

Selective preservation of organic-walled dinoflagellate cysts  
in Quaternary marine sediments: An oxygen effect and its  
application to paleoceanography

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*“What has happened can happen again”*

Reid A. Bryson  
(climate scientist)

## PREFACE

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The thesis is cumulative and includes four manuscripts (Chapter 2-5) which are, respectively, preceded by a general introduction (Chapter 1) and followed by conclusions and scientific perspectives (Chapter 6). The first chapter portrays the scientific context of the thesis and summarizes selected aspects that are not discussed in detail within the separate manuscripts but might be important to the reader’s comprehension. The first manuscript presents published results of work to which I contributed sample material, statistical analysis and co-authorship. The three remaining manuscripts are all first-authorships and are either under revision or have been submitted to peer-reviewed journals. References to cited literature in the text are given at the end of each chapter. All data presented in this thesis are available from the public database Pangaea (<http://www.pangaea.de>).

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## EXECUTIVE SUMMARY

Twenty years after the discovery of major glacial-interglacial cycles in atmospheric CO<sub>2</sub>, one of the hottest topics in paleoceanographic research is the global carbon cycle. Motivated by public concerns considerable progress has been made in pinning down the ocean's role as a source and sink for atmospheric CO<sub>2</sub>. Yet, we remain ignorant of several key issues. Are physical processes primarily responsible for carbon storage in the ocean or is marine biology the dominant player? Has ocean productivity changed over ice ages? How much carbon sequestered by primary production ultimately preserves in marine sediments? Was the O<sub>2</sub> content of the glacial deep-ocean much lower than today? To answer some of these questions we critically depend on methods that can separate productivity from preservation and enable to estimate deep-ocean ventilation. It is this story with which this thesis is concerned.

The ultimate goal of this work is to develop and evaluate methods that enable to transform the paleoenvironmental signal of organic-walled dinoflagellate cysts (dinocysts) into estimates of export production, organic matter preservation, and oxygen contents of the ocean's deepest water. Why dinocysts? First, dinocyst assemblages in marine sediments bear important information on ocean productivity, notably in neritic settings where dinoflagellates contribute essentially to primary production. Moreover, after buried to surface sediment their fossil remains comprise an archive for the reconstruction of sea surface temperature, salinity, nutrient availability, and physical mixing. Second, certain dinocysts (S-cysts) exhibit lower degradation rates under anoxic as compared with oxic conditions. As a result, S-cysts are less efficiently preserved when oxygen is present than dinocysts that protect themselves against decay by aromatic substances in their wall structure (R-cysts). Recent advances proof that the lower preservation potential of S-cysts remains stable for different environments while the high preservation potential of R-cysts exceeds that of pollen, lipids, and n-alkanes. Together, these attributes suggest that dinocysts might be an ideal tool to link export production, organic matter preservation, and oxygenation of bottom water to the fossil record.

The first step toward a reasonable working model on selective dinocyst preservation is to test how R-cysts and S-cysts relate to environmental conditions as they pertain to different regions of the oceans, notably to bottom water oxygen contents and conditions in the upper water column where dinocysts are produced. For this purpose, a compilation of dinocyst accumulation rates generated from surface sediments of the Arabian Sea, the subtropical East Atlantic, the western Equatorial Atlantic, the South-East Atlantic, and the Atlantic sector of the Southern Ocean is used. The statistical analysis reveals significant relationships between R-cysts and chlorophyll *a* concentration in surface waters as well as between S-cysts and bottom water oxygen concentration. In contrast, relationships are insignificant or weak between R-cysts and bottom water oxygenation and between S-cysts and surface water chlorophyll *a* contents, temperature, salinity, and nutrient levels. These results suggest that S-cyst accumulation reflects export production and surface water conditions only in low oxygen settings while R-cyst accumulation is a reliable indicator of export production regardless of the environment under consideration.

Furthermore, calculation of a degradation index assesses S-cysts decay as a high-order process with a degradation rate that is dependent on the bottom water oxygen content.

The conclusion of the former study makes it necessary to verify the model performance by comparing it to independent proxies. For this reason, a core from the subtropical North-East Atlantic (GeoB 4216) is chosen. Former studies used the Ba/Al ratio and redox-sensitive element distributions (Fe, Mn, and U) to explain the ambiguous productivity signals in the TOC profile of the last glacial-interglacial sediment horizon in this sediment core. The high-resolution dinocyst record reveals that these signals are also imprinted on the record of S-cysts where they likely reflect post-depositional degradation, i.e. “burn-down” events. In contrast, the record of R-cysts parallels Ba/Al ratios throughout the studied section and thus, is assumed to reflect the initial productivity signal for the entire period. Moreover, using the degradation index as a measure of oxygen supply into the sediment largely explains the formation of redox-sensitive element enrichments due to a chemical adjustment of the pore water equilibrium after non-steady state situations. Because these diagenetic conditions often result from changes in particle flux and/or deep water circulation, it is suggested that they have a causal connection to the major climate transitions of the last deglaciation (Older Dryas - Bölling-Allerød - Younger Dryas - Holocene). Uncertainties in the performance of R-cysts, S-cysts, and the degradation index stem largely from the unknown accuracy of accumulation rates, which relies on the temporal resolution of the age model and precise estimation of dry bulk densities.

In order to circumvent the problem associated with the use of accumulation rates, it is necessary to scrutinise the relevance of selective dinocyst preservation using relative abundances. For this purpose, relative abundance data on the dinocyst associations in surface sediments of the Benguela upwelling system are used to explore the relationship between community variability and oceanographic parameters that potentially govern species distribution. It is shown that dinocyst associations in regions where oxygen minimum zones impinge on the sea floor differ in species composition compared with ventilated areas. The statistical analysis reveals that this pattern cannot be explained only by the ecological requirements of the different cyst forming species and lateral transport but also significantly correlates to the oxygenation of bottom waters. This makes a plausible case that post-depositional degradation in oxygenated settings selectively removes S-cysts (notably *Brigantedinium* spp.) and alters assemblage structures toward R-cysts (notably the genus *Impagidinium* and *Nematosphaeropsis labyrinthus*). As such, the results provide convincing proof that the use of relative abundances instead of accumulation rates does not challenge the concept of selective dinocyst preservation.

The former findings give reason to use selective cyst preservation for the reconstruction of bottom water oxygen concentration over geological timescales. Therefore, count data on the modern cyst distribution in the Benguela upwelling system are used as calibration dataset to derive an oxygen index. This index enables to transform the late Pleistocene dinocyst record of a sediment core (GeoB 1710) from the lower continental slope off Namibia into quantitative estimates on bottom water oxygenation. It is possible to show that lowest oxygen contents typified glacial cold phases of the last 150,000 years consistent with the timing of weaker deep water

formation in the North Atlantic. Rapid returns to present-day oxygen levels proceed during the resumption of meridional overturning circulation and the subsequent inflow of oxygen-rich North Atlantic Deep Water that filled up the deep basin at the expense of oxygen-depleted southern component water. The comparison to ventilation scenarios based on stable isotopes, carbonate dissolution, and benthic foraminiferal assemblages confirm the high-quality of proxy performance. Moreover, the incorporation of selective dinocyst preservation enhances the quality of existing productivity reconstructions at the studied site as it emphasizes the effect of organic matter oxidation.

This thesis provides important new insights into the use dinocysts as indicators for marine export production, organic matter preservation, and deep-ocean ventilation. The perspective that is generated draws attention to the potential of degradation models for estimating the diagenetic status of geological records, which is difficult to accomplish using conventional criteria but crucial to avoid spurious interpretations on past changes in marine bioproduction, biogeochemical cycles, and ocean circulation. In this regard, dinocysts are an ideal tool due to the large difference between the preservation potential of R-cysts and S-cysts and their similar behaviour to factors such as transport and bioturbation. Because dinocysts are abundant in almost all marine environments since the Early Jurassic, the proposed method is potentially widely applicable, notably in key areas of both high marine production (e.g., Southern Ocean) and ocean circulation (e.g., Agulhas Current and Indonesian Flow Through). Moreover, the general idea to use differences in degradation rates it is not bound to dinocysts. Applying it to land-derived organic matter may elucidate transport of terrestrial material to the marine environment, which could facilitate the modelling of ancient wind patterns and carbon fluxes into the ocean. To be clear, much work remains to be done and the presented results of this thesis should be recognised as a promising but certainly not complete attempt. Next steps will require a quantitative appreciation of the impact of degradation on dinocyst assemblages as well as the exploration of molecular geochemical applications. If this is successful then selective cyst preservation will become much more tangible and as such could gain some of the raw information to be included in models of the ocean carbon cycle. In turn, better estimates will enable to better predict ecosystem change and global climate in the future.

## KURZFASSUNG

Zwanzig Jahre nach Entdeckung der beträchtlichen Glazial-Interglazial Zyklen im CO<sub>2</sub> Gehalt der Atmosphäre ist die Erforschung des globalen Kohlenstoffkreislaufs ein Kernthema der Paläozeanographie. Unter dem Druck gesellschaftlicher Interessen, konnte die Rolle der Ozeane als Quelle und Senke atmosphärischen CO<sub>2</sub> bereits wesentlich konkretisiert werden. Dennoch bleibt eine Vielzahl von Kernfragen ungelöst. Sind hauptsächlich physikalische Prozesse für die Speicherung von Kohlenstoff im Ozean verantwortlich oder ist die Biologie der dominierende Faktor? Hat sich die Produktivität der Ozeane während der Eiszeiten verändert? Welcher Anteil des durch Primärproduktion gebundenen Kohlenstoffs bleibt in marinen Sedimenten letztendlich erhalten? War der Sauerstoffgehalt im Tiefenwasser des glazialen Ozeans deutlich geringer als heute? Um einige Fragen zu beantworten bedarf es Methoden, die es ermöglichen, Produktivität von Erhaltung zu trennen und die eine Abschätzung über die Ventilation des Tiefenwassers zulassen. Es sind diese Themen, denen sich die vorliegende Arbeit widmet.

Ziel der Arbeit ist die Entwicklung und Bewertung von Methoden, die es ermöglichen, das Paläo-Umweltsignal organisch-wandiger Dinoflagellatenzysten (Dinozysten) zur Abschätzung von Exportproduktion, Erhaltung organischen Materials und dem Sauerstoffgehalt im Tiefenwasser zu nutzen. Warum Dinozysten? Erstens, Dinozysten-Vergesellschaftungen in marinen Sedimenten liefern wichtige Informationen über die Produktivität im Ozean, insbesondere in neritischen Gebieten, in denen Dinoflagellaten wesentlich zur Primärproduktion beitragen. Darüber hinaus bilden die fossilen Überreste nach Einlagerung im Oberflächensediment ein umfassendes Archiv zur Rekonstruktion von Paläo-Umweltbedingungen der Meeresoberfläche wie beispielsweise Temperatur, Salinität, Nährstoffgehalt und physikalische Durchmischung. Zweitens sind die Abbauraten bestimmter Dinozysten (S-Zysten) unter anoxischen Bedingungen niedriger als im oxischen Milieu. Dies hat zur Folge, dass die Erhaltung der S-Zysten unter dem Einfluss von Sauerstoff deutlich schlechter ist als bei Arten, die den Abbauprozess durch die Synthetisierung aromatischer Substanzen in ihre Wandstruktur verlangsamen (R-Zysten). Neueste Studien belegen ein gleich bleibend geringes Erhaltungspotential der S-Zysten in verschiedenen Meeresgebieten, während das hohe Erhaltungspotential von R-Zysten das von Pollen, Lipiden und n-Alkanen übersteigt. Die Verbindung dieser Eigenschaften lässt vermuten, dass Dinozysten ein ideales Hilfsmittel sind, um Exportproduktion, Erhaltung organischen Materials und Sauerstoffgehalte des tiefen Ozeans aus dem Fossilbericht abzuleiten.

Um ein adäquates, auf selektiver Erhaltung von Dinozysten basierendes Arbeitsmodell zu erarbeiten, ist es zunächst notwendig, die die Verteilung von R-Zysten und S-Zysten in Sedimenten aus unterschiedlichen Regionen der Ozeane mit Umweltbedingungen in Beziehung zu setzen, insbesondere dem Sauerstoffgehalt des Bodenwassers sowie den physikalisch/chemischen Bedingungen in der oberen Wassersäule, wo Dinozysten produziert werden. Hierfür werden Akkumulationsraten von Dinozysten herangezogen, die aus Oberflächensedimenten des Arabischen Meeres, des subtropischen Nordost-Atlantik, des westlich-äquatorialen Atlantik, des Südost-Atlantik und dem atlantischen Sektor des Südozeans berechnet wurden. Die statistische Auswertung zeigt signifikante Korrelationen zwischen R-Zysten und der Chlorophyll *a*

Konzentration im Oberflächenwasser sowie zwischen S-Zysten und dem Sauerstoffgehalt im Bodenwasser. Im Gegensatz dazu bestehen keine oder nur sehr schwache Korrelationen zwischen R-Zysten und dem Sauerstoffgehalt im Bodenwasser sowie zwischen S-Zysten und der Chlorophyll *a* Konzentration, der Temperatur, dem Salzgehalt sowie dem Nährstoffangebot in der oberen Wassersäule. Die Ergebnisse implizieren, dass die Akkumulation von S-Zysten nur in Gebieten mit niedrigem Sauerstoffgehalt im Bodenwasser ein Anzeiger für Exportproduktion und Umweltbedingungen in der oberen Wassersäule ist, während die Akkumulation von R-Zysten zuverlässige Angaben über Exportproduktion liefert und dies unabhängig vom betrachteten Gebiet. Darüber hinaus zeigt sich durch die Berechnung eines Abbau-Index, dass die oxidative Lösung von S-Zysten einem Prozess höherer Ordnung unterliegt, mit einer Abbaurrate, die vom Sauerstoffgehalt im Bodenwasser abhängig ist.

Die vorhergehende Schlussfolgerung macht es erforderlich, die Effizienz des Modells anhand eines Vergleichs zu unabhängigen Proxies zu verifizieren. Zu diesem Zweck wird ein Sedimentkern (GeoB 4216) aus dem subtropischen Nordost-Atlantik herangezogen. Vorherige Studien haben anhand von Ba/Al-Verhältnissen und redox-sensitiven Elementgehalten (Fe, Mn, U) versucht, die im letzten glazial-interglazialen Kernabschnitt auftretenden fragwürdigen Produktivitätssignale im TOC-Profil zu erklären. Der hoch auflösende Fossilbericht der Dinozysten zeigt, dass diese Signale ebenfalls im Fossilbericht der S-Zysten zu beobachten sind, wo sie wahrscheinlich durch Abbau nach der Einlagerung ins Sediment entstanden sind, d.h. so genannte „burn-down“ Events darstellen. Im Gegensatz dazu findet sich eine Übereinstimmung zwischen dem Fossilbericht der R-Zysten mit dem Ba/Al-Verhältnis über die gesamte Kernlänge, was darauf hinweist, dass der Fossilbericht der R-Zysten das primäre Produktionssignal der untersuchten Zeitspanne reflektiert. Das Heranziehen des Abbau-Index als Indikator für die Sauerstoffversorgung des Sediments kann darüber hinaus die Anreicherungen der redox-sensitiven Elemente erklären, die durch diagenetisch instabile Bedingungen und der daraus resultierenden chemischen Angleichung des Porenwasser-Gleichgewichts entstanden sind. Da solche Situationen oft das Resultat von Veränderungen im Partikelfluss und/oder der Tiefenwasserzirkulation sind, ist anzunehmen, dass sie in einem kausalen Bezug zu den größeren Klimawechseln des letzten Deglazial stehen (Ältere Dryas - Bölling-Allerød - Jüngere Dryas - Holozän). Unsicherheiten bei der Interpretation von R-Zysten, S-Zysten und des Abbau-Index sind vorwiegend durch die Genauigkeit der Berechnung von Akkumulationsraten bedingt, die wiederum von der Auflösung des Altersmodells und einer präzisen Berechnung der Trockenraumdichte abhängt.

Um das Problem zu umgehen, das mit der Verwendung von Akkumulationsraten verbunden ist, erscheint es notwendig, die Bedeutung selektiver Erhaltung von Dinozysten auf Basis relativer Häufigkeiten zu überprüfen. Zu diesem Zweck werden relative Häufigkeiten von Dinozysten-Vergesellschaftungen aus Oberflächensedimenten des Benguela Auftriebsgebiets in Beziehung zu ozeanographischen Parametern mit potentielltem Einfluss auf die Artenverbreitung gebracht. Es zeigt sich, dass Vergesellschaftungen aus Bereichen der Sauerstoff-Minimum-Zone deutliche Unterschiede zu denen belüfteter Gebiete aufweisen. Eine anschließende statistische Analyse beweist, dass dieses Muster nicht nur durch ökologische Ansprüche der verschiedenen Dinozysten produzierenden Arten und lateralen Transport hervorgerufen wird, sondern auch eine

signifikante Relation zum Sauerstoffgehalt des Bodenwassers aufweist. Eine plausible Erklärung dafür ist, dass selektiver Abbau von S-Zysten (insbesondere *Brigantedinium* spp.) unter oxischen Bedingungen die Assoziation zu Gunsten widerstandsfähiger Zysten verändert. Die Daten liefern darüber hinaus eindeutige Beweise, dass die Anwendung relativer Häufigkeiten anstelle von Akkumulationsraten das grundlegende Konzept der selektiven Erhaltung von Dinozysten nicht in Frage stellt.

Die Ergebnisse der vorherigen Studie geben Anlass dazu, die selektive Erhaltung der Dinozysten zur Rekonstruktion des Sauerstoffgehalts im Bodenwasser auf erdgeschichtlicher Zeitskala einzusetzen. Dazu wird mittels der Zysten-Daten aus dem Benguela Auftriebsgebiet ein Sauerstoff-Index abgeleitet. Der Index wird dazu benutzt, aus dem spät-pleistozänen Fossilbericht eines Sedimentkerns (GeoB 1710) vom unteren Kontinentalhang Namibias Sauerstoffgehalte im Bodenwasser zu berechnen. Es zeigte sich, dass Warmzeiten der letzten 150,000 Jahre niedrige Sauerstoffgehalte aufwiesen, was mit der zeitgleichen Verringerung der Tiefenwasserbildung im Nordatlantik übereinstimmt. Ein abrupter Anstieg der Sauerstoffkonzentration erfolgt nach dem Wiedereinsetzen der meridionalen Zirkulation und dem damit einhergehenden Zustrom von sauerstoffreichem Nordatlantischem Tiefenwassers, das das Becken auf Kosten sauerstoffärmeren Wassers südlichen Ursprungs füllte. Ein Vergleich zu Ventilationsszenarien basierend auf stabilen Isotopen, Karbonatlösung und benthischen Foraminiferen-Vergesellschaftungen bestätigte die hohe Qualität der Rekonstruktion. Durch die Einbeziehung selektiver Erhaltung von Dinozysten zeigt sich darüber hinaus, dass die Interpretation vorhandener Produktivitätssignale durch Berücksichtigung von Oxidation labilen organischen Materials verbessert werden kann.

Diese Dissertation liefert neue nützliche Erkenntnisse über den Nutzen von Dinozysten als Indikatoren für Exportproduktion, Erhaltung organischen Materials und Tiefenwasserventilation. Die Perspektive, die sich daraus ergibt, richtet die Aufmerksamkeit auf das Potential von Abbau-Modellen zur Einschätzung des diagenetischen Zustands von geologischen Archiven. Dies ist auf Basis herkömmlicher Kriterien nur schwierig zu erreichen, jedoch entscheidend, um fehlerhafte Interpretationen bezüglich Veränderungen in der marinen Bioproduktion, den biogeochemischen Stoffkreisläufen und der Ozeanzirkulation zu vermeiden. In dieser Hinsicht sind Dinozysten aufgrund der großen Unterschiede in Erhaltungspotential von R-Zysten und S-Zysten und dem gleichzeitig adäquaten Verhalten gegenüber Transport und Bioturbation ein optimales Mittel. Da Dinozysten zudem in fast allen marinen Lebensräumen seit dem frühen Jura anzutreffen sind, ist die vorgeschlagene Methode potenziell breit einsetzbar, insbesondere in Schlüsselregionen der marinen Produktion (z.B. Südozean) und Ozeanzirkulation (z.B. Agulhas Strom und Indonesischer Durchstrom). Darüber hinaus ist die grundlegende Idee der Nutzung von unterschiedlichen Abbauraten nicht auf Dinozysten beschränkt. Die Anwendung auf organisches Material, das von Land eingetragen wird, könnte Aufschluss über den Transport terrestrischen Materials in den Ozean geben und damit die Modellierung von Windfeldern und Flussraten von Kohlenstoff erleichtern. Sicherlich besteht derzeit noch Forschungsbedarf und die Ergebnisse dieser Arbeit sollten deshalb als viel versprechende aber gewiss nicht vollständige Abhandlung verstanden werden. In weiteren Schritten wird es erforderlich sein, eine quantitative Abschätzung des

Einflusses von Abbau auf Dinozysten-Vergesellschaftungen zu erlangen sowie deren Nutzung auf molekular-geochemischer Ebene zu erforschen. Sollte dies erfolgreich sein, wird die selektive Erhaltung von Dinozysten sehr viel greifbarer und würde wichtige Informationen für die Modellierung des marinen Kohlenstoffkreislaufs liefern. Genauere Abschätzungen würden wiederum Veränderungen der Ökosysteme und die globale Klimaentwicklung besser vorhersagbar machen.

## CHAPTER 1

### 1.1. Introduction

The study of the carbon cycle requires a view both humbled by the knowledge of past global transformations and emboldened by the imagination of details not seen in the fragments of the rock record. Understanding the present-day carbon cycle has become a matter of societal urgency because of concerns about the effects of human activities on atmospheric chemistry and global climate. This public limelight has had far-reaching consequences for research on the geologic history of the carbon cycle that claims among its adherents many geologists as well as biologists, and chemists. The pace of change in local weather systems demand that studies of the geologic history of the carbon cycle cannot be isolated from the context of present and future events. Today, the role of the oceans in the global carbon cycle is ever more apparent and the international community is seeking answers to questions on the range of variation in marine bioproduction, ocean circulation, and carbon sequestration and how this is linked to the atmospheric  $p\text{CO}_2$  variation during Earth's history. However, proper constraints on the processes that control carbon fluxes between the ocean and the atmosphere are still lacking.

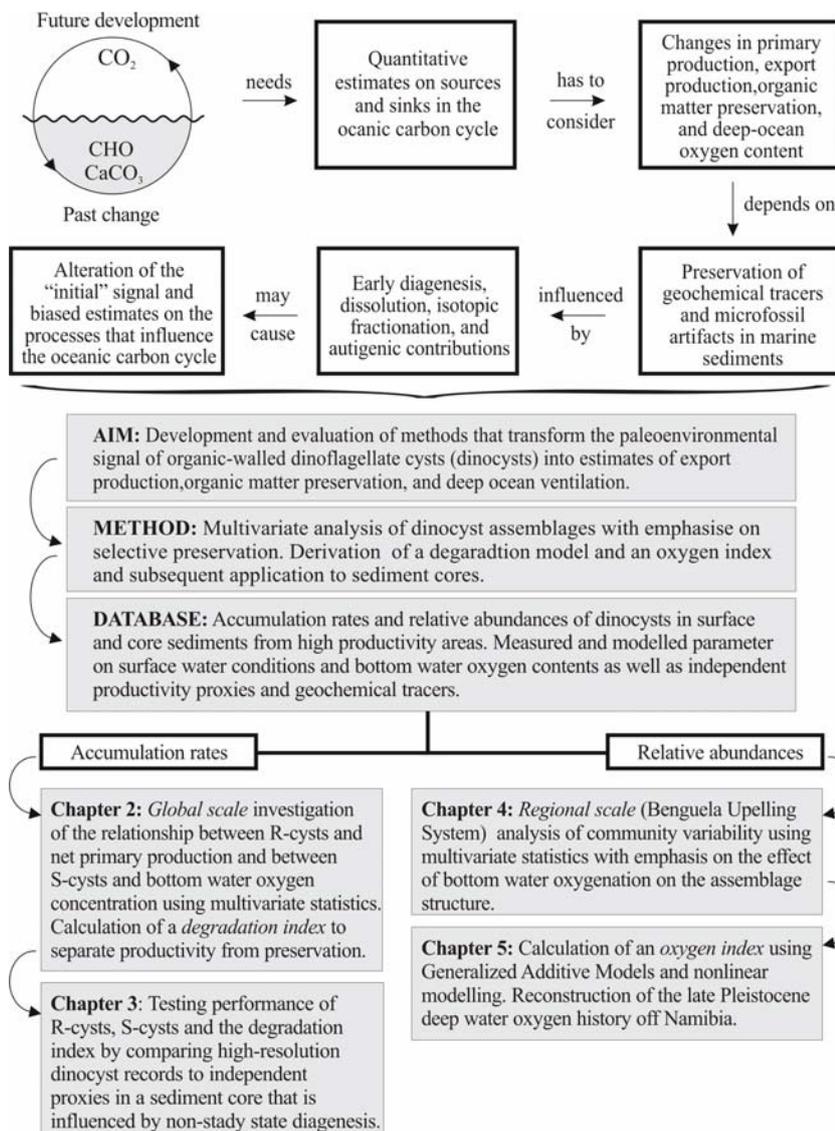
Most of the carbon on Earth is incorporated into carbonaceous rocks, but this pool turns over too slowly to account for the  $p\text{CO}_2$  changes during climate cycles (BERNER *et al.*, 1983). The terrestrial biosphere holds only about 5% the amount of carbon that resides in the ocean and any release from forest soils and vegetation retreat should usually be balanced by  $\text{CO}_2$  uptake in the deep-ocean reservoir (BROECKER & PENG, 1986). Thus, on timescales that are adequately long ( $\geq 500$  yr) to allow the deep-sea to communicate with the surface-ocean and the atmosphere, carbon storage in the ocean all but sets the atmospheric  $\text{CO}_2$  concentration. As yet, the exact mechanisms are matter of debate. Some hypothesizes call upon changes in sea ice coverage (STEPHENS & KEELING, 2000), Southern Ocean stratification (FRANÇOIS *et al.*, 1997), deep-ocean ventilation (TOGGWEILER, 1999), and ocean alkalinity (ARCHER & MAIER-REIMER, 1994) to account for the  $p\text{CO}_2$  reduction during glacial times. In other efforts marine scientists frequently refer to the ocean's biologically driven sequestration of carbon as the "biological pump", notably in the context of low versus high latitude efficiency and  $\text{CaCO}_3$  cycling (e.g., MARTIN, 1990; Broecker and Henderson, 1998, ARCHER *et al.*, 2000; SIGMAN & HAUG, 2003). There is, however, no broadly accepted explanation for the ocean's role in the regulation of atmospheric  $p\text{CO}_2$  that is consistent with all the evidence from ice cores, isotope measurements, and temperature records.

The numerous attempts to yield information on the sources and sinks in the oceanic carbon cycle have unearthed a range of potentially useful proxies that enable estimates on primary productivity, export production, nutrient cycling, deep-ocean circulation, and carbonate chemistry (e.g., BROECKER & PENG, 1983; KUMAR *et al.*, 1993; FISCHER & WEFER, 1999; LYNCH-STIEGLITZ, 2003; POURMAND *et al.*, 2005; TRIBOVILLARD *et al.*, 2006). However, several of these markers and tracers are subjected to roughly the same limitations as they can suffer from post-depositional degradation, diagenetic alteration, and fractionation (e.g., DE LANGE *et al.*, 1994; LEHMANN *et al.*, 2002; SINNINGHE DAMSTE *et al.*, 2002; MOODLEY *et al.*, 2005), and thus

possibly forfeit their “primary signal.” The organic carbon (OC) content in marine sediments, for instance, does not only depend on ocean productivity, export flux, sedimentation rate, and water depth but also on the origin and diagenetic history of the organic matter (OM). Origin and diagenetic fate may vary for different environments and critically depend on the availability of the inorganic electron acceptors at different stages of degradation. This could lead to preferential preservation of certain compounds (JUMARS *et al.*, 1989) and, as a consequence, may alter dramatically the composition of OM and its isotopic signal. Other productivity signals that are related to biogeochemical and benthic fluxes may only be preserved under certain diagenetic conditions. Barium, in its sedimentary solid phase, becomes mobile under sulfate-reducing conditions and is subsequently precipitated to produce authigenic barite fronts (TORRES *et al.*, 1996). Furthermore, redox-sensitive element distributions (e.g., Mn and U) at glacial-interglacial transitions have been explained by geochemical mobilization alone (WALLACE *et al.*, 1988; MANGINI *et al.*, 2001). The bulk carbonate content, and isotopic ratios and trace element compositions in shells of calcite or silicate manufacturing organisms yield records on past surface water temperatures and salinity, continental ice volume, and carbon storage in terrestrial biomass, and are primary carriers of information on bioproduction, nutrient distribution, and strength of the biological pump. However, these proxies cannot always be interpreted straightforward taking at face that a lowering of the pH during oxic decomposition of OM promotes dissolution and isotopic fractionation (e.g., MACKENSEN *et al.*, 1993; MCCORKLE, 1995, EMERSON & HEDGES, 2003). Prominent rate tracers such as the  $^{231}\text{Pa}/^{230}\text{Th}$  ratio and Nd-isotopes are less affected by early diagenetic processes but their sedimentary signal may suffer from authigenic and lithogenic contributions, and different particle affinities (LYNCH-STIEGLITZ, 2003; GEIBERT & USBECK, 2004). These are only a few examples of the limitations placed on the use of paleo-proxies that demonstrate why the quantity of work on proxy development has increased markedly over the last decade and must continue to support a vanguard in search of untapped constraints. In this regard the quantification of key processes within the marine carbon cycle such as the export of carbon fixed by primary production and the degradation of OM during early diagenesis remains at high priority. Progress in this study is, among others, tied to our ability to separate productivity from preservation – a major task of world-wide operating research programs.

The dissolved  $\text{O}_2$  concentration of ocean bottom water is commonly thought to be a master variable that controls the degradation of OM reaching the sediment-water interface and influences its diagenetic fate upon further burial. Where oxygen minimum zones impinge continental margins  $\text{O}_2$  deficiency eventually promotes the generation of fossil fuel (GÉLINAS *et al.*, 2001), essentially the only process that accounts for the accumulation of atmospheric  $\text{O}_2$  and intimately links the global cycles of C, S, and O over geological time (BERNER, 1982). Over periods of hundreds to thousands of years, exposure to molecular  $\text{O}_2$  appears to affect the amount and composition of OM preserved in marine sediments (HARNETT *et al.*, 1998; HEDGES *et al.*, 1999) and has a meaning with respect to nutrient cycling, deep ocean carbonate chemistry, and ultimately the atmospheric  $p\text{CO}_2$  level (BROECKER & HENDERSON, 1998). We know, for instance, that oxygen minimum zones of the global ocean varied in response to climate upheaval with implications for the release of greenhouse gases (ALTABET, 2002) and possible feedbacks on the supposed “positive” effects

of fertilization connected to climatic change (FUHRMAN & CAPONE, 1991). We also have realized that mechanisms associated with ocean-atmosphere carbon partition such as biological pumping call on roughly the same tie between the atmospheric  $p\text{CO}_2$  and deep water  $\text{O}_2$  concentration, because they demand a major reduction in the deep water  $\text{O}_2$  content to explain the lower  $p\text{CO}_2$  of the glacial atmosphere (SIGMAN & HAUG, 2003). There is as yet no strong message from marine sediments that widespread glacial deep water anoxia have existed, but we need to consider glacial bottom water  $\text{O}_2$  contents that were at least considerably lower (BOYLE, 1988; MARCHITTO *et al.*, 1998). For this reason, testing the biological pump hypothesis by reconstructing deep-ocean  $\text{O}_2$  will require more than simply search for extensive deep-ocean anoxia but demands for quantitative indicators of dissolved  $\text{O}_2$  that work at intermediate  $\text{O}_2$  concentrations. While interesting data have been put forward in support of various approaches (HASTINGS *et al.*, 1996; YARINCIK *et al.*, 2000; NAMEROFF *et al.*, 2004), it seems fair to argue that the paleoceanographic community still lacks a reliable set of methods for the reconstruction of deep-ocean dissolved  $\text{O}_2$  contents.



**Figure 1.1.** Flowchart illustrating the thematic background and conceptual design of the present thesis.

Palynologists, like other scientists, tend to view the geological record of marine sediments through the lens of their particular training and experience. Studying contemporary and fossil palynomorphs they are both amazed by unexpected discoveries and reassured by the extent to which “the present is the key to the past.” In particular, organic-walled dinoflagellate cysts (dinocysts) have been proven as reliable indicators of (paleo)environmental conditions given the fact that fossil associations sensitively reflect even small changes in temperature, salinity, and nutrient availability (e.g., DE VERNAL *et al.*, 1994; ESPER *et al.*, 2002; RADI & DE VERNAL, 2004; SLUIJS *et al.*, 2005). Recent efforts to communicate compositional features of dinocyst associations revealed that oxic degradation can dramatically influence the assemblage structure preserved in fossil records (e.g., ZONNEVELD *et al.*, 2001; HOPKINS & MCCARTHY, 2002). Moreover, it was found that oxidation resistant (R-cysts) and sensitive dinocyst (S-cysts) taxa are, respectively, more and less efficiently preserved as compared to various OM compounds such as pollen, lipids, and hydrocarbons (VERSTEEGH & ZONNEVELD, 2002). It is this large difference in the preservation potential of dinocysts that sets the scene for the present study.

This thesis aims to place more accurate constraints on the use of selective dinocyst preservation in paleoceanographic applications. It summarizes attempts to develop and evaluate methods that may enable to detach diagenetic effects from the productivity signal reflected in marine sediments and could provide a mean to transform the fossil record of assemblages into quantitative estimates on past bottom water O<sub>2</sub> contents (cp. Fig. 1.1). The following sections of this chapter outline some selected aspects of our current understanding of the marine carbon cycle and OM preservation as it pertains to marine sediments and briefly overview the potentials and limits of extant dinocysts as carriers of paleoenvironmental information. **Chapter 2** then proceeds to highlight results of a data compilation that relate to the output of this thesis due to the contribution of surface sediment data and the implementation of statistical evaluation. The study explicitly emphasizes the relationship between accumulation of R-cysts and primary production in surface waters as well as accumulation of S-cysts and bottom water O<sub>2</sub> concentration as they emerge from surface sediments of different environments. The scientific perspective that is generated also provides new insights into the principles of S-cyst degradation and eventually accounts for the refinement of degradation models. **Chapter 3** gives an example of how our present-day knowledge of selective dinocyst preservation can be applied to records of the past. Throughout this chapter three themes are prominent. One is that R-cyst accumulation reflects productivity in surface waters over geological time while S-cyst accumulation documents the diagenetic history of the sedimentary archive. A second theme is that relatively abrupt changes in depositional conditions play a central role in the post-depositional transformation of proxy records, notably the record of export production. The third theme is that these non-steady state diagenetic conditions may represent a common case of carbon sequestration in marine sediments and thus need to be considered in order to advance our understanding of the oceanic carbon cycle. Then, **Chapter 4** and **Chapter 5** focus on the Benguela upwelling system – a key area of marine high productivity that holds a crucial role in controlling the oceanic carbon budget and a prime setting for natural experiments in diagenesis. Both studies place new constraints on the concept of selective dinocyst preservation due to the unique regional character and the use of relative

abundances instead of accumulation rates. Chapter 4 describes changes in the assemblage structure of dinocysts among surface sediments from different ocean domains as a result of variable bottom water oxygen concentration. The processes responsible for the distribution of R-cysts and S-cysts are discussed from the perspective of selective preservation, and the chapter concludes with a prospect for their use as a paleo-O<sub>2</sub> proxy. After having built this reasonable working hypothesis Chapter 5 extends the view into the past by transforming a late Pleistocene dinocyst record into quantitative estimates on bottom water oxygenation. The description of events reveals a particularly illuminating array of details about interactions among deep-ocean ventilation, carbon sequestration, and carbonate dissolution – a subset of processes that must be understood in order to comprehend carbon cycling over nearly all timescales. Finally, a short outline addresses new as well as unresolved questions which provide future challenges for palynologists and organic biogeochemists, and discusses emerging approaches that may encourage the use of dinocysts in paleoceanographic research beyond current fields of application.

