because of insufficient foraminifera material for stable isotope analysis due to higher selective carbonate dissolution and higher dilution by finer material, mainly coccolithophores and diatoms (Section 6.4). Information for the “biogenic boom” (green shading) is thus missing from these records.

As an introduction to this discussion, I will briefly summarize the results of Paper III with respect of $\delta^{13}C$, and $\delta^{18}O$, which the following discussion builds on. Given that from Paper II and Paper III it has been demonstrated that the stable isotope composition of bulk carbonate and fine fractions (including $<$63 $\mu$m, $<$38 $\mu$m and $<$20 $\mu$m sediment fractions) reflects the stable isotope composition of calcareous nannofossils,
in the discussion below I refer to them as calcareous nanofossil (or nanofossil) $\delta^{13}$C and $\delta^{18}$O. Looking at the longer 5 Myrs record (Paper III, Figure 8, reproduced here as Figure 15), we see that calcareous nanofossil $\delta^{13}$C signals from Site 851 show values that are higher than those of benthic foraminifera records and generally lower values than the surface dwelling planktic foraminifera G. sacculifer. Calcareous nanofossil and G. sacculifer $\delta^{13}$C shows fairly coherent variability. However, there are also some key deviations that imply oceanic changes in the EEP. This is seen as distinct shifts in the EEP calcareous nanofossil $\delta^{13}$C at certain times, not paralleled in planktic foraminifera records, i.e. during the late Miocene and the early Pliocene (7.0-4.6 Ma), and during two intervals of the Pleistocene: a short interval centered at 2 Ma and another between 0.5 Ma and 0.3 Ma. These shifts result in significantly reduced $\delta^{13}$C offsets between calcareous nanofossil and G. sacculifer $\delta^{13}$C at these times. In Paper III these episodes were interpreted as reflecting biological production changes in the upper mixed layer. This idea is supported at Site 851 by lower calcareous nanofossils $\delta^{18}$O, increased sedimentation rates and biosilica content during the time intervals of high calcareous nanofossil $\delta^{13}$C.

Calcareous nanofossil $\delta^{18}$O shows lower values than benthic foraminifera $\delta^{18}$O and higher values than G. sacculifer $\delta^{18}$O (by on average 0.8 ‰) over the last 5 Myrs (Figure 15). As for $\delta^{13}$C, nanofossil $\delta^{18}$O and G. sacculifer $\delta^{18}$O display coherent variability, including, typically, the magnitude of characteristic patterns of variability over the studied interval. Calcareous nanofossil should have a lower $\delta^{18}$O due to the warmer, shallower habitat of coccolithophores compared to planktic foraminifera (a prediction of classic $\delta^{18}$O-temperature theory), that live slightly deeper in the mixed layer [Grant and Dickens, 2002]. However, calcareous nanofossils consistently register higher $\delta^{18}$O compared to G. sacculifer. In Paper III the higher calcareous nanofossils $\delta^{18}$O compared to than G. sacculifer $\delta^{18}$O was explained by coccolithophore vital effects, which have the effect of increasing the $\delta^{18}$O values [Dudley et al., 1986; Steinmetz, 1994; Zivieri et al., 2003]. Over the last 0.56 Ma the offset between calcareous nanofossils $\delta^{18}$O and G. sacculifer $\delta^{18}$O at Site 851 is higher during the glacial intervals compared to during interglacial intervals (Figure 16). In Paper III, this was interpreted as a higher magnitude of coccoliths vital effects during glacial compared to interglacial periods, generated by lowered atmospheric CO$_2$ concentrations [Bolton and Stoll, 2013; Hermoso, 2016]. The idea here is to further explore calcareous nanofossils stable isotopes over the glacial interglacial cycles of the last 0.56 Ma, which spans the last 14 Marine Isotope Stages (MIS), and see if similar changes were occurring in the tropical Atlantic at the same time.

In Figure 16, we see an expanded view of the EEP Pleistocene surface ocean $\delta^{13}$C and $\delta^{18}$O variability for the 0.56-0 Ma time period, now with comparative data from the Caribbean added. The EEP records comprise the fine fraction (<20 µm sediment), which gives the nanofossil signal, and G. sacculifer data from Site 851 and P. wuellerstorfi data from Site 849 (Paper III). For the Caribbean, published records from Core P6304-4, DSDP Site 502 and ODP Site 999 are used [Emiliani, 1972; Anderson and Steinmetz, 1981; deMenocal et al., 1992; Schmidt et al., 2006].
Figure 16. Comparison between fine fraction, surface water dwelling planktic foraminifera and benthic foraminifera stable isotope records from the eastern equatorial Pacific Ocean and the Caribbean Sea over the last 0.56 Ma. Core P6304-4 G. sacculifer data are from [Emiliani, 1972] whereas fine fraction (3-25 µm) data are from [Anderson and Steinmetz, 1981]. Site 502 P. wuellerstorfi data are from [deMenocal et al., 1992]. Site 849 P. wuellerstorfi data are from [Mix et al., 1995]. Site 851 G. sacculifer data are from [Cannariato and Ravelo, 1997] while fine fraction (<20 µm) data are from Paper III. Site 999 G. ruber data are from [Schmidt et al., 2006]. Note that data age estimations are based on the age model presented by deMenocal et al., [1992] (Site 502), Cannariato and Ravelo [1997] (Site 851) and Hermoso [2016] (Core P6304-4 and Site 999). Green arrows highlight abrupt shifts of fine fraction δ13C not paralleled by correlative shifts in foraminiferal signals. These shifts are interpreted as changes of biological production in the upper mixed layer between 0.56 and 0.30 Ma. Note also that fine fraction δ18O glacial-interglacial fluctuations are much higher in the Caribbean Sea (Core P6204-4) than in the EEP (Site 851). MIS refers to the Marine Isotope Stage system of numbering glacials and interglacials of the Pleistocene, with grey shading identifying interglacials [Lisiecki and Raymo, 2005].