## **1.2. The carbon cycle**

The carbon cycle is important for at least three reasons. First, carbon forms the structure of all life on the planet, making up 50% of the dry weight of living things. Second, the cycling of carbon approximates the flows of energy around the Earth, the metabolism of natural, human, and industrial systems. The increased use of fossil fuels leads to a third reason for interest in the carbon cycle. Carbon, in the form of carbon dioxide and methane forms two of the most important greenhouse gases. Additions of these gases to the atmosphere from industrial activity are increasing their concentrations, enhancing the greenhouse effect, and starting to warm the Earth. The rate and extent of the warming depend, in part, on the global carbon cycle. For instance, if the rate at which the oceans remove CO<sub>2</sub> from the atmosphere were faster, concentrations of CO<sub>2</sub> would have increased less over the last century. If the processes removing carbon from the atmosphere and storing it on land were to diminish, concentrations of CO<sub>2</sub> would increase more rapidly than projected on the basis of recent history. However, the processes responsible for adding carbon to and withdrawing it from the atmosphere are not well enough understood to predict future levels of *p*CO<sub>2</sub> with great accuracy.

### *1.2.1. Between the ocean and the atmosphere*

There is ~ 50 times more carbon in the ocean than in the atmosphere, and it is the amount of dissolved inorganic carbon (DIC) in seawater that determines the atmospheric concentration of CO<sub>2</sub> (SIEGENTHALER & SARMIENTO, 1993). The amount of DIC in the oceans is ~3.7 x 10<sup>4</sup> Gt, and the amount of OC is ~1,000 Gt. Most of this oceanic carbon is stored in intermediate and deep waters, while only a small fraction resides in surface layers in direct contact with the atmosphere. The carbon pool in reactive ocean sediments (~6,000 Gt) is generally not considered as part of the short-term, carbon cycle, but important in determining the long-term *p*CO<sub>2</sub> in the atmosphere and oceans (HOUGHTON, 2003).

Carbon is transferred within the ocean by sinking of particles and from regions of cooling to regions of heating via ocean circulation, producing, respectively, vertical gradients and north-

south transports of carbon within the ocean (BROECKER AND PENG, 1992; HOLFORT *et al.*, 1998). This spatial separation of natural sources and sinks dominates the regional distribution of net annual air-sea fluxes. The most important process determining the exchanges of carbon between the oceans and the atmosphere is the chemical equilibrium of dissolved CO<sub>2</sub>, bicarbonate, and carbonate in the seawater. However, the rate at which the oceans take up or release carbon is slow on a century timescale, because of lags in circulation and changes in the availability of calcium ions. Two additional processes besides carbon chemistry keep the atmospheric *p*CO<sub>2</sub> lower than it otherwise would be. One process is referred to as the “solubility pump” and the other as the “biological pump” (BROECKER & PENG, 1986, RAVEN & FALKOWSKI, 1999). The solubility pump is based on the fact that CO<sub>2</sub> is ~ 2 times more soluble in the cold mid-depth and deep waters than in the warm surface waters near the equator. Sinking of cold, CO<sub>2</sub> enriched surface waters in Arctic and Antarctic regions forms these mid-depth and deep waters that keep the atmospheric *p*CO<sub>2</sub> lower than the average concentration of surface waters.

The biological pump transfers carbon sequestered by photosynthesis to the intermediate and deep ocean. Not all of this OM is respired in surface waters but some sinks to deeper water, where it is eventually decomposed and reaches the surface again through ocean circulation. The net effect maintains higher DIC concentrations at depth and cause atmospheric *p*CO<sub>2</sub> to be ~200 ppm lower than would be the case in the absence of such mechanism (SARMIENTO & TOGGWEILER, 1984; MAIER-REIMER *et al.*, 1996). There is another biological pump, called the carbonate pump, but its effect in reducing the atmospheric *p*CO<sub>2</sub> is small, because the precipitation of CaCO<sub>3</sub> in the surface waters increases the *p*CO<sub>2</sub>, and the evasion of this CO<sub>2</sub> to the atmosphere offsets the sinking of carbonate carbon. Moreover, the effect of CaCO<sub>3</sub> formation on surface water *p*CO<sub>2</sub> and air-sea fluxes is counter to the effect of OC production. For the surface ocean globally, the ratio between the export of OC and the CaCO<sub>3</sub> rain ratio is a critical factor controlling the overall effect of biological activity on surface ocean *p*CO<sub>2</sub> (ARCHER & MAIER-REIMER, 1994).

Since BROECKER & PENG (1982) summarized basic outlines for the carbon cycle in the ocean, ongoing research has unearthed new sensitivities including ideas about the role of the oceans in glacial-interglacial variations of atmospheric *p*CO<sub>2</sub>. One of the first proposed mechanisms to lower the atmospheric *p*CO<sub>2</sub> during glacials was to increase the rate of biological productivity in surface waters of the ocean. Thereby the *p*CO<sub>2</sub> of the atmosphere was shown to be extremely sensitive to the biological pump in high latitudes and insensitive to low-latitude forcing (SARMIENTO & TOGGWEILER, 1984). Either an increase in the ocean inventory of nutrients, or a change in the ratio of nutrient to carbon in phytoplankton, could have stimulated the biological pump in this way (SIEGENTHALER & WENK, 1984; BROECKER & HENDERSON, 1998). It has also been suggested that the productivity of marine phytoplankton was promoted by an increased flux of iron-bearing dust to the Southern Ocean (e.g., MARTIN *et al.*, 1990), decreased denitrification (ALTABET *et al.*, 1995), or a northward shift of the region of high productivity in the Southern Ocean (KUMAR *et al.*, 1995). However, paleo-nutrient proxies have also been used to argue against large changes in high-latitude productivity (BOYLE, 1988; ELDERFIELD & RICKABY, 2000).

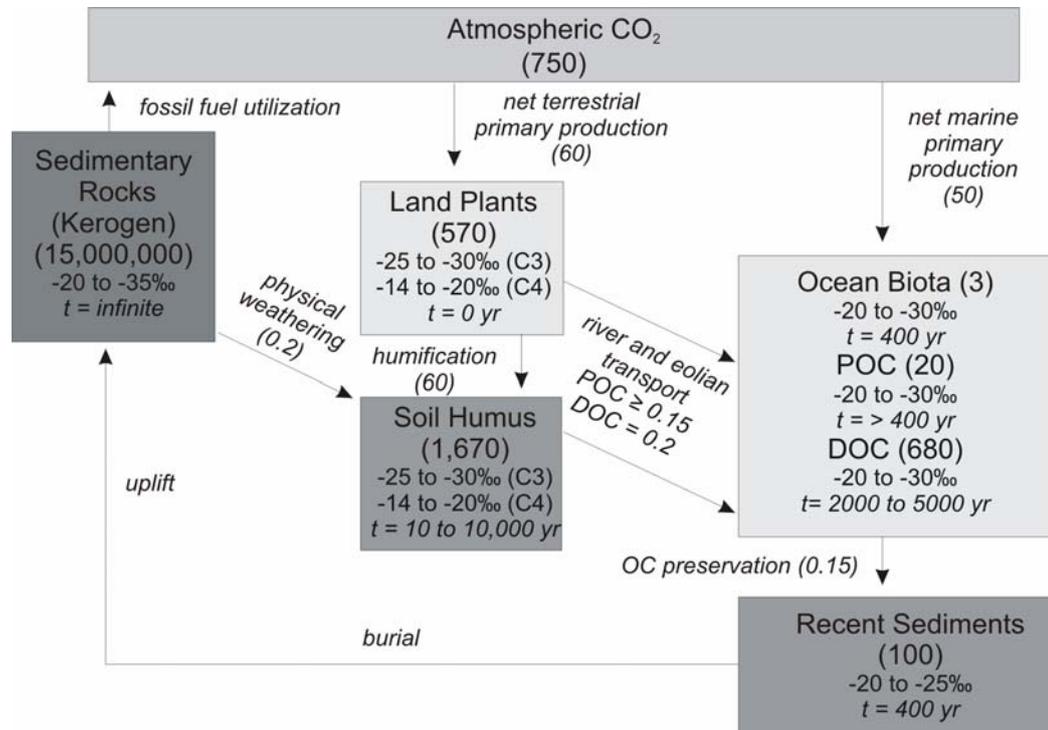
Another family of hypotheses relies on physical mechanisms that could change dissolution and outgassing of CO<sub>2</sub> in the ocean. Thereby, glacial cooling (i.e. increased solubility) can account

for only a small fraction of the observed  $p\text{CO}_2$  drawdown, because this effect is partly balanced by higher salinities (SIGMAN & BOYLE, 2000). STEPHENS & KEELING (2000) have proposed that extended winter sea ice prevented outgassing of upwelled,  $\text{CO}_2$ -rich water around Antarctica during glacial times. During summer a melt-water lens may have further restricted evasion of  $\text{CO}_2$  (FRANÇOIS *et al.*, 1997). These mechanisms could explain the parallel increases of Antarctic temperature and atmospheric  $p\text{CO}_2$  during deglaciations (PETIT *et al.*, 1999), but require less vertical mixing to occur at low latitudes than is normally assumed (ARCHER *et al.*, 2000). Alternatively, TOGGWEILER (1999) considered the boundary between intermediate and deep water as a chemical divide that separates low  $\text{CO}_2$  water above from high  $\text{CO}_2$  water below. Higher  $\text{CO}_2$  concentration below the divide is caused by reduced ventilation of bottom water creating strongly depleted  $\delta^{13}\text{C}$  values without an attendant change in nutrient concentrations (BOYLE, 1988) but from the combined effects of decreased ventilation and carbonate alkalinity response. Such changes in ocean alkalinity have been inferred from a variety of mechanisms (e.g., ARCHER & MAIER-REIMER, 1994; KLEYPAS, 1997), yet higher ocean pH during glacials remain a controversial issue (SANYAL *et al.*, 1995, ANDERSON & ARCHER, 2002). Moreover, large increases in ocean alkalinity would result in a much deeper lysocline and enhanced  $\text{CaCO}_3$  preservation that is not observed in deep-sea sediments (CATUBIG *et al.*, 1998; SIGMAN *et al.*, 1998). Given the complex timing of changes in climate and atmospheric  $p\text{CO}_2$ , it is plausible that more than one mechanism has been in operation. Important with respect to the magnitude of past climate change, the variation in atmospheric  $p\text{CO}_2$  might have amplified the small insolation changes of the Milankovich orbital cycles to produce the large shifts in global climate on glacial-interglacial timescales (WEAVER *et al.*, 1998).

### 1.2.2. Organic carbon

Greater than 99.9% of all carbon in the Earth's crust is stored in sedimentary rocks (BERNER, 1989). About 20% of this total ( $1.5 \times 10^7$  Gt) is OC, and the majority (>90%) of the OC in these consolidated sediments is kerogen (Fig. 1.2). Organic-rich deposits that include the World's fossil fuel reserves account for less than 0.1% of total sedimentary OC (HUNT, 1996). Of the small fraction of OM that is not sequestered in ancient sedimentary rocks, almost two-thirds reside on the continents in form of standing biomass, litter, and soil humus (POST, 1993). Marine biota comprise only ~3 Gt of OC, while sinking and suspended particulate OC (POC) account for further 10 - 20 Gt. The majority of OC in the oceans is in the form of dissolved OC (DOC) and sequestered in the upper meter of marine sediments (HEDGES, 1992). Concentrations of marine DOC in the upper ocean typically range between 60 - 80  $\mu\text{M}$  but may exceed 200  $\mu\text{M}$  in coastal zones (VLAHOS *et al.*, 2002). The inventory of marine OC is fixed by the concentration of DOC in the deep ocean, which is relatively constant, suggesting a very tightly controlled feedback between production and degradation (EGLINTON & REPETA, 2003). The sinking of dead organisms and detritus together with vertical transfer of DOC create the downward flux of OC known as export production. Of this material only a small fraction reaches the sediments, notably at continental margins, where greater than 90% of all OC burial occurs in deltaic, continental shelf, and upper continental slope deposits (BERNER, 1989; HEDGES & KEIL, 1995), making the margins one of the

largest sinks in the global carbon budget. Continental margins are also sites of intense recycling of OM, and thus are a dynamic component of the global carbon cycle (BERELSON *et al.*, 1996).



**Figure 1.2.** The global organic carbon cycle (ca. 1950). Numbers in parentheses are approximate reservoir sizes ( $10^{15}\text{gC} = \text{Gt}$ ) and italicized are approximate fluxes ( $10^{15}\text{gC yr}^{-1}$ ). Nonitalicized numbers are approximate ranges for stable carbon isotopic compositions ( $\delta^{13}\text{C}$ , per mil) and italicized numbers are approximate radiocarbon ages (yr BP) (from EGLINTON & REPETA, 2003, after HEDGES, 1992).

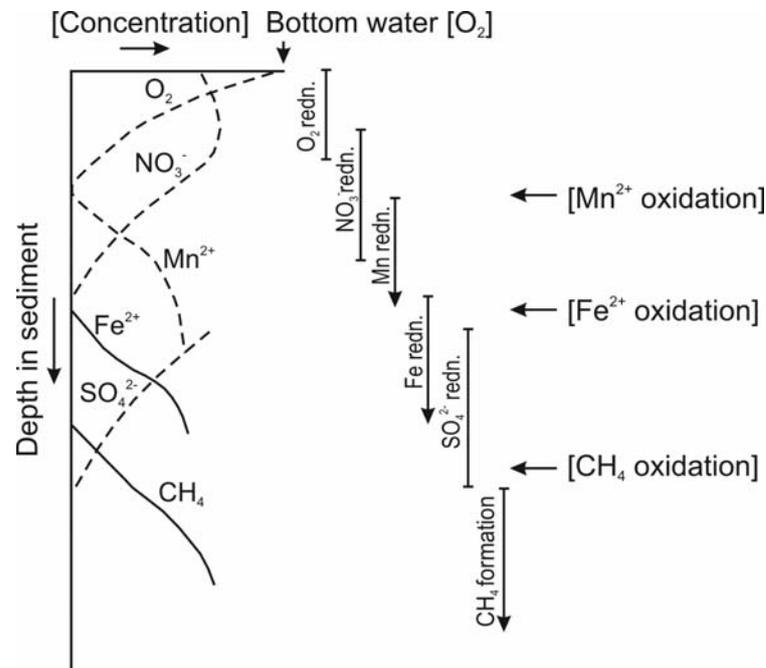
Marine photosynthesis by unicellular phytoplankton produces OC at a comparable rate to land plants (HEDGES, 1992) and accounts for ~ 95% of the annual primary production in the oceans. The rate of production varies spatially and temporally as a function of nutrient supply and insolation. In today's oceans, ~80% of new production takes place in the open ocean while the balance is concentrated in only about 10% of the oceanic area, notably at continental margins characterized by coastal upwelling (KILLOPS & KILLOPS, 1993). On average, only ~10% of the net primary production escapes the upper 100 m of the water column in form of sinking faecal pellets and as aggregates of cellular debris (i.e. marine snow). The rain of POC out of the surface ocean attenuates exponentially through the water column, and only about 10% of the OC that leaves the photic zone reaches an average depth of 4,000 m (SUESS, 1980). Subsequent to remineralization during settling through the water column, further 90% or more of the OM deposited on the seafloor is degraded, leaving ~ 0.1% of the material originally synthesized in surface waters to be ultimately preserved in sediments underlying most of the open ocean (WAKEHAM *et al.*, 1997). However, global burial efficiencies exceed 0.1%, because a significant amount of OM is deposited on continental margins and in oxygen-deficient regions where burial efficiencies are considerably higher (BERNER, 1989).

As a dominant biological component in marine sediments, measurements of OC contents seem a logical choice to infer production in overlying surface waters. Consequently, empirical equations have been proposed that quantitatively relate OC export to water depth (Suess, 1980) and sediment accumulation rates of OC to primary production (Müller & Suess, 1979) or carbon flux to the sea floor (Sarnthein *et al.*, 1988). The equations have been used to reconstruct paleoproductivity in different oceanic basins and over various timescales (e.g., Müller & Suess, 1979; Pedersen, 1983; Sarnthein *et al.*, 1992). However, the actual mechanisms that determine the OC content in marine sediments are not known well enough to predict that geographical variations also apply to a single location that undergoes productivity changes with time (e.g., Fischer & Weyer, 1996). There is evidence that some of these mechanisms are directly related to the bulk sediment accumulation rate (Henrichs & Reeburgh, 1987), bottom water oxygen concentration (Emerson, 1985), oxygen exposure time (Hartnett *et al.* 1998), and OC to mineral surface area ratio (Hedges *et al.*, 2001). It seems likely that all factors play a role to some extent but distinguishing between them is difficult, because they often vary in concert. For example, higher burial efficiencies are encountered in many continental margin sediments, yet it is unclear whether this reflects greater input of recalcitrant OM, higher OC fluxes, or shorter oxygen exposure times due to the elevated particle flux. Moreover, export of re-deposited organic material from the shelf (Inthorn *et al.*, 2006) and OM supply from terrestrial sources (Goni *et al.*, 1998) can further influence results considerably, as can the loss from continuing decay (Hedges & Keil, 1995). A great precision suggested by more complicated formulations for the estimation of export productivity must therefore be treated with suspicion.

### **1.3. Controls on organic matter preservation**

Roughly 90% of the OM that exits the euphotic zone of the ocean is degraded in the water column. The 10% of the OC flux that reaches the seafloor drives the reactions that control sediment diagenesis and benthic flux. Finally, only about one-tenth escapes oxidation and is buried in marine sediments. Among this material a wide range of organic compounds are sequestered, including (in)direct products of marine photoautotrophy, vascular plant debris, and relict OC derived from sedimentary rock weathering. The means by which this OM escapes degradation has been the subject of much debate and reasons given to explain the perceived pattern of increased OM preservation have been extensively reviewed (e.g., Emerson & Hedges, 1988; Henrichs, 1992; EGLINTON & REPATA, 2003). While the processes and mechanisms remain elusive, it is evident that there are several principal factors that contribute to the seemingly universal slowing of OM decomposition with time. One of these is that the physical form and distribution of organic matter within sediments is not uniform (Ransom *et al.*, 1997). A second is that the rate and extent of organic matter degradation can vary with the different inorganic electron acceptors available at different stages of degradation (Bernier, 1980, Fig. 1.3). Finally, the structural features of the residual organic matter mixture may vary over time as more readily utilized components are oxidized or converted into less-reactive products (Boudreau & Ruddick, 1991). Of greatest importance are these processes that determine the degradation of OM and the resulting fluxes

across the sediment-water interface as they influence the biogeochemical cycle and the pH of the sea, and, eventually affect the abundance of plankton in the ocean.



**Figure 1.3.** A schematic representation of the pore-water result of organic matter degradation by sequential use of electron acceptors.

Nowadays many studies integrate OM characteristics to understand OM preservation in marine sediments but there is no consensus as to which factor(s) control this mechanism. One group proposed that productivity has a major influence (e.g., PEDERSEN & CALVERT, 1990; CALVERT *et al.* 1996) while others suggested that the availability of oxygen is the major factor regulating the preservation of OM in sediments (e.g., PAROPKARI *et al.*, 1992; INGALL *et al.*, 1993; HARNETT & DEVOL, 2003). In this regard, oxygen exposure time has been successfully related to changes in OM content and composition (HARNETT *et al.*, 1998; HEDGES *et al.*, 1999). Another important concept refers to OM preservation as physical protection by association with mineral matrices (KEIL *et al.*, 1994). However, preservation of OM may also depend on properties of the material itself, its source and environment in which it is deposited, and the strength of sediment reworking (EMERSON, 1985; EMERSON & HEDGES, 1988; HEDGES *et al.*, 1988). Moreover, the observed spread in OM preservation might be primarily driven by differences in sedimentation rates (BETTS & HOLLAND, 1991), which vary by a factor of hundred or so more than %OC, and they are subjected to variations introduced by dilution of organic-rich debris with coarse minerals such as quartz sand, but also calcite or opal tests (MIDDELBURG *et al.*, 1993).

In general, all these investigations showed that sediments accumulated under upwelling cells, and where an oxygen minimum zone (OMZ) impinges on the sea floor, present OC concentrations higher than oceanic mean. Additional processes must therefore account for that fact

that open ocean sediments, which cover ~80% of total sea floor, amount to less than 5% of global OC burial (BERNER, 1989; HEDGES & KEIL, 1995). The residual OM in such sediments is often inferred to be highly refractory, and it has to be assumed that the structural attributes of the material may be pivotal in dictating its survival. These geochemical and microfossil inventory that remain after diagenesis in marine deposits are the artifacts used for interpreting past changes in marine bioproduction, biogeochemical cycles, and ocean circulation.

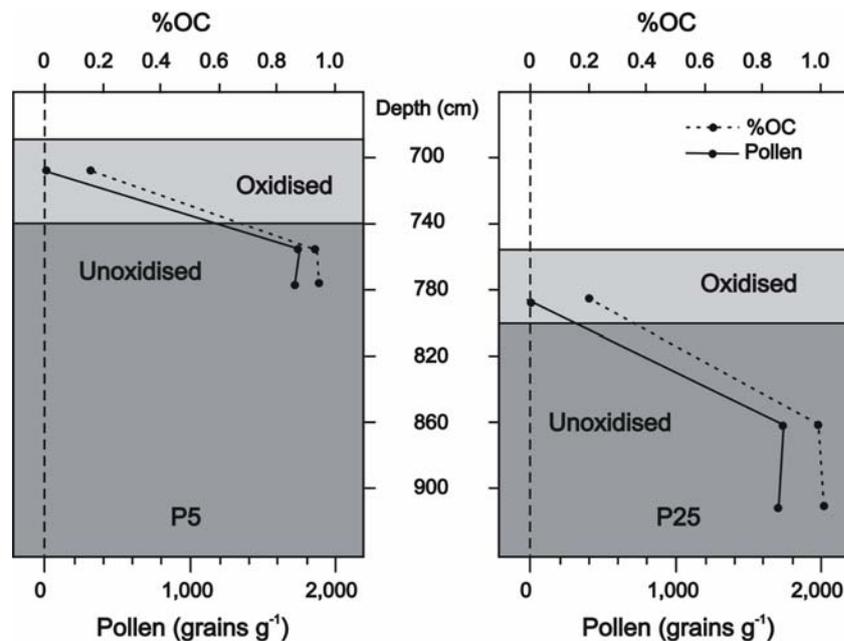
### 1.3.1. The role of oxygen

Various approaches have been taken towards assessing the role of oxygen in OM degradation. Laboratory incubations have provided information on the influence of aerobic versus anaerobic microbial degradation of phytoplankton biomass (e.g., ANDERSEN, 1996; HARVEY *et al.*, 1995; HARVEY & MACKO, 1997). Investigation of natural systems includes examination of depth transects traversing OMZs that impinge on continental margins (e.g., KEIL & COWIE, 1999, VAN DER WEIJDEN *et al.*, 1999), comparison of turbidites overlying pelagic sediments that were subjected to oxygen “burn-down” (e.g., WILSON *et al.*, 1985; COWIE *et al.*, 1995; PRAHL *et al.*, 1997), and studies on the relationship between OC and the mineral surface area in relation to bottom water oxygen concentrations (KEIL & COWIE, 1999). As an extension of the latter study HEDGES *et al.* (1999) hypothesized that OM preservation in continental margin sediments is controlled by the average residential period of accumulating organic particles in the water column and in the oxygenated pore waters immediately beneath the sediment-water interface. However, it has proven especially difficult to determine the length of time over which the OM is exposed to oxygen. Given evidence that even brief, periodic re-exposure to oxygenated conditions (e.g. by bioturbation and irrigation) can result in more complete and sometimes rapid OM degradation (HULTHE *et al.*, 1998), calculations of oxygen exposure time based on steady state conditions may critically underestimate cumulative degradation under oscillating redox conditions (ALLER, 1994).

**Table 1.1.** The importance (in percent) of various oxidants at some representative sites (after MIDDELBURG, 1992)

Site	O <sub>2</sub>	NO <sub>3</sub>	Mn/FeO <sub>x</sub>	SO <sub>4</sub>	CH <sub>4</sub>
<i>Coastal sediments</i>					
Danish coastal sediments	39.9	3.1	-	57	-
Cape Lookout Bight	-	-	-	68	32
Saanich Inlet	-	-	-	76	24
<i>Continental slope and rise</i>					
Indian Ocean	86.6	12.5	0.3	0.6	-
Hatteras Contin. Rise	76	8.3	1.7	13.8	-
Bermuda Rise	78.2	11.7	1.4	8.7	-
Savu Basin	60.9	25.4	6.5	7.2	-
<i>Deep Sea</i>					
Manop H	99.2	0.8	0.4	-	-
Manop M	90.7	6.9	0.9	1.1	-
Hatteras Abyssal Plain	96	4	-	-	-

While the extent of exposure to oxygen prior to entering the anoxic realm is frequently considered as a master variable influencing OM preservation (DEMAISON *et al.*, 1991), much debate persists concerning the factors leading to enhanced OM burial under oxygen deficient or anoxic conditions. One group argues that decomposition is more efficient with O<sub>2</sub>, and hence, OC will be preferentially oxidized in its presence, and preserved in its absence. Another group argues that the kinetics of OM decomposition are similar in the presence and absence of O<sub>2</sub>, and there should be no influence of O<sub>2</sub> on preservation. Indeed, there is a causal or even correlative relation between the presence of a minimum in bottom water oxygen concentration and the preservation of OM matter in underlying marine sediments (COWIE & HEDGES, 1992), but the proportion of OM that reaches the sediment-water interface and is then ultimately preserved in the sediments (i.e. burial efficiency) may be partly or entirely independent of the dissolved oxygen concentration in bottom waters at high rates of sedimentation (TYSON, 1995). Moreover, in areas well away from the continents, where rain rate of organic material to the sea floor is so low today that sediments are nearly free of OM, it is entirely possible that this situation would prevail even if the O<sub>2</sub> content of the bottom waters were quite a bit lower. However, in most open ocean areas with slower sediment accumulation rates and deeper O<sub>2</sub> penetration, the top few decimetres of sediments are oxic and O<sub>2</sub> is by far the dominant electron acceptor for OC diagenetic degradation (JAHNKE & JACKSON, 1992). BENDER & HEGGIE, (1984) found that greater than ~90% of the OM in these sediments is degraded by oxygen consumption and that oxic degradation rates are much faster than those by denitrification and Mn, Fe, SO<sub>4</sub> reduction. In coastal sediments, however, sulfate may be as or even more important than oxygen (Table 1.1) and the rate of OC oxidation by secondary oxidants becomes significant in governing the burial of bioactive elements into sediments.



**Figure 1.4.** Profiles of the %OC and pollen abundances down two sequences of the f-turbidite from the Madeira Abyssal Plain (from EMERSON & HEDGES 2003, after COWIE *et al.*, 1995).

The most direct evidence that the extent of OM preservation is affected by exposure to bottom water oxygen comes from oxidation fronts in deep-sea turbidites and sapropels of various ages and depositional settings (e.g., WILSON *et al.*, 1985; VAN SANVOORT *et al.*, 1996; PRAHL *et al.*, 1997; MOODLEY *et al.*, 2005). One of these deposits in which the timing of exposure to oxic and anoxic conditions is well known, is the relict f-turbidite from the Madeira Abyssal Plain. In this originally homogeneous deposit, ~ 80% of the OM and essentially all pollen that has been stable for 140 kyr in the presence of pore-water sulfate have been degraded in the upper section as a result of long-term exposure to dissolved O<sub>2</sub> (COWIE *et al.*, 1995; Fig. 1.4). However, this setting is a special case and generally does not reflect the conditions of carbon sequestration in the marine environment. Instead, continental shelves and slopes where most of the OC is buried tend to be in the focal point of debates between proponents of anoxia- versus productivity-induced preservation of OM. In these areas changes in bottom water oxygen content were probably accompanied by increases in productivity during past glacial ages, so that the factors controlling preservation may be more than simple correlations to bottom water oxygen contents but more properly described by a host of processes that prevail under oxic conditions. Nevertheless, it seems fair to argue that exposure to oxygen beyond a threshold of centuries to millennia affect OM preservation (HEDGES & KEIL, 1995), and that in special cases “oxic effects” can be apparent at timescales of decades or less (HARTNETT *et al.*, 1998). Because these oxic effects have a meaning with respect to nutrient cycling, deep-ocean carbonate chemistry, and atmospheric *p*CO<sub>2</sub>, it is essential to identify whether the areal extent of anoxic waters expanded or retracted in response to paleoceanographic changes. Unfortunately, our ability to reconstruct paleo-O<sub>2</sub> in bottom waters is not good and evidence for changes on glacial-interglacial timescales is seen in sediments from only very limited parts of the sea floor (BOYLE, 1988; MARCHITTO *et al.*, 1998, NAMEROFF *et al.*, 2004).

### 1.3.2. Degradation rate models

Marine geologists are mainly interested in the preservation of OM in marine sediments. The focus is on burial of OM rather than remineralization since it is the preserved OM that can be studied in the sedimentary record. However, conceptual models of early diagenetic processes in sedimentary deposits guide interpretation and investigation of compositional patterns, elemental fluxes, and biogeochemical cycling. Many of the reactions and processes that occur in the water column and sediments are related either directly or indirectly to OM degradation and knowledge of the rate of decomposition is therefore of utmost importance (e.g., BERNER, 1980; EMERSON *et al.*, 1987). Though it is generally accepted that early rates of OM degradation in marine environments are determined largely by the quality and concentration of the available substrate, the ultimate extent of preservation in the same sediment may involve very different types and processes (HEDGES & KEIL, 1995). On a qualitative basis organic geochemists are able to predict the lability (or conversely the preservation potential) of specific compounds (e.g., TEGELAAR *et al.*, 1989), but marine OM is made of hundreds if not thousands of different organic components that show a continuum of reactivities (MIDDELBURG *et al.*, 1993). These rates of degradation are known to vary over orders of magnitude due to variations in the amount and lability of the OM being degraded (EMERSON & HEDGES, 1988), leading to the seemingly universal slowing of OM

decomposition with time. These “long-tailed” decreases in OM with time are the rule, rather than the exception, for sediments of many types and ages (WESTRICH AND BERNER, 1984; BOUDREAU, 1997).

Most models of OM degradation have derived in some way from the early studies by Berner on this subject (e.g., BERNER, 1964; 1980). The most widely applied one is the first-order (one-G) model. In this model it is assumed that reactive OM decomposes at an overall rate directly proportional to its own concentration (i.e. by first-order kinetics):

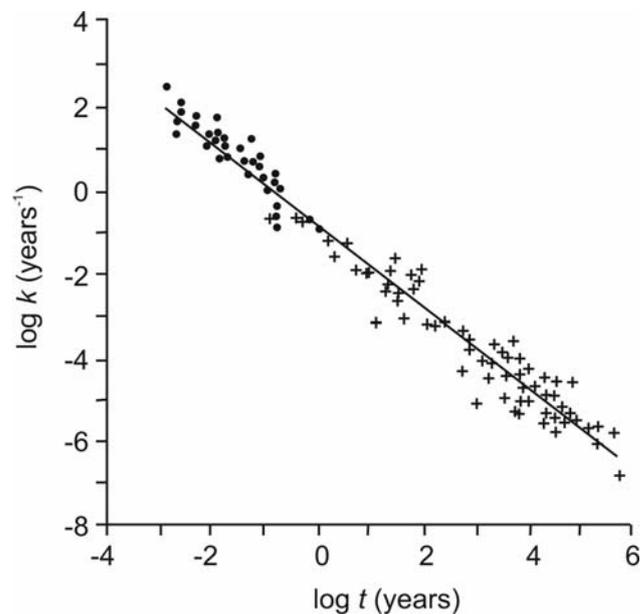
$$dG_m / dt = -kG_m, \quad (1)$$

where  $G_m$  is the concentration of metabolizable OC,  $k$  is the first-order rate constant, and  $t$  is time. Equation 1 can be integrated for the boundary conditions,  $t = 0, G_m = G_0, t = \infty, G_m \rightarrow 0$  to obtain:

$$G_m(t) = G_0[\exp(-kt)]. \quad (2)$$

Expressed in this way, the concentration of OM and its rate of decay both decreases exponentially with time and explicitly dependent on the amount and reactivity of the decomposable material. Thereby, the first-order rate constant  $k$  (i.e. the OM reactivity) is assumed to be constant. While true for individual OM components (MIDDELBURG, 1989; HEDGES *et al.*, 1999), laboratory and field studies have shown that OM substrates are sequentially decomposed, the more reactive components being degraded first (e.g., BENNER *et al.*, 1987; EMERSON & HEDGES, 1988; SUN & WAKEHAM, 1994). A result of this broad continuum is that the reactivity of sedimentary OM decreases with time but can be observed to degrade on essentially all timescales.

An alternative to the one-G model is to treat sedimentary OM as containing a continuum of multiple components whose distribution changes over time. Such kinetics can be variously described. In “multi-G” models sums of different organic components degrade with different first-order rates (BERNER, 1980, WESTRICH AND BERNER, 1984). Selective removal according to the reactivity of each compound (or group) accounts for the change in reactivity and the amount of OM with time. The number of groups and their reactivities must be determined empirically as curve fitting parameters. Canfield’s “pseudo-G” model differs from the former in that the degradation of more refractory OM components is linked to the decay rate of more labile constituents (CANFIELD, 1994). In other words, the most labile fraction is consumed first and controls the overall metabolic activity of the sediment. Continuum models are not based on this highly subjective partitioning of OM into labile and refractory components, since they consider a continuum of  $k$  values rather than a few discrete values. The two most relevant models are the “power” model (MIDDELBURG, 1989) and the “reactive continuum” model (BOUDREAU & RUDDICK, 1991). The power model is based on the premise that the reactivity of organic matter gradually decreases with time. Thus, the apparent rate constant becomes a continuously varying parameter that follows a power functional decrease with time and degree of mineralization. The reactive continuum model is based on a gamma distribution of OM reactive types and degradation rate constants decrease as a function of time (BOUDREAU AND RUDDICK, 1991). Substantially, all these discrete and continuum models capture the fundamental feature that bulk OM breaks down at an increasingly slower rate as it degrades.



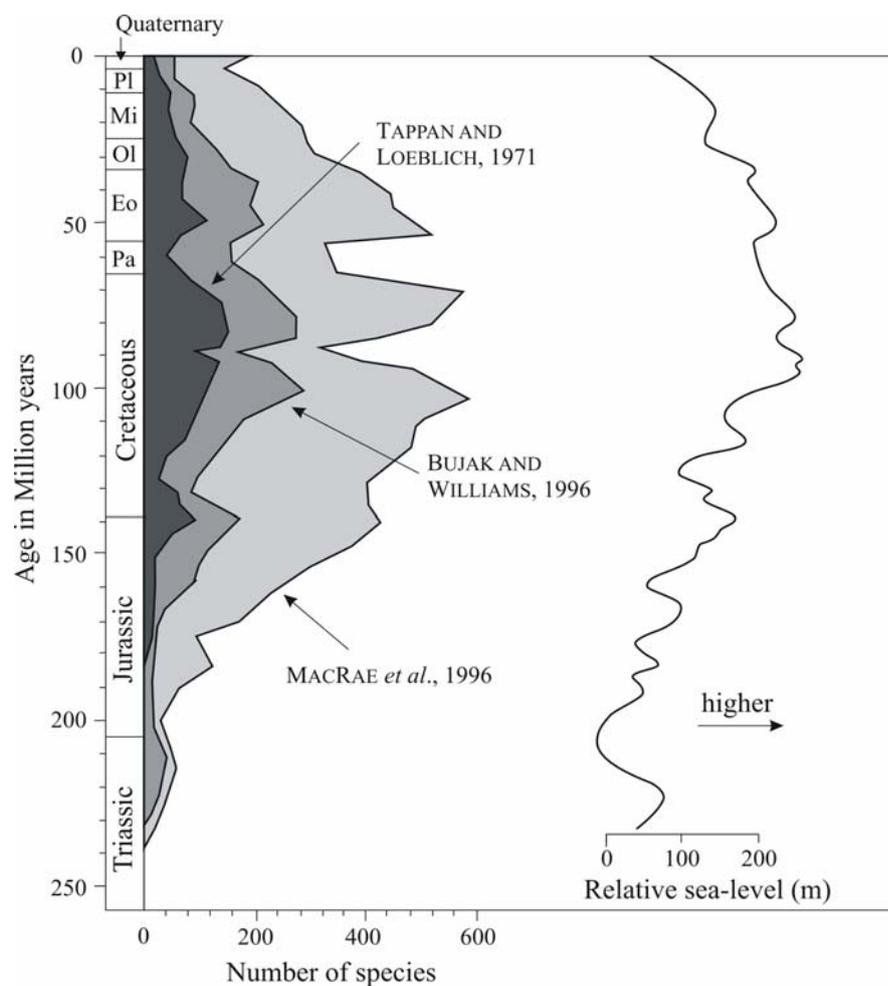
**Figure 1.5.** The reactivity of OC ( $k$ ) versus time ( $t$ ), determined from the power model. Dots and crosses represent data from laboratory experiments and OC vs. depth profiles (from MIDDELBURG, 1989).

The partition between labile and refractory OM components is very subjective and depends largely on the time scale and environment under consideration. For example, part of the seemingly refractory OM from environments with high accumulation rates is labile when transported to an oxygenated environment with low accumulation rates (e.g., WILSON *et al.*, 1986). Moreover, freshly dissolved organic substrates, polysaccharide- and protein rich materials are often degraded at similar rates in the presence or absence of molecular oxygen, while aged OM may show much slower and less efficient anoxic degradation (KRISTENSEN & HOLMER, 2001). This apparent contradiction may be partly explained by selective initial decay of easily decomposable proteins and polysaccharides and the resulting concentration of carbon-rich, hydrolysis-resistant substrates such as lipids and lignin whose effective degradation requires oxygen (EMERSON & HEDGES, 1988). As a consequence, slightly different degradation rates may be measured for various OM types of the sedimentary mixture, while the range of absolute values of the rate constants closely corresponds to the time span of observations. This correspondence extends over eight order of magnitudes from days to million of years (MIDDELBURG, 1989; Fig. 1.5). A result of the high-order kinetics is that components of sedimentary mixtures that react more slowly will become a much greater fraction with time while the reaction rate constant and its curvature is mainly described by the more labile components.

#### 1.4. Dinoflagellates

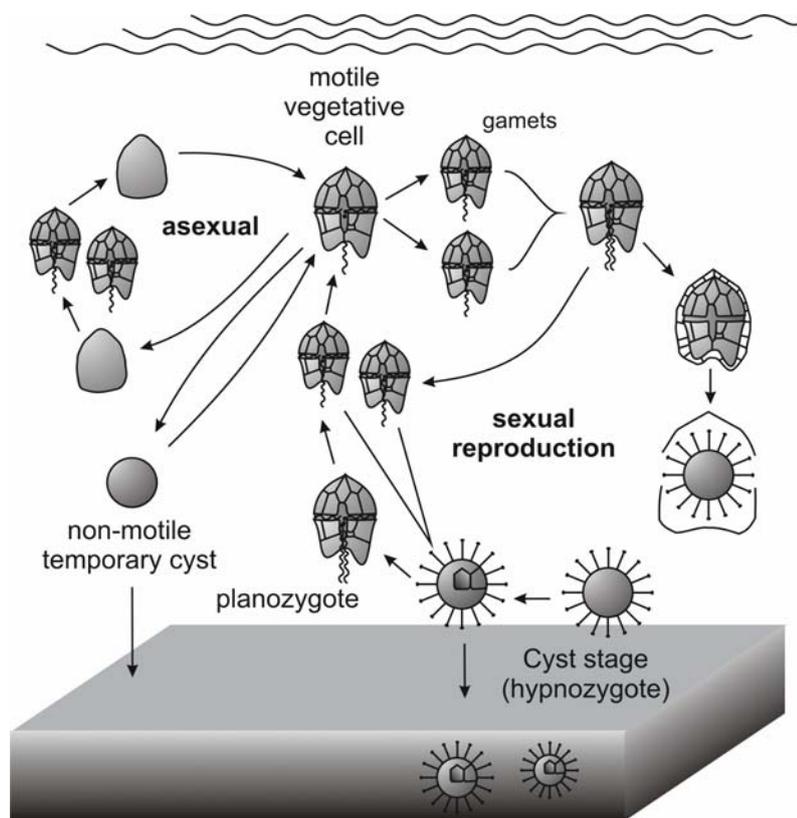
Dinoflagellates appear to be a diverse group of single-celled, eukaryotic protists. Most are small ( $\sim 30 - 100\mu\text{m}$ ), free-living, biflagellate, photosynthetic cells that thrive in the upper water

column of oceans and lakes but some species are also known to survive in rivers, ponds, and even ice (FENSOME *et al.*, 1996). The total number of extant dinoflagellate species has been estimated at over 2000 (Taylor, 1987), the bulk being amongst the more important primary producers of the current oceans and seas (TAYLOR, 1987a). The record of dinoflagellates possessing similar morphological characteristics to those of today basically starts in the Mesozoic, with a major adaptive radiation occurring in the Late Triassic and Early Jurassic (MACRAE *et al.*, 1996; Fig.1.6). Because of their high stratigraphic resolution, dinoflagellates (i.e. their fossil record) have become increasingly used in hydrocarbon exploration where they are now consulted as a routine tool in biostratigraphy (GRADSTEIN *et al.*, 1992). As photosynthetic symbionts (zooxanthellae), dinoflagellates play a substantial role in the calcification processes of other protists and invertebrates, notably corals, and are therefore important in reef ecosystems. Headline events are due to the disastrous toxic effect of some dinoflagellate species on coastal marine ecosystems through the development of “red tides” (HEIL *et al.*, 2001), which may cause massive fish kills and can be fatal to humans (i.e. by paralytic shellfish poisoning; e.g., BACKER *et al.*, 2003).



**Figure 1.6.** Diversity of dinoflagellates through the Mesozoic and Cenozoic. Correlation with sea-level (HAQ *et al.*, 1987) has been proposed to result from feedbacks between sea level variation and degree of ecological variance in shelf environments (from SLUIJS *et al.*, 2005, modified after MACRAE *et al.*, 1996).

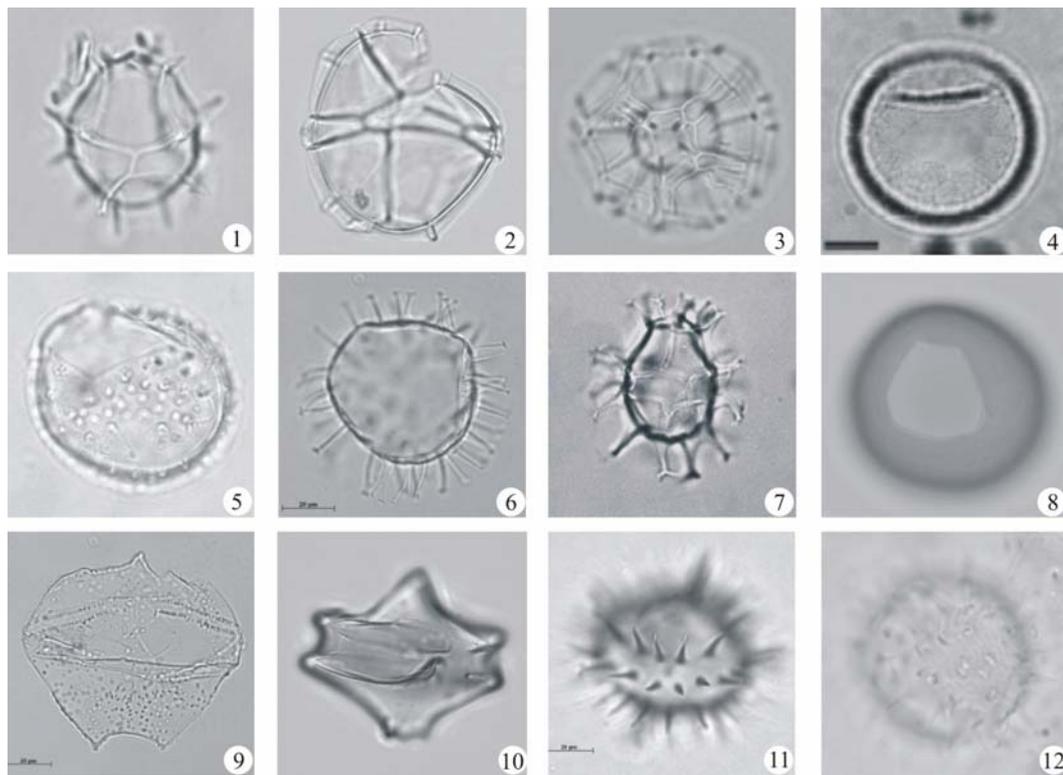
Marine dinoflagellates, representing the majority of species (~90%), are found in almost all climatic regimes from the tropical realm to the high latitude polar regions, but show greatest diversity in the tropics and in neritic temperate waters (e.g., STOVER *et al.*, 1996). In these environments dinoflagellates constitute to the majority of marine phytoplankton and together with diatoms and coccolithophorids are among the most important primary producers. Besides an autotrophic metabolism, half of the extant genera embark on either auxotrophic (photosynthetic but requiring extra vitamins), heterotrophic (feeding mainly on diatoms or decaying or dissolved OM), or mixotrophic (combination of autotrophic and heterotrophic) strategies (e.g., DALE, 1983). Motile cells are capable of diel vertical migration, but are generally found nearest the surface reflecting their fragility and light requirements.



**Figure 1.7.** Simplified life cycle of cyst-producing dinoflagellates (after DALE, 1986).

The life cycle of dinoflagellates is simple to complex and typically includes motile cells covered by a cellulosic, non-fossilisable theca. In addition, about 260 (~16%; HEAD, 1996) of the known species produce non-motile cysts, which are either metabolically active in case of vegetative cysts or inactive in case of resting cysts (hereafter termed dinocysts). These fossilisable stages are surrounded by a continuous wall that consists of acid-resistant organic material known as sporopollenin (KOKINOS *et al.*, 1998) or, in fewer cases, of calcite or silica (e.g., HEAD, 1996). It is generally thought that the majority of dinocysts is produced as part of the sexual reproduction cycle of dinoflagellates (TAYLOR, 1987b, Fig. 1.7). The hypnozygote develops a thick cyst wall

around itself and after a certain dormancy period the protoplast hatches through an excystment aperture known as the archeopyle. Often, the process of encystment seems to follow exponential population growth and commonly occurs after blooms. However, cysts formation may also conduce to survive adverse condition such as anoxia, low temperatures, or nutrient and light limitation (ANDERSON *et al.*, 1987; BRAVO & ANDERSON, 1994) and has a meaning with respect to population dynamics and dispersal.



**Figure 1.8.** Organic-walled dinoflagellate cysts. 1) *Impagidinium aculatum*, 2) *Impagidinium patulum*, 3) *Nematosphaeropsis labyrinthus*, 4) *Pyxidinospis reticulata*, 5) *Operculodinium israelianum*, 6) *Polysphaeridium zoharyi*, 7) *Spiniferitis bentori*, 8) cyst of *Protoperidinium* spp., 9) *Trinovantedinium applanatum*, 10) *Selenopemphix nephroides*, 11), *Selenopemphix quanta*, 12) *Echinidinium granulatum*.

Though heterospory (i.e. different species producing the same cyst) does occur, dinocyst morphology is generally species specific. The link between the motile and dinocyst populations is most often made by observing living dinocysts within the thecate cell in plankton tows or by inference from the similarity of cell-wall plate arrangement (tabulation) of theca and cysts (e.g., HEAD, 1996). The preferred methods, however, are germination experiments on of living cysts. Such studies not only confirm the theca-cyst taxonomic relationship but also provide experimental data on the environmental conditions (e.g. temperature, salinity, light and nutrients) that determine the onset of cyst production. Calibration of theca and dinocyst production can also be achieved by comparing annual export production from deployment of sediment traps (HARLAND & PUDSEY, 1999). Because, there are two different taxonomic systems based on planktology and paleontology,

it is not unusual that the same species has two different scientific names. The dinocysts studied in this work possess organic walls and belong to the orders Gonyaulacales, Peridinales, and Gymnodinales (see Fig. 1.8 for examples). Taxonomy of subfamilies and higher taxonomic levels follows FENSOME *et al.* (1996). Species citations generally follow WILLIAMS *et al.* (1998) and represent cyst names where possible. Cyst-theca relationships are discussed and listed in HEAD (1996).

#### 1.4.1. *The fossil record of modern dinoflagellates*

Generally, dinocyst ecology is best understood for Quaternary assemblages due to the high number of extant taxa that can be studied. Since the first comprehensive studies in the 70's (e.g., WALL *et al.*, 1977), our knowledge on ecological preferences of modern cyst-forming species has increased tremendously and today covers information on species-environmental relations from various marine ecosystems (cf. MARRET & ZONNEVELD, 2003 for an overview). Concurrently, fossil archives became increasingly explored for paleoenvironmental reconstructions (e.g., MUDIE *et al.*, 2001; ESPER *et al.*, 2004; DE VERNAL *et al.*, 2005), given the fact that associations can sensitively reflect even small changes in temperature, salinity or nutrient availability. Especially at high latitudes and in neritic settings, where dinoflagellates constitute to the bulk of phytoplankton, this efficiency greatly expanded the understanding of paleoecological conditions (e.g., by using transfer functions: DE VERNAL *et al.* 1994). This paleoclimatic information is important and complementary to the data derived from typically more offshore groups such as planktonic foraminifera, coccolithophorids and radiolaria.

The increased importance assigned to dinocysts for paleoceanography has stimulated research on the distribution of dinocysts in modern sediments and their statistical correlation with physical/chemical parameters of the upper water column. Large data matrixes of dinocyst assemblages and environmental parameters were compiled for quantitative reconstruction of past sea-surface temperature, salinity and sea-ice cover (duration) with an accuracy similar to that of modern synoptic oceanography (e.g., ROCHON *et al.*, 1999; DE VERNAL *et al.*, 2001, 2005). This sensitivity is particular valuable at high latitudes where common indicators such as planktonic foraminifera, diatoms, and radiolaria may dissolve in carbonate/silicate undersaturated water. These developments have rapidly opened up the field of ultra-high resolution (decadal- to centennial time-scale) studies of natural oscillations in climate and phytoplankton responses prior to the historical period of anthropogenic changes and global warming. However, the inferences from observations of dinocyst assemblages are not perfect for several reasons. First, motile dinoflagellates in plankton associations correspond to an instantaneous time interval, whereas the cysts in sediments may represent several years or decades of sedimentary fluxes. Second, little is known about the frequency of reproduction, and when we turn to the proportion of dinocysts that is produced in given population information becomes even more limited. Third, several dinocyst species tend to have broad distributions and may at least in part reflect the ease with which they can be transported from their point of origin to the site of sedimentation. Some authors, in fact, consider the vast majority of dinocysts beyond the shelfbreak to have been transported there from neritic environments (e.g., DALE, 1983, 1996). Finally, at small regional scales, parameters other

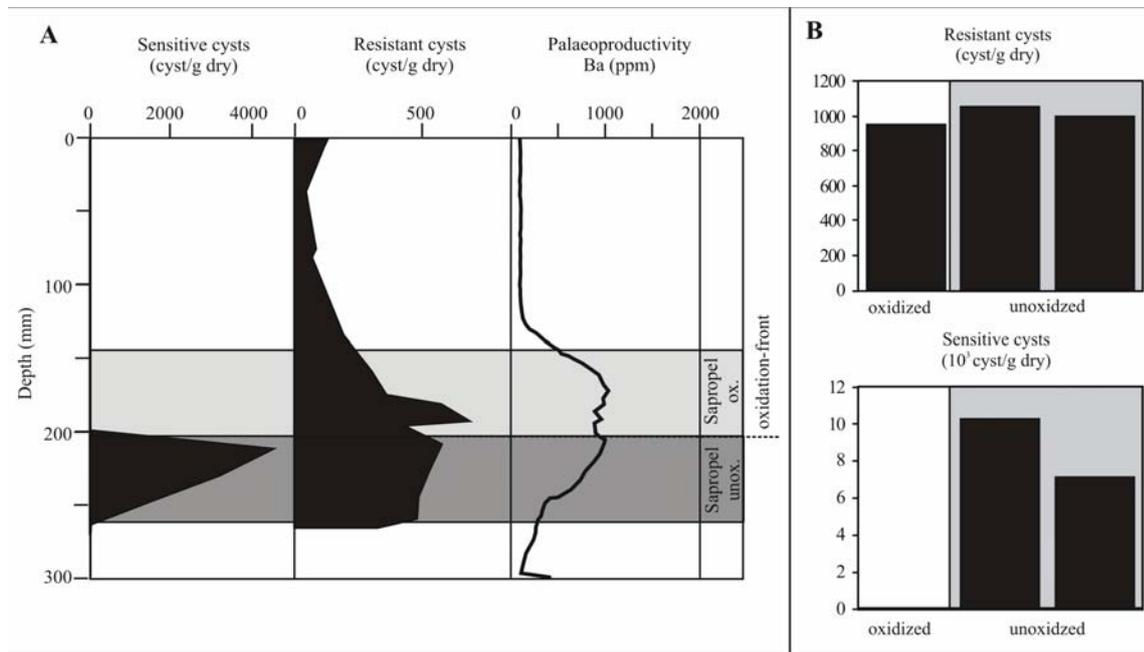
than temperature or salinity may determine dinocyst assemblages such as at northeast Pacific margins and western equatorial Atlantic, where, respectively, productivity and river discharge seem to be the parameter that are most closely related to the spatial distribution of dinocysts (VINK *et al.*, 2000; RADI & DE VERNAL, 2004).

Simple increases in microfossil abundance have long been interpreted as an index of high paleoproductivity (e.g., WEFER *et al.*, 1999) and there has been a strong tendency to relate high diatom concentrations to nutrient-rich upwelling conditions and high carbon burial. Likewise, high abundance of heterotrophic dinocysts (notably cysts of *Protoperidinium*) has been interpreted as indicative of upwelling conditions (e.g., DALE, 1996; HAMEL *et al.* 2002; REICHAERT & BRINKHUIS, 2003; RADI & DE VERNAL, 2004). Indeed, most peridinioid species tend to characterise nearshore/inner-outer neritic environments, where large amounts of nutrients are available in order to support their predominantly heterotrophic feeding strategy, whereas autotrophic gonyaulacoid genera (notably *Impagidinium* and *Nematosphaeropsis*) are considered to be good indicators of oligotrophic, open ocean conditions. This has led to the early believe that the ratio between heterotrophic peridinioid and autotrophic gonyaulacoid species (G/P) generally tends to increase offshore and can be associated with both climate and nutrition (e.g., WALL *et al.*, 1977; HARLAND 1983, DALE, 1996). This approach has, however, been criticised for various reasons. First of all, not all peridinioid dinoflagellates are necessarily heterotrophic. Second, DALE & FJELLSÅ (1994) drew attention to the fact that modern heterotrophic dinoflagellates also occur in regions other than high productivity areas, such as sea ice dominated settings. Moreover, McMinn (1992) stated that oligotrophic areas with periodical nutrient supply may also yield assemblages dominated by protoperidinioid species. Finally, and probably most important, some peridinioid species are far more susceptible to oxic degradation than their gonyaulacoid relatives, which may cause selective destruction of the former and overrepresentation of the latter (e.g., ZONNEVELD *et al.*, 2001; **Chapter 4**). Indeed, McCarthy *et al.* (2003) suggest that the common observation that the G/P ratio tends to increase offshore may result primarily from selective destruction of protoperidinioid cysts under oxidizing conditions rather than reflecting the true distribution of dinoflagellates in surface waters. Therefore, caution is advised when interpreting palynomorphs assemblages from basins where oxidation may completely alter the climatic signal of sedimentary assemblages.

#### 1.4.2. Selective dinocyst preservation

One of the main advantages of palynology over other branches of micropaleontology is the extraordinary resistance of sporopollenin to chemical degradation. Nevertheless, strong acids, acetolysis, and base treatments are avoided as much as possible upon processing of assemblages. The reason is that such procedures would destroy many peridinioid species, notably the brown-walled taxa (i.e. protoperidinioids). The selective destruction of protoperidinioid cysts is already evident at relatively low levels of oxidation and skews the sample toward the more resistant gonyaulacoid dinocyst (HOPKINS & MCCARTHY, 2002). This is most likely subscribed to a fundamental difference in the cyst wall chemistry. According to VERSTEEGH & BLOKKER, (2004), the gonyaulacoid cyst wall consists mainly of carbon and ether-linked macromolecule building

blocks with a high proportion of aromatic moieties, whereas the building blocks of peridinioid cyst walls are much more ester linked and aliphatic in nature.



**Figure 1.9.** Effect of post-depositional selective degradation displayed in the different concentration of R-cysts and S-cysts across oxidation fronts in sediment horizons of: A) core ABC-26 of the S1-sapropel (eastern Mediterranean), B) Madeira Abyssal Plain f-turbidite (equatorial Atlantic), modified after ZONNEVELD *et al.* (1997, 2001).

Although early recognized by differences in fluorescence, vulnerability to staining or oxidative laboratory treatments (e.g., DALE, 1976; MARRET, 1993), many palynologists consider the relevance of selective dinocyst preservation in marine sediments with scepticism. However, several studies provide strong evidence that the resistance of cysts to in situ oxidation parallels their resistance to chemical treatment in the laboratory. For instance, post-depositional aerobic OM degradation at natural oxidation fronts in the Madeira Abyssal Plain f-turbidite and the eastern Mediterranean S1 sapropel causes S-cysts to vanish rapidly in sediments immediately above the oxidation front (ZONNEVELD *et al.* 1997, 2001; Fig. 1.9). In the Arabian Sea, S-cysts are highly enriched in sediments underlying the oxygen minimum compared with sediments outside this zone, although sea-surface and water-column conditions in this area are comparable (ZONNEVELD, 1997). Furthermore, comparison of sediment-trap and bottom samples from oxic and anoxic sites indicates rapid aerobic degradation of S-cysts, whereas trap and sediment-based fluxes of R-cysts correspond well in all cases (ZONNEVELD & BRUMMER, 2000). So far, such trap studies revealed no evidence that dinocysts are prone to degradation during their transport within the water column, probably due to the fact that cyst accumulation tends to be accelerated by faecal pellet transportation, self sedimentation or aggregation, resulting in a relatively short reaction time.

The extent of dinocyst preservation in marine sediments appears to reflect the average period during which accumulating S-cysts are exposed to oxic sedimentary conditions. Such an “oxygen effect” is also evident from lower degradation rates exhibited by recalcitrant OM particles and macromolecules such as pollen (KEIL *et al.*, 1994), lignin (BENNER *et al.*, 1984), hydrocarbons (ATLAS, 1981), and algaenans (GELIN *et al.*, 1997) under anoxic as compared with oxic conditions. Comparing dinocyst degradation rates with these OM compounds, VERSTEEGH & ZONNEVELD (2002) found that oxidation resistant R-cysts and sensitive S-cysts taxa are, respectively, more and less efficiently preserved, whereby S-cyst degradation typically follows first-order decay. They concluded that this “ranking” is stable for different environments and can be used to separate productivity from OM preservation in time series. Moreover, the changing abundances of these uniform and easily counted bodies might be used to directly calibrate an absolute scale of oxic exposure, without complications from diffusive losses. This is particularly important in continental margin settings, where sea level fluctuations can result in very different preservational conditions over relatively short time spans, causing erroneous interpretations if the role of OM degradation is not considered. The more accurate the attempted paleoenvironmental interpretation is (e.g. quantitative reconstructions using transfer functions), the more important it is to determine the relative significance of selective preservation on the palynological assemblage being studied. Understanding this process through “calibration” is important to interpret better the paleoenvironment records inferred from sediments cores analysis.

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## CHAPTER 2

### Selective preservation of organic-walled dinoflagellate cysts as a tool to quantify past net primary production and bottom water oxygen concentrations

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#### **Abstract**

To understand the role of the ocean within the global carbon cycle, detailed information is required on key-processes within the marine carbon cycle; bio-production in the upper ocean, export of the produced material to the deep ocean and the storage of carbon in oceanic sediments. Quantification of these processes requires the separation of signals of net primary production and the rate of organic matter decay as reflected in fossil sediments. This study examines the large differences in degradation rates of organic-walled dinoflagellate cyst species to separate these degradation and productivity signals. For this, accumulation rates of cyst species known to be resistant (R-cysts) or sensitive (S-cysts) to aerobic degradation of 62 sites are compared to mean annual chlorophyll *a*, sea-surface temperature, sea-surface salinity, nitrate and phosphate concentrations of the upper waters and deep-water oxygen concentrations. Furthermore, the degradation of sensitive cysts, as expressed by the degradation constant *k* and reaction time *t*, has been related to bottom water oxygen concentration. The studied sediments were taken from the Arabian Sea, north-western African Margin (North Atlantic), western-equatorial Atlantic Ocean/Caribbean, south-western African margin (South Atlantic) and Southern Ocean (Atlantic sector).

Significant relationships are observed between (a) accumulation rates of R-cysts and upper water chlorophyll *a* concentrations, (b) accumulation rates of S-cysts and bottom water oxygen and (c) degradation rates of S-cysts and bottom water oxygen concentrations. Relationships that are extremely weak or are clearly insignificant on all confidence intervals are between (1) S-cyst accumulation rates and chlorophyll *a* concentrations, sea-surface temperature, sea-surface salinity, phosphate concentrations, and nitrate concentrations, (2) between R-cyst accumulation rates and bottom water oxygen concentration, sea-surface temperature, sea-surface salinity, phosphate, and nitrate concentrations, and between (3) degradation rates of S-cysts and water depth. Co-variance is present between the parameters nitrate and phosphate, nitrate, phosphate and chlorophyll *a*, bottom water oxygen, and water depth. Correcting for this co-variance does not influence the significance of the relationship given above.

The possible applicability of dinoflagellate cyst degradation to estimate past net primary production and deep ocean ventilation is discussed.

KEYWORDS: dinoflagellate cysts; early diagenesis; organic matter; preservation; oxygen

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*Appendix A1:* Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.margeo.2006.10.023.

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## 2.1. Introduction

The fate of organic matter (OM) in the ocean has intrigued scientists over years. Especially in the last decades the role of the ocean within the global carbon cycle has been subject of intense focus as the concern grows about the possible effects of industrial-induced atmospheric  $p\text{CO}_2$  increase on global climate. To understand the role of the oceans, detailed information is needed on key-processes within the marine carbon cycle such as bio-production in the upper ocean, especially primary production, the export of the produced material to the deep-ocean, the storage of carbon in sediments and the redistribution of carbon from the ocean to the atmosphere. The present-day marine net global production of phytoplankton has been estimated to be more or less comparable to the production of land plants (ocean  $\sim 45\text{--}50 \text{ Gt C year}^{-1}$ , land plants about  $45\text{--}68 \text{ Gt C year}^{-1}$ ; LONGHURST *et al.*, 1995; CAO *et al.*, 2005). Although estimates of the above mentioned processes are thought to give more or less adequate results for the modern environments, quantification of these processes in the past is largely hampered by the difficulty to separate past bio-productivity signals from those induced by (early-) diagenetic processes. As results, separating “export productivity from diagenesis” forms a key-target of world-wide operating research programs (e.g., IMAGES, JGOFS and WCRP).

Degradation of OM in surficial sediments occurs by either aerobic or anaerobic pathways. After oxygen is consumed, a series of electron acceptors are used by bacteria to decompose organic compounds in a sequence that depends on the yield of metabolic free energy (e.g., JØRGENSEN, 2000; SUN *et al.*, 2002). Studies on natural diffusion-limited, oxidation phenomena, often referred to as “burn-down” events as well as laboratory experiments, reveal that early aerobic diagenesis is highly selective and that the rate of degradation with respect to the concentration of labile organic matter seems to be a typically first-order process. (e.g., HEDGES & PRAHL, 1993 and references therein; COWIE *et al.*, 1995; DE LANGE, 1998; PRAHL *et al.*, 2003). The rate of degradation of a given concentration of labile organic matter component (G) can be expressed as  $dG/dt = -kG$  where  $t$  is the reaction time and  $k$  is the first-order decay constant (HEDGES & PRAHL, 1993). This equation can be integrated between the boundary conditions  $t = 0$ ,  $G = G_0$  and  $t \rightarrow \infty$  to obtain  $G_t = G_0 \exp^{-kt}$ . Hence, degradation depends on the lability of the OM expressed by the constant  $k$ , and the reaction time  $t$ .

Recently VERSTEEGH & ZONNEVELD (2002) suggested a method to separate production and preservation signals as archived in fossil sediments by using the different lability of OM components in relation to aerobic degradation. Their studies of post-depositional aerobic OM degradation at natural oxidation fronts in late Quaternary sediments of the Madeira Abyssal Plain f-turbidite, the mid-Holocene Eastern Mediterranean S1 sapropel and the modern Arabian Sea Oxygen Minimum Zone (OMZ) and surrounding sediments, show that the ranking of different OM components, with respect to their degree of degradation, is similar in all studied regions and time intervals. End-members on this scale of lability are groups of organic-walled dinoflagellate cyst (dinocysts) species (ZONNEVELD *et al.*, 1997, 2001). VERSTEEGH & ZONNEVELD (2002) concluded that concentrations of components resistant against degradation within (fossil) sediments are a reflection of the initial export production (with export production being the amount of material exported from the photic zone prior to degradation) of the component whereas the final concentrations of more labile components are the result of their export production and the aerobic degradation process within the water column and the sediments. Variability in accumulation rates of resistant components can therefore be used as proxy to reconstruct past component production by assuming minimal degradation within the water column. The rate of (post-depositional) decay ( $kt$ ) can be calculated using the stable ranking of the components with respect to their lability.

Here we aim to develop this method further and discuss if this method can be used to quantify past productivity and the rate of degradation. For this, we concentrate on dinocyst species which form the end members of the “lability ranking”. Dinoflagellates are a diverse group of eukaryotic, primarily unicellular organisms with two distinctive flagella which give the organisms a (species-) characteristic spiral motion. Many planktonic dinoflagellates show diel vertical migration as result of endogenous rhythms and their geotactic and phototactic (e.g., ANDERSON & STOLZENBACH, 1985; LIEBERMAN *et al.*, 1994; KAMYKOWSKI *et al.*, 1998). Although species dependent, their migration ability is limited to several meters only, as result of their small size (the majority of species have sizes between 10–60  $\mu\text{m}$ ). Together with diatoms and coccolithophorids, dinoflagellates constitute the majority of marine eukaryotic phytoplankton and are, therefore, important primary producers. Fossilizable dinocysts are thought to be formed during the sexual life-cycle of dinoflagellates. During formation they lose their flagella and sink through the water column most probably as part of faecal pellets, aggregates and/or marine snow (MUDIE, 1996). Field studies reveal that maximal cyst formation occurs during, or just after periods of maximal vegetative cell division (e.g., ISHIKAWA & TANIGUCHI, 1996; MONTRESOR *et al.*, 1998; KREMP and HEISKANEN, 1999; GODHE *et al.*, 2001; Matsuoka, 2001). The cyst species that have been classified as resistant against aerobic decay by VERSTEEGH & ZONNEVELD (2002; R-cysts) are all able to photosynthesize although most, if not all of them are thought to be mixotrophic (SCHNEPF & ELBRÄCHTER, 1992). It is assumed that their vegetative production is positively influenced by enhanced availability of nutrients and/or trace elements when other biologic and a-biotic factors remain constant. Dinocysts that are extremely sensitive for aerobic decay (S-cysts) are found, or thought, to be heterotrophic. Their vegetative growth is likely enhanced as more prey is available when other factors being equal. To investigate if cyst production of both groups of dinocysts can

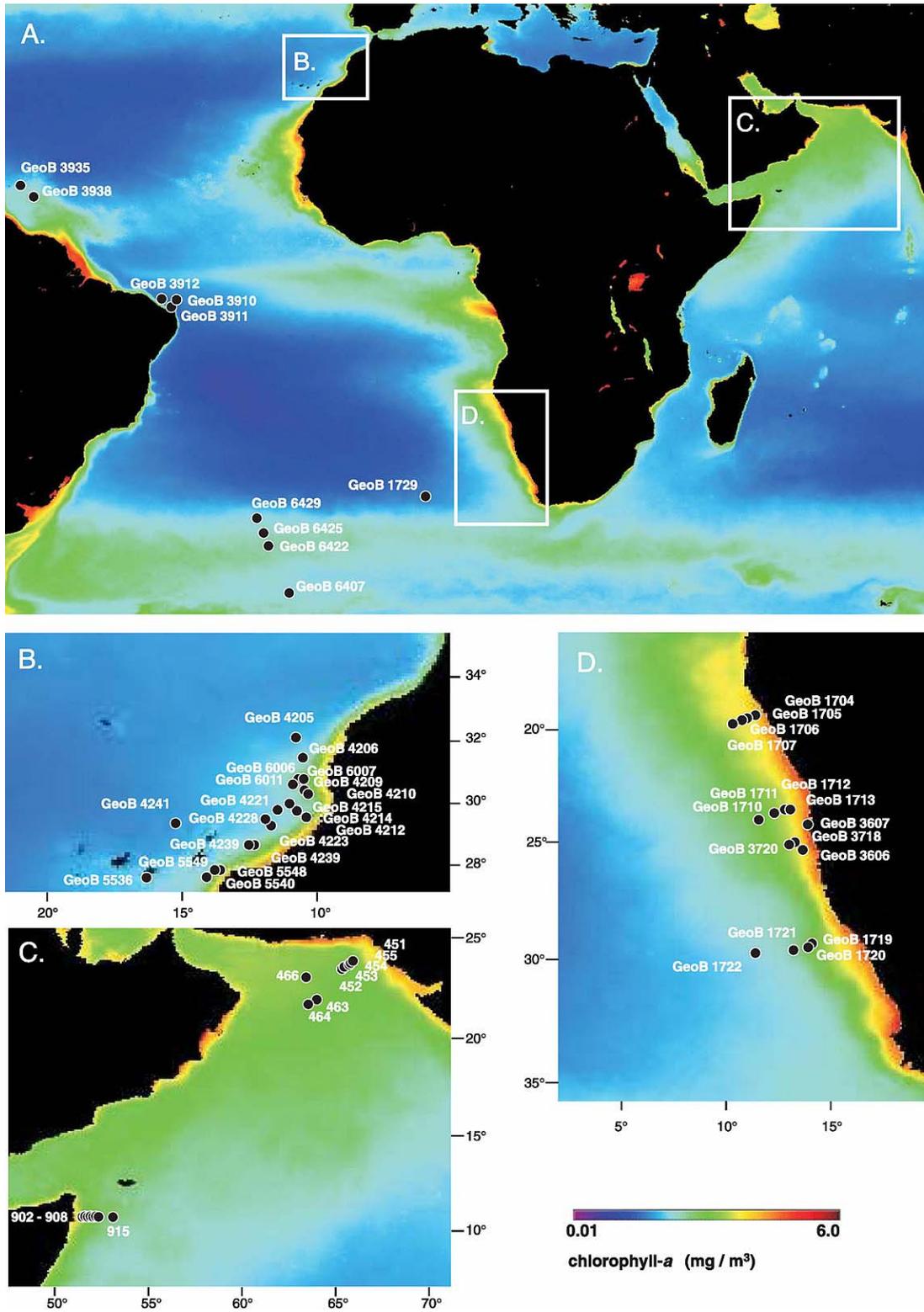
be related to net primary production or other environmental parameters we correlated cyst accumulation rates of S-cysts and R-cysts with mean annual chlorophyll *a* concentrations, mean annual sea-surface temperature (SST), mean annual sea-surface salinity (SSS), mean annual nitrate concentrations [NO<sub>3</sub>], and mean annual phosphate concentrations [PO<sub>4</sub>] of the upper waters at the sampling sites (Fig. 2.1).

To investigate if the rate of decay of S-cysts might be useful to reconstruct ventilation of the deep-ocean, we correlated their accumulation rates as well as the degradation of S-cysts expressed by the “*kt*”-value with bottom water oxygen concentration [O<sub>2</sub>] at the above mentioned sites.