Core P6304-4 was retrieved in 1963 from 15°27’N latitude and 70°43’W longitude (Figure 14), at a water depth of 4136 m by Emiliani [1966]. Data derived from the associated studies used in the early stages of paleoceanographic proxy development and application [Emiliani, 1972; Anderson and Steinmetz, 1981; 1983]. The late Pleistocene sequence recovered in Core P6304-4 comprised 11.9 m of “globigerina” ooze. The stable isotopes analyzed in sediment from this core particularly suit the purpose of this comparison because, as for Site 851, measurements were made on the sediment fine fraction (3-25 µm) [Anderson and Steinmetz, 1981] and G. sacculifer, although only the δ18O data are available for G. sacculifer [Emiliani, 1972]. Thus, the comparison between calcareous nannofossil and surface dwelling planktic foraminifera δ13C from the Caribbean Sea was done using the G. ruber δ13C data from neighbor Site 999 [Schmidt et al., 2006; Hermoso, 2016]. ODP Site 999, a 1066.4 mbsf long sequence of nannofossil sediment mixed with “foraminifera and clays”, was piston cored by the ODP at 12°45’N latitude and 78°4’W longitude at a
water depth of 2828 m [Sigurdsson et al., 1997]. For this core, *G. ruber* $\delta^{13}$C and $\delta^{18}$O are available but not bulk or fine fraction data. DSDP Site 502 is located at 11°29’N latitude and 79° 23’W longitude at a water depth of 3051 m and comprises a 215 mbsf long sediment sequence of predominantly foraminifera-nannofossils marls [Prell et al., 1982]. The *P. wuellerstorfi* stable isotope records from this site (deMenocal et al., 1992) are here used as a reference of the Caribbean Sea deep ocean chemistry and to compare it with surface water signals.

6.2.1 Caribbean - EEP $\delta^{13}$C comparison

![Figure 17](image.png)

*Figure 17.* Location of sediment cores in which an abrupt shift in calcareous nannofossils $\delta^{13}$C (see the arrows in Figure 16) was described between MIS 14 and MIS 8 [Anderson and Steinmetz, 1981; Schiffelbein and Thierstein, 1981; Dudley and Nelson, 1989; Liu et al., 2002]. These $\delta^{13}$C were described in multiple EEP cores, at Core P6304-4 in the Caribbean Sea, at DSDP Site 593 in the southern Tasman Sea and at ODP Site 1143 in the south China Sea. Bathymetric data and map are from GEBCO Compilation Group [2019].

Some key observations can be made regarding the calcareous nannofossils records. First, in Figure 16 we see the zoomed in view of EEP the $\delta^{13}$C record, showing the relatively lower calcareous nannofossil $\delta^{13}$C compared to the surface-dwelling *G. sacculifer* and the close coherency of these signals. The calcareous nannofossils $\delta^{13}$C from Site 851 (EEP) and Core P6304-4 (Caribbean Sea) show correlative changes over the last 0.56 Ma. Site 851 calcareous nannofossil $\delta^{13}$C displays a ~1.2 ‰ increase at 0.52 Ma and a ~1.2 ‰ decrease at 0.30 Ma. A similar pattern is seen in the fine fraction $\delta^{13}$C of in Core P6304-4, where the $\delta^{13}$C displays a 1.2 ‰ increase at 0.48 Ma and a 0.9 ‰ decrease at 0.30 Ma (Figure 16). Other studies observed similar $\delta^{13}$C shifts across the global ocean (Figure 17) at this time including (i) in multiple cores from the Pacific Ocean, between MIS 14 (ca 0.56 Ma) and MIS 8 (ca 0.30 Ma) [Schiffelbein and Thierstein, 1981], ii) in the southern Tasman Sea, at DSDP Site 593, where Dudley and Nelson [1989] reported a +1.2
‰ calcareous nanofossil δ¹³C shift in MIS 14 followed by an abrupt -1.5 ‰ shift in MIS 8, and iii) in the south China Sea, at ODP Site 1143, involving a 1.0 ‰ δ¹³C increase during MIS 14, decreasing again by 0.7 ‰ in MIS 8 [Liu et al., 2002]. As for Site 851, these coccolith carbonate δ¹³C perturbations are not paralleled by correlative shifts in surface dwelling planktic foraminifera δ¹³C from the same sites (Figure 16) [Schiffelbein and Thierstein, 1981; Dudley and Nelson, 1989; Liu et al., 2002].

Given these observations, these isotopic shifts have been interpreted as a global phenomenon [Dudley and Nelson, 1989; Liu et al., 2002] but the causes are debated. Anderson and Steinmetz [1983] ruled out changes in the magnitude of coccolithophorid vital effects and in the composition of the calcareous nanofossils assemblage. They also noted that the calcareous nanofossils δ¹³C of Core P-6304-4 is higher during glacials compared to interglacials between MIS 6 and MIS 1. They speculated that the low calcareous nanofossils δ¹³C during MIS 1, 3 and 5 was derived from increased local upwelling of ¹²C-rich waters at the core location [Anderson and Steinmetz, 1983]. In contrast, Dudley and Nelson [1989] suggested that changes in the magnitude of coccolithophorid vital effects could explain at least part of these δ¹³C shifts. Liu et al. [2002] found a negative relationship between calcareous nanofossil δ¹³C and the percentage of the species Florisphaera profunda, and interpreted the low percentages of F. profunda and high calcareous nanofossil δ¹³C between MIS 14 and MIS 8 as indicative of enhanced biological production at Site 1143. The higher calcareous nanofossils δ¹³C is indicative of higher surface water DIC δ¹³C, which in turn reflects enhanced biological productivity as phytoplankton preferentially fixes ¹²C into organic matter [Kroopnick, 1974; Grant and Dickens, 2002]. Lower content of F. profunda is also a proxy for enhanced biological production Liu et al. [2002]. Liu et al. [2002] concluded that calcareous nanofossil δ¹³C can be used as an indicator of surface water paleoproductivity, as was proposed by Kroopnick et al., [1977] and Goodney et al. [1980]. All the above observations and the EEP-Caribbean Sea comparison presented here, support ideas presented in Paper III. That is that distinctive calcareous nanofossil δ¹³C shifts most likely reflect changes of biological production in the upper mixed layer rather than changes in vital effects or in the composition of calcareous nanofossil assemblages. The absence of correlative δ¹³C fluctuations in the G. sacculifer δ¹³C was explained by the deeper calcification depth of this latter species [Rippert et al., 2016] and implied that calcareous nanofossil δ¹³C was a better proxy of surface water primary production compared to G. sacculifer. Hence, it is concluded that calcareous nanofossil δ¹³C is a tracer of upper mixed layer productivity also in the Caribbean Sea at least for the 0.56-0 Ma period. To verify if this is true also in other time periods, as in the EEP case, in the future new bulk, fine fraction and foraminiferal stable isotope records that extends from the late Miocene to present need to be produced from the Caribbean Sea.

With the EEP-Caribbean Sea comparison it is possible to verify whether paleoproductivity changes recorded in coccolith δ¹³C are also captured in the shallowest-dwelling planktic foraminifera species such as G. ruber δ¹³C. The latter calcifies in shallower water than G. sacculifer, at a maximum depth of 95 m [Rippert et al., 2016]. In addition, it has been observed that G. sacculifer stable isotopes record a mixture
of thermocline and mixed layer water properties. Thus, *G. sacculifer* would not be appropriate for surface water paleoceanographic applications [Spero, 2003]. The latter observation can itself explain the absence of *G. sacculifer* δ13C shifts between MIS 14 and MIS 8. The Site 999 *G. ruber* δ13C might be predicted to parallel the fine fraction record, however it does not do so especially well (Figure 16). Similar observations come also from Site 1143 where the MIS 14 through MIS 8 calcareous nannofossil δ13C fluctuations are not paralleled by coherent shifts in the *G. ruber* δ13C [Liu et al., 2002]. As for *G. sacculifer*, *G. ruber* δ13C clearly do not show the coherent abrupt changes of calcareous nannofossil δ13C records during the late Pleistocene at multiple locations in the global ocean.

Despite some broad similarities in the pattern of secular δ13C change over the past 0.56 Myrs, the inter-basin stable isotope comparison shows a large discrepancy in absolute δ13C values of calcareous nannofossil archives. Between 0.56-0 Ma EEP nannofossil δ13C is on average ca 0.94 ‰ lower compared to the Caribbean Sea (Figure 16). A similar Caribbean-EEP δ13C offset is also present between benthic foraminifera signals. This offset between benthic signals might reflect richer nutrient content in EEP bottom waters (Antarctic bottom water, thus with lower δ13C) compared to the Atlantic intermediate waters bathing the deep Caribbean Sea [Oppo and Fairbanks, 1990; Calvo et al., 2011]. While the relative difference between EEP and Caribbean fine fraction δ13C are at least in the same direction as the corresponding benthic offsets, i.e. EEP δ13C is lower than the Caribbean, the precise mechanisms of the EEP-Caribbean nannofossil δ13C offset, remains a puzzle. The next paragraphs dissect the problems in more detail.