## 2.2. Materials and methods

Surface sediments derived from 62 samples of well-dated multi-cores from the western-equatorial Atlantic Ocean, the northwest African margin (North Atlantic), southwest African margin (South Atlantic), the Southern Ocean (Atlantic sector) and the Arabian Sea, have been collected from box- and multicores during cruises of the R/V *Meteor* and R/V *Tyro* (Fig. 2.1, Table 2.1). Sediment samples have been processed using standard palynological techniques according to the aliquot method described in MARRET & ZONNEVELD (2003). Accumulation rates are calculated by multiplying the numbers of dinocysts per gram of dry sediment with the dry bulk density and the sedimentation rate at the sample sites. Sedimentation rates have been estimated based on linear interpolation between the <sup>14</sup>C-AMS dates of the studied multi cores (Table 2.1). Accumulation rates of both R-cysts and S-cysts (Table 2.2) have been compared to chlorophyll *a*, SST, SSS, NO<sub>3</sub>, and PO<sub>4</sub> concentrations of the upper waters at the sampling sites and bottom water oxygen concentrations. Chlorophyll *a* values have been extracted from the SEAWIFS satellite images that depict mean annual chlorophyll *a* data compiled from 30 October, 1978–1 June, 2005 using the program NCSA JHV 2.7. Bottom water [O<sub>2</sub>], SST, SSS, [NO<sub>3</sub>], and [PO<sub>4</sub>] have been derived from the NOAA, 1998 dataset (Appendix A1).

The degradation of S-cysts expressed by “*kt*” has been calculated assuming a first-order decay process:  $kt = \ln(X_i / X_f)$ , with  $X_f$  = final dinocyst concentration (cysts cm<sup>-2</sup> kyr<sup>-1</sup>), and  $X_i$  = initial cyst concentration (cysts cm<sup>-2</sup> kyr<sup>-1</sup>). We assume that in regions with minimal aerobic degradation surface sediments, such as oxygen-minimum zones (OMZ), the accumulation rate (AR) of R-cysts and S-cysts reflect their initial export production. Material from the surface samples of OMZs of the Arabian Sea and the Namibian shelf (SE-Atlantic) as well as sediment traps (western Arabian Sea) indicate that the ARs of R-cysts and S-cysts relate to the equation:  $AR_{S-cysts} = 68 \times AR_{R-cyst}$  (Appendix A1, ZONNEVELD & BRUMMER, 2000). Based on this relationship initial concentrations of S-cysts can be calculated by multiplying the AR of R-cysts in the surface sediments by 68 and by using the above mentioned first-order decay function to determine the degradation index (*kt*). The *kt* values of the studied samples have been compared to mean annual bottom water oxygen values.



**Figure 2.1.** Maps of the Atlantic Ocean and Indian Ocean showing mean annual chlorophyll *a* concentrations of surface waters and sample positions of surface sediment samples. (A) Overview map of the studied regions, (B) Detailed map of the NW-African margin (C) Detailed map of the Arabian Sea, (D) Detailed map of the studied region off SW Africa.

Sample GeoB 1711 has been excluded from the analyses since accumulation rates of the cysts appeared a factor 10 higher than the surrounding samples. ARZE showed a remarkable difference in association as samples in its close vicinity and is excluded as well. Since both sites are not characterized by exceptional sedimentation regimes or deviant environmental conditions in the water column we ascribe these discrepancies to “errors” during the counting process.

**Table 2.1.** List of samples with information about the sample position, water depth, sedimentation rates, and stratigraphy.

Sample	Lat. (N)	Long. (E)	Depth (m)	SR	Stratigraphy	continued	Sample	Lat. (N)	Long. (E)	Depth (m)	SR	Stratigraphy
GeoB4205	32.182	-11.648	272	1.83	KUHLMANN <i>et al.</i> (2002)		ARZE906	10.48	52.07	2020	20	IVANOVA (2000)
GeoB4206	31.498	-11.015	1855	4.67	KUHLMANN <i>et al.</i> (2002)		ARZE907	10.48	52.14	2807	14	IVANOVA (2000)
GeoB4209	30.357	-11.083	2150	4.17	KUHLMANN <i>et al.</i> (2002)		ARZE908	10.46	52.54	3572	8	IVANOVA (2000)
GeoB4211	30.193	-10.821	1173	3.83	KUHLMANN <i>et al.</i> (2002)		ARZE915	10.41	53.31	4035	5	IVANOVA (2000)
GeoB4212	29.603	-10.95	1256	4.42	KUHLMANN <i>et al.</i> (2002)		GeoB1704	-19.4	11.62	395	3.6	MOLLENHAUER (2002)
GeoB4214	29.781	-11.198	1788	3.08	KUHLMANN <i>et al.</i> (2002)		GeoB1705	-19.5	11.38	647	13.1	MOLLENHAUER (2002)
GeoB4215	30.036	-11.553	2106	3	KUHLMANN <i>et al.</i> (2002)		GeoB1706	-19.57	11.18	980	9	MOLLENHAUER (2002)
GeoB4221	29.775	-12.338	1826	3.08	KUHLMANN <i>et al.</i> (2002)		GeoB1707	-19.7	10.65	1234	9.4	MOLLENHAUER (2002)
GeoB4223	29.018	-12.467	777	11.17	KUHLMANN <i>et al.</i> (2002)		GeoB1710	-23.43	11.68	2995	5.3	MOLLENHAUER (2002)
GeoB4228	29.47	-12.99	1633	6.67	KUHLMANN <i>et al.</i> (2002)		GeoB1711	-23.32	12.37	1975	10	MOLLENHAUER (2002)
GeoB4237	28.493	-13.18	800	6.5	KUHLMANN <i>et al.</i> (2002)		GeoB1712	-23.25	12.80	1004	8	MOLLENHAUER (2002)
GeoB4239	28.493	-13.18	881	10.75	KUHLMANN <i>et al.</i> (2002)		GeoB1713	-23.22	13.020	600	7.7	MOLLENHAUER (2002)
GeoB4241	29.167	-15.453	3610	3.08	KUHLMANN <i>et al.</i> (2002)		GeoB1719	-28.93	14.17	1023	6.5	MOLLENHAUER (2002)
GeoB5536	27.537	-16.135	3456	6.5	KUHLMANN <i>et al.</i> (2002)		GeoB1720	-29.	13.8	2011	4	MOLLENHAUER (2002)
GeoB5540	27.535	-14.175	2035	9.92	KUHLMANN <i>et al.</i> (2002)		GeoB1721	-29.18	13.08	3079	2.9	MOLLENHAUER (2002)
GeoB5548	27.992	-13.518	1162	8.83	KUHLMANN <i>et al.</i> (2002)		GeoB1722	-29.45	11.75	3971	1.9	MOLLENHAUER (2002)
GeoB5549	27.978	-13.695	1454	11.25	KUHLMANN <i>et al.</i> (2002)		GeoB1729	-28.9	01.0	4401	1.45	THIEBEN (1993)
GeoB6006	30.868	-10.63	1282	5.92	KUHLMANN <i>et al.</i> (2002)		GeoB3606	-25.46	13.08	1793	7.38	MOLLENHAUER (2002)
GeoB6007	30.852	-10.267	899	86.75	KUHLMANN <i>et al.</i> (2002)		GeoB3607	-23.88	14.33	97	60	MOLLENHAUER (2002)
GeoB6011	30.315	-10.288	993	6.83	KUHLMANN <i>et al.</i> (2002)		GeoB3718	-24.9	13.17	1313	7.7	MOLLENHAUER (2002)
ARZ451	23.41	66.02	495	25.5	VANDER WEIJDEN <i>et al.</i> (1999)		GeoB3720	-25.07	12.67	2517	10.5	MOLLENHAUER (2002)
ARZ452	22.56	65.28	2001	5	VANDER WEIJDEN <i>et al.</i> (1999)		GeoB3910	-04.245	-36.347	2359	3.56	MOLLENHAUER (2002)
ARZ453	23.14	65.44	1555	8.1	VANDER WEIJDEN <i>et al.</i> (1999)		GeoB3911	-04.613	-36.635	825	14.29	MOLLENHAUER (2002)
ARZ455	23.33	65.57	998	10.1	VANDER WEIJDEN <i>et al.</i> (1999)		GeoB3912	-03.665	-37.718	773	3.45	MOLLENHAUER (2002)
ARZ463	22.33	64.03	970	16	VANDER WEIJDEN <i>et al.</i> (1999)		GeoB3935	12.613	-59.388	1556	2.63	MOLLENHAUER (2002)
ARZ464	22.15	63.35	1511	15	VANDER WEIJDEN <i>et al.</i> (1999)		GeoB3938	12.257	-58.33	1972	1.32	MOLLENHAUER (2002)
ARZ466	23.36	63.48	1960	6.4	VANDER WEIJDEN <i>et al.</i> (1999)		GeoB6407	-42.05	-19.5	3354	1.76	FRANKE <i>et al.</i> (2004)
ARZ902	10.46	51.34	459	8.1	IVANOVA (2000)		GeoB6422	-35.71	-22.44	3972	1.77	FRANKE <i>et al.</i> (2004)
ARZ903	10.46	51.39	789	48	IVANOVA (2000)		GeoB6425	-33.83	-23.59	4352	1.05	FRANKE <i>et al.</i> (2004)
ARZE904	10.47	51.46	1194	40	IVANOVA (2000)		GeoB6429	-31.95	-24.25	4335	2	SCHMIEDER (2004)
ARZE905	10.54	51.56	1567	29	IVANOVA (2000)							

Accumulation rates of R-cysts, S-cysts and the degradation index (*kt*) have been compared with oxygen concentrations of bottom waters, and upper water mean annual chlorophyll *a*, SST, SSS, NO<sub>3</sub> and PO<sub>4</sub> concentrations using the multivariate ordination methods Redundancy Analysis (RDA) using the CANOCO for Windows software package (JONGMAN *et al.*, 1987; TER BRAAK & SMILAUER, 1998). Seasonal values of SST and SSS at the investigated sites strongly co-vary to each other (Fig. 2.2). As a result seasonal differences can be considered as of minor importance and annual values have been included within our analyses. As seasonal data of [PO<sub>4</sub>] and [NO<sub>3</sub>] are available for a few sites only, we have included annual data. Nitrate and phosphate values co-vary strongly (Fig 2.3, Table 2.3). Slight co-variation between chlorophyll *a* and NO<sub>3</sub>, PO<sub>4</sub> concentrations and between bottom water [O<sub>2</sub>] and water depth occurs. For this co-variance is corrected in the RDA analysis.

The performed analyses are based on the assumption of a linear response of the species in relation to environmental variables. A detrended correspondence analysis carried out before the analysis confirmed such a linear response model.

**Table 2.2.** List of cyst-species included within the S-cyst and R-cyst groups.

R-cysts	S-cysts
<i>Dalella chathamensis</i>	<i>Brigantedinium</i> spp.
<i>Impagidinium aculeatum</i>	cyst of <i>Diplopelta parva</i>
<i>Impagidinium pallidum</i>	cyst of <i>Diplopelta symmetrica</i>
<i>Impagidinium paradoxum</i>	cyst of <i>Protoperidinium avellanum</i>
<i>Impagidinium patulum</i>	cyst of <i>Protoperidinium americanum</i>
<i>Impagidinium plicatum</i>	cyst of <i>Protoperidinium monospinum</i>
<i>Impagidinium sphaericum</i>	cyst of <i>Protoperidinium nudum</i>
<i>Impagidinium striolatum</i>	cyst of <i>Protoperidinium stellatum</i>
<i>Impagidinium variaseptum</i>	<i>Echinidinium aculeatum</i>
<i>Impagidinium velorum</i>	<i>Echinidinium granulatum</i>
<i>Impagidinium</i> spp.	<i>Echinidinium transparantum</i>
<i>Nematosphaeropsis labyrinthus</i>	<i>Echinidinium delicatum</i>
<i>Operculodinium israelianum</i>	<i>Echinidinium</i> spp.
<i>Pentapharsodinium dalei</i>	<i>Lejeunecysta oliva</i>
<i>Polysphaeridium zoharyi</i>	<i>Lejeunecysta sabrina</i>
<i>Quinquecuspis concreta</i>	
<i>Selenopemphix antarctica</i>	
<i>Selenopemphix nephroides</i>	
<i>Selenopemphix quanta</i>	
<i>Stelladinium robustum</i>	
<i>Trinovantedinium applanatum</i>	
<i>Votadinium calvum</i>	
<i>Votadinium spinosum</i>	
<i>Xandarodinium xanthum</i>	

### 2.3. Results

Accumulation rates of S-cysts ( $s$ ) show an exponential decrease with oxygen concentrations ( $y_{O_2}$ ) in bottom water that is significant on all significance levels (Fig. 2.4, Table 2.4) according to:

$$y_{O_2} = 4.3374 e^{-0.00001s}, \text{ with } R^2 = 0.73 \quad (1)$$

R-cyst accumulation rates and bottom water oxygen concentrations show an insignificant correlation ( $R^2 = 0.23$ ; Fig. 2.5, Table 2.4).

Accumulation rates of R-cysts ( $r$ ) show a significant linear relationship with chlorophyll  $a$  concentrations ( $y_{Chla}$ ) in the upper water column (Fig. 2.6, Table 2.4) according to the equation:

$$y_{Chla} = 0,0002r + 0.2271, \text{ with } R^2 = 0.70 \quad (2)$$

**Table 2.3.** Correlation matrix of the environmental variables depicting the rate of co-variance.

Correlation matrix	O <sub>2</sub>	chl <i>a</i>	SST	SSS	PO <sub>4</sub>	NO <sub>3</sub>	water depth	A	B
O <sub>2</sub> (ml l <sup>-1</sup> )	1							51%	51%
chl <i>a</i> (mg m <sup>-3</sup> )	-0.409	1						19%	3%
SST (°C)	-0.389	-0.206	1					7%	0%
SSS (psu)	-0.150	0.020	0.130	1				1%	0%
PO <sub>4</sub> (mM)	-0.331	0.448	-0.045	-0.075	1			14%	2%
NO <sub>3</sub> (mM)	-0.171	0.441	-0.281	-0.034	0.829	1		5%	1%
water depth (m)	0.495	-0.363	-0.013	-0.243	-0.146	-0.195	1	19%	1%

Amount of variance in the dataset explained by the environmental variables.  
A = without co-variance correction, B = with co-variance correction.

Site GeoB 3607 is located at the edge of an active upwelling cell along the Namibian coast (Fig. 2.1) and is characterized by extreme high chlorophyll *a* values that are a factor 100 higher than the other studied samples. This sample has been excluded from the establishment of equation no. 2.

Although by visual examination a positive relationship between accumulation rates of S-cyst with chlorophyll *a* concentrations seems to be present, this trend is extremely weak and not significant (Fig. 2.7, Table 2.4). The *kt*-values show a clear relationship with bottom water [O<sub>2</sub>] according to the equation (Fig. 2.8A, Table 2.4):

$$[O_2] = 5.184 = 1 / e^{-1.131(kt-1.98)}, \text{ with } R^2 = 0.73 \quad (3)$$

When samples GeoB 5540 (NW-African margin) and GeoB 1704 (SW-African margin) are excluded from the dataset a relationship between oxygen concentration and the degradation index (*kt*) according to the following equation can be observed (Fig. 2.8B, Table 2.4):

$$[O_2] = 5.17 = 1 / e^{-1.23(kt-2.058)}, \text{ with } R^2 = 0.846 \quad (4)$$

A weak relationship ( $R^2 = 0.42$ ) can be observed between water depth and *kt* (Fig. 2.9, Table 2.4). The *kt*-values decrease with increasing sedimentation rates (Fig. 2.10, Table 2.4). Mean annual SST, SSS, [PO<sub>4</sub>], and [NO<sub>3</sub>] show no significant or only a weak relationship between with R-cysts and S-cyst accumulation rates (Fig. 2.11, Table 2.3). By correcting for this co-variation the variables water depth, SST, SSS, [PO<sub>4</sub>], and [NO<sub>3</sub>] did not account for variation within the dataset (Table 2.3).

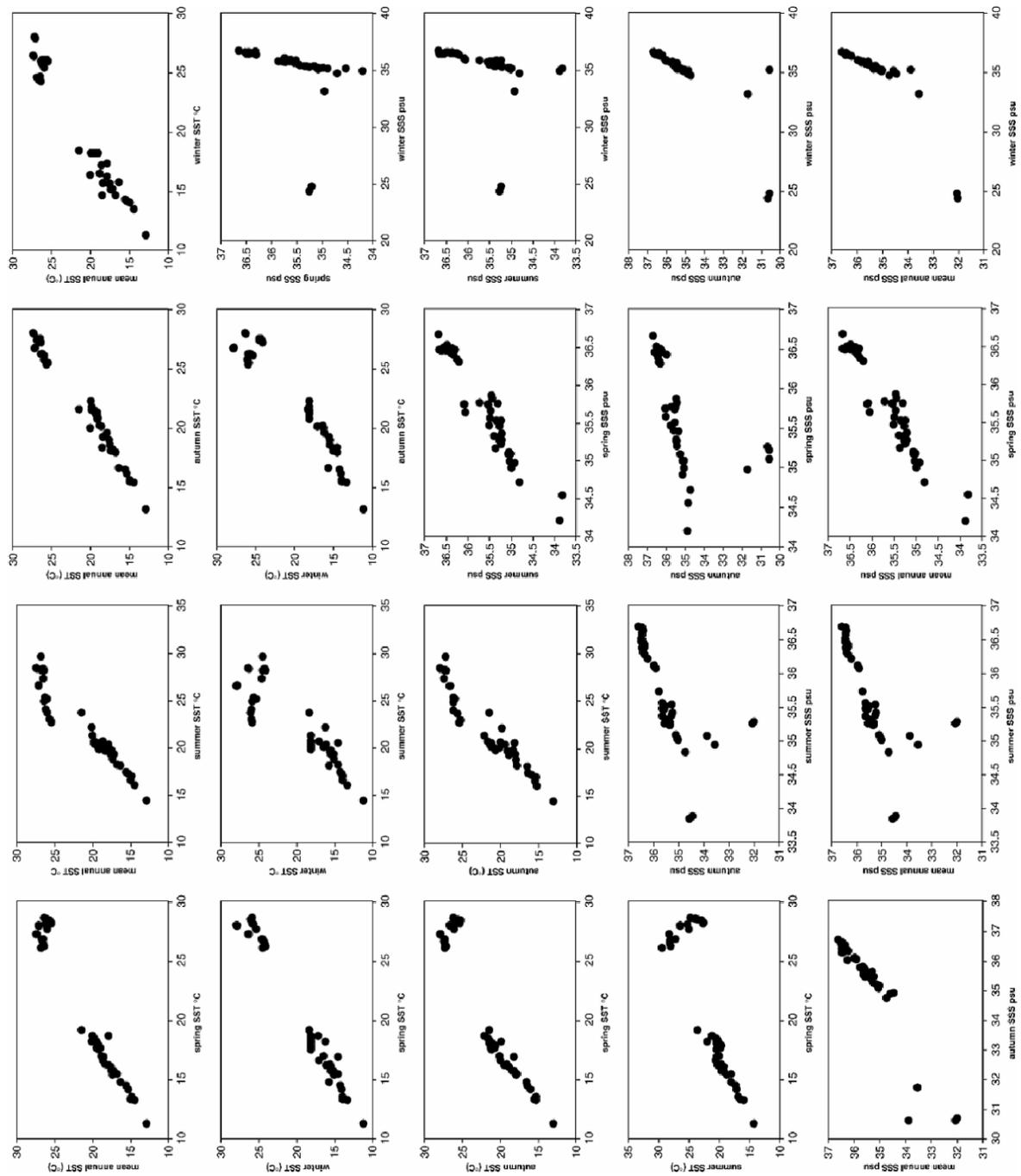


Figure 2.2. Draftman's plots of the seasonal variables of SST and SSS

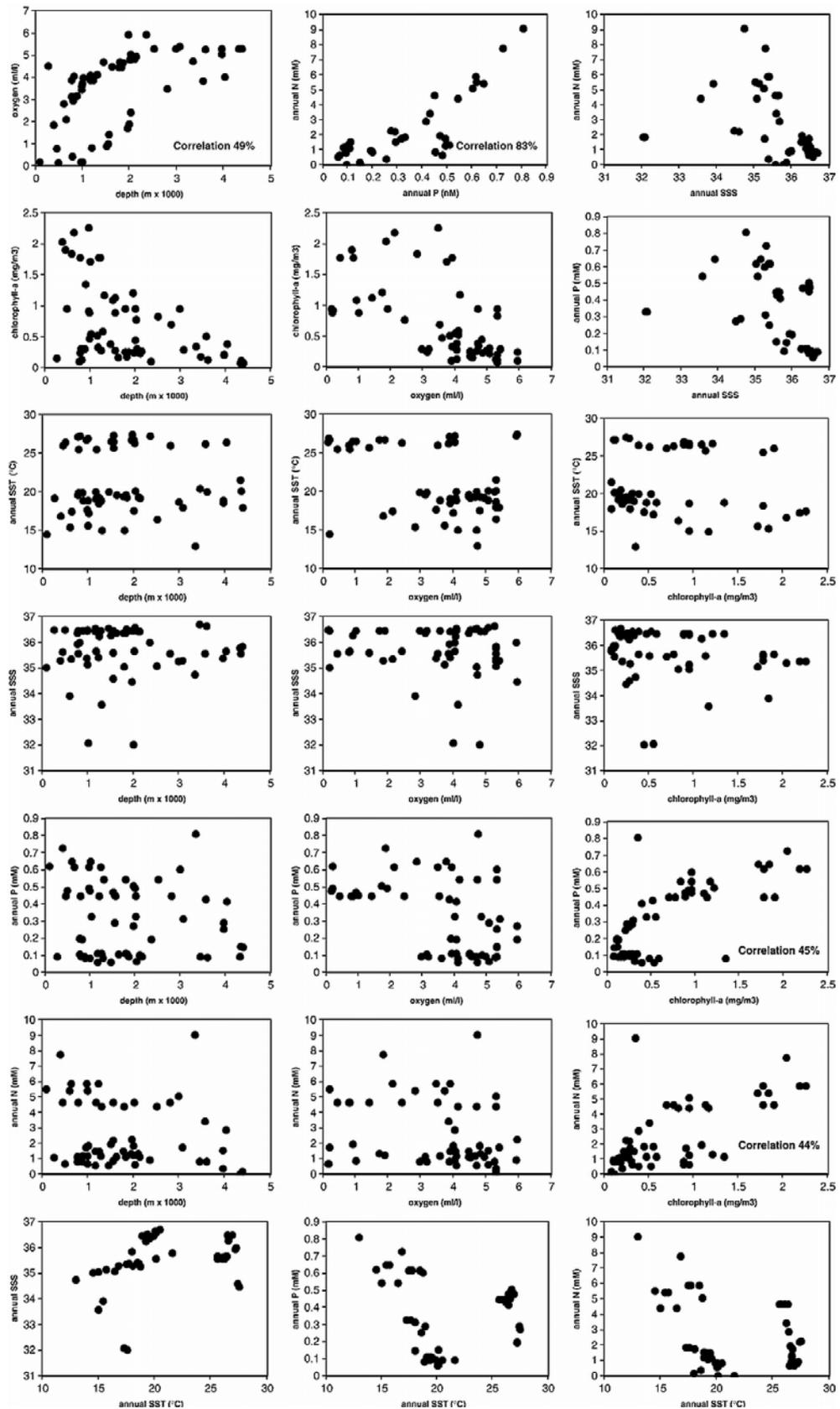
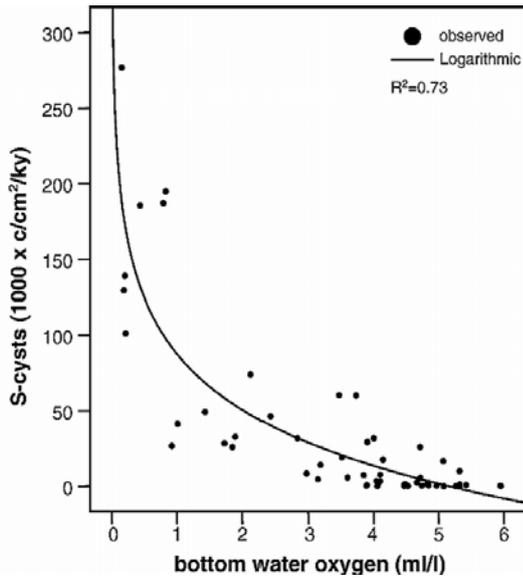
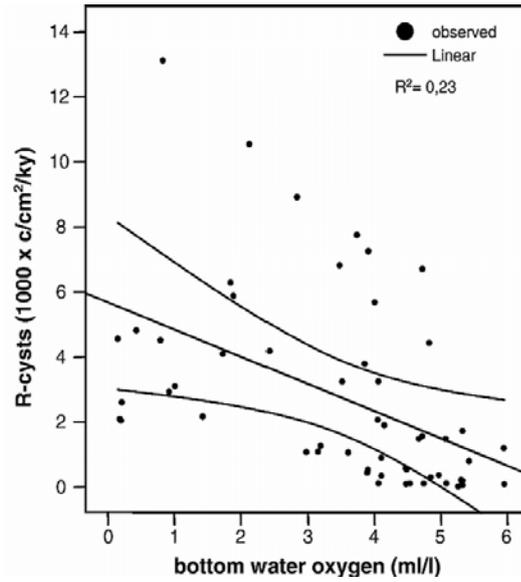


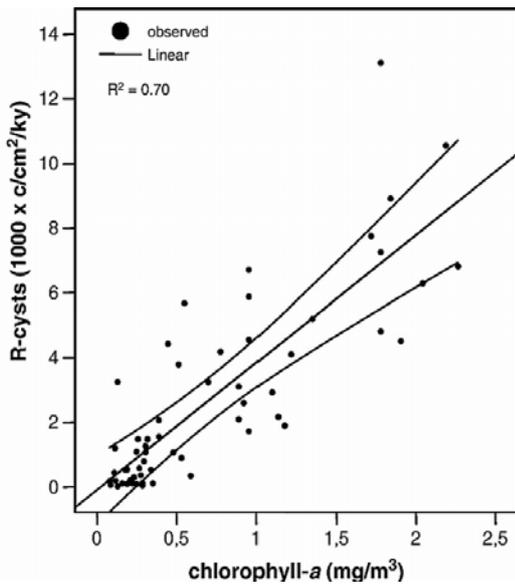
Figure 2.3. Draftman's plot of the analysed variables



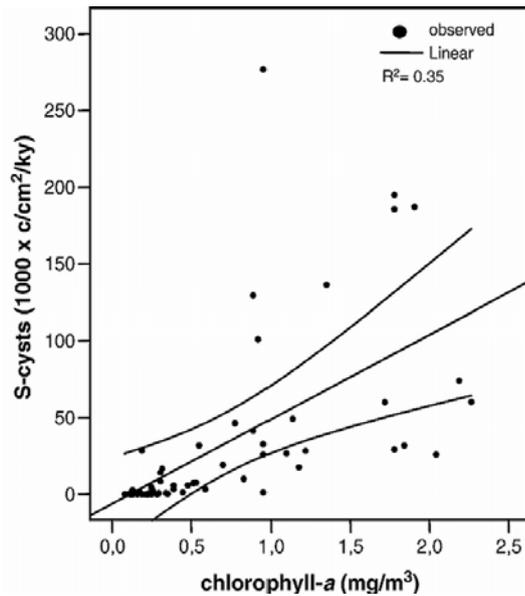
**Figure 2.4.** Relationship between accumulation rates of S-cysts and bottom water oxygen.



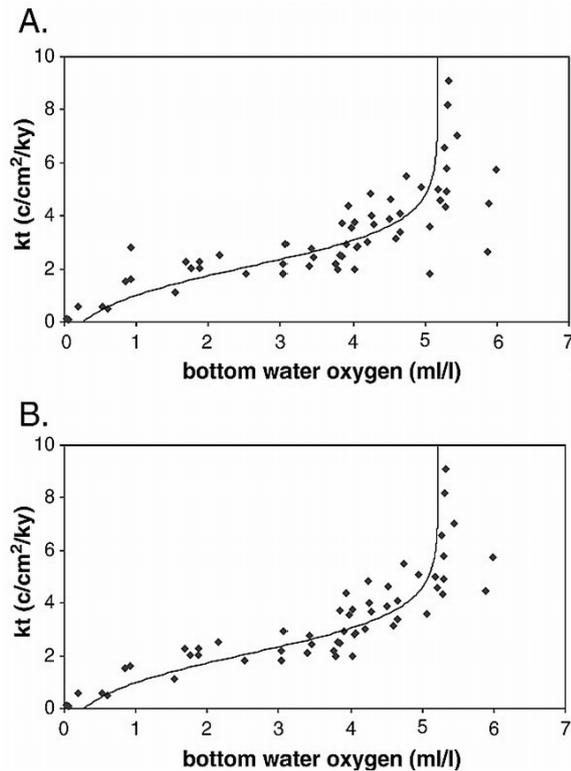
**Figure 2.5.** Relationship between accumulation rates of R-cysts and bottom water oxygen. Estimated linear relationship with 99.9% confidence limits of mean.



**Figure 2.6.** Relationship between accumulation rates of R-cysts and mean annual upper water chlorophyll a concentrations. Estimated linear relationship with 99.9% confidence limits of mean.



**Figure 2.7.** Relationship between accumulation rates of S-cysts and mean annual upper water chlorophyll a concentrations. Estimated linear relationship with 99.9% confidence limit of mean.



**Figure 2.8.** Relationship between the degradation expressed of S-cysts by  $kt$  and bottom water [O<sub>2</sub>]. (A) with outliers, (B) without outliers.

## 2.4. Discussion

Our results document marked difference in relation ship of accumulation rates of R-cysts and S-cysts to environmental gradients in upper water masses and bottom waters. The final recovery of dinocysts depends on numerous factors such as initial dinocyst production, degradation within the water column and sediment as result of bacterial activity and chemical processes, and lateral translocation during downward transport through the water column or post-depositional due to sediment winnowing. The following chapters discuss how these processes are related to our results.

### 2.4.1. Cyst production

The initiation of dinoflagellate sexuality and, as a result, cyst production is influenced by environmental conditions in surface waters such as nutrient availability, temperature, irradiance, turbulence and by endogenic encystment rhythms. (e.g., PFIESTER & ANDERSON, 1987). Although salinity is an important parameter influencing the geographic distribution of dinoflagellates, it is not known to trigger or influence their sexuality and dinocyst production. Laboratory experiments show that cyst production can often be induced when phototrophic dinoflagellates are grown under nitrogen or phosphate limitation and when cultures of heterotrophic dinoflagellates are exposed to food limitation (e.g., ANDERSON & LINDQUIST, 1985; ISHIKAWA & TANIGUCHI, 1996; MONTRESOR *et al.*, 1998; SGROSSO *et al.*, 2001; OLLI & ANDERSON, 2002). However, studies in

natural environments show that maximal cyst production occurs during or just after dinoflagellate cyst blooms, when nutrients in the water column are not limiting (ISHIKAWA & TANIGUCHI, 1996; MONTRESOR *et al.*, 1998; KREMP & HEISKANEN, 1999; GODHE *et al.*, 2001). Results of a long-term sediment trap study from just outside the upwelling region off NW-Africa covering a time interval of 5 years show that dinocyst export production of phototrophic dinoflagellates increases when more nutrients are available in the upper water column. Thereby, dinocyst production of some heterotrophic dinoflagellates is positively related to the export production of diatoms. In turn, export production of diatoms, the main food source of heterotrophic dinoflagellates, follows nutrient availability in upper waters (SUSEK *et al.*, 2005). As a possible explanation for this paradox it is suggested that at maximal vegetative growth, nutrient depletion can occur within individual cells or their microhabitat and as such triggering enhanced sexuality. The amount of gametes produced is therefore related to the amount of motile cells but individual specimens are triggered to produce gametes by nutrient or food depletion. Nevertheless, independent of the question if this hypothesis is true or not, in natural environments, for both groups of dinocysts (R-cysts and S-cysts) increased production is related to enhanced production of motile cells, which in turn is observed when nutrient, trace element or food conditions are favourable.

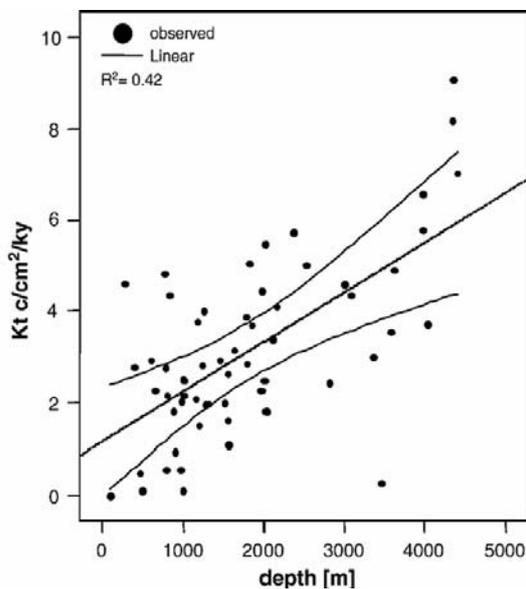
**Table 2.4.** Regression table of the factors compared. Dependent variables: S-cyst ( $1000 \times \text{cysts cm}^{-2} \text{ kyr}^{-1}$ ), R-cyst ( $1000 \times \text{cysts cm}^{-2} \text{ kyr}^{-1}$ ), *kt* ( $\text{cysts cm}^{-2} \text{ kyr}^{-1}$ ).

Regression variables	Model	R	R <sup>2</sup>	df <sub>regr</sub>	df <sub>res</sub>	F-value
S-cysts – O <sub>2</sub>	logarithmic	0.85	0.73	1	55	145.53
S-cysts – chlorophyll <i>a</i>	linear	0.59	0.35	1	57	30.36
S-cysts – SST	linear	0.26	0.07	1	58	4.35
S-cysts – SSS	linear	0.04	0.002	1	57	0.11
S-cysts – PO <sub>4</sub>	linear	0.37	0.13	1	58	9
S-cysts – NO <sub>3</sub>	linear	0.23	0.05	1	58	3.14
R-cysts – O <sub>2</sub>	linear	0.48	0.23	1	54	16.17
R-cysts – chlorophyll <i>a</i>	linear	0.84	0.7	1	56	128.98
R-cysts – SST	linear	0.0048	0.00002	1	57	0.0013
R-cysts – SSS	linear	0.31	0.1	1	56	6.13
R-cysts – PO <sub>4</sub>	linear	0.62	0.38	1	57	35.58
R-cysts – NO <sub>3</sub>	linear	0.56	0.31	1	57	25.42
<i>kt</i> – O <sub>2</sub>	logistic	0.92	0.85	3	54	55.8
<i>kt</i> – water depth	linear	0.64	0.42	1	58	41.26
<i>kt</i> – sedimentation rate	linear	0.75	0.56	1	58	74.96

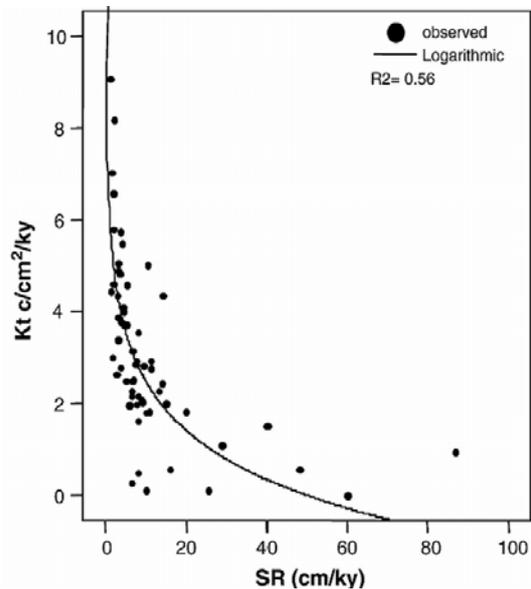
Independent variables: O<sub>2</sub> (ml l<sup>-1</sup>), chlorophyll *a* (mg m<sup>-3</sup>), SST (°C), SSS (psu), PO<sub>4</sub> (mM), NO<sub>3</sub> (mM), water depth (m), and sedimentation rate (cm kyr<sup>-1</sup>). df<sub>regr</sub> = degrees of freedom for regression, df<sub>res</sub> = degrees of freedom of residuals. F-value is the measurement of the distance between individual distributions. As F goes up, *p*-value goes down (i.e., more confidence in the difference between two means).