A first factor to consider is the local surface ocean DIC δ13C. Coccolithophores calcifying in the mixed layer might be expected to record the local DIC δ13C, albeit with a vital effect-related offset. Samples of surface ocean DIC δ13C from the EEP and Caribbean, however, are similar, ∼1.4 ‰ at both Site 851 and Core P6304-4 locations [Tagliabue and Bopp, 2008; Schmittner et al., 2013], suggesting that the different coccolith δ13C signals cannot easily be explained by different upper ocean chemistry, e.g. related to inter-ocean differences in productivity intensity or the chemistry of different upwelling waters. On the other hand, the similar surface water DIC δ13C measurements are perhaps curious on their own, given the higher biological production in the EEP compared to the Caribbean Sea (Figure 6), in which case higher productivity in the EEP should be associated with relatively higher DIC δ13C and in turn to higher calcareous nannofossil δ13C in the Caribbean Sea. One possibility is that the upwelling signals are quite seasonal or patchy, meaning that more continuous water column DIC measurements are needed to constrain the dynamics of EEP upwelling, primary production and, thus, water column and coccolith chemistry.

Potentially, it’s possible that despite our reasoning, coccolithophore vital effects are playing a part in regulating the stable isotope composition of calcareous nannofossil calcite in these different settings. In this respect it’s tempting to revisit the potential role of CO2 efflux to surface waters and the atmosphere in the EEP (Figure 18) [McPhaden et al., 2006; Takahashi et al., 2009; Martinez-Botí et al., 2015a], something
that is not occurring in large scale in the Caribbean, but potentially important for coccolith calcification pathways. Something else to consider, requiring future work, is the impact on calcite stable isotope composition of differences in coccolithophore nutrient use efficiency, relative to nutrient supply, including differences in the supply of preformed nutrients to the Caribbean compared to the EEP. In the EEP preformed nutrients, i.e. nutrients that were subducted where the subsurface water originally sank, are supplied to the Equatorial Undercurrent that feeds the upwelling system from the Antarctic and North Pacific [Raifer and Charles, 2012]. To what extent this impacted coccolith primary production and $^{12}$C fractionation is to my knowledge unknown.

Figure 18. Mean annual net air-sea flux for CO$_2$ (grams C m$^{-2}$ year$^{-1}$) for the year 2000. Air-sea flux is here estimated using the difference between sea-air pCO$_2$ and air-sea gas transfer rate [Takahashi et al., 2002; 2008; 2009]. The air-sea gas transfer rate is parameterized as a function of wind speed with a scaling factor of 0.26. Red-yellow areas indicate that the ocean is a source for atmospheric CO$_2$, and blue-purple areas indicate that the ocean is a CO$_2$ sink.

In conclusion, the Caribbean Sea -EEP stable isotope comparison support ideas presented in Paper III that calcareous nannofossil $\delta^{13}$C reflects variability in upper mixed layer conditions and hence primary productivity both in the EEP and in the Caribbean Sea. The calcareous nannofossils $\delta^{13}$C seems to be a better indicator of upper mixed layer water conditions compared to surface dwelling planktic foraminifera, including G. sacculifer and G. ruber, as was previously suggested [Kroopnick et al., 1977; Goodney et al., 1980]. The $\sim$1‰ lower absolute values of nannofossils $\delta^{13}$C in the EEP compared to the Caribbean cannot be explained solely with inter-basin differences in surface water conditions. Thus, some other factor must be at play, and the likely culprit is coccolithophore vital effects.
6.2.2 Caribbean - EEP δ¹⁸O comparison

Comparison of the Caribbean and EEP δ¹⁸O records reveals something quite different. Fine fraction, planktic and benthic foraminifera δ¹⁸O from both regions show the classic mid-late Pleistocene isotope stages of increasing and decreasing δ¹⁸O [Lisiecki and Raymo, 2005]. However, while EEP and Caribbean nanofossils δ¹³C records show comparable glacial-interglacial variability, the amplitude changes in the accompanying Caribbean nanofossils δ¹⁸O are significantly larger (2-3 times) than that seen in the EEP (Figure 16). These glacial-interglacial changes are on the order of 2.5-3 ‰ and thus are even larger than those of benthic foraminifera δ¹⁸O, which are on the order of 2 ‰. Moreover, the calcareous nanofossil δ¹⁸O form the EEP is on average 1.21 ‰ lower compared to the Caribbean Sea record (Figure 16). The EEP calcareous nanofossils δ¹⁸O, is dampened compared to the other δ¹⁸O signals, with on average 1 ‰ glacial-interglacial changes, except at MIS 12 - MIS 11 deglaciation (ca 0.44 Ma, the highest-amplitude deglacial warming in the last 5 Myrs). The absolute differences between the Caribbean and the EEP coccolith δ¹⁸O are smallest (<1 ‰) at interglacial maxima whereas the offset is largest during glacial maxima (>2 ‰). Thus, the average 1.21 ‰ offset between these records is mainly due to glacial δ¹⁸O offsets.

When originally published [Anderson and Steinmetz, 1981], the surprisingly strong coccolith signal was interpreted, as recording the ‘true’ global sea water glacial-interglacial δ¹⁸O signal, and thus ice volume signal, implying that the planktic foraminifer record was dampened due to selective dissolution and recrystallization during interglacials. Differences in assemblages between glacials and interglacials were ruled out [Anderson and Steinmetz, 1981]. Numerous benthic and planktic records from around the world now indicate that this is likely not the case and that the calcareous nanofossil record is the anomaly. So, what is the explanation?

Assuming that the fine fraction carbonate δ¹⁸O reflects the surface ocean calcification habitat of coccolithophores, the offset in δ¹⁸O might relate to differences in surface salinity and temperature between the two tropical ocean regions. EEP surfaces waters have lower salinity compared to the Caribbean Sea (Figure 19) [Wang et al., 2010]. In modern ocean conditions, salinity at 50 m depth, the depth of maximum coccolithophore abundance, is 34.7 psu at Site 851 and 35.9 psu at P6304-4 [Locarnini et al., 2013]. Higher salinities are associated with higher δ¹⁸O, hence the modern salinity difference (ca 0 Ma in Figure 16), representative of interglacial conditions, would account for the ca 0.4 ‰ of higher calcareous nanofossil δ¹⁸O in the Caribbean Sea compared to the EEP seen in the comparison [Conroy et al., 2014]. What about glacials where the EEP-Caribbean offsets are largest? In a recent study, Sepulcre et al. [2011] proposed that during all glacial periods of the last ca 1 Ma surface water salinity at low latitude oceans was higher compared to interglacial periods because of the southward position of the ITCZ and a reduced Atlantic Meridional Overturning Circulation (AMOC). So, could higher glacial surface salinity in the tropical Atlantic explain the large Caribbean coccolith δ¹⁸O swings? Figure 19 (panel a) shows that the salinity
difference between the two sites increases with depth until 150 m depth. Thus, the salinity difference can account for more than 0.4‰ δ18O, if a coccolithophore calcification depth was saltier at 50 m or the habitat deepened to > 50 m. A problem with this is that similar signals are not seen in the surface dwelling planktic foraminifera from the Caribbean. Moreover, the other factor to consider is water temperature, which is a key controller of biogenic calcite δ18O. In modern times, at 50 m depth the temperature is on average ca 5°C colder at Site 851, due to upwelling, compared to Site P6304-4, which is well stratified (Figure 19, panel b) [Locarnini et al., 2013]. This water temperature difference would add 1-1.2‰ δ18O in the EEP, using a standard δ18O-temperature relationship. However, it can be seen that the EEP nannofossil δ18O is consistently lower than the Caribbean nannofossil δ18O. Hence, while the modern lower salinity in the EEP compared to the Caribbean Sea partially explains the lower nannofossils δ18O in the EEP, the same is not true for inter-basin temperature differences, they work in opposite direction with respect to the δ18O signal. The colder surface water temperatures in the EEP, that likely occurred both during interglacial and glacial periods, should result in higher nannofossil δ18O values in the EEP compared to the Caribbean Sea, but instead relatively lower δ18O values are recorded in the EEP (Figure 16). Temperature and salinity on their own, thus do not seem to be able to explain the large swings in Caribbean nannofossil δ18O.

Here again coccolithophore vita effects must be considered. In a recent study of the Core P6304-4 nannofossil δ18O, Hermoso [2016] explained the high amplitude changes (>2.5‰) over glacial-interglacial cycles by invoking stronger vital effects during glacial intervals, generated by low atmospheric CO2
concentrations. Hence, a possible cause for the >2‰ higher calcareous nannofossils δ¹⁸O in the Caribbean Sea compared to the EEP during glacial periods is a combination of higher Caribbean seawater salinity and larger coccolith vital effects in the Caribbean Sea compared to the EEP. Similarly changes in vital effects associate with changes in nutrient availability and nutrient use efficiency could possibly produce a similar effect, although, as mentioned above this is currently untested. This idea is stimulated by recent research by Poggemann et al., [2017] who suggest changes in nutrient content of Antarctic Intermediate Water feeding temporary tropical Atlantic productivity zones between glacial and interglacials.