Numerous studies show that dinoflagellates have complex ecologies with the cyst production of every species dependent on biotic and a-biotic factors (e.g., MARRET & ZONNEVELD, 2003; ROCHON & MARRET, 2004; HARLAND *et al.*, 2004). Within this study we have grouped cysts with different ecologies. By doing so, we expect that environmental factors that influence the cyst production, transport and preservation of all species in the group in a similar way, will have a strong relationship with the total dinocyst accumulation of that group. On the

contrary, a damped effect is expected for factors that influence only part of the species within the group, or influence individual species of the group in different ways. We have correlated the abiotic environmental factors; bottom water [O<sub>2</sub>], water depth, mean annual chlorophyll *a*, SST, SSS, nitrate and phosphate concentrations, with total accumulation rates of R-cysts and S-cysts. The multivariate ordination analysis shows that mean annual SST, SSS, nitrate and phosphate concentrations do not show a significant relationship to the variation in accumulation rates of R-cysts or S-cysts (Fig. 2.11, Table 2.4). We therefore suggest that they had differential effects on the production of individual cyst species within the groups. Only the factors bottom water [O<sub>2</sub>], chlorophyll *a* and water depth showed a significant relationship with accumulation rates of R-cysts and S-cysts. With exception of chlorophyll *a* these factors can not directly influence dinocyst production in upper water masses.



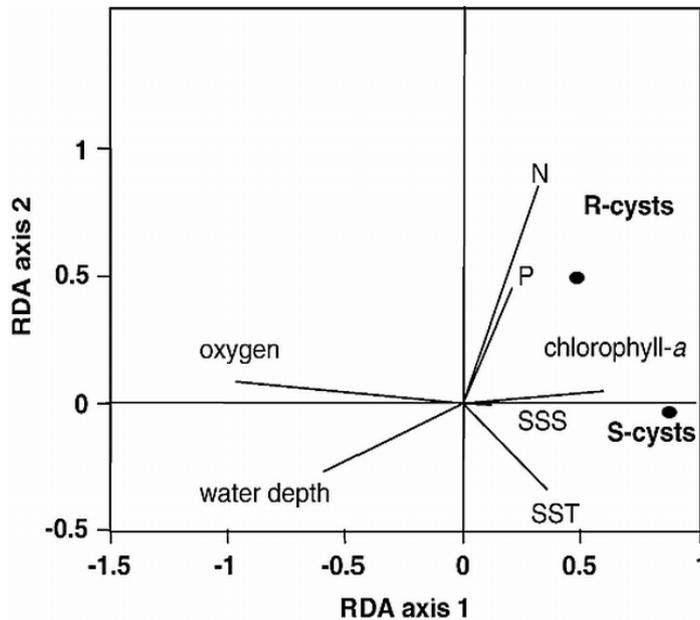
**Figure 2.9.** Relationship between the degradation of S-cysts expressed by *kt* and water depth. Estimated linear relationship with 99.9% confidence limits of mean.



**Figure 2.10.** Relationship between the degradation of S-cysts expressed by *kt* and sedimentation rate.

To date, satellite measurements routinely provide global chlorophyll *a* biomass. Since the remote sensing determination of phytoplankton carbon has been proven to be elusive, net primary production estimates use chlorophyll *a* as an index of phytoplankton biomass (e.g., CAMPBELL *et al.*, 2002). Although the above mentioned method has constraints and it is assumed that about 30% of daily water column photosynthesis is missed by satellite based estimates (e.g., BEHRENFELD *et al.*, 2005; MOUW & YODER, 2005), we can safely assume that mean annual chlorophyll *a* is a qualitative reflection of mean annual net primary production. Assuming that more cysts of heterotrophic dinoflagellates might be produced when more food is available we could expect to find a positive causal relationship between mean annual chlorophyll *a* concentration and S-cyst accumulation rates. However, although a trend is visible the relationship is weak ( $R^2 = 0.35$ , F-

value = 30.36, df= 57; Fig. 2.7, Table 2.4). A possible explanation for could be that production of S-cysts relates to the presence of individual phytoplankton prey species rather than to the phytoplankton community as a whole.



**Figure 2.11.** RDA diagram of R-cyst and S-cyst accumulation rates with environmental variables.

The positive relationship between R-cysts and upper water mean annual chlorophyll *a* concentrations suggests that the accumulation of R-cysts is somehow related to the total phytoplankton production in upper waters (Fig. 2.5). We do not think this relationship to be causal but assume that chlorophyll *a* and R-cyst accumulation rates react on similar factors, although we can not exclude a causal relationship completely, given the fact that many, if not all, dinoflagellates that are capable of photosynthesis, are capable of heterotrophy (SCHNEPF & ELBRÄCHTER, 1999; SMAYDA & REYNOLDS, 2003 and references therein). However, within our database we find one exception at site GeoB 3607. At this site chlorophyll *a* values are a factor 100 higher than at the other studied sites whereas accumulation rates of R-cysts have intermediate values. This sample is located at the edge of an active upwelling cell along the Namibian coast. In contrast to all other studied sites, considerable mixing of waters takes place in the upper water column at this site. Field and laboratory studies show that dinoflagellate growth and cyst production can be strongly (negatively) influenced by turbulence intensity and the duration of turbulent phases (e.g., THOMAS *et al.*, 1995; GIBSON & THOMAS, 1995; GIBSON, 2000; SMAYDA & REYNOLDS, 2001). They appear to be much more sensible for turbulence than other groups of primary producers such as diatoms. In high productivity areas such as upwelling regions it is often observed that dinoflagellates become abundant in the phytoplankton at times of upwelling relaxation when the water column becomes more stratified or in the more stratified upwelling filaments (e.g., SHANNON & PILLAR, 1986; MITCHELL-INNES & WALKER, 1991; PITCHER *et al.*,

1991; VELDHUIS *et al.*, 1997; SMAYDA & REYNOLDS, 2003). At site GeoB 3607 turbulence might therefore be the limiting factor for cyst production.

#### 2.4.2. Transport

Apart from reflecting differences in initial production and preservation processes at the sediment-water interface, accumulation rates can be affected by processes of winnowing or focusing. Winnowing or focusing result in an underestimation or overestimation of the accumulation rates compared to the real influx of cysts into the sediments. Regarding the fact that the size and cyst-outlines of the grouped species are comparable indicates that the processes of winnowing/focusing will have a similar effect on both groups. The marked differences in relationship of R- and S-cysts with upper water and bottom water conditions can, therefore, not be the result of winnowing or focusing.

Several authors have suggested that lateral transportation of cysts during downward migration within the water column or after deposition might form an important factor affecting the cyst distribution (e.g., DALE & DALE, 1992; HARLAND & PUDSEY, 1999). However, except for mass transport (e.g., turbidites) studies on the distribution pattern of dinocysts in modern, undisturbed sediments as well as sediment trap studies document small scale transport only (e.g., ZONNEVELD & BRUMMER, 2000; MARRET & ZONNEVELD, 2003; SUSEK *et al.*, 2005). As far as we know no evidence is found that species selective cyst transport occurs in natural environments. We therefore assume that transport of dinocysts does not cause the observed differences in relationship between R-cysts and S-cysts and bottom water [O<sub>2</sub>], water depth and upper water chlorophyll *a*.

#### 2.4.3. Preservation

We observe a significant exponential relationship between S-cysts accumulation rates and bottom water [O<sub>2</sub>] (Fig. 2.4, Table 2.4). As discussed above, this relationship can not be explained by differential production related to upper water conditions and selective transport. Our results are consistent to earlier studies that conclude S-cysts to be extremely sensitive for degradation based on similar relationships and comparison with chemical data (ZONNEVELD & BRUMMER, 2000; ZONNEVELD *et al.*, 2001; VERSTEEGH & ZONNEVELD, 2002; Hopkins & MCCARTHY, 2002; REICHART & BRINKHUIS, 2003; **Chapter 3**) Again consistent with earlier studies we find no clear relationship between R-cysts accumulation rates and bottom water [O<sub>2</sub>] subscribing the assumption that they are minimally affected by aerobic degradation (Fig. 2.5, Table 2.4). We assume that the difference in relationship between R-cysts and S-cysts with bottom water [O<sub>2</sub>] can be subscribed to a fundamental difference in the chemistry of the cyst walls of both groups. Such a difference has previously been evidenced by differences in fluorescence, vulnerability to staining or oxidative laboratory treatments by various authors (e.g., DALE, 1976; MARRET, 1993; ELBRÄCHTER, 1994 and references therein). To date, chemical data of dinoflagellate cyst walls are limited but indicate that they are composed of complex biomolecules (KOKINOS *et al.*, 1998; VERSTEEGH & BLOKKER, 2004; DE LEEUW *et al.*, 2006). Nuclear magnetic resonance (NMR) analysis of the Fossilizable organic inner-wall of *Scrippsiella* sp. (a peridinioid) cysts that are included into the species *Brigantedinium* spp. By palynologists, suggests that the macromolecules contain a

substantial aliphatic component (HEMSLEY *et al.*, 1994). A comparable aliphatic component is absent in the dinoflagellate cyst walls of *Lingulodinium polyedrum* (gonyaulacoid) in contrast to the presence of condensed and predominantly aromatic components (KOKINOS *et al.*, 1998). Furthermore, laboratory experiments based on dinocyst cultures and sediments suggest that gonyaulacoid cyst walls consists to a high proportion of carbon and ether-linked macromolecular building blocks, whereas the macromolecular building blocks of peridinioid cyst walls are much more ester linked (for an overview see VERSTEEGH & BLOKKER, 2004). VERSTEEGH & BLOKKER (2004) suggested that there are two variables influencing cyst wall composition, (i) the proportion of aliphatic versus aromatic moieties and (ii) the proportion of ether- and carbon-bonds versus ester-bonds.

Sediment trap studies have so far revealed no evidence that organic-walled dinoflagellate cysts are prone to degradation during their transport within the water column (ZONNEVELD & BRUMMER, 2000; SUSEK *et al.*, 2005). This might be the result of the fact that cyst accumulation is thought to be a rather fast process resulting in a relatively short reaction time. Within this study we observe a weak negative relationship between S-cysts accumulation rates and water depth that might suggest a degradation of these cysts within the water column. However, water depth co-varies with bottom water [O<sub>2</sub>] and after correction for co-variance, no significant relationship can be found (Table 2.3).

#### *2.4.4. Cyst accumulation rates as a tool to estimate past net primary productivity*

One of the aims of this study is to discuss if we can use accumulation rates of R-cysts to estimate past net primary productivity. We observe a significant positive relationship between accumulation rates of R-cysts and chlorophyll *a*, according to equation no. 2 (Fig. 2.6, Table 2.4). Given the discussion above we can assume that this equation has the potential to be used as a past productivity proxy. We realize that this suggestion will cause controversy within the palynological community given the discussions about the attempts to digitalize past environmental conditions using dinoflagellate cyst associations (e.g., DALE *et al.*, 2002; DE VERNAL *et al.*, 2005). However, we suggest this relationship to be tested in paleo-studies to obtain insight into potentials and limitations. We already pointed out that this relationship cannot be used in environments that are characterized by strong or long-lasting turbulence or in regions where environmental factors influence dinoflagellate growth and dinocyst production differently compared with the production of other phytoplankton groups. Nevertheless, the empirical relationship appears to be clear in a large variety of environments.

#### *2.4.5. Degradation rates of dinocysts as a tool to estimate past deep-ocean oxygen*

The calculation of the degradation index (expressed by *kt*) of S-cyst assumes that the initial production is related to the production of R-cysts in all studied environments. This is based on the relationship we found in various regions, in sediment trap samples and samples from anoxic environments, where selective degradation can be expected to be minimal and where cyst accumulation rates of both groups can be assumed to reflect changes in their initial production

(e.g., REICHART & BRINKHUIS, 2003). As far as we know, there is no evidence from the literature that our assumption does not hold. Furthermore, if our assumption is wrong we would expect to find a random signal between  $kt$  and environmental gradients (such as bottom water [O<sub>2</sub>]; Fig. 2.8).

A logical question arises; how causal is the relationship between  $kt$  and bottom water [O<sub>2</sub>]. As explained in the Introduction part, individual OM components typically show a first order decay (e.g., MIDDELBURG, 1989; HARTNETT *et al.*, 1998; HEDGES *et al.*, 1999). The cyst wall degradation can be considered to depend on the degradability of its biomolecules (expressed by their degradation constants  $k$ ) and the oxygen exposure time ( $t$ ). Other factors that are known to influence the rate of aerobic decay of organic matter such as bioturbation and sedimentation rates, oxygen concentration and water depth, are considered to actually modulate the effects of the oxygen exposure time (e.g., HARTNETT *et al.*, 1998; SUN *et al.*, 2002; KEIL *et al.*, 2004). A decrease in rate of aerobic decay of organic matter with reaction time has often been observed and several mechanisms have been proposed to explain this phenomenon such as organic recalcitrance and biotic exclusion (e.g., TEGELAAR *et al.*, 1989; DERENNE & LARGEAU, 2001; MAYER, 2004). For instance, complex biomolecules vary in their ease to disassembly, at monomer, polymer or supra-molecular scales of organization. In the case of dinocysts it is therefore possible that for S-cysts the degradation constant “ $k$ ” is not completely constant with the most labile species degrading first, therefore increasing the relative amount of the less sensitive species through time. Through biotic exclusion, some organisms, or their digestive agents, are excluded or inhibited from access to organic matter, for instance through the accumulation of harmful metabolites or by transporting material to anoxic environments through bioturbation processes. Indeed  $kt$  shows a decreasing relationship to increasing sedimentation rates (Fig. 2.10) which suggests that the degradation processes might take place in the upper sediments or at the sediment-water interface.

If dinocyst degradation is a first-order process there should be a constant or decreasing relationship between  $kt$  and all the factors reflecting oxygen exposure time. The relationship between  $kt$  and bottom water [O<sub>2</sub>] is however more complex, suggesting a high-order degradation process. At low bottom water [O<sub>2</sub>] there is a strong increase in the degradation with increasing bottom water [O<sub>2</sub>] that becomes less intense at intermediate bottom water [O<sub>2</sub>]. Above a bottom water [O<sub>2</sub>] at 4 ml l<sup>-1</sup> there is an exponential increase. This pattern can be explained when cysts are being degraded though a process with oxygen concentration being the limiting factor inhibiting the growth rate of degrading organisms (JORGE & LIVINGSTON, 1999; GUERRA-GARCÍA and GARCÍA-GÓMEZ, 2005). With the degrading organisms increasing in numbers with increasing oxygen concentration the rate of degradation will also increase. However, at a certain threshold oxygen concentration the population of the degrader increases to a point where all S-cysts are being consumed and  $kt$ -values increase exponentially to infinity.

There are several methods to estimate past deep-ocean ventilation based on the sediment structure and the (bio-)chemical content of sediments including, numerical models, as well as the chemical and isotopic composition of microfossils (e.g., FRANCOIS *et al.*, 1997; TOGGWEILER, 1999; NINNEMANN & CHARLES, 2002; MATEAR & HIRST, 2003; MCMANUS *et al.*, 2004; IVANOCHKO & PEDERSEN, 2004). However, the estimation of past bottom oxygen concentrations is still problematic. The relationship documented here might form the basis of a new method that

makes quantitative estimations of past deep-ocean oxygen concentrations possible. First applications of this method in sediments deposited during the last deglaciation, last 140 kyr and between 3.2 and 2.5 Ma years BP imply ventilation changes of the deep Equatorial Atlantic, South Atlantic and Southern Ocean (Atlantic Sector; VERSTEEGH & ZONNEVELD, 2002; **Chapter 3 & 5**). Further studies are required to determine the accuracy and restrictions of the method.

#### 2.4.6. General remarks

Our results are in opposition to the strong traditional belief within the dinoflagellate research community, that cyst forming dinoflagellates with a heterotrophic life strategy prefer high productivity regions characterized by eutrophic conditions, whereas phototrophic cyst-forming dinoflagellates prefer low productivity, oligotrophic environments. This belief finds its basis in the results of the first pioneering studies on the geographic distribution of dinoflagellate cysts in modern environments carried out in the 60's and 70's of the last century. A strong dominance of cysts of photosynthetic species in the central oceanic basins was documented whereas the cyst associations of most coastal sediments appeared to be dominated by cyst of heterotrophic species (see overviews in WALL *et al.*, 1977; HARLAND, 1983 and references therein). However, the lack of good dating methods prevented the calculation of accumulation rates in these studies. The recent compilation of large worldwide datasets show, that there are many sites from “low productivity, oligotrophic” regions that are dominated by heterotrophic taxa and vice versa (DE VERNAL *et al.*, 2001; MARRET & ZONNEVELD, 2003). Furthermore, several photosynthetic R-cyst species have their highest abundances in regions where eutrophic conditions prevail. For instance *Dalella chathamensis* can dominate assemblages in sediments of the eutrophic Southern Ocean frontal zones (MARRET & ZONNEVELD, 2003). *Nematosphaeropsis labyrinthus*, *Pentapharsodinium dalei* and *Pyxidinosia reticulata* can dominate cyst associations in regions characterized by eutrophic upper water conditions whereas the distribution of *Impagidinium pallidum*, is even restricted to these environments (MARRET & ZONNEVELD, 2003). Several heterotrophic dinoflagellates have their highest abundances in “oligotrophic regions”. For instance *Polykrikos* species (such as *Polykrikos kofoidii* and *Polykrikos schwarzii*) and *Votadinium spinosum* have high or even their highest relative abundances in the oligotrophic part of the China Sea. These datasets indicate therefore, that the environmental “preferences” of cyst forming dinoflagellate species should not be generalized but have to be considered on an aut-ecological level and that the initial concept is due for revision.

Also in recent years many studies document that the cyst association of high productivity areas is dominated by heterotrophic species and conclude that dominance of heterotrophic species are characteristic for these regions (e.g., HAMEL *et al.*, 2002; RADI & DE VERNAL, 2004). These studies do, however, not consider the possible effect of selective preservation on the relative abundances of cysts and do not correct for differences in sedimentation rates in the studied region. Hence, although the conclusions that eutrophic regions are often characterized by a dinoflagellate association dominated by dinocysts of heterotrophic species while oligotrophic regions are characterized by a dominance of dinocysts of photosynthetic species are valid, the conclusion that cysts of both groups are produced in higher amounts in the respective regions can not be drawn.

These studies give no support to the idea that heterotrophic dinoflagellates or phototrophic species “prefer” eutrophic or oligotrophic regions respectively. Our results indicate that cyst production has to be considered at an aut-ecologic scale and that only in case of excellent preservation (as can occur in regions characterized by oxygen minimum zones) cyst accumulation rates of S-cysts reflect their export production. It can be expected that in these extreme conditions their accumulation rates co-vary with changes in total export productivity (REICHART & BRINKHUIS, 2003). Consequently, the results of this study clearly demonstrate that the traditional view about the ecology of cyst forming dinoflagellates has to be evaluated.

## 2.5. Conclusions

Accumulation rates of dinoflagellate cyst species known to be resistant against (post-depositional) aerobic decay show a significant positive relationship with upper water chlorophyll *a* concentrations (equation no. 2). No relationship with bottom water oxygen concentrations, annual sea-surface temperature, salinity, nitrate and phosphate concentrations can be observed. This is in contrast to the general opinion that species producing these cysts are being produced in higher amounts in oligotrophic environments. The reason for this seemingly paradox is that previous studies considered relative abundances of cysts in sediments, did not correct of differential sedimentation rates or did not consider the possible effect of species selective preservation. Our study suggests that R-cyst accumulation rates might be a useful proxy to estimate net primary production in the past. Exception is found in regions with environments that are characterized by strong or long-lasting turbulence or in case other environmental factors influence dinoflagellate growth and cyst production differently from production of other phytoplankton groups.

Accumulation rates of dinocysts known to be sensitive for aerobic degradation show an exponential decrease in relation to bottom water oxygen concentration (equation no. 1; Fig. 2.4). Only a weak correlation can be found with upper water chlorophyll *a* concentrations (Fig. 2.5). This suggests that aerobic degradations might strongly overprint the initial production signal. Only in case of excellent preservation (as can occur in regions characterized by oxygen minimum zones) cyst accumulation rates of S-cysts reflect their export production.

The observed relationships between *kt*, water depth and sedimentation rates suggest that processes of organic recalcitrance and biotic exclusion might take place in the upper sediments rather than within the water column.

The positive relationship between degradation rate of S-cysts and bottom water [O<sub>2</sub>] (equation no. 4; Fig. 2.8) suggests that S-cysts are being degraded according to a higher order decay process. This relationship forms the basis for a proxy that can be used to estimate past bottom water oxygen concentration.

## 2.6. References

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## CHAPTER 3

# Decoupling productivity from organic matter preservation using selective degradation of organic-walled dinoflagellate cysts

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### **Abstract**

A high resolution organic-walled dinoflagellate cyst record from a hemipelagic core site off northwest Africa documents distinct periods of post-depositional organic matter mineralization punctuating the last glacial-interglacial climate transition. Two 'burn-down' events, imprinted on the fossil record of species with reduced preservation capacities in oxic milieus, have produced signals that are unrelated to changes in export productivity. Instead they reflect diagenetic processes related to post-burial degradation of labile organic matter compounds during non-steady state conditions. This is evident from comparison of the degradation resistant and sensitive fraction of the dinoflagellate cyst assemblage and explains the ambiguous productivity patterns reconstructed from TOC and the Ba/Al ratio. Indications for mobilization and (re-)precipitation in the solid-phase element distributions of Mn, Fe, and U point to an adjustment of the pore water equilibrium to variable redox-conditions. The incidence of changing preservation quality at times of deglacial climate upheaval suggest a causal connection to variable particle flux and/or bottom water oxygen supply during reorganization in North Atlantic deep water circulation. Important with respect to diagenetic overprints our results draw attention to the potential of dinoflagellate cysts as sensitive recorders of the transformation of geological archives.

KEYWORDS: Dinoflagellate cysts, preservation, productivity, diagenesis, ocean ventilation

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*Appendix A2:* Dinocyst data of core GeoB 4216, calculated initial S-cyst abundance and degradation index (*kt*).

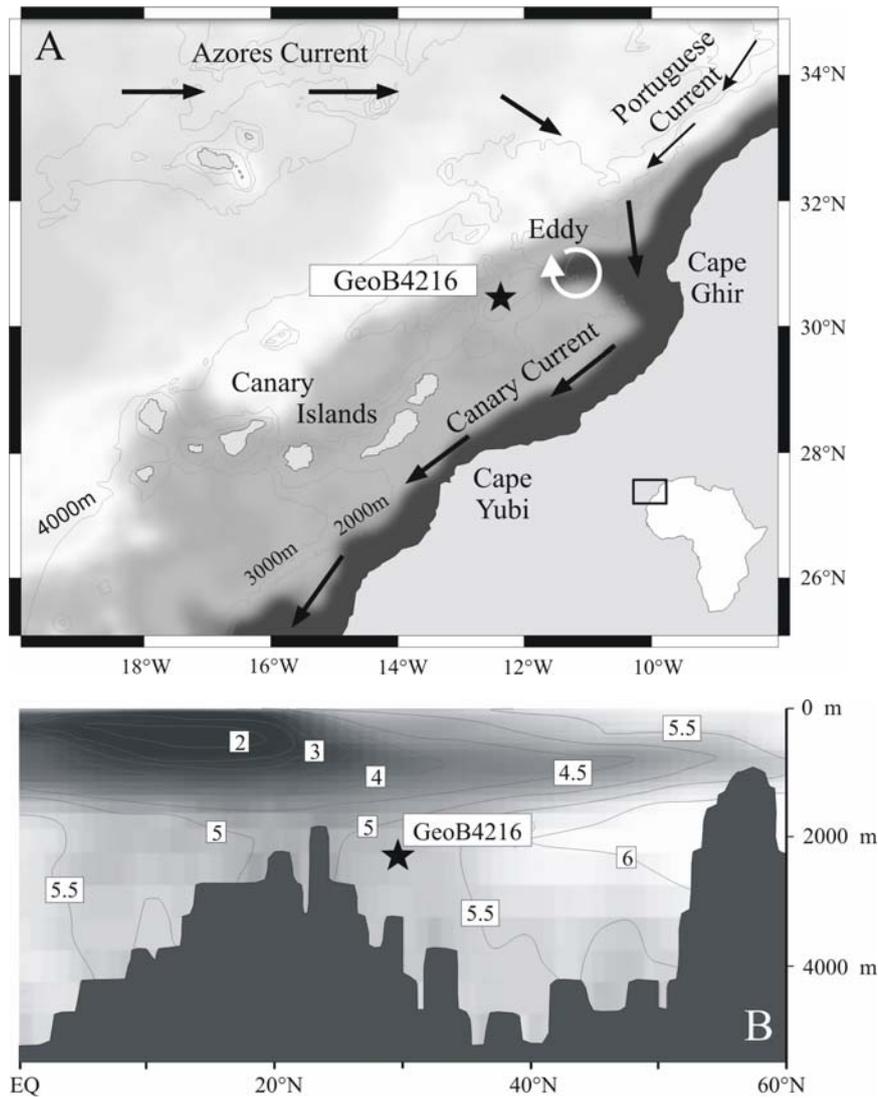
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### **3.1. Introduction**

During the last decades many studies on ocean paleoproductivity were based on the assumption that sedimentary organic matter (OM) is well preserved since deposition in marine sediments or they focused on the refractory component to provide constraints on the “diagenetic status” of proxy records. Along with present-day efforts evidence is growing that several markers traditionally used to estimate past states of marine export production suffer from post-depositional degradation and diagenetic alteration (e.g., LEHMANN *et al.*, 2002; SINNINGHE DAMSTE *et al.*, 2002; MOODLEY *et al.*, 2005). Unfortunately, we critically depend on unbiased reconstructions of marine export production to fully understand atmospheric CO<sub>2</sub> regulation, nutrient cycling, and deep-ocean (carbonate) chemistry on climatically relevant timescales (e.g., BROECKER and HENDERSON, 1998; ARCHER, 2003). Because this situation demands intensified research, the separation of productivity from OM preservation became a major task of world-wide operating research programs such as IMAGES, JGOFS, or WCRP.

VERSTEEGH & ZONNEVELD (2002) proposed a method to isolate effects of oxygen exposure on sedimentary OM preservation. Their approach bases on observations across oxidation fronts in sapropelic and turbiditic deposits which reveal that several species of organic walled dinoflagellate cysts (dinocysts) are rapidly degraded under oxic conditions whereas others are extremely resistant and persist (ZONNEVELD *et al.*, 1997; 2001). They used the species-specific preservation capacity to estimate the influence of degradation on different OM compounds and reconstructed the productivity history of a southeast Atlantic upwelling site for the past 145,000 years. Besides the large difference in degradability of resistant and sensitive cysts, further advantages are due to their similar behaviour to other factors, such as transport. Moreover, they are abundant in practically all marine environments since the Early Jurassic, and thus potentially widely applicable. However, whether the idea to use selective degradation of dinocysts provides an accurate way to reconstruct productivity has still to be assessed. In particular, studies must account for various productivity proxies and include information on geochemical processes that accompany non-steady state diagenesis.

The aim of the present study is to test whether selective dinocyst preservation enables to separate productivity from OM preservation. Therefore a high resolution dinocyst record is established for the last glacial-interglacial sediment section of an upwelling influenced core taken off Morocco (NW Africa). A former study carried out by KASTEN *et al.* (2003) reveals discrepancies between TOC and Ba based productivity reconstructions for this site. Upon applying the a priori classification in oxidation resistant and sensitive dinocysts, the productivity signals of both groups are compared to the TOC content and the Ba/Al ratios. According to the method described in VERSTEEGH & ZONNEVELD (2002) and **Chapter 2** a degradation indicator is calculated to assess the temporal variability of OM preservation. Beyond, solid phase element data of Mn, Fe and U provide information on the redox history of the investigated time period and support the characterization of geochemical conditions.



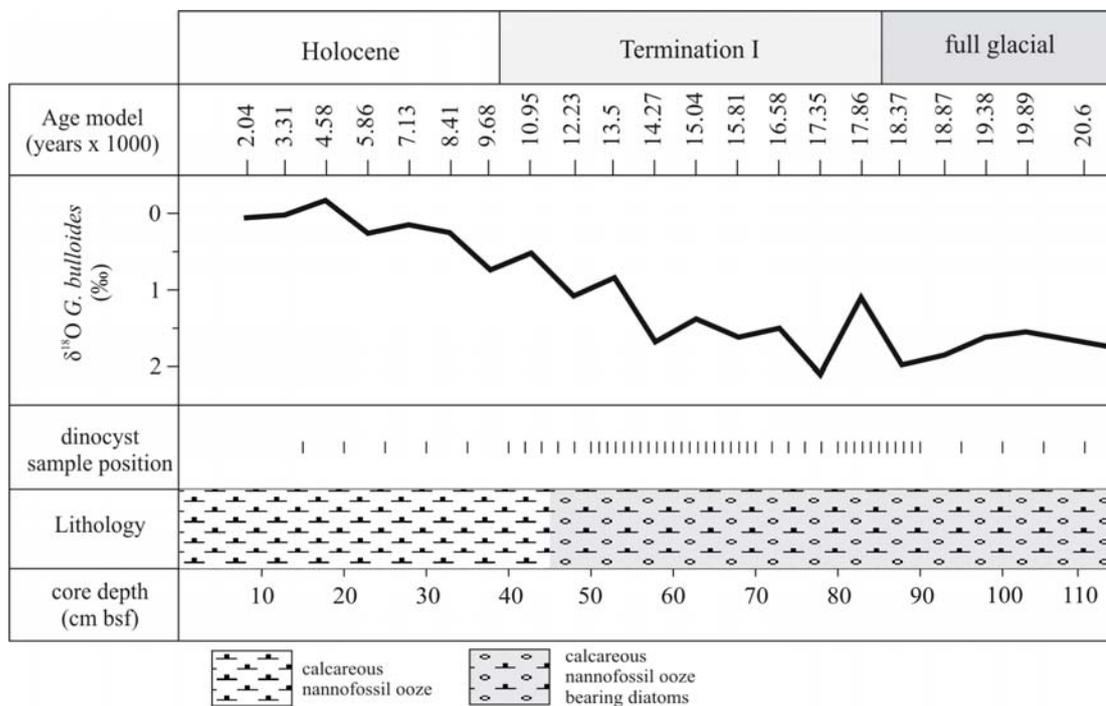
**Figure 3.1.** (A) Bathymetric map showing the investigation area and core location of GeoB 4216. Major surface currents are indicated by arrows. SeaWiFS-derived chlorophyll *a* concentrations averaged from year 1999 are shaded dark grey ( $> 1 \text{ mg m}^{-3}$ ), grey ( $0.25 - 1 \text{ mg m}^{-3}$ ) and light grey ( $< 0.25 \text{ mg m}^{-3}$ ). (B) Core location projected horizontally on a vertical ocean transect across the eastern North Atlantic at  $18.5^\circ\text{W}$ . Shading indicates  $\text{O}_2$  concentration ([www.ingrid.ldeo.columbia.edu/SOURCES/LEVITUS94](http://www.ingrid.ldeo.columbia.edu/SOURCES/LEVITUS94)).

### 3.2. Regional settings

Figure 3.1A depicts the principal surface water characteristics north of the Canary Islands off NW-Africa. The dominant surface water current is the Canary Current (CC), the easternmost branch of the Azores Current. The CC transports Subtropical Surface Water and North Atlantic Central Water southward (MITTELSTAEDT, 1991). During the last deglaciation, when major cooling events caused changes in North Atlantic surface water properties (e.g., RUDDIMAN & MCINTYRE, 1981; BARD *et al.*, 2000), the CC was possibly a vector of iceberg movement (Baas *et al.*, 1997) and experienced prominent cooling (KIM *et al.*, 2002). Today, the alongshore flow results in upwelling which is most intensive during summer and early fall, when the position of the

subtropical high pressure system strengthen the NE trades (NYKJÆR & VAN CAMP, 1994). Coastal Zone Color Scanner show highest chlorophyll *a* concentrations along the shelf, but the formation of filaments causes lateral advection of nutrient-rich waters off Cape Ghir (VAN CAMP *et al.*, 1991; HAGEN *et al.*, 1996). The filaments can reach far into the subtropical gyre region and their enhanced biological activity is documented by dinocysts (TARGARONA *et al.*, 1999), diatoms (NAVE *et al.*, 2001), and geochemical parameters (MEGGERS *et al.*, 2002). Sedimentation of terrigenous material is mainly due to dust transport of particles with high iron contents (TORRES-PADRÓN *et al.*, 2002). This input has implications for water column sedimentation processes (RATMEYER *et al.*, 1999) and accelerates phytoplankton growth in this region (DUCE & TINDALE, 1991).

Within the investigation area the principle water mass stratification corresponds to North Atlantic Central Water (NACW) between 100 – 600 m, Mediterranean Outflow Water (MOW) centred at about 1200 m and North Atlantic Deep Water (NADW) between 1700 – 3500 m (e.g., SIEDLER & ONKEN, 1996). Additionally, relatively fresh Antarctic Intermediate Water (AAIW) can be conveyed by a pole-ward undercurrent and intrudes this region between 600 and 1000 m (LLINÁS *et al.*, 2002). At present, all water masses are well oxygenated (Fig. 3.1B). At abyssal depth, below 3500 m, low oxygenated Antarctic Bottom Water (AABW) is supplied into the North Canary Basin. To the north this progression is bounded by the east Azores fracture zone scarps. This barrier possesses only two narrow passages and has been noted as an important feature for the control of glacial deep water circulation (MCCARTNEY *et al.*, 1991; SARNTHEIN *et al.*, 1994).



**Figure 3.2.** Lithological column of the analyzed core section (after WEFER *et al.*, 1997) and dinocyst sample positions.  $\delta^{18}\text{O}$  of the planktonic foraminifera *Globigerina bulloides* and age model are taken from FREUDENTHAL *et al.* (2002).

### 3.3. Material and methods

#### 3.3.1. Core site and description

Site GeoB 4216-1 (30°37.8'N; 12°23.7'W, 2324 m) is located in the path of major filament transport off Cape Ghir, Morocco (Fig. 3.1A) and was cored during R/V *Meteor* cruise M37/1 (WEFER *et al.*, 1997). At present, the fertile waters of Cape Ghir filaments only occasionally extend to this site and surface sediments reflect oligotrophic conditions (MEGGERS *et al.*, 2002). Bottom waters consist of well oxygenated NADW (Fig. 3.1B). We studied the top meter of gravity core GeoB 4216, which comprises the last 20,000 years BP. Sedimentation rates for this period vary between 3 - 10 cm kyr<sup>-1</sup>. The corresponding stratigraphy is according to FREUDENTHAL *et al.* (2002) and bases on the correlation of  $\delta^{18}\text{O}$  values of the planktonic foraminifera *Globigerina bulloides* with the SPECMAP standard record. The investigated interval shows a continuous sedimentation of light brownish to olive-grey nannofossil ooze (Fig. 3.2). The OM content is low (0,15 – 0,9% of weight) and mainly derived by marine sources (FREUDENTHAL *et al.*, 2002). Silt sized quartz and iron rich minerals represent the largest fraction of terrigenous material (WEFER *et al.*, 1997).

#### 3.3.2. Data acquisition

For dinocyst analyses 50 sediment samples were taken between 15 and 110 cm (3,820 - 20,600 years BP; Fig. 3.2). The temporal resolution varies between 100 - 510 years (glacial/interglacial transition) and 510 - 1300 years (full glacial and Holocene). For each sample approximately 1 cm<sup>3</sup> of dry sediment was treated with 10% hydrochloric acid in order to remove the carbonate content. Afterwards, they were washed repeatedly, decanted and subsequently treated with cold 38% hydrofluoric acid in order to remove silicates. After having stood for two days samples were neutralized with 40% potassium hydroxide. To avoid dinocyst dissolution care was taken that the solution did not become alkaline at any time. By sieving over a nickel precision sieve (Stork Veco, mesh 570) the size fraction > 20  $\mu\text{m}$  was collected. The residue was centrifuged (3500 r.p.m. for 8 min) and transferred into a 1.5 ml Eppendorf reaction vessel. After re-centrifugation samples were concentrated to 1 ml. Finally 50 or 100  $\mu\text{l}$  of the homogenized residue was placed on a microscope slide, embedded in glycerine jelly, and sealed with paraffin wax. At least one slide was counted for dinocyst species. When slides contained fewer than 200 dinocysts, additional slides were counted. As a basis for further calculations dinocyst concentrations (cysts cm<sup>-3</sup>; further referred to as abundance) were calculated (Appendix A2).