6.3 The puzzle of coccolith vital effects on glacial-interglacial cycles

Given the above considerations and discussion in Paper II and Paper III, a crucial point still not fully understood is the extent to which bulk carbonate stable isotope records are influenced by changing strengths of coccolith vital effects over glacial-interglacial cycles. As introduced in Section 4.1.1 of this kappa and Paper II and Paper III, the isotopic composition of calcareous nannofossil calcite is not the same as that of the seawater in which the coccolithophores lived. Carbon and oxygen isotope fractionation occurs during the precipitation of calcium carbonate from DIC because of equilibrium fractionation effects [Emrich et al., 1970; McConnaughey, 1989; Romanek et al., 1992] and because of biological or “vital” effects [Ziveri et al., 2003; Bolton and Stoll, 2013]. Cultures of coccolithophores have shown that these vital effects can alter both carbon and oxygen isotopes by up to 5‰ [Ziveri et al., 2003]. Vital effects have also been described to depend on cell size and grow rate [Ziveri et al., 2003; Rickaby et al., 2010; McClelland et al., 2017] and on atmospheric and aqueous CO₂ levels [Bolton et al., 2012; Bolton and Stoll, 2013; Hermoso et al., 2016]. Early Cenozoic perspectives suggest that coccolith vital effects were absent in calcareous nannofossil calcite during the hyperthermal events of the Paleocene [Bolton et al., 2012], when atmospheric CO₂ reconstructions suggest CO₂ on the order of 1000-2000 ppm [Zachos et al., 2008; Pälike et al., 2012], but became increasingly important between 7 and 5 Ma, when the atmospheric CO₂ fell below a critical threshold of ca 500 ppm (Figure 7) [Bolton and Stoll, 2013].

In Paper III, larger coccolithophores vital effects during glacial periods were invoked to explain larger amplitude δ¹⁸O of calcareous nannofossils compared to planktic foraminifera at Site 851. The Caribbean-EEP comparison shows that glacial-interglacial δ¹⁸O fluctuations are much larger at P6304-4 compared to Site 851 suggesting lower vital effects during glacials in the EEP compared to the Caribbean Sea. From a broad ocean-scale view, this idea is consistent with the fact the oceanography and biogeochemistry of the two ocean basins is very different. The EEP is the ocean region located near the Equator where upwelling is strongest, where CO₂ is release to the atmosphere; here the supply of CO₂-rich intermediate waters to the mixed layer maintains a disequilibrium with the CO₂ concentration between atmosphere and surface ocean (Figure 18) [McPhaden et al., 2006; Takahashi et al., 2009]. This disequilibrium would limit the invasion of atmospheric CO₂ into the surface ocean both during interglacial and glacial periods. Hence, in the EEP area of strong wind-driven upwelling, the surface water CO₂ concentration would be higher than atmospheric CO₂ limiting coccolith vital effects on carbonate stable isotopes. In contrast, the Caribbean
Sea surface water would be more influenced by glacial-interglacial CO₂ fluctuations because of water column stratification, generating stronger vital effects in glacial periods when the atmospheric CO₂ concentration is low.

Following this rationale and the ideas presented in the section above, higher coccolithophores vital effects in the Caribbean Sea and an increased salinity difference between the Caribbean Sea and the EEP during the Pleistocene glacial periods can explain the higher calcareous nannofossils δ¹⁸O offsets between the Caribbean Sea and the EEP. The idea of stronger δ¹⁸O vital effects in the Caribbean Sea compared to the EEP however contrast with the ca 1‰ lower δ¹³C at Site 851 compared to Core P6304-4 during the 0.56-0 Ma. In fact, the magnitude of vital effects seems to be correlative with carbon and oxygen stable isotopes [Bolton and Stoll, 2013; Hermoso, 2016; Jin et al., 2018]. Thus, vital effects would not explain the ca 1‰ lower nannofossils δ¹³C in EEP compared to the Caribbean.

6.4 Sediment grain size since the late Miocene

One fascinating aspect of EEP sediments that has not been fully investigated yet are changes of coarse fraction sediment content and composition since the late Miocene. Figure 20 shows CaCO₃ %, CF % and abundances of >63 µm sediment components at Site 851 over the last 7 Ma. Clearly, foraminifera content decreases whereas biosilica content (radiolarians, diatoms and sponge spicules) increases with increasing age. These changes are paralleled by an abrupt decrease in the CF %, from 17.0 % on average during the 0.56-0 Ma interval to 2.7 % on average during the 6.8-6.4 Ma interval, and by a smaller decrease in CaCO₃ %, from 82.3 % on average during the 0.56-0 Ma interval to 71.9 % on average during the 6.8-6.4 Ma interval (Paper III). Similar trends have been described at Site U1338 (Paper I and Paper II) and at Site 573 (Paper II). However, at Sites U1338 and 573 CaCO₃ % increased by about 5 % on average from the 0.56-0 Ma interval to 6.8-6.4 Ma interval (Papers I and II supplementary tables). Apparently, sediment grain size distribution and coarse fraction composition vary significantly from the late Miocene to the late Pleistocene at EEP sites located near the Equator. These data together bring information on changes in carbonate dissolution related to the lysocline depth and/or changes in the relative amount of carbonate and biosilica particles produced in the surface ocean [Broecker and Clarrck, 1999; Broecker, 2008; Lyle et al., in review]. Thus, understanding the reason for these changes in sedimentary records is important in the effort of better understanding the EEP paleoclimate evolution.