Data on solid phase element distributions of Ba are taken from KASTEN *et al.* (2003) and the Fe, Mn and U data are obtained from JACQUET (2000). TOC data are taken from FREUDENTHAL *et al.* (2002). While the former are measured in 1 cm sample intervals, the latter have a resolution of 5 cm.

#### 3.3.3. Proxy definitions

Among organic-walled dinoflagellate cysts, two groups of species can be distinguished with respect to preservation potential. In the following we refer to oxidation resistant cysts as 'R-cysts' and sensitive species as 'S-cysts' (Table 3.1). R-cysts belong to a group of species that is

hardly susceptible to aerobic decay, because their wall structure contains oxidation resistant polymers (KOKINOS *et al.*, 1998; VERSTEEGH & BLOKKER, 2004). The corresponding motile forms tolerate a wide range of environmental conditions as they are found in open marine, coastal and frontal habitats in the tropics as well as in higher latitudes (MARRET & ZONNEVELD, 2003 and references therein). Because degradation of R-cysts during settling through the water column has never been evidenced, we referred to this group as a productivity proxy that is unaffected by aerobic decay (**Chapter 2**).

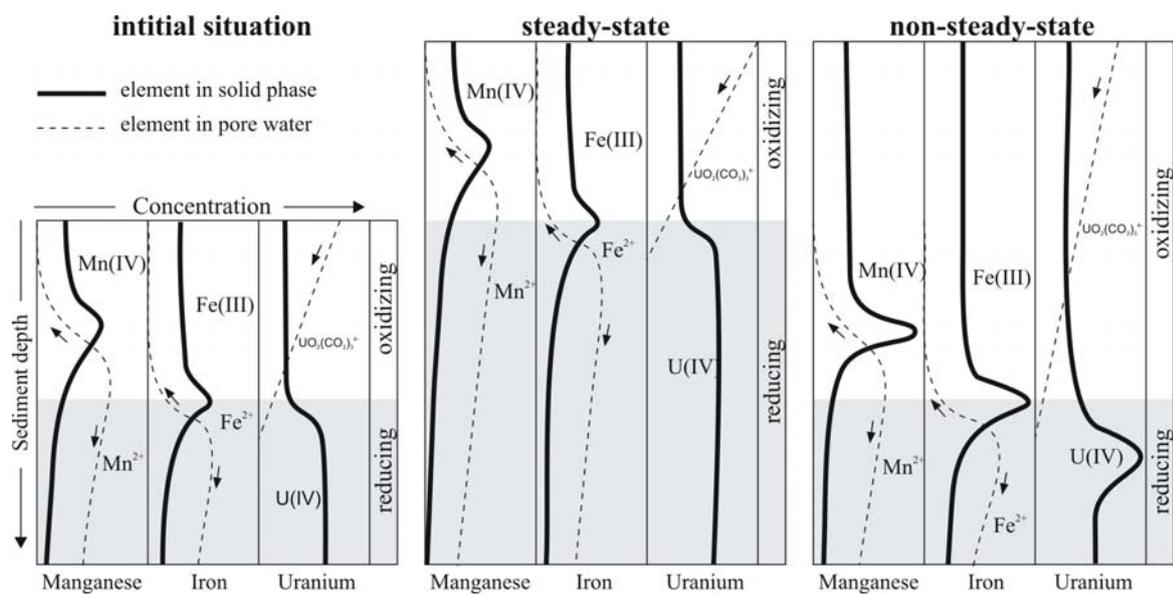
We used the abundance of S-cysts in each sample as a productivity proxy with low preservation potential. Studies of post-depositional OM degradation at natural oxidation fronts in the Madeira Abyssal Plain f-turbidite and the eastern Mediterranean S1 sapropel have shown that this group of dinocysts easily degrades under oxic conditions (ZONNEVELD *et al.*, 1997; 2001). Corresponding dinocysts vanish rapidly in sediments immediately above the oxidation fronts compared with sediments below. S-cysts typically belong to the genus *Protoperidinium* (notably *Brigantedinium* spp.) and *Echinidinium* (ZONNEVELD *et al.*, 2001). Their motile forms have broad ecological niches, as they are found in open marine environments, river plumes, frontal zones, and upwelling regions (WALL *et al.*, 1977; ROCHON *et al.*, 1999; MARRET & ZONNEVELD, 2003).

**Table 3.1.** List of cyst-species included within the S-cyst and R-cyst groups.

R-cysts	S-cysts
<i>Impagidinium aculeatum</i>	<i>Brigantedinium</i> spp.
<i>Impagidinium pallidum</i>	<i>Multispinula quanta</i>
<i>Impagidinium paradoxum</i>	<i>Trinovantedinium capitatum</i>
<i>Impagidinium patulum</i>	<i>Selenopemphix nephroides</i>
<i>Impagidinium plicatum</i>	<i>Echinidinium aculeatum</i>
<i>Impagidinium sphaericum</i>	<i>Echinidinium granulatum</i>
<i>Impagidinium strialatum</i>	<i>Echinidinium transparantum</i>
<i>Impagidinium</i> spp.	<i>Echinidinium delicatum</i>
<i>Nematosphaeropsis labyrinthus</i>	<i>Echinidinium</i> spp.
<i>Operculodinium israelianum</i>	
<i>Polysphaeridium zoharyi</i>	
<i>Pentapharsodinium dalei</i>	

Given the different preservation potentials of R-cysts and S-cysts, we calculated a measure of degradation using to the method described in VERSTEEGH & ZONNEVELD (2002) and **Chapter 2**. Accordingly, we described S-cyst degradation as a first-order decay process (MIDDELBURG, 1989):  $X_f = X_i e^{-kt}$ , so  $\ln(X_i) - \ln(X_f) = kt$ , where  $X_f$  = final concentration,  $X_i$  = initial concentration,  $k$  = degradation constant and  $t$  = reaction time. In order to quantify the first-order rate constant for degradation and reaction time ( $kt$ ) for each core sample the  $X_i$  of S-cysts had to be set. We used the S-cysts/R-cysts ratio of 68 obtained in **Chapter 2** and referred to this value as constant through time. We assumed that it represented the initial S-cysts/R-cysts ratio prior to any degradation ( $t = 0$ ) and calculated the  $X_i$  of S-cysts relative to resistant ones for each sample.

Similar to S-cysts, we used TOC record as a productivity proxy which suffers from aerobic decay. The TOC content is one of the most frequently applied proxies for paleoproductivity reconstructions, but afflicted with certain insecurities, because only a little of the TOC produced in surface waters becomes preserved in sediments of deep sea environments (BERGER *et al.*, 1989). Among other factors the preservation of OM is intrinsically linked to bottom water oxygen concentrations (BETTS & HOLLAND, 1991), availability of O<sub>2</sub> (HULTHE *et al.*, 1998), oxygen exposure time (COWIE *et al.* 1995), primary productivity (TYSON, 2001), and sediment accumulation rates (HENRICH, 1992). The sensitivity of TOC to aerobic decay is reflected by its high degradation factor (VERSTEEGH & ZONNEVELD, 2002) and has been demonstrated elsewhere (e.g., HARTNETT *et al.*, 1998; RULLKÖTTER, 2000).



**Figure 3.3.** Schematic illustration of the formation of solid-phase enrichments of manganese, iron and uranium under steady state and non-steady state depositional and diagenetic conditions (modified after KASTEN *et al.*, 2003). Dotted Lines represent pore water profiles, solid lines show solid-phase concentration profiles.

We used the Ba/Al ratio as an oxidation resistant proxy for export production. Barium in its sedimentary solid phase of barite (BaSO<sub>4</sub>) is used for productivity reconstructions and algorithms have been developed that link its accumulation in sediments to export production (e.g., DYMOND *et al.*, 1992). Barium based productivity estimations have been successfully applied in environments of hemipelagic (e.g., GINGELE & DAHMKE, 1994) and pelagic sedimentation (NÜRNBERG *et al.*, 1997; THOMPSON & SCHMITZ, 1997). An advantage of using barium is its more predictable preservation in oxic to sub-oxic sediments, where supersaturation of barite in interstitial waters prevents its dissolution after burial (PAYTAN & KASTNER, 1995). A problem is due to dissolution of barite in anoxic horizons, when pore water sulphate has been depleted by microorganisms and subsequent re-precipitation as an authigenic front at higher sediment levels occurs (TORRES *et al.*, 1996). According to pore water data (WEFER *et al.*, 1997), these conditions

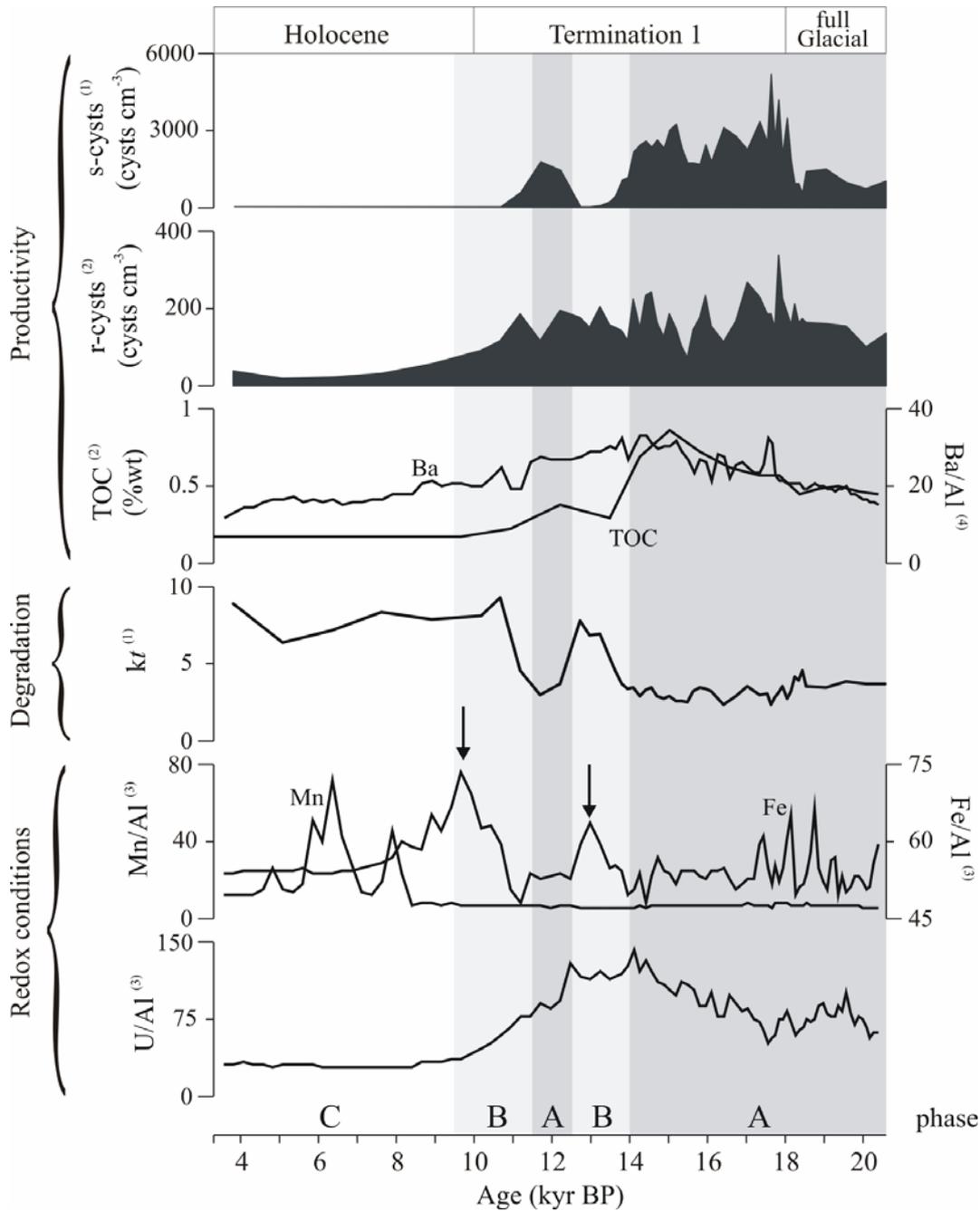
are not observed in the study region. Thus, neither dissolution, nor aerobic decay is expected to have a significant effect on the barium record.

We used the element/Al profiles of solid phase Fe, Mn and U to provide insights into the redox history of the investigated core section and to assess changes in bottom and pore water oxygenation. Sudden changes in organic carbon input, sedimentation rates or supply of O<sub>2</sub> during non-steady state situations are accompanied by significant changes in sediment geochemistry. Apart from the 'burn down' of OM, such conditions can produce higher solid phase concentrations of redox-sensitive elements as observed under steady state equilibrium (e.g., WILSON *et al.*, 1986; VAN SANTVOORT *et al.*, 1996). Because of their different redox sensitivity, enrichments of Mn, Fe and U are typically found in a characteristic depth succession (THOMSON *et al.*, 1995, 1996; Fig. 3.3). Typically, peaks of Fe(-hydroxides) are located below the maximum of Mn(-hydroxide), because dissolved Fe<sup>2+</sup> tolerates lower O<sub>2</sub> concentrations than Mn<sup>2+</sup> before being oxidized. Concentrations typical of average shale or enrichments of solid phase Mn and Fe are thus indicative of relative bottom water oxygenation. Authigenic enrichments of solid phase U result from precipitation and/or adsorption to reactive surfaces. After dissolved U has diffused from seawater into the sediment it becomes immobilized in anoxic sediments below the Fe redox boundary (KASTEN *et al.*, 2003). The presence of high authigenic U concentrations in glacial sediment sections has been attributed to lower than present-day O<sub>2</sub> levels in the glacial Atlantic Ocean (THOMSON *et al.*, 1990).

### **3.4. Results**

A total of ten resistant and five sensitive dinocyst species were identified and counted in samples of core GeoB 4216 (Tab. 3.1). The records of both groups showed a comparable long-term trend with higher abundances in the deeper core section towards lower in the upper part (Fig. 3.4). Thereby, S-cysts clearly exceeded R-cyst abundance in most cases, except for samples taken between 50 -53 cm and in Holocene deposits (15 – 42 cm), where the former were almost absent. An exceptional high abundance of sensitive as well as resistant dinocysts was observed in samples from 80 – 83 cm, which also revealed higher Ba/Al ratios. Similar to the dinocysts, TOC and the Ba/Al ratio had, on average, higher values in samples from the lowermost compared to the uppermost core section (Fig. 3.4). For these two productivity proxies highest values were determined for the interval from 56 – 63 cm. Their trends corresponded well in the core section below the TOC maximum, but clearly differ above, whereby the Ba/Al ratio resembled the R-cyst profile and TOC that of S-cysts. Quantitative calculation of *kt* revealed large variations of the degradation indicator over the investigated core interval (Fig. 3.4). Lowest values were obtained for samples between 56 – 110 cm and for the short interval from 46 – 50 cm. On top of each interval an abrupt increase of the degradation index occurred within a few centimetres. Above the lowermost increase the degradation index dropped abruptly, while values of Holocene samples remained high. Among the redox sensitive elements, Fe displayed two broad maxima between 49 – 53 cm and 34 – 43 cm, respectively. Above the uppermost Fe peak Mn spikes were observed at 25 cm and 29 cm, respectively (Fig. 3.4). Below the uppermost Fe peak the U/Al ratio was high and reached its maximum in between 49 – 53 cm (Fig. 3.4).

Upon evaluation of the different proxy records the investigated core interval was divided into characteristic horizons. We related these intervals to the corresponding age model and distinguished three characteristic phases.

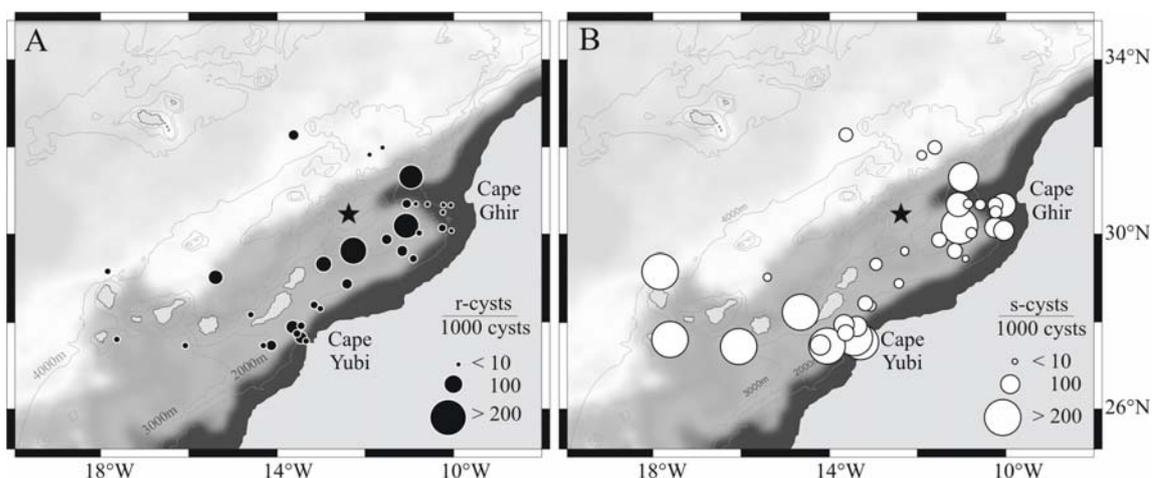


**Figure 3.4.** Results of dinocyst, geochemical and solid phase element analyses for core GeoB 4216; (1) this study, (2) FREUDENTHAL *et al.* (2002), (3) JACQUET, (2000), (4) KASTEN *et al.* (2003). Periods of good preservation are shaded grey (phase A), of decreasing preservation light grey (phase B) and bad preservation are not shaded (phase C). Arrows indicate the position of ‘fossil’ oxidation fronts.

Phase A comprised two intervals. The first comprised the period from 20,600 – 14,000 years BP and the other to a short sequence between 12,500 – 11,500 years BP. For the corresponding samples low values of the degradation indicator had been calculated suggesting good preservation during both periods. All productivity proxies indicated high production, whereby two maxima were obtained. The first maximum occurred around the onset of the glacial termination (~ 18,000 years BP) and was reflected in the records of R-cysts, S-cysts, and Ba/Al. The second maximum was observed around 14,500 years BP and most pronounced in the TOC signal and the Ba/Al ratio. Among the redox sensitive elements uranium showed highest concentrations.

Phase B covered two core horizons including the periods from 14,000 – 12,500 years BP and 9,500 – 11,500 years BP. Both intervals were characterized by abrupt increases of the degradation indicator  $kt$  pointing to deterioration of OM preservation. Solid phase Fe maxima at the upper boundary of the corresponding sediment sections demarked the position of fossil oxidation fronts, while increasing U/Al ratios below indicated downward diffusion of dissolved uranium and subsequent precipitation as authigenic uranium in the anoxic horizons. Both period of phase B showed productivity records different for oxidation resistant (R-cysts, Ba) and decay susceptible proxies (S-cysts, TOC).

Phase C comprised only Holocene deposits starting at around 9,500 years BP. During this period the degradation index ( $kt$ ) remained at high values indicating deterioration of OM preservation. Values of all productivity proxies declined to a minimum suggesting lowest surface water production of the entire core section. Among the redox sensitive elements Mn showed two spikes between 8,000 - 6,000 years BP.



**Figure 3.5.** Surface distribution patterns of (A) R-cysts and (B) S-cysts in the investigation area (data after TARGARONA *et al.*, 1999; HOLZWARTH (unpublished data). Black star marks location of site GeoB 4216. Chlorophyll *a* concentration is indicated as in Figure 3.1A.

### 3.5. Discussion

#### 3.5.1. Separating productivity from preservation

The high resolution dinocyst analysis presented in this study provides a detailed record of productivity and preservation at site GeoB 4216 during the past 20,000 years. Highest abundances of R-cysts and S-cysts are observed at the glacial termination, consistent with the Ba/Al ratio and TOC record as well as with grain-size patterns and geochemical parameters (FREUDENTHAL *et al.*, 2002; MORENO *et al.*, 2002). It also accords to reconstructions of contemporary productivity patterns along the NW-African margin (MATTHEWSON *et al.*, 1995; ZHAO *et al.*, 2000) and off Portugal (THOMSON *et al.*, 2000). Because dinoflagellates are capable of forming immense blooms under extreme conditions (CODISPOTI, 1983), we suggest that they took advantage of high nutrient concentrations in surface waters and strong filament activity off Cape Ghir at this time. Two factors could have caused such conditions. First, intrusion of cold, nutrient-rich melt water from high latitudes into the eastern subtropical Atlantic via the CC (ZHAO *et al.*, 1995; HARRIS *et al.*, 1996). Second, the accompanied lowering of the sea surface temperatures would have strengthened the Azores high-pressure system, intensified trade winds, and ultimately amplified upwelling (OVERPECK *et al.*, 1989).

Enhanced productivity in mid and low latitudes could be responsible for most of the observed  $p\text{CO}_2$  reduction during glacials, while a weakening might be the main factor that caused the rapid rise of atmospheric  $p\text{CO}_2$  and delayed  $\text{CO}_2$  depletion of the deep ocean towards interglacial times (NEWELL & HSUING, 1984; SARNTHEIN *et al.*, 1988). If such hypotheses are based on oxidation susceptible tracers, such as S-cysts and TOC, they can bear a high risk of misleading interpretation, because aerobic decay may have affected their geological record. In core GeoB 4216 abrupt changes in the abundance of S-cysts and TOC evidence a significant influence of post-depositional OM degradation. Conditions for preservation deteriorated abruptly during phase B and were constantly unfavourable during phase C (Fig. 3.4). In these intervals only degradation resistant proxies like R-cysts and the Ba/Al ratio can reflect the OM input to the sediment. The assumption of a high preservation quality during phase A is confirmed by the good agreement between R-cysts and S-cysts and between TOC and the Ba/Al ratio in corresponding intervals. The postulation that post-depositional OM degradation affected the records of S-cysts and TOC during phase B is supported by observations of similar oxidation effect found sapropelic and turbiditic core layers (THOMSON *et al.*, 1995; VAN SANTVOORT *et al.*, 1996; ZONNEVELD *et al.*, 1997; 2001). Resting cysts of dinoflagellates show the same behaviour with respect to factors like transport or bioturbation. Hence, the hypothesis that strong degradation occurred during phase C can only be challenged if S-cyst formation would have dropped below the production ratio of R-cysts. According to TARGARONA *et al.* (1999) and HOLZWARTH (unpublished data) modern distribution patterns of both groups are comparable, suggesting a similar respond to upper water mass conditions (Fig. 3.5). Because the modern assemblages are usually dominated by S-cysts, selective dissolution is most likely responsible for their low abundance during phase C rather than less dinocyst production. This theory is corroborated by observations from the eastern Arabian Sea and the southeast Atlantic, where S-cysts abundance is conspicuously higher beneath oxygen

minimum zones compared to well oxygenated sediments outside, where degradation occurs (ZONNEVELD, 1997; **Chapter 4**).

In this study we observe a good correlation between R-cyst abundance and the Ba/Al ratio. Barium peaks at terminations, as observed for this core, are recorded in sediments of the northwest African (MATTHEWSON *et al.*, 1995; MORENO *et al.*, 2002), the Portuguese margin (THOMSON *et al.*, 2000), the Ontong Java Plateau (SCHWARZ *et al.*, 1996), and the Sierra Leone and Ceará Rise (Kasten *et al.*, 2001). It is, however, possible that the Ba/Al record suffered from post-depositional redistribution/dissolution of barite (SCHENAU *et al.*, 2001), irregular high contribution from lithogenic sources (NÜRNBERG *et al.*, 1997; Paytan *et al.*, 1996) and/or increasing Ba<sup>2+</sup> concentrations in intermediate and deep waters (DYMOND *et al.*, 1992). If these processes would have biased the Ba record we should expect inconsistency between the Ba/Al ratio and the TOC record in core horizons unaffected by oxidation, which is not the case. We rather observe accordance between the Ba/Al and TOC in these intervals, which supports the reliability of Ba and thus, R-cysts as productivity indicators.

The quantitative relationship between R-cyst formation and bioproduction has still to be assessed, but data from various environments show a significant correlation between R-cyst abundance in surface sediments and chlorophyll *a* concentration in surface waters (Fig. 2.6 in **Chapter 2**). If R-cyst abundance in core GeoB 4216 would not reflect export production, their modern distribution in the investigation area should be unrelated to present-day productivity conditions. Figure 3.5 shows that higher abundance of R-cysts generally occurs in areas of strong present-day upwelling. This coherence is also observed by several studies which report higher R-cyst flux during times of strong primary production in surface waters (e.g., HARLAND & PUDSEY, 1999; ZONNEVELD & BRUMMER, 2000) and dependence to overlying productivity gradients (e.g., MARRET & DE VERNAL, 1997; VINK *et al.*, 2000).

### *3.5.2. Assessing bottom and pore water oxygen history*

Basically, two factors may account for the variability in OM preservation at site GeoB 4216, variable sedimentation rates and/or changes in the sedimentary redox environment. Higher sedimentation rates during phase A may have protected OM from significant oxidation, while a decrease to a critical value, as proposed by JUNG *et al.* (1997), could explain the lack of correlation between the different productivity proxies during phase B and C, by allowing deeper penetration of oxygen into the sediment. However, the last glacial termination was accompanied by reorganization of ocean thermohaline circulation. It is supposed that circulation changed from a sluggish mode during glacials towards the present-day situation with deep water formation in the North Atlantic (e.g., ADKINS *et al.*, 1997; MCMANUS *et al.*, 2004). There is evidence that the transition to better ventilation was interrupted by rapid returns to glacial conditions during the Older Dryas cooling, sustained by Heinrich event 1, and the Younger Dryas cold snap. Bottom water formation and thermohaline overturn during either of these climate reversals was possibly weakened (e.g., PAILLARD & LABEYRIE, 1994; ZAHN *et al.*, 1997; CAME *et al.*, 2003) and may have been switched on and off rapidly. Most drastic changes to strong, present-day-like NADW ventilation occurred during the Bølling/Allerød warming and at the onset of the Holocene (BOYLE

& KEIGWIN, 1987; AUSTIN & KROON, 2001). Changes in the thermohaline overturn may have influenced the ventilation of bottom waters and, ultimately, could explain part of the preservation history at the core site. It is, however, difficult to assess the influence of sedimentation rates and we thus conclude that changes in preservation conditions are causative to a combined effect of oxygen supply by bottom waters and variable particle flux.

The assumption of  $t = 0$  at times of lowest degradation and  $k = \text{constant}$  throughout the studied core interval are only approximations, so that the calculation of the degradation index ( $kt$ ) remains a qualitative attempt. However, combined dinocysts data from different environments show a significant correlation between  $kt$ -values inferred from surface sediments and bottom water oxygen concentrations (Fig. 2.8 in **Chapter 2**). Albeit  $\delta^{13}\text{C}$  values of benthic foraminifera from our core provide only vague evidence for a lowering of bottom water oxygen concentrations at site GeoB 4216 (FREUDENTHAL *et al.*, 2002), oxygen concentrations off Portugal, north of the investigation area and at similar depths may have dropped from recently 5 - 6  $\mu\text{mol l}^{-1}$  to less than 0.5  $\mu\text{mol l}^{-1}$  around Heinrich event 1 (BAAS *et al.*, 1998). Our theory also accords with study results of SARNTHEIN *et al.* (1994), who suggest that during distinct intervals of the last glacial termination ventilation was at minimum in the northeast Atlantic below 1800 m, well above the depth range of core GeoB 4216. The accompanied lowering of bottom water oxygen levels by a slow-down of the meridional overturning circulation or uplift of NADW to intermediate depth was possibly amplified by admixture of low oxygenated AABW (LOTOTSKAYA & GANSEN, 1999). In addition, higher sedimentation rates at this time may have promoted rapid burial of OM and thus significantly shortened the time period of oxygen exposure.

Proof for the use of degradation index as a proxy for changes in bottom and pore water oxygenation is provided by the records of redox-sensitive elements. Along with the abrupt increase of  $kt$ -values during phase B we observe peaks in the solid phase element distribution of iron (Fig. 3.4). The high values may originate from Fe-(hydroxide) precipitation within or close to oxic/post-oxic boundaries that were possibly sustained at a particular level for a prolonged period of time in response to re-oxygenation of bottom waters and/or changes in particle flux rates. The uppermost Fe peak is placed in a typical depth arrangement of redox sensitive elements with enrichments of solid phase Mn above and authigenic U below (cf. Fig. 3.3). This succession typically occurs in sapropel/hemipelagic (e.g., THOMSON *et al.*, 1995; VAN SANTVOORT *et al.*, 1996) and turbiditic/hemipelagic deposits (e.g., WILSON *et al.*, 1986; COWIE *et al.*, 1998), where it indicates adjustment of the pore water equilibrium to non-steady state conditions. Similar patterns are reported for sediment intervals of glacial/interglacial transitions in the east equatorial Pacific (BERGER *et al.*, 1983), the northeast Atlantic (WALLACE *et al.*, 1988; THOMSON *et al.*, 1996), central Atlantic (REITZ *et al.*, 2004), and eastern equatorial Atlantic (THOMSON *et al.*, 1984). It is possible that initially there existed a second Mn peak slightly above the lower Fe peak. The development of sub-oxic conditions upon further burial, however, may have caused the dissolution of the Mn (-hydroxides) which were subsequently re-precipitated at the “modern” redoxcline (DE LANGE *et al.*, 1994). Although being prone to dissolution under post-oxic and anoxic conditions, a relict of the lower Fe enrichment is still present due to slower reduction kinetics of Fe compared to Mn (KASTEN *et al.*, 2003). A closer look at the profiles of degradation resistant and

sensitive productivity proxies in the vicinity of the lower and upper iron redox boundaries reveals a discrepancy between these two groups immediately above the S-cyst and TOC enriched sediment horizons. The higher Ba contents and abundance of R-cyst in these intervals suggests that there has not only been a fixation but also a slight downward movement of the oxidation front. This progression is likely to have caused an efficient post-depositional 'burn-down' of TOC and S-cysts, leaving Ba and R-cysts as a relict.

### 3.6. Conclusions

In our example selective degradation of organic-walled dinoflagellate cysts forms the ideal tool to tackle the difficulties in discriminating productivity and preservation. It is concluded that variations in the abundance of R-cysts are related to bioproduction in surface waters throughout the analysed core section. In contrast, the abundance of S-cysts reflects productivity only in case of excellent preservation and provides information on the diagenetic status of geological archives. The calculated degradation index ( $kt$ ) is assumed to mirror past variations in bottom and pore-water oxygenation and largely explains the formation of redox-sensitive element enrichments. For the studied core GeoB 4216 the proposed method points to a climatically related variability in the rate of degradation with a good preservation of the productivity signal during colder intervals and high rates of OM degradation during the warmer intervals of the last 20,000 years. The degree of preservation may largely depend on rapid changes in deep ocean ventilation and productivity induced particle flux rates.

Dinocysts are equally affected by transport, bioturbation, and irrigation, and they are abundant in almost all marine environments since the Early Jurassic. Hence, incorporation of selective degradation is potentially widely applicable and may support the application of other paleoproductivity proxies. As an independent approach it can also provide information on sediment geochemistry, deep-ocean circulation and thus may improve our understanding of carbon cycling in the ocean.

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**Appendix A2:** Dinocyst data of core GeoB 4216, calculated initial S-cyst abundance ( $X_i = 288 \times R\text{-cysts}$ ), and degradation index [ $kt = \ln(X_i) - \ln(X_f)$ ].

Comp. depth (cm)	Age (years BP)	R-cysts (no. cm <sup>-3</sup> )	$X_f$ of S-cysts (no. cm <sup>-3</sup> )	$X_i$ of S-cysts (no. cm <sup>-3</sup> )	$kt$
15	3,820	35	1	10128	8.86
20	5,090	18	9	5299	6.36
25	6,370	19	5	5471	7.09
30	7,640	30	2	8702	8.30
35	8,920	55	6	15911	7.83
40	10,190	90	8	25798	8.06
42	10,700	114	3	32744	9.22
44	11,210	185	571	53245	4.53
46	11,720	115	1764	33109	2.93
48	12,230	195	1449	56123	3.66
50	12,740	176	21	50556	7.79
51	12,990	149	47	42936	6.82
52	13,250	204	61	58882	6.87
53	13,500	155	200	44669	5.41
54	13,650	149	450	42861	4.56
55	13,810	139	1054	40136	3.64
56	13,960	114	1146	32875	3.36
57	14,120	222	2127	63813	3.40
58	14,270	147	2441	42358	2.85
59	14,420	233	2560	67032	3.27
60	14,580	242	2347	69559	3.39
61	14,730	163	2601	46818	2.89
62	14,890	123	2304	35425	2.73
63	15,040	185	2995	53185	2.88
64	15,200	147	3218	42321	2.58
65	15,350	100	2280	28757	2.53
66	15,500	72	1713	20724	2.49
67	15,660	144	1728	41341	3.18
68	15,810	176	1692	50641	3.40
69	15,970	231	2418	66533	3.31
70	16,120	154	1781	44294	3.21
72	16,430	113	3095	32643	2.36
74	16,740	166	2772	47858	2.85
76	17,040	267	2239	77001	3.54
78	17,350	228	3353	65562	2.97
80	17,560	183	2504	52577	3.04
81	17,660	183	5159	52685	2.32
82	17,760	146	2554	42167	2.80
83	17,860	336	4196	96678	3.14
84	17,960	225	2000	64720	3.48
85	18,060	186	3449	53618	2.74
86	18,160	155	1885	44717	3.17
87	18,270	211	937	60782	4.17
88	18,370	163	940	46884	3.91
89	18,470	171	545	49309	4.50
90	18,570	161	1372	46337	3.52
95	19,080	159	1469	45728	3.44
100	19,580	152	949	43823	3.83
105	20,090	99	747	28385	3.64
110	20,600	134	1025	38701	3.63

## CHAPTER 4

### Environmental control of organic-walled dinoflagellate cyst distribution in surface sediments of the Benguela upwelling region (eastern South Atlantic): Does oxygen matter?

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#### **Abstract**

Organic-walled dinoflagellate cyst assemblages in surface sediments of the Benguela Current Upwelling System (eastern South Atlantic) show geographic patterns that cannot entirely originate from cyst production or transport. Aimed at answering how far these variations are due to taphonomic control, this study investigated a possible correlation with changes in bottom water oxygen concentrations typifying this region. Based on thirty-six samples, multivariate statistics were used to analyze community variability with respect bottom water oxygen concentration, temperature, salinity, nutrient content, chlorophyll *a* concentration, the organic carbon content of surface sediments, and a measure of water column stratification. Dinoflagellate cyst production shows specific requirements regarding salinity, nutrient supply, nutrition, and environmental steadiness, while transport in the nepheloid layers may introduce variability prior to burial in surface sediments. Species distributions coincided with expected degradation behaviours separating susceptible protoperidinaean types from their oxidation resistant gonyaulacacean relatives. Bottom water oxygenation significantly relates to this pattern and upon elimination of co-variation is among the parameters best explaining community variability. This study shows that selective preservation is of importance to species distribution and taphonomic control is responsible for much more of the presence of dinoflagellate cysts in the geological record than presently acknowledged.

Keywords: dinocysts, community variability, selective preservation, bottom water oxygen

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#### 4.1. Introduction

Distribution patterns of organic-walled dinoflagellate cysts (or dinocysts) in marine sediments have been intensively studied throughout the world's oceans. Thereby, knowledge on ecological preferences of modern cyst-forming species has steadily grown and today covers information on species-environmental relations from various marine ecosystems (cf. MARRET & ZONNEVELD 2003 for an overview). Concurrently, fossil archives became increasingly explored for palaeoenvironmental reconstructions (MUDIE *et al.* 2001), given the fact that associations can sensitively reflect even small changes in temperature, salinity or nutrient availability. Especially at high latitudes and in neritic settings, where calcareous microfossils are rare, this efficiency greatly expanded the understanding of (paleo)ecological conditions (e.g., by using transfer functions: DE VERNAL *et al.* 1994). Nevertheless, drawing conclusions on species affinities or paleoenvironments necessarily premises that associations remain unchanged beyond initial production. DALE (1992) pointed out that such an assumption potentially violates allochthonous contributions, and ever since consideration of long-distance transport is inherent to an accurate data analysis. At present, another problem bothers the palynological community, the possibility that dinocyst associations could be substantially skewed by taphonomic control, notably differential preservation (ZONNEVELD *et al.* 2001*b*; HOPKINS & MCCARTHY 2002).

Preservation of dinocysts is most likely sustained by aromatic substances in their wall structures. For decades their high preservation potential has constituted a fundamental concept in palynology which has often been stressed as advantageous to the use of siliceous and calcareous microfossils. However, the use of strong acids, acetolysis, and base treatment are avoided as much as possible upon processing of assemblages. The reason is that such procedures would destroy many peridinioid species, notably the brown-walled taxa (HOPKINS & MCCARTHY 2002). Though long recognized by palynologists (e.g., DALE 1976), most attribute this effect to inappropriate laboratory processing and consider the relevance in natural setting with great scepticism. Few reports contrast this canon, as they have qualitatively inferred the differential preservation of Quaternary cyst taxa from sediment cores (e.g., ZONNEVELD *et al.* 2001*b*). However, this does not provide convincing proof for a direct relation between groups of dinocysts and bottom water oxygen contents, so that an occurrence of selective 'in situ' degradation is still limited to speculations. This situation demands intensified research to fuller understand how preservation can affect dinocyst associations.

Studies on species-environmental relationships coming from areas with strong bottom water oxygen gradients probably contribute most to a better understanding of taphonomic effects on dinocyst distribution patterns. We focused on the Benguela Current Upwelling System off Namibia (herein referred to as the BCUS), where hydrography and atmospheric conditions promote intense production, high particle flux rates, and ultimately, severe bottom water oxygen deficiencies (O<sub>2</sub> <2 ml l<sup>-1</sup>) that locally give way to quasi permanent oxygen minimum zones (Chapman and Shannon 1985). Although parameters commonly associated with dinocyst distribution are found as steep gradients, associations in surface sediments show patterns that are difficult to explain by differences in cyst production or lateral transport (e.g., DAVEY & ROGERS 1975; ZONNEVELD *et al.* 2001*a*). Instead, they are possibly a response to deposition in different

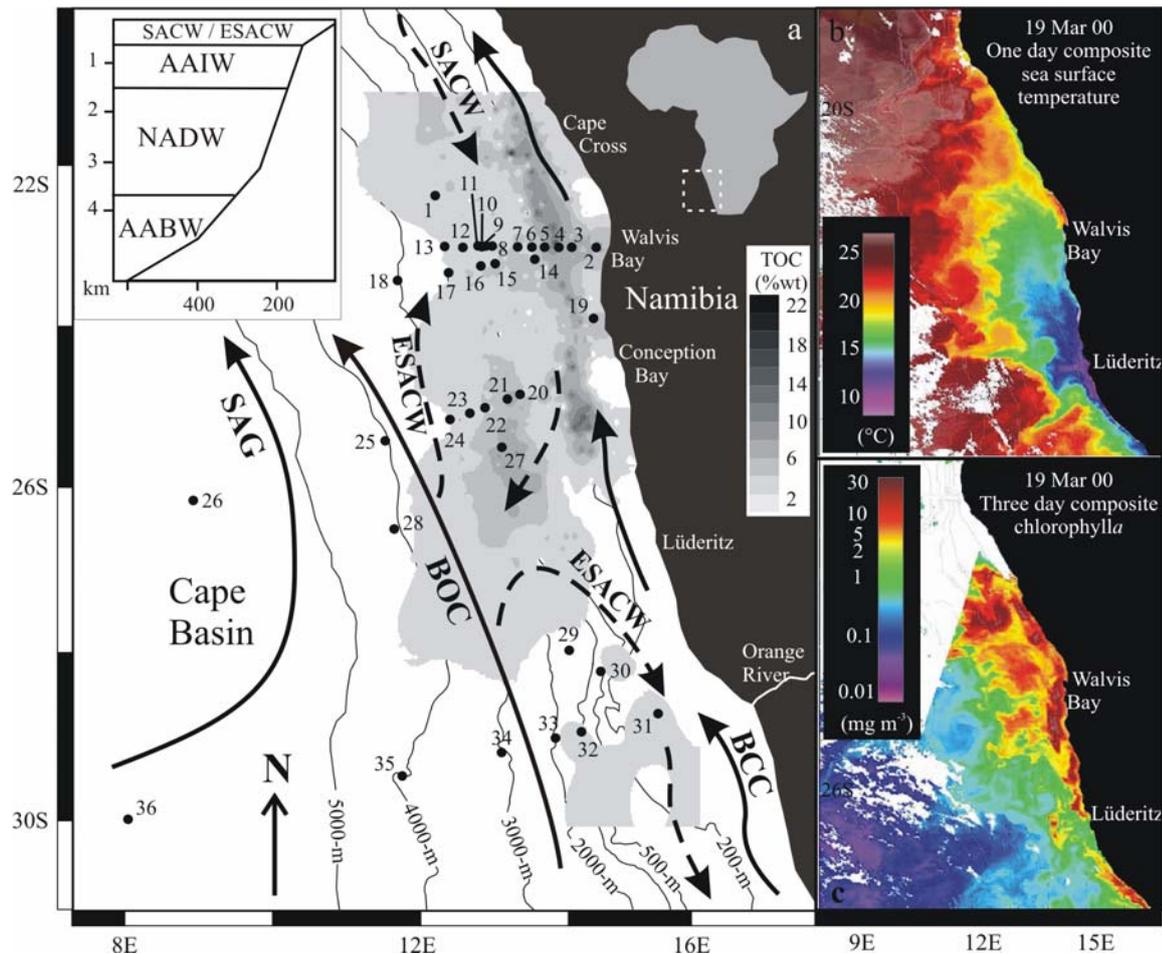
bottom waters oxygen regimes. To test this hypothesis, we raised species inventories of thirty-six surface sediment samples and analyzed the data with respect to physical, chemical, and biological factors applying multivariate techniques of ordination. Aimed at identifying taphonomic control our approach attaches importance to the role of oxygen exposure and may facilitate the understanding of marine palynomorph behaviour as sedimentary organic particles.

## 4.2. Material and methods

### 4.2.1. Study area

The study area stretches along the Namibian coast between 22°S to 30°S and in its largest offshore extension reaches the Cape Basin at about 8°E, where water depths exceed 5000 m (Fig. 4.1). Surface hydrography relates to the equator-ward flow of the Benguela Current (SHANNON & NELSON 1996). Shoreward, the flow of the Benguela Coastal Current and prevailing south-easterly winds drive upwelling of nutrient-rich water from depths between 200 – 300 m. This water can comprise different proportions of South Atlantic Central Water (SACW) and East SACW (ESACW). The former is bounded by the shelf and travels south by a pole-ward undercurrent. Low oxygenation of SACW ( $<1 \text{ ml l}^{-1}$ ) and ongoing oxygen consumption during bacterial break down of organic matter promote the establishment of oxygen minimum zones over the shelf and upper slope at depth between 100 to 450 m (BAILEY 1991; cf. Fig. 4.2). Off the shelf, an increasing fraction of ESACW accounts for the northward advection of oxygen rich, but nutrient depleted water from the Agulhas Retroflexion that is transported by the Benguela Oceanic Current. Cross-shelf circulation intensifies south of  $\sim 26.5^\circ\text{S}$ , where well ventilated ESACW becomes the dominant water mass limiting the southward extension of SACW to the latitude of Lüderitz. Below the thermocline, the flow of salty, less oxygenated Antarctic Intermediate Water ( $\sim 3$  to  $4 \text{ ml l}^{-1}$ ) is similar to overlying waters. Beneath, a southward flowing stratum of high saline, oxygenated North Atlantic Deep Water reaches down to depth of about 3800-m and overlies Antarctic Bottom Water at abyssal depth (SHANNON & NELSON 1996).

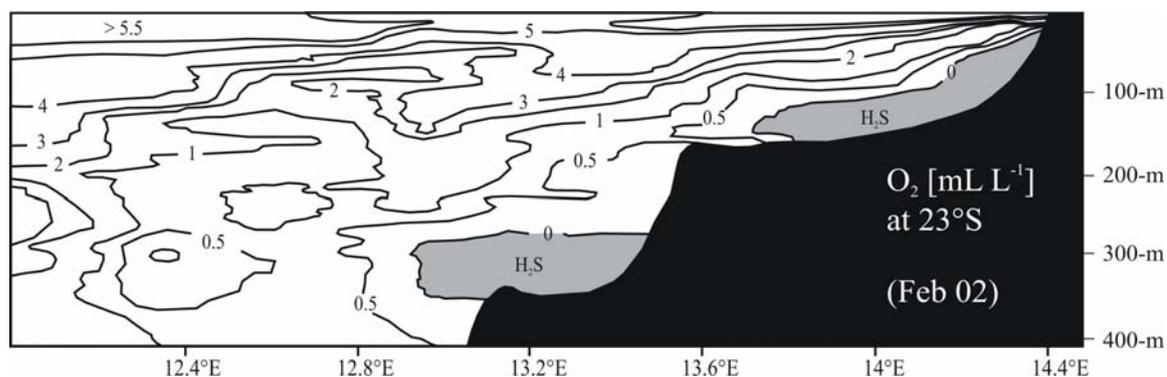
For much of the year strongest upwelling prevails in cells along the continental shelf, but Ekman transport in corridors of strong winds and the interaction of tides and topography may induce enhanced productivity above the shelf edge and upper slope (LUTJEHARMS & MEEUWIS 1987). During austral summer and early autumn the relaxation of wind stress and subsequent intrusion of warm, saline waters from the Angola Basin weaken the upwelling intensity. Usually, a thermal front at the shelf edge separates cold, productive water from warm, subtropical water, but recurrently is penetrated by eddies, filaments, and plums (Fig. 4.1). Nutrient concentrations of upwelled water can attain up to  $20 \mu\text{mol l}^{-1}$  of nitrate,  $1.5 \mu\text{mol l}^{-1}$  of phosphate, and  $15\text{-}20 \mu\text{mol l}^{-1}$  of silicate (CHAPMAN & SHANNON 1985). The average production north of the Orange river amounts to  $\sim 2 \text{ g C m}^{-2} \text{ d}^{-1}$  (SHANNON *et al.* 1986), whereby chlorophyll *a* (Chl *a*) concentrations are lower during intense upwelling, but increase during quiescent phases, when stratification recovers. They are also lower off Lüderitz ( $\sim 27^\circ\text{S}$ ), but higher downstream of the cell (BAILEY 1991). Diatoms bloom in the turbulent, nutrient rich waters of upwelling centres, while the phytoplankton community changes towards flagellate dominated assemblages under stratified, nutrient depleted conditions over middle and outer shelf (SHANNON & PILLAR 1986).



**Figure 4.1.** (A) Map showing surface (solid arrows) and subsurface currents (dashed arrows) and the principal water mass stratification in the Benguela Current upwelling region. BCC = Benguela Coastal Current, BOC = Benguela Oceanic Current, SAG = South Atlantic gyre, SACW = South Atlantic Central Water, ESACW = East SACW, AAIW = Antarctic Intermediate Water, NADW = North Atlantic Intermediate Water, AABW = Antarctic Bottom Water. Modified after SHANNON & NELSON (1996). TOC contents of surface sediments and sample positions (filled circles) are indicated. (B) One day composite of sea surface temperature showing strongest upwelling of cold, thermocline water at latitude of Lüderitz. (C) One day composite of chlorophyll *a* concentrations in surface waters showing highest pigment contents north of Lüderitz and filament induced offshore transport.

The bottom topography is characteristic of an inner and outer shelf break at the 140 to 180 m and 360 to 400 m contours, respectively. Except for few inner shelf areas, nannofossil and foraminiferal ooze constitute the bulk of sediments accumulating at high rates on the continental margin (ROGERS & BREMNER 1991). Among the biogenic deposits on the shelf, highest amounts of organic carbon (>15%) are recorded in a diatomaceous mud-belt between 21°S – 25.5°S (INTHORN *et al.* 2006). A distinct depo-center with enhanced organic carbon loads (~9%) exists on the upper continental slope between 24°S – 26.5°S in water depths of 400 to 1500 m. Terrigenous material supplied by perennial river discharge (Orange River) and aeolian dust from the Namibian desert has little influence on the sediment texture (SHANNON & NELSON 1996). Erosion and export of organic matter from the middle and outer shelf to the slope is provoked by cross-shelf

circulation and lateral transport of particles in nepheloid layers (INTHORN *et al.* 2006). Due to the topography we assume that slumps or slides do not represent significant transport processes.



**Figure 4.2.** Section of dissolved O<sub>2</sub> in the upper 400 m along 23°W. In shaded areas free H<sub>2</sub>S can occur in the water column. (A coloured image is available at [www.ifm-geomar.de/index.php?id=meteor\\_berichte](http://www.ifm-geomar.de/index.php?id=meteor_berichte)).

#### 4.2.2. Samples and processing

Dinocyst counts refer to thirty-six surface sediment samples, recovered during R/V *Meteor* cruises M20/2, M34/2, M34/1, M57/2, and M57/3; Fig. 4.1 and Table 4.1. The samples comprised the top centimetre of multi- and box-cores. They mainly consisted of diatomaceous mud or calcareous ooze with varying proportions of sand and clay. Due to areal changes in sedimentation rates (MOLLENHAUER *et al.* 2004), sediments are likely younger in near-shore settings and older in deep-sea regions, but information inferred from oxygen isotope and AMS <sup>14</sup>C dated cores taken at, or in the vicinity of the sample positions implies that all are late Holocene in age (see data archived by LOCHTE & ROMANKEVICH 1998; MOLLENHAUER 2002*b*). Since climatic and oceanographic conditions during the late Holocene were relatively stable and similar to those prevailing today, samples are presumed to represent present-day dinocyst associations with an acceptable degree of accuracy.

Quantitative dinocysts analyses were conducted with approximately 1 cm<sup>3</sup> of dried sediment (at 60°C overnight), which were dissolved in 10% hydrochloric acid to remove the carbonate content. Afterwards, they have been washed thoroughly, decanted, and subsequently treated with cold 38% hydrofluoric acid to remove silicates. Upon two days of exposure samples were neutralized with 40% potassium hydroxide. Neutralization was essential, as the precision sieve is not resistant to either acids or bases. To avoid dinocyst dissolution care was taken that the solution did not become alkaline at any time. By sieving over a nickel precision sieve (Stork Veco, mesh 570) the size fraction >20 µm was collected. The residue was centrifuged (3500 r.p.m. for 8 min) and transferred into a 1.5 ml Eppendorf reaction vessel. After re-centrifugation samples were concentrated to 1-mL. Finally, an aliquot of the homogenized residue, depending on the amount of remaining material, was placed on a microscope slide, embedded in glycerine jelly, and sealed with paraffin wax. At least one whole slide was counted for dinocyst species. Whenever a slide contained fewer than 200 dinocysts, an additional one was counted.

Dinocysts have been termed according to their fossil names, as application of motile names was insufficient to differentiate them down to species level (for cyst-theca relationships cf. HEAD 1996). Generic groups designated with ‘spp.’ include species of a similar genus that were not identifiable at species level due to unsuitable orientation, adherence of debris or the inability to spot typical taxonomic features. The group *Brigantedinium* spp. comprises all spherical brown protoperidinioid cysts without processes. The taxonomy used for this study is in accordance to WILLIAMS *et al.* (1998). Species of the genus *Echinidinium* are described in ZONNEVELD (1997).

**Table 4.1.** Station list, basic lithology, and total dinocyst concentrations of analyzed samples.

No.	Event label	Cruise	Gear <sup>a</sup>	Latitude (deg. S)	Longitude (deg. E)	Depth (m)	Lithology	dinocysts (no. g <sup>-1</sup> )
1	GeoB3608-1	M57/3	MUC	22°21.69	12°12.09	1972	foram.-nannofos. ooze	9250
2	184-3	M20/2	MUC	23°00.00	14°22.05	44	diatomaceous ooze	49438
3	187-3	M20/2	MUC	23°00.03	14°02.94	130	diatomaceous ooze	77993
4	188-3	M57/3	MUC	22°59.94	13°51.94	143	diatomaceous ooze	46120
5	212-3	M57/3	MUC	22°59.97	13°41.01	152	diatomaceous ooze	8997
6	213-3	M57/3	MUC	22°59.97	13°29.94	234	clay.-nannofos. ooze	11995
7	191-5	M57/3	MUC	23°00.00	13°18.72	360	clay.-nannofos. ooze	11663
8	173-2	M57/3	MUC	22°59.97	12°56.98	591	clay.-nannofos. ooze	15895
9	GeoB8482-2	M57/3	MUC	22°59.97	12°53.52	706	calcareous ooze	27618
10	GeoB8483-1	M57/3	MUC	22°59.64	12°50.64	805	foram.-nannofos. ooze	15489
11	GeoB8484-3	M20/2	BC	23°00.00	12°46.98	953	calcareous ooze	14926
12	GeoB8498-2	M20/2	MUC	23°00.03	12°34.95	1439	foram.-nannofos. ooze	18492
13	176-3	M20/2	BC	23°00.06	12°20.01	2073	calcareous ooze	6586
14	GeoB1714-1	M20/2	BC	23°08.19	13°32.49	200	clay.-nannofos. ooze	10809
15	GeoB1713-5	M20/2	BC	23°13.00	13°00.70	600	clay.-nannofos. ooze	21131
16	GeoB1712-2	M20/2	BC	23°15.19	12°48.30	1004	clay. foram.-nannofos. ooze	37095
17	GeoB1711-5	M20/2	BC	23°19.00	12°22.39	1975	foram.-nannofos. ooze	16932
18	GeoB1710-2	M20/2	BC	23°25.80	11°41.40	2995	foram.-nannofos. ooze	3699
19	GeoB3607-1	M20/2	BC	23°53.28	14°19.89	97	diatomaceous ooze	172800
20	GeoB3717-1	M20/2	BC	24°49.99	13°21.00	855	clay. foram.-nannofos. ooze	60813
21	GeoB3718-8	M20/2	BC	24°53.70	13°09.69	1313	clay. foram.-nannofos. ooze	20833
22	GeoB3719-2	M20/2	MUC	24°59.70	12°52.29	1995	clay.-nannofos. ooze	15333
23	GeoB3720-1	M34/1	BC	25°04.08	12°40.08	2516	foram.-nannofos. ooze	14179
24	GeoB3721-4	M34/1	MUC	25°09.09	12°24.00	3014	clay. nannofos. ooze	14340
25	GeoB3723-2	M34/1	MUC	25°23.70	11°31.59	4004	clay. foram.-nannofos. ooze	6377
26	GeoB3724-1	M34/2	MUC	26°08.29	8°55.60	4766	nannofossil ooze	4063
27	GeoB3606-2	M34/2	MUC	25°27.99	13°04.98	1793	silicious nannofossil ooze	66217
28	GeoB1715-1	M34/2	MUC	26°28.59	11°38.19	4097	foram.-nannofos. ooze	6480
29	GeoB1716-2	M34/2	MUC	27°57.10	14°00.19	1485	foram.-nannofos. ooze	42738
30	GeoB1717-2	M34/2	MUC	28°12.49	14°25.39	603	sandy+clay.-nannofos. ooze	5121
31	GeoB1718-1	M34/2	MUC	28°42.49	15°12.60	167	sandy+clay.-nannofos. ooze	4645
32	GeoB1719-5	M34/2	MUC	28°55.60	14°10.39	1023	foram.-nannofos. ooze	25639
33	GeoB1720-4	M57/2	MUC	29°00.00	13°49.69	2011	foram.-nannofos. ooze	8675
34	GeoB1721-4	M57/2	MUC	29°10.50	13°05.29	3079	foram.-nannofos. ooze	559
35	GeoB1722-3	M57/2	MUC	29°26.89	11°45.00	3971	nannofossil ooze	333
36	GeoB1724-4	M57/2	MUC	29°58.30	8°02.50	5102	clay.-nannofos. ooze	1139

<sup>a</sup> MUC = multicorer; BC = box corer/grab

#### 4.2.3. Environmental data

The environmental parameters selected for this study go conform to literature records and cover a wide range of potentially important gradients (MARRET & ZONNEVELD 2003 and references therein). Besides the oxygen content of bottom water, we considered the temperature, salinity, nutrient availability, and measures of stratification, primary, and export production.

Values on annual mean bottom water oxygen concentrations (adO<sub>2</sub>) were derived from model results gained with a regional implementation of the Modular Ocean Model-31 (MOM-31); Geophysical Fluid Dynamics Laboratory, NOAA Department of Commerce, Princeton, NJ, ([www.gfdl.noaa.gov](http://www.gfdl.noaa.gov)). Theory and concept of MOM-31 are explained elsewhere (PACANOWSKI & GRIFFIES 1999). The circulation model is coupled with an ecosystem model as described in FENNEL & NEUMANN (2004). Oxygen sources are photosynthesis and exchange with the atmosphere. Consumption is due to respiration and bacterial mineralization of detritus in the sediment and water column. Lateral ventilation by the Ekman compensation current and by the pole-ward undercurrent plays an important role to maintain the permanent oxygen deficit of the shelf water. The horizontal model resolution in the area of investigation is about 8 km and compares with the cross shelf station distance. Simulations were run over five model years for 1999 to 2005. The calculated adO<sub>2</sub> values used in this study correspond to 2003.

Information on total organic carbon contents in surface sediments (TOC) has been gathered from the data archive PANGAEA (LOCHTE & ROMANKEVICH 1998; MOLLENHAUER 2002*a,b*) and from literature records (ROGERS 1977; BREMNER 1981; CALVERT & PRICE 1983). In total, data include 602 locations, of which 83% are from stations above 1000-m water depth, resulting in a higher data density for the shelf and upper slope. Average summer and winter sea surface temperature (SSST, WSST) and salinity (SSSS, WSSS) values, as well as annual mean sea surface concentrations of phosphate (aPO<sub>4</sub>) and nitrate (aNO<sub>3</sub>) were derived from the World Ocean Atlas 2001 Data Set, National Oceanographic Data Center, Silver Springs, MD ([www.nodc.noaa.gov/OC5](http://www.nodc.noaa.gov/OC5)). Upper water column stratification during summer (SSI) and winter (WSI) was indicated by the Brunt-Väisälä frequency [ $N = \sqrt{(9.8\delta D)/(1026\delta z)}$ ], where  $\delta D$  represents the density difference calculated from the temperature and salinity change over  $\delta z$  (in this case 50 m) taking the standard NICMM equation. Seasonal concentrations of Chl *a* (SChl *a*, WChl *a*) for 2001 have been inferred from ocean colour scan images that are available by the SeaWiFS Project, NASA Goddard Space Flight Center, ([oceancolor.gsfc.nasa.gov/SeaWiFS](http://oceancolor.gsfc.nasa.gov/SeaWiFS)) at a grid size of ¼ degree. In all cases seasonality refers to northern hemisphere summer (Jul - Sep) and winter (Jan - Mar), respectively. Depth was not considered separately within the statistical analyses, because its relationship to species distribution is clearly coincidental with any dependence of other variables on depth. To finally determine a value at each of the 36 sample locations, all environmental variables have been interpolated horizontally with inverse distance weighting, a mapping method build in Surfer v8, Golden Software, Inc.

#### 4.2.4. Statistical analysis

Eleven dinocyst species were removed from the original data set because they occurred only in three or fewer samples. The remaining twenty-eight species accounted for at least 94% of

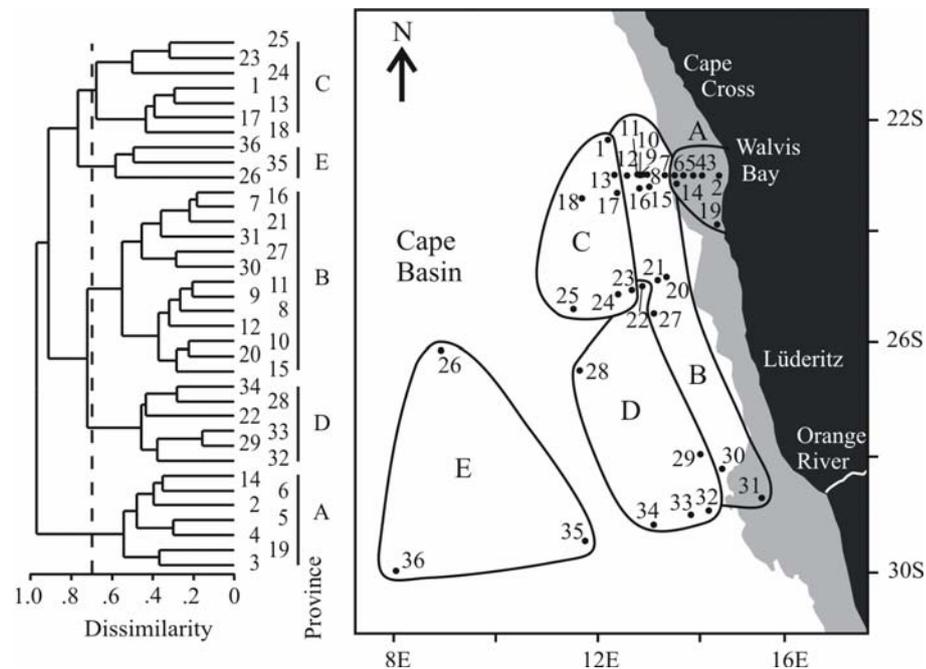
the total assemblage at each station and have been retained for statistical analyses (Table 4.2). Relative frequencies were used instead of concentrations per gram of sediment, because of the extreme ranges in the dataset.

**Table 4.2.** List of species included in statistical analysis, their nutrition, and taxonomic classification.

Peridinioid	Abbr.	Trophy	Gonyaulacoid	Abbr.	Trophy
<i>Echinidinium aculeatum</i>	<i>Eacu</i>	heterotr.	<i>Bitectatodinium tepikiense</i>	<i>Btep</i>	autotr.
<i>Echinidinium delicatum</i>	<i>Edel</i>	heterotr.	<i>Impagidinium aculeatum</i>	<i>Iacu</i>	autotr.
<i>Echinidinium granulatum</i>	<i>Egra</i>	heterotr.	<i>Impagidinium paradoxum</i>	<i>Ipar</i>	autotr.
<i>Echinidinium</i> spp.	<i>Espp</i>	heterotr.	<i>Impagidinium patulum</i>	<i>Ipat</i>	autotr.
<i>Echinidinium transparentum</i>	<i>Etra</i>	heterotr.	<i>Impagidinium plicatum</i>	<i>Ipli</i>	autotr.
cyst of <i>Protoperidinium americanum</i>	<i>Pame</i>	heterotr.	<i>Impagidinium sphaericum</i>	<i>Isph</i>	autotr.
cyst of <i>Pentapharsodinium dalei</i>	<i>Pdal</i>	heterotr.	<i>Impagidinium striolatum</i>	<i>Istr</i>	autotr.
<i>Multispimula quanta</i>	<i>Mqua</i>	heterotr.	<i>Impagidinium variaseptum</i>	<i>Ivar</i>	autotr.
<i>Polykrikos kofoidii</i>	<i>Pkof</i>	heterotr.	<i>Nematosphaeropsis labyrinthus</i>	<i>Nlab</i>	autotr.
<i>Trinovatedinium capitatum</i>	<i>Tcap</i>	heterotr.	cyst of <i>Protoceratium reticulatum</i>	<i>Pret</i>	autotr.
<i>Brigantedinium</i> spp.	<i>Bspp</i>	heterotr.	<i>Pyxidinopsis reticulata</i>	<i>Pyxr</i>	autotr.
<i>Selenopemphix nephroides</i>	<i>Snep</i>		<i>Operculodinium israelianum</i>	<i>Oisr</i>	autotr.
			<i>Spiniferites mirabilis</i>	<i>Smir</i>	autotr.
			<i>Spiniferites patchydermus</i>	<i>Spat</i>	autotr.
			<i>Spiniferites ramosus</i>	<i>Sram</i>	autotr.
			<i>Spiniferites</i> spp.	<i>Sspp</i>	autotr.

A cluster analysis (Euclidean distances) based on the Jaccard (Ružička) index was conducted to identify provinces of similar assemblage structure, while species common to a province, in the sense that they appear at consistent (high) percentages in the corresponding samples, were inferred from SIMPER-analysis (Similarity Percentage). In order to point out relationships to latent environmental gradients data were processed with detrended correspondence analysis (DCA; detrending by 2<sup>nd</sup> order polynomial). This method demands for species data only (indirect), but interpretation was facilitated by including the available environmental information. Subsequent to DCA constrained (or canonical) correspondence analysis (CCA) was applied. This technique accounts for variability that can be explained ‘best’ by the measured environmental parameters (direct). Therefore, variables had to be standardized to mean 0 and variance 1 in order to make them comparable. In CCA it is very popular to use all available parameters simultaneously. This, however, coevally relaxes constraining if the number of variables is high, so that the results become similar to unconstrained ordination. Hence, CCA modeling has been accomplished to limit the number of variables to the most important ones. This was done by single term addition (forward selection) of variables that met the AIC (Akaike Information Criterion) goodness-of-fit criterion. Each selection was assessed by evaluating its contribution in terms of total deviance explained. Thereby, variables had to be significant at  $p < 0.05$  of a Chi-square test. As strong correlations exist among the candidate predictors, variance inflation factors (VIFs) were consulted as a measure of redundancy. The results obtained from ordination were finally cross-checked consulting discriminant analysis in order to determine the degree of consistency between the final model and cluster analysis. For detailed background information on the statistical techniques mentioned above we refer to more sophisticated literature (e.g., JONGMAN *et al.* 1987;

LEGENRE & LEGENDRE 1998). All computations were done with R (R CORE DEVELOPMENT TEAM 2005), a programming environment for data analysis and graphics.



**Figure 4.3.** (A) Results of cluster analysis. Dendrogram of species data showing groups of sample stations at the 70% dissimilarity cut-off level (dashed line). (B) The map indicates geographic locations of the identified provinces (A-E).

### 4.3. Results

After removing rare species from the dataset species richness corresponded to 13–24 taxa per sample, assuming that counting more than 200 specimens per sample eliminated further diversity. The total concentration of dinocysts per gram of sediment varied largely among sites (cf. Table 4.1), but generally declined between coastal and open-ocean as well as northern and southern stations. The latter tendency was less pronounced. Cluster analysis identified five groups of stations at a dissimilarity cut-off level of 70% which we assigned to oceanic provinces (A-E; Fig. 4.3). Province-A comprised epeiric sites above 250 m, located within the oxygen minimum zone off Walvis Bay. Province-B ran parallel to the coast and merged most sites from the slope above 2000 m and the sample from the Orange River mouth (31). Province-C contained sites from the continental rise between 2000 to 4000 m north of ~25.5°S and province-D mainly sites from a similar depth range but south of ~25.5°S. Province-E comprised the remaining three sites that located in the Cape Basin abyssal plain below 4000 m. The relative contributions of single species to the similarity in each province were determined by SIMPER-analysis (Table 4.3). Many species did not contribute to a large extent and they were therefore not considered in great detail. Those with tendencies to dominate associations in the different provinces were *Brigantedinium* spp., cyst of *P. reticulatum*, *N. labyrinthus*, and *I. aculeatum*. Generally, these species represented the good discriminators between provinces. Most conspicuous trends were observed for cysts of

heterotrophic dinoflagellates which accounted for ~81% similarity in province-A. In province-B and C they declined considerably and were largely displaced by the cyst of *P. reticulatum* and *N. labyrinthus*, respectively. In province-D the relative abundance of cysts of heterotrophic dinoflagellates did not exceed 10% and became insignificant in province-E, where *I. aculeatum* contributed most.

**Table 4.3.** Results of SIMPER-analysis.

Province	Species/taxon	Average abund. %	Average similarity	Contrib. %	Cum. %
A	<i>Pspp</i>	46.03	41.22	56.64	56.64
	<i>Espp</i>	12.26	8.93	12.27	68.91
	<i>Eacu</i>	6.43	4.55	6.25	75.16
	<i>Pcon</i>	6.39	4.21	5.79	80.95
	<i>Nlab</i>	6.42	3.89	5.35	86.29
	<i>Ocen</i>	6.09	3.12	4.28	90.57
B	<i>Ocen</i>	45.49	41.54	52.86	52.86
	<i>Pspp</i>	25.54	20.34	25.89	78.74
	<i>Espp</i>	6.23	4.60	5.85	84.60
	<i>Nlab</i>	6.55	4.28	5.44	90.04
C	<i>Nlab</i>	32.65	26.28	39.05	39.05
	<i>Ocen</i>	18.41	13.99	20.79	59.84
	<i>Pspp</i>	18.74	12.11	17.99	77.83
	<i>Ipar</i>	3.38	2.43	3.62	81.45
	<i>Pret</i>	3.55	2.11	3.14	84.59
	<i>Iacu</i>	3.41	2.07	3.08	87.67
	<i>Espp</i>	4.35	2.02	3.00	90.68
D	<i>Ocen</i>	56.02	49.19	64.09	64.09
	<i>Nlab</i>	12.88	9.24	12.04	76.13
	<i>Pspp</i>	10.25	6.93	9.02	85.15
	<i>Sram</i>	7.59	5.70	7.43	92.58
E	<i>Iacu</i>	26.90	19.34	30.11	30.11
	<i>Nlab</i>	17.10	15.05	23.43	53.54
	<i>Ipar</i>	9.32	8.54	13.30	66.84
	<i>Ocen</i>	17.71	8.15	12.69	79.53
	<i>Pret</i>	2.73	2.14	3.34	82.87
	<i>Isph</i>	3.71	2.00	3.12	85.99
	<i>Sram</i>	2.84	1.80	2.80	88.79
	<i>Sspp</i>	3.21	1.75	2.73	91.52

Graphical presentation of the DCA results allowed for the discrimination of the same provinces that had been identified by cluster analysis (Fig. 4.4). The first axis explained the largest part of the variation and represented a gradient (or combination of gradients) of proximal-distal (coastal-neritic-oceanic) change. The axis achieved maximal contrast between most shelf-ward stations bundled on the negative scale (province-A) and samples from furthest offshore on the positive extreme (province-E). The second DCA axis accounted for a smaller part of the variation and separated stations of province-A and C on the positive scale from samples corresponding to province-B, D, and E on the negative part. The distribution of species scores illustrated affinities with respect to the underlying gradient(s). Opposed on the first DCA axis most cysts of the heterotrophic genera plotted on the shelf-ward scale, while the cysts of autotrophic gonyaulacoids were distributed on the neritic to oceanic intercept. Most of the dinocysts that scored towards the extremes of DCA axis 2 were associated with a cosmopolitan distribution. The environmental predictors correlated significantly ( $p < 0.05$ ) but differently strong with the site scores of the first DCA axis, and in the case of WSSS explained 91% of the association captured by ordination (Table 4.4). The second DCA axis proved a weak but significant relationship to WChl *a*.

**Table 4.4.** DCA summary and inter set correlations of environmental variables with axes scores. Estimates in bold are significant at  $p < 0.05$ .

	DCA1	DCA2	DCA3	DCA4
Eigenvalue	0.385	0.166	0.067	0.041
Cum. % of var.	36.4	52.2	58.5	62.4
adO <sub>2</sub>	<b>0.707</b>	0.104	0.061	-0.058
TOC	<b>-0.662</b>	0.119	-0.042	0.035
aPO <sub>4</sub>	<b>-0.835</b>	0.323	-0.048	0.014
aNO <sub>3</sub>	<b>-0.860</b>	0.237	-0.023	0.061
SSST	<b>0.865</b>	-0.081	0.107	0.062
WSST	<b>0.837</b>	-0.143	-0.010	0.037
SSSS	<b>0.856</b>	-0.117	-0.205	-0.057
WSSS	<b>0.911</b>	-0.156	-0.179	-0.040
SChl <i>a</i>	<b>-0.628</b>	0.256	-0.102	-0.064
WChl <i>a</i>	<b>-0.467</b>	<b>0.329</b>	0.081	-0.170
SSI	<b>-0.812</b>	0.234	0.012	0.151
WSI	<b>-0.702</b>	0.219	0.111	0.170

From the available quantity of variables the combination explaining best community variability was determined by stepwise CCA modelling. Forward selection identified a model composed of WSSS, WChl *a*, adO<sub>2</sub>, and aPO<sub>4</sub> (Table 4.5). The linear combination of these parameters and its direct relation to variations in assemblage composition was statistically significant (Monte Carlo Permutation test:  $p < 0.005$ ). The VIF of the variables did not exceed the critical value of ten so that each addition accounted for independent information (i.e., covariance was negligible). This became apparent when their values were plotted against the site scores of the first CCA axis (Fig. 4.5). Vectors of WSSS and aPO<sub>4</sub> ran opposite one another and were linearly correlated to the first axis. In contrast, WChl *a* and adO<sub>2</sub> revealed a significant connection with variability on the first axis by means of exponential and logistic coherence, respectively. The relationship between community variability and the conditionally significant parameters (i.e., covariance eliminated) has been summarized in Table 4.6. Constraining rendered only a part of the environmental ties, but in most cases at least one parameter explained a significant proportion of species variability.