Overall, the combination of low foraminiferal material content in the coarse fraction, low CF % and almost unvaried CaCO₃ % suggests enhanced carbonate dissolution during the late Miocene compared to more recent times at EEP on-equator sites. Enhanced dissolution related to the shallowing of the lysocline would lower the CF % by removing the foraminiferal material but would not lower the CaCO₃ % as much because coccoliths are less susceptible to dissolution than foraminifera [Berger, 1973; Broecker and Clarrck, 1999; 2009; Chiu and Broecker, 2008]. Enhanced dissolution is also supported by the poor preservation of foraminifera carbonate in the late Miocene compared to more recent times (Figure 20). Dilution of
carbonate by biosilica particles would be ruled out as a first cause of low foraminiferal material content and low CF % because dilution by biosilica should also generate much lower CaCO$_3$ % as diatoms are mostly smaller than 63 $\mu$m. However, dilution can still be a major cause for low CF % and low foraminifera content over short time intervals of low CaCO$_3$ % in the late Miocene (<60 %, Figure 20). To further test this hypothesis and to shed new light on whether dissolution or dilution or a combination of both are responsible for the EEP sediment grain-size distribution changes a step forward would be to measure WBD, CaCO$_3$ % and weight of bulk, <20 $\mu$m, <63 $\mu$m and >63 $\mu$m sediment fractions and estimate the relative abundance on carbonate and biosilica particles in each of these sediment fractions.

![Figure 20](image.png)

**Figure 20.** Comparison between coarse fraction content (CF %), bulk carbonate content (CaCO$_3$ %) and abundances of coarse fraction (>63 $\mu$m) sediment components over 7 Ma at Site 851. Note that bio-silica components (mainly radiolaria, large diatom tests and sponge spicules) are the most abundant >63 $\mu$m sediment component during the late Miocene and the early Pliocene whereas calcareous planktic foraminifera are the most abundant >63 $\mu$m sediment component during more recent times. The grey shade indicates poor preservation of CaCO$_3$ particles (mainly planktic foraminifera) here interpreted as enhanced carbonate dissolution during the late Miocene and early Pliocene. In more recent times foraminifera preservation is generally better. Abundance estimations were performed using a Lecia M250C stereomicroscope equipped with a Leica DFC295 digital microscope camera.
6.5 Summary of EEP paleoceanography

This thesis work has produced data demonstrating that the geochemical signals in the bulk sediment archive contain fundamental information to help better understand the evolution of EEP paleoceanography, as well as global carbon cycling and ocean circulation. This involved using multiple approaches to disentangle the oceanographic signals hidden in bulk sediment δ18O and δ13C. With this new knowledge, bulk sediment geochemistry and physical properties become more powerful tools in the palaeoceanographic tool box, with value for understanding the development and dynamics of the EEP system during warm climates of the late Miocene and the early Pliocene, to strong climatic swings of the Pleistocene glacial. The most important finding is that the bulk sediment δ18O and δ13C represents surface ocean conditions, although the absolute isotopic values deviate from ambient seawater values due to strong coccolith vital effects.

The data produced suggest important variation in the EEP paleoceanography from the late Miocene to the present. A key observation has been the impressively coherent bulk sediment δ13C that can be traced across the EEP. The results of the on-equator compared to off-equator studies, including measurements of bulk stable isotopes, grain size, carbonate and biosilica content, and sedimentation rates, suggest a more focused wind-driven equatorial upwelling and higher biological production between 8.0 Ma and 4.6 Ma compared to the present day (Paper II and Paper III). Overall the data support the ‘biogenic bloom’, and are inconsistent with the alternate palaeoceanographic interpretation for changes during this time, based on planktic foraminifera, invoking permanent El Niño conditions [e.g. Wara et al., 2005; Dekens et al., 2007; Ford et al., 2015]. Latest theories proposing coexisting warm SST and enhanced biological production during the late Miocene [Lyle and Baldwaf, 2015; Zhang et al., 2017] on one hand are consistent with evidences from paleoproductivity proxies presented here but, on the other hand, warm SSTs during the late Miocene are difficult to reconcile with high calcareous nanofossils δ18O at on-equator sites.

The enhanced wind-driven upwelling and surface productivity typical of the biogenic bloom suggests major late Miocene early Pliocene perturbation of the global climate and carbon cycle [Grant and Dickens, 2002; Herbert et al., 2016]. The increase in temperature gradients between the equator and the polar regions would have strengthened the Hadley Cell [Herbert et al., 2016], intensifying the trade winds and hence the wind-driven upwelling in the EEP [Hovan, 1995] and in other low-latitude upwelling areas of the global Ocean [Grant and Dickens, 2002; Herbert et al., 2016]. The changes in atmospheric and ocean circulation, were paralleled by decreasing atmospheric CO2. The associated climate cooling was accompanied by terrestrial aridification and diversification of C4 plants, which are specialists of lower CO2 and water conservation [Diester-Haas, 2006; Herbert et al., 2016]. In addition, mountain uplift increased during the late Miocene [Raymo et al., 1988]. As a result, these terrestrial changes increased the supply of nutrients to the ocean because of i) greater soil erosion of 13C-depleted organic matter and ii) higher aeolian dust input into the oceans [Hovan, 1995; Grant and Dickens, 2002; Diester-Haas, 2006; Herbert et al., 2016] fostering biological production. Together with the strengthening of trade winds and nutrients supply to the oceans, the biogenic bloom was probably sustained by changes in ocean nutrients distribution linked to changes in...
global oceanography \cite{Grant_Dickens_2002}. The simultaneous progressive restriction of the Indonesian Throughflow and, most importantly for the EEP case, of the CAS, might have played an important role in changing the water, nutrients and heat fluxes between different water masses further supporting conditions for the biogenic bloom \cite{Brierley_Fedorov_2016,Sentman_2018}.

From 4.6 to 2.4 Ma, EEP biological production decreased, SST warmed and the wind-driven circulation system was potentially weaker compared to the 8.0-4.6 Ma interval and the present-day conditions, which is consistent with the sustained global warmth during the Pliocene \cite{Seki_2012}. In more recent times, SST progressively and gradually cooled. Bulk sediment signals suggest high biological production, cooler SST and enhanced wind-driven circulation at about 2.0 Ma and between 0.5 Ma and 0.3 Ma. After 0.3 Ma, the wind-driven circulation and biological production decreased to present day conditions.

6.6 Unresolved questions and future research

Despite the detailed treatment of sedimentary data from the EEP undertaken here, the findings of this thesis raise a series of unresolved questions, each of which requires specific further research work. The most significant of these questions are briefly discussed below.

From Paper I, it is still not clear whether the dominant factor generating WBD changes with depth is sediment compaction or variations in sediment composition. From the discussion presented in section 6.4, it is clear that significant changes in sediment composition have occurred since the late Miocene, in particular with respect to coarse fraction data. The decreasing >63 µm foraminifera content with increasing age in theory could itself explain increasing WBD with increasing depth/age. Our results also indicate a greater mass loss after sample rinsing than that predicted by modelling. Thus, is not clear if the CaCO$_3$ % of rinsed samples are more precise than that of unrinsed samples. Further analyses are needed to estimate how much of the mass loss is derived from the removal of salt and how much from the removal of sediments during the rinsing process.

From Paper II and Paper III, it remains unclear how bulk carbonate sediments, reflecting coccolith carbonate, and thus a surface water signal, acquire their absolute isotopic signature in the first place. The strong deviations from surface ocean DIC δ$^{13}$C and δ$^{18}$O are generated by vital effects, and although there is broad understanding that this reflects biochemical processes occurring inside the coccolithophore cell associated with coccolith calcification (internal pH modifications), an univocal view on exactly what how coccolithophorid precipitation works is still missing. Furthermore, it is not clear how the magnitude of carbon and oxygen vital effects changes under different atmospheric CO$_2$ concentrations, such as over glacial/interglacial cycles of the Pleistocene, and how vital effects varies in relation to different ocean basins (Section 6.3). And what role does the high CO$_2$ efflux to the atmosphere due to upwelling in the EEP impact this process compared to other ocean regions? Differences in absolute values and amplitude of calcareous
nannofossil δ^{13}C and δ^{18}O between the EEP and Caribbean Sea, the Caribbean being more salinity stratified, provide a tantalizing future for exploring this further.

The precise timing and cause of the high amplitude (>2 ‰) bulk calcareous nannofossil δ^{13}C changes in the EEP are still unclear. The remarkable coherency of some bulk carbonate stable isotope records across the EEP was interpreted to reflect a diffuse gradient in surface water DIC δ^{13}C despite heterogeneity of surface water conditions across the EEP. An in depth understanding of the factors controlling surface water DIC δ^{13}C remain elusive. How and in what extent CO_{2} outgassing in the EEP is impacting DIC δ^{13}C and nannofossils δ^{15}C and δ^{18}O? For a deeper understanding of how coccolithophores acquire their stable isotope signature, a step forward would be to examine the stable isotope composition of bulk, fine sediment fractions, coarse sediment and microfiltered species-specific coccolithophorids at multiple locations in the EEP, where SST and DIC δ^{13}C vary significantly. This should also be extended to other low latitude ocean areas.

From this thesis it has been learned that the study of bulk properties is crucial for a better understanding of EEP paleoceanography. Despite factors complicating the understanding of bulk sediment properties and bulk carbonate stable isotopes, e.g. mixed particles composition, vital effects or differential dissolution, bulk sediment preserves information on surface ocean properties. Thus, bulk sediment is probably a more reliable archive of proxies for EEP paleoceanography since the late Miocene than foraminifera that instead are deeply altered by diagenetic alterations and/or are scarce in several time intervals.

The data produced and the ideas proposed in this work represent the starting point in the effort to understand the potential of bulk sediment records for deciphering the EEP paleoceanography history. Certainly, this potential revealed to be far greater than being merely a stratigraphy and correlation tool.
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Appended Papers