A major influence on ordination could be ascribed to species that accounted for the main differences between the provinces. Although these species obtained highest weights in CCA, model building carried out without them resulted in the same solution. After combining evidence inferred from regressions and correlations between species abundance and the determined predictors, five categories of dinocysts were recognized (note that the relationships always refer to the mean of a variable): (1) Species whose relative abundance showed a strong connection to increasing salinity values. This concerns *Impagidinium* species (except for *I. variaseptum*). (2) Species whose distribution showed a strong relationship to Chl *a* concentrations in surface waters. Positive relationships were determined for *Brigantedinium* spp., *M. quanta*, *Echinidinium* spp., *E. aculeatum*, and *P. kofoidii*. Relationships were negative in case of *I. aculeatum*, *I. sphaericum*, and *S. mirabilis*. (3) Species whose relative abundance showed changes in the course of varying

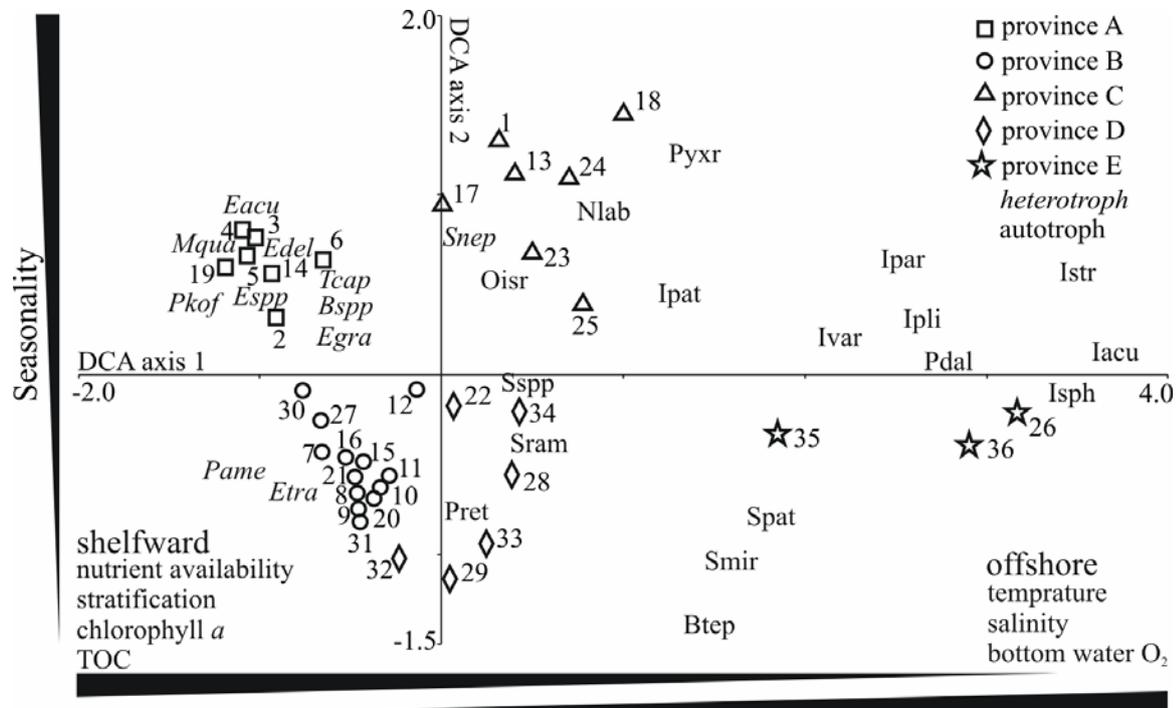
bottom water oxygen concentrations. Inverse correlations were observed for cysts of *E. transparentum*, *T. capitatum*, cyst of *P. americanum*, and *M. quanta*. Positive relationships were determined for *P. reticulata*, *N. labyrinthus*, *S. ramosus*, and *I. patulum*. (4) Species whose contributions to the assemblage showed dependency on phosphate concentrations in surface waters. Positive relationships were shown by cysts of *Brigantedinium* spp., *Echinidinium* spp., *E. delicatum*, and *E. granulatum*. Negative relationships were assessed for *N. labyrinthus*, *P. reticulata*, *S. ramosus*, *S. mirabilis*, and *B. tepikiense*. (5) Species whose distribution pattern had little or no relation to any of the given variables (i.e., cyst of *P. reticulatum*, *O. israelianum*, *P. dalei*, *I. variaseptum*, *S. patchydermus*, *Spiniferites* spp., and *S. nephroides*).

**Table 4.5.** Description and results of stepwise CCA model building.

	CCA1	CCA2	CCA3	CCA4	df	AIC	Deviance	Residual deviance	% of dev. explained	Pr ( $\chi^2$ ) <sup>a</sup>	VIF <sup>b</sup>
Eigenvalues	0.333	0.125	0.067	0.038							
Cum % var.	31.5	43.4	49.7	53.3							
none					-	169.64	3790.54	-	-	-	-
WSSS					-1	158.26	1177.07	2613.47	31.1%	0.00025	7.43
WSSS + WChl <i>a</i>					-2	154.70	373.91	2239.56	40.9%	0.01839	1.57
WSSS + WChl <i>a</i> + adO <sub>2</sub>					-3	152.52	245.22	1994.34	47.4%	0.04103	2.14
WSSS + WChl <i>a</i> + adO <sub>2</sub> + aPO <sub>4</sub>					-4	150.15	228.07	1766.27	53.4%	0.03654	7.12

<sup>a</sup> refers to the addition of the variable

<sup>b</sup> value of added variable in the final model



**Figure 4.4.** DCA plot showing the variation between samples and variability in species distribution. Axes lengths are expressed in unit standard deviation. Relationships between sample scores and the environmental parameters are indicated by filled triangles.

The results of discriminant analysis are shown in Table 4.7. The use of WSSS, WChl *a*, adO<sub>2</sub>, and aPO<sub>4</sub> as explanatory variables was highly significant (Wilk's Lambda = 0.051, df = 12,  $p < 0.001$ ) and accounted for a total of 81% correctly predicted classifications. Two stations of province-A (6, 14) were incorrectly assigned to province-B, three stations (12, 21, 25) of province-B were grouped in province-C and two stations (22, 27) were confused between province-C and D. Stations of province-E were classified correctly throughout. Classifications that did not correspond to the results of cluster analysis were in most cases attached to stations from the upper slope.

**Table 4.6.** Simplified results of CCA. Multiple linear regressions between species distribution and the best CCA model and rank correlations between environmental variables and species.

Species/ taxon	CCA weight	adj. $R^2$ model <sup>a</sup>	WSSS	WChl <i>a</i>	adO <sub>2</sub>	aPO <sub>4</sub>
<i>Edel</i>	14.61	*0.262	—	+	—	(+)
<i>Egra</i>	52.30	0.234	—	+	—	(+)
<i>Bspp</i>	854.79	*0.609	—	(+)	—	(+)
<i>Espp</i>	210.01	*0.568	—	(+)	—	(+)
<i>Eacu</i>	72.04	*0.678	—	(+)	—	+
<i>Pkof</i>	6.86	*0.281	—	(+)	—	+
<i>Mqua</i>	74.26	*0.349	—	(+)	(—)	+
<i>Pame</i>	31.96	*0.564	—	+	(—)	+
<i>Tcap</i>	68.02	0.157	—	+	(—)	+
<i>Etra</i>	26.57	*0.299	—	+	(—)	+
<i>Snep</i>	34.37	0.242				
<i>Oisr</i>	8.32	0.004				
<i>Sspp</i>	46.28	0.207				
<i>Pret</i>	1152.06	*0.283		( )		
<i>Pdal</i>	11.89	0.203	( )			
<i>Spat</i>	5.69	0.225	( )			
<i>Ivar</i>	14.10	*0.372	( )			( )
<i>Ipat</i>	14.78	*0.262	(+)	—	(+)	—
<i>Ipli</i>	3.78	*0.421	(+)	—	+	
<i>Ipar</i>	61.29	*0.657	(+)	—	+	—
<i>Istr</i>	8.76	*0.473	(+)	—	+	—
<i>Isph</i>	15.70	*0.624	(+)	(—)	+	—
<i>Iacu</i>	115.88	*0.604	(+)	(—)	+	—
<i>Smir</i>	17.09	*0.624	+	(—)	+	(—)
<i>Btep</i>	2.89	0.157	+	—		(—)
<i>Sram</i>	128.92	*0.629	( )		(+)	(—)
<i>Nlab</i>	487.24	*0.485	+	—	(+)	(—)
<i>Pyxr</i>	45.42	*0.449	+	—	(+)	(—)

<sup>a</sup>significant ( $p < 0.01$ ) multiple regressions have an asterisk.

Spearman rank correlation: +/- = positive/negative ( $p < 0.05$ ); else insignificant. Brackets indicate parameter explaining significant proportion of species variability ( $p < 0.05$ ).

#### 4.4. Discussion

Apart from preservation, dinocyst assemblages are always controlled by the balance of initial cyst supply and transportation, and therefore do not necessarily reflect selective degradation of cysts after burial to sediments. These processes are crucial to the interpretation of statistical

results and their influence must be considered carefully before we attach importance to taphonomic control.

#### 4.4.1. Cyst production

Traditional tenets in palynology associate heterotrophic dinoflagellates, notably of the genus *Protoperidinium*, with high productivity regimes where ample food supply supports the copious production of cysts (WALL *et al.* 1977; HARLAND & PUDSEY 1999). In contrast, autotrophic species are supposed to produce cysts in predictable and nutrient poor habitats that satisfy their fragility and light requirements (WALL *et al.* 1977; HARLAND *et al.* 1998). Our results show that cysts of heterotrophic dinoflagellates dominate the assemblage close to coastal upwelling, whereas cysts of autotrophic species typify neritic to oceanic environments (cf. Table 4.3). This analogy indicates that community variability in surface sediments of the BCUS results from different cyst production. For several reasons we, however, cannot determine how far it explains the observed patterns.

First of all, little is known about cyst assemblages within the water column or benthic boundary layer. Consequently, there is no proof whether production of cysts in surface waters directly connects to their distribution in the sediments. We also do not know the frequencies of sexual reproduction. Usually, we expect maximal encystment to occur when thecal cell concentrations are highest (ANDERSON & KEAFER 1987). However, endogenous rhythms unique to each species may exert control on cyst formation, but timing and scale of response can be modulated by the environment, notably nutrient depletion, temperature decrease, and light limitation (PFIESTER & ANDERSON 1987; BLANCO 1995). When we turn to the proportion of cells that forms gametes in a given population, information becomes even sparser. Though efficiencies can differ greatly (DALE 1976), cyst production may ultimately depend on thresholds (WYATT & JENKINSON 1997). Second, dinoflagellates with preservable cysts are of minor relevance to the community in the BCUS, whereupon cyst assemblages in sediments do not necessarily correlate to maximum proliferation in surface waters (DAVEY & ROGERS 1975; PITCHER *et al.* 1998). In consequence, prevalence of peridinioid cysts close to the upwelling domain may result from the dominance of autotrophic dinoflagellates with no known resting stage rather than copious production. Third, trap studies off northwest Africa and in the Arabian Sea have shown that the abundance of some autotrophic dinoflagellates positively relates to nutrient supply (ZONNEVELD & BRUMMER 2000; SUSEK *et al.* 2005). Moreover, some autotrophic species are capable of heterotrophy as well (SMAYDA & REYNOLDS 2003), which together makes a plausible case that cysts production may increase with elevated or episodic nutrient delivery. Finally, the persistent or periodical oxygen depletion of bottom waters on the Namibian shelf may inhibit excystment of some dinoflagellates eventually causing them to die (ANDERSON *et al.* 1987). Species with long maturation times consequently run a greater risk, so that their contribution to bloom initiation and subsequent cyst production would decline (LECKIE *et al.* 1992). Apparently, it is impossible to monitor all underlying mechanisms that drive cyst production and further studies will be necessary to demonstrate effects on distributional change in dinocyst associations unequivocally.

The dinocyst assemblage at a given location does not necessarily reflect production, notably beyond shelf breaks where lateral input and removal may exceed vertical supply (DALE 1992). Studies on particle flux, carbon turnover, and sedimentation processes point to the relevance of lateral transport in the BCUS (INTHORN *et al.* 2006). Accordingly, shelf break and upper slope may receive cyst input from the outer shelf due to transport in benthic and intermediate nepheloid layers. This process could explain the deviant grouping of some upper slope stations observed by cluster analysis and discriminant analysis (Table 4.7). On the shelf, dinoflagellates are probably also displaced from the upwelling centre by the equator-ward current, but cyst flux into the pole-ward undercurrent may prevent washout from the inner shelf. Such a re-circulating loop is described for diatoms in an upwelling area off southwest Africa (PITCHER 1990). The major consequence for cyst transport is that the bulk of cysts produced over the inner and middle shelf is most likely not transferred to outer domains, but accumulates in the mud-belt north of Lüderitz and below the Walvis Bay upwelling cell.

**Table 4.7.** Jackknifed matrix of discriminant analysis showing the classification of sample stations by the final CCA model (cases in row categories classified into columns).

Province	A	B	C	D	E	% correct
A	5	2	0	0	0	71
B	0	10	3	0	0	77
C	0	0	6	1	0	86
D	0	0	1	5	0	83
E	0	0	0	0	3	100
total	5	12	10	6	3	81

#### 4.4.2. Transport

Most cysts behave like silt particles and could cover long distances from their point of formation to the site of sedimentation by both, surface and deep water transport (WALL *et al.* 1977). We found high contributions of cysts of *P. reticulatum* and *S. ramosus*, which also prevail in the Agulhas Current region and the south-western shelf of Africa, respectively (DAVEY & ROGERS 1975). Transport associated with the Benguela Current could have supplied these species to the BCUS, notably to stations influenced by ESACW (cp. Fig. 4.1). However, ZONNEVELD *et al.* (2001a) conclude that cyst contribution from different remote sources has marginal influence on assemblage structures in the BCUS. A predominately autochthonous character of the association is also inferred from our database that only sporadically includes species typical for the Atlantic sector of the Southern Ocean (ESPER & ZONNEVELD 2002), the south Indian Ocean (MARRET & DE VERNAL 1997), or the Angola Basin (DALE *et al.* 2002).

Some mechanisms accelerate the export of cysts to bottom sediments and thus reduce the time span for transportation including agglomeration/flocculation in ‘marine snow’ (LAMPITT *et al.* 1993) and faecal pellet transport (MUDIE 1996). Once settled most cysts tend to accumulate in the flocculent layer, because they are less dense than sand or clay particles and (DALE 1979).

Hence, bottom current speed typical of the Benguela Current (10-30 cm s<sup>-1</sup>; Shannon and Nelson 1996) may be capable of resuspending dinocysts. For this reason, sampling may account for the majority of cysts at a given location but at other stations could fail due to preferential burial of cysts (ANDERSON *et al.* 1985). In other words, where vast quantities of 'round-brown' protoperidinioid cysts dominate the assemblage, cysts of autotrophic species that are mostly equipped for flotation may have remained in suspension and thus not sampled. The extent to which the above mentioned processes operate in the BCUS is vague, and additional data such as grain size populations are required to determine how much they affect dinocyst distribution.

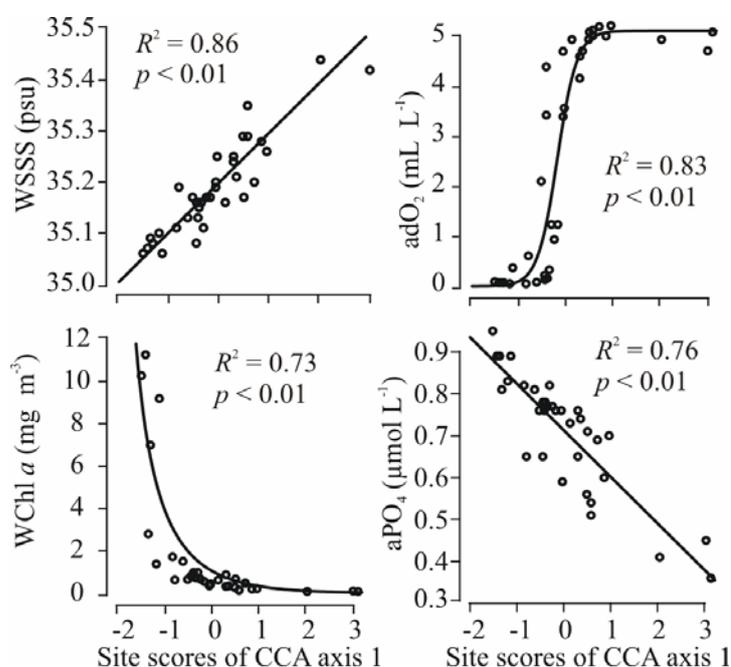
#### 4.4.3. Environmental control: Sea surface conditions

According to our results, a part of community variability explained by CCA modeling connects to winter salinity, which influences the distribution of *Impagidinium* species, *P. dalei*, *S. ramosus*, and *S. patchydermus* (Table 4.6). This is in contrast to findings of ZONNEVELD *et al.* (2001a), who identified a strong stratification signal in their study of the Benguela region. However, their sampling covered more stations near to Orange River outflow, so that the stratification gradient was possibly steeper. In our study area, salinity differences are greatest between active upwelling centres and the open ocean domain. This may be more important than water column stability, because salinity is a prime factor for the control of osmotic exchange and plays a decisive role in the distribution of dinoflagellates (DE VERNAL *et al.* 1994).

The Chl *a* concentration, in particular, is an indicator for primary production and in our study WChl *a* explains a significant proportion of community variability. This parameter positively relates to the distribution of some peridinioid species (Table 4.6), which suggests an indirect relationship to phytoplankton growth. Because their motiles mainly feed on diatoms (WALL *et al.* 1977; HARLAND & PUDSEY 1999), encystment may attain highest rates during austral summer after phytoplankton blooms have formed in response to weaker upwelling. Some species are negatively related to winter chlorophyll *a*. They are all produced by autotrophic dinoflagellates and predominantly described from oligotrophic habitats that accord to their light requirements (MARRET & ZONNEVELD 2003). The link between WChl *a* and community variability may further cover a seasonal component. This is indicated by DCA (Table 4.4, Fig. 4.4). The second axis opposes cysts of heterotrophic dinoflagellates that are adapted to seasonal cues (EDWARDS 1993) and most *Spiniferites* species which prefer areas of little seasonal contrast (DE VERNAL *et al.* 1994; VINK *et al.* 2000). The former are abundant in areas of strong seasonal changes in Chl *a* concentration (i.e., near to upwelling cells and in the filament sector), while the latter tend to make higher contributions in more predictable provinces of the BCUS.

Nutrient concentrations in surface waters exert strong control on the distribution of dinocysts (MARRET & ZONNEVELD 2003). CCA model building has selected the annual phosphate concentration, which shows a positive relation with cysts of *Brigantedinium* spp. and most *Echinidinium* species. In modern sediments vast numbers of the former are found in areas of elevated nutrient contents (ROCHON *et al.* 1999), but they are also prominent in habitats with periodical nutrient enrichment (MCMINN 1992). In the eastern South Atlantic cysts of the genus *Echinidinium* are observed in the vicinity of upwelling of fertile waters (ZONNEVELD *et al.* 2001a)

and in the western equatorial Atlantic in association with high nutrient input from river discharge (VINK *et al.* 2000). Species with negative relations to phosphate, in particular of the genera *Impagidinium* and *Nematosphaeropsis*, are often related to rather nutrient-poor environments (WALL *et al.* 1977). This agrees with the association of province-E, but our results suggest that they can also prosper in areas where filament activity causes episodic nutrient delivery, so that high relative abundances do not necessarily mirror an oligotrophic open ocean environment. Most studies infer a stronger nitrogen control on dinoflagellates (e.g., DEVILLERS & DE VERNAL 2000). However, nitrogen is the limiting component in the BCUS (CHAPMAN & SHANNON 1985), and we assume that phosphate better explains community variability, because it is less homogeneously distributed.



**Figure 4.5.** Regressions between site scores of the first CCA axis and the environmental parameter included in the final CCA model. Different trend lines have been fitted to the data: WSSS and aPO<sub>4</sub> = linear, WChl *a* = exponential, adO<sub>2</sub> = logistic.

#### 4.4.4. Taphonomic control: The role of oxygen

To the authors' knowledge this approach is among the first to quantitatively include information on bottom waters oxygen concentration in an analysis of dinocyst distribution in surface sediments (**Chapter 2**). For terrestrial palynomorphs differential susceptibility to oxidation is evident from the study of Quaternary pollen (CAMPBELL 1999). By comparison to terrestrial compounds, VERSTEEGH & ZONNEVELD (2002) hypothesized that gonyaulacoid and peridinioid cysts represent end-members in a degradability 'ranking'. They expected significant shifts in assemblage compositions towards the former, once the availability of oxygen in bottom and pore waters increases. Their theory agrees well with the result of SIMPER-analysis in this study (Table 4.3). It also corresponds to the discrimination of heterotrophic peridinioids and autotrophic gonyaulacoids

along the first DCA axis (Fig. 4.4). The low scattering of peridinioid cysts relative to stations of province-A suggest that their sedimentary distribution particularly relates strong oxygen deficiency. Similar conclusions have been drawn from a sediment-trap study in the eastern Arabian Sea (ZONNEVELD & BRUMMER 2000), where sensitive cysts are enriched in sediments beneath the oxygen minimum zone compared to well-oxygenated sediments outside this zone.

MCCARTHY *et al.* (2003) argued that the common observation of an offshore increase in the gonyaulacoid:peridinioid ratio may result primarily from destruction of peridinioid cysts under oxidizing conditions rather than reflecting the true distribution of dinoflagellates in surface waters. In our study, the pattern emerging from community variability roughly depicts the local hydrography and ground level oxygenation off Namibia as is described in BAILEY (1991) and CHAPMAN & SHANNON (1985). Moreover, results of CCA emphasize that the distribution of certain peridinioid taxa may particularly relate to this factor (Table 4.6; Fig. 4.5). This is corroborated by laboratory experiments which reveal the different degradation behaviours of marine palynomorphs (HOPKINS & MCCARTHY 2002). These tests, however, suggest also that oxidation initially changes relative abundances towards certain taxa, whereas prolonged exposure may favour other taxa and could cause a step-like change rather than a gradual decrease. Nevertheless, reports on post-depositional organic matter degradation at natural oxidation fronts indicate that resistance of dinocyst to oxidation in natural settings parallels their susceptibility to chemical treatment (ZONNEVELD *et al.* 2001b). According to these observations, species could be classified in ascending order of resistance as: (1) highly sensitive (cysts formed by genera *Protoperidinium* and *Echinidinium*); (2) moderately sensitive (e.g., cyst of *P. reticulatum* and *Spiniferites* species); and (3) resistant (e.g., *Impagidinium* species, *N. labyrinthus* and *O. israelianum*). An analogy to the present study exists in case of the sensitive categorization, but it is vague with respect to moderately sensitive and resistant dinocysts. This, however, seems reasonable, since factors other than taphonomic ones ought to gain stronger influence on the distribution of resistance cyst. The positive relationships to oxygenation of bottom waters assessed for some gonyaulacoid species may point out that their spatial variability is particularly governed by selective degradation of sensitive cysts.

Selective dinocyst degradation during settling through the water column has never been proven, but a factor worth mentioning is the oxygen exposure time. According to FERDELMAN & SCHULZ (1999), probably ~90% of the total oxygen uptake in organic-rich sediments from the continental slope of Namibia can be attributed to oxidation of hydrogen sulphide. In this case dinocyst degradation/preservation may predominantly relate to the oxygen exposure time, as has been pointed out for fluxes of lipid biomarkers to surface sediments in the eastern South Atlantic (SCHEFUß *et al.* 2004). Apparently, it is difficult to account for all factors influencing the oxygen exposure time such as sedimentation rates, re-suspension, bioturbation, export production and amounts, states and reactivity of compounds available for oxidation. We assume that most factors covary with changes in bottom water oxygen contents, so that differences in cyst preservation between shelfward and oceanic areas would be exaggerated if the oxygen exposure time were corrected for. Nevertheless, the ultimate preservation of assemblages reaching the sediment-water interface may be partly or entirely independent of the dissolved oxygen level at high rates of

sedimentation (TYSON 2001). In this case bottom waters could be ventilated while pore waters may not, because of rapid burial and enhanced oxygen consumption by bacteria. The sparse information on pore water profiles at the studied sites makes it impossible to decide whether variations in export fluxes could offset the usage of bottom water oxygen concentrations.

#### 4.5. Concluding remarks

The ubiquitous occurrence of dinocysts in marine sediments allows for their use as stratigraphic markers and paleoenvironmental proxies. Although taphonomy is a factor in any palynological assemblage and should be recognized to avoid spurious interpretations, its significance is rarely addressed in Quaternary dinocyst studies. Given the lack of evidence, we designed this study to test if varying bottom water oxygenation can account for spatial variability in dinocyst assemblages in the BCUS. Trends in assemblage composition were revealed and compared to environmental factors with a probable connection to species distribution. From the pool of variables we computed a model composed of sea surface parameter (WSSS, WChl *a*, and aPO<sub>4</sub>), and one taphonomic factor (adO<sub>2</sub>). The results suggest that selective degradation, to some degree, altered the initial pattern in species associations after cysts were buried to surface sediments. In consideration of the factors discussed above, we conclude that the dinocyst thanatocoenosis in bottom sediments of the BCUS reflects five domains: (1) The upwelling zone. This domain concerns the eutrophic, inner shelf area off Walvis Bay, where an oxygen minimum zone is developed for most of the year. Well preserved, highest amounts of sensitive cysts produced by opportunistic species (i.e., of the genera *Protoperidinium* and *Echinidinium*) reflect high nutrient and pigment concentrations derived from intense but seasonal upwelling. Transport occurs downstream of the upwelling cell but is of minor importance in terms of community variability. (2) The transport realm. Including the shelf break front, this belt stretches parallel to the coastline covering the outer shelf and upper slope, where lateral transport in nepheloid layers and resuspension by bottom currents are of particular importance. An association typically dominated by the cyst of *P. reticulatum* relates to cyst production in matured waters. Though high contributions of *Brigantedinium* spp. can be observed, varying oxygenation of bottom waters and local changes in sedimentation rates probably provoke spatial heterogeneity in preservation of sensitive species. (3) The seasonal domain. Located in the pathway of major filament activity, this area over the lower continental slope receives periodical nutrient delivery in dependence on seasonal changes in meridional wind stress. Higher abundances of *N. labyrinthus* compared to cysts of *P. reticulatum* or *Spiniferites* species are probably the result of a better adaptation to a relatively unstable environment. *Brigantedinium* spp. takes advantage of the fertile waters associated with filament formation and cysts production is sufficient to enable relatively high deposition in sediments despite the permanent oxidation stress. (4) The Benguela Current domain. South of 25.5°S conditions become more stable in terms of seasonality, while hydrography relates to a stronger influence of ESACW. The dinocyst association is characterized by highest contributions of cysts of *P. reticulatum* and the characteristic appearance of *S. ramosus*, both possibly also transported to the north along the advection path of the Benguela Oceanic Current. Degradation of sensitive cysts considerably proceeds due to sufficient oxygenation of bottom waters. *Brigantedinium* spp. is still present in the sediments, but the abundance probably does not reflect

production in overlying waters. (5) The open ocean realm. Furthest offshore, towards the oligotrophic waters of South Atlantic gyre, conditions are favourable for photosynthesis. Cyst production in surface waters is likely low and the typical representatives of the dinocyst association in sediments at abyssal depth are almost exclusively gonyaulacoids. Species of the genus *Impagidinium* become more important, but the extremely slow sedimentation rates and conditions favourable for selective degradation do not allow for a direct comparison to the plankton assemblage.

Certainly, the use of relative abundances for statistical analysis gave more weight to dominant species and potentially underestimated trends of less abundant cysts ('closed-sum effect'). Absolute numbers, however, were inappropriate for the analysis of community variability due to the extreme ranges in our dataset, a disproportional weighting of rare cysts, and the effect of dilution by varying sedimentation rates. Despite the use of modelled oxygen data, the paucity of samples at our disposal and the uncertain time frames involved, we advocate that selective preservation of dinocysts has to receive more attention as presently acknowledged. There are, however, positive applications of palynomorph taphonomy, such as in distinguishing distal turbidites from pelagites (MCCARTHY *et al.* 2004), or the separation of preservation from productivity (VERSTEEGH & ZONNEVELD 2002), which is difficult to accomplish using conventional criteria. Next steps will require not only a qualitative appreciation of the impact of taphonomy on assemblages, but a quantitative way to measure and adjust for this skewing. In this regard, incorporation of selective degradation may prove to be a sensitive indicator of sediment geochemistry, facilitate environmental reconstruction and redirect attention to those areas and periods where discrepancies remain. Essential to the understanding of dinocysts distribution in different depositional regimes, such information can ultimately encourage the relevance of dinocysts in paleoenvironmental and paleoceanographic studies beyond current fields of application.

#### 4.6. References

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## CHAPTER 5

### Relating organic-walled dinoflagellate cysts to bottom water oxygenation: A case study and paleoceanographic application from the southeast Atlantic

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#### **Abstract**

Testing the biological pump hypothesis for lowering atmospheric  $p\text{CO}_2$  by reconstructing deep-ocean  $\text{O}_2$  requires more than simply search for extensive deep-ocean anoxia but demands for quantitative indicators of dissolved  $\text{O}_2$  that work at intermediate  $\text{O}_2$  concentrations. Analyses of organic-walled dinoflagellate cysts associations in surface sediments of the Benguela Current Upwelling System reveal that species pattern bears quantitative information on bottom water  $\text{O}_2$  conditions. Statistical evaluation evidences two cyst categories, referred to as oxidation resistant and sensitive end-members, and enables to derive a bottom water oxygen index. Upon calibration with present-day oxygen data this new proxy allows to trace the late Pleistocene history of bottom water  $\text{O}_2$  concentration at the lower continental slope of Namibia. In this area lowest  $\text{O}_2$  contents typify glacial cold phases of the last 150 kyr consistent with the timing of weaker deep water formation in the North Atlantic. Comparison to ventilation scenarios based on stable isotopes, carbonate dissolution, and benthic foraminiferal assemblages confirm the good proxy performance. Moreover, incorporation of selective preservation enhances reconstruction quality and largely explains the considerably higher organic carbon loads seen in some sections of the core.

Index terms: 4952 Paleocyanography : Palynology; 0473 Biogeoscience : Paleoclimatology and Paleocyanography; 1635 Global Change : Oceans; 4219 Oceanography – General: Continental shelf and slope processes

Keywords: bottom water oxygen, dinoflagellate cysts, preservation, deep water circulation, productivity

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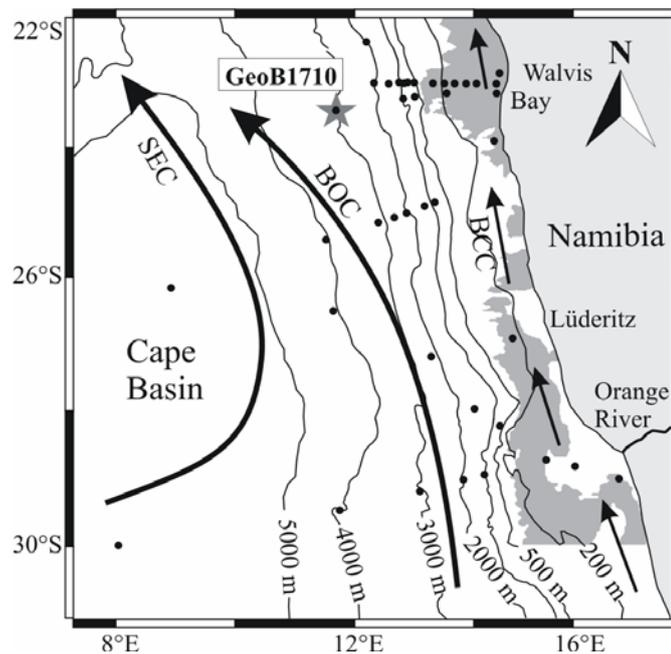
## 5.1. Introduction

The dissolved  $O_2$  concentration of ocean bottom water is commonly thought to be a master variable controlling the fate of organic matter (OM) that reaches the sediment-water interface. Where oxygen minimum zones impinge continental margins the  $O_2$  deficiency eventually promotes carbon burial and the generation of fossil fuel (GÉLINAS *et al.*, 2001), essentially the only process that accounts for the accumulation of atmospheric  $O_2$  and intimately links the global cycles of C, S, and O over geological time (BERNER, 1982). Over periods of hundreds to thousands of years, exposure to molecular  $O_2$  appears to affect the amount and composition of OM preserved in sediments (HARNETT *et al.*, 1998; HEDGES *et al.*, 1999) and has a meaning with respect to nutrient cycling, deep ocean carbonate chemistry, and ultimately the atmospheric  $pCO_2$  level (BROECKER & HENDERSON, 1998). However, estimates on the variability of bottom water  $O_2$  concentration on climatically relevant timescales are rare (e.g., YARINCIK *et al.*, 2000; NAMEROFF *et al.*, 2004) and effort needs to be directed to the quantification.

Many studies infer ‘oxygen effects’ on labile OM in sapropels and turbidites (e.g., RUTTEN *et al.*, 1999; PRAHL *et al.*, 2003), but these settings represents special cases and generally do not reflect the conditions of carbon sequestration in the marine environment, especially on continental shelf and slope areas, where most of the organic carbon is buried. Hence, to better estimate oxygen contents of the ocean’s deepest water during the past compositional parameters are required which reflect the degradative histories of sedimentary OM components. Such indices do exist and include pollen (KEIL *et al.*, 1994) and recalcitrant macromolecules such as algalenans (GELIN *et al.*, 1997) and hydrocarbons (ATLAS, 1981) which exhibit lower degradation rates under anoxic as compared with oxic conditions. Likewise, some species of organic-walled dinoflagellate cysts (or dinocysts) (TAYLOR, 1987), notably of the order Peridiniales, have been demonstrated to easily disintegrate during harsh oxidation procedures while others are robust and persist (MARRET, 1993; HOPKINS & MCCARTHY, 2002). This unlike preservation capacity is subscribed to a fundamental difference in the chemistry of the cyst walls (VERSTEEGH & BLOKKER, 2004) and distinguishes dinocyst that are very resistant (R-cysts) and particularly sensitive (S-cysts) with respect to ‘in situ’ oxidation. Palynology as yet has provided convincing proof that selective dinocyst preservation is a promising tool for paleoenvironmental reconstruction (e.g., VERSTEEGH & ZONNEVELD, 2002; MCCARTHY *et al.*, 2003; **Chapter 3**).

A potential use of statistical models is proxy calibration, where biotic data are used to estimate past environmental conditions. Such calibration sets, when analyzed by appropriate procedures, have the potential to transform the fossil record from sediment cores into quantitative estimates of the past environment. Within this study we aimed to derive a bottom water  $O_2$  proxy using as calibration dataset the modern distribution of dinocyst species in surface sediments of the northern Benguela Current Upwelling System, southeast Atlantic (herein referred to as BCUS). Like other eastern boundary upwelling system, this regime is typified by organic-rich sediments and severe bottom water oxygen gradients that locally give way to quasi permanent oxygen minimum zones (BAILY, 1991), providing a prime setting for natural experiments in diagenesis. We first raised species inventories of forty surface sediment samples, explored their spatial distribution with respect to the bottom water  $O_2$  gradient, and classified the R-cysts end-member

group. We defined the S-cyst end-member group by analyzing environmental dependencies of potential candidates with respect to physical, chemical and biological factors using Generalized Additive Models (GAMs). In a second step we calculated a bottom water oxygen index (BWOI) as the weighted ratio of both end-member groups ( $R/(R+S)$ ) and calibrated this proxy with the available O<sub>2</sub> data. We finally quantified late Pleistocene deep water ventilation changes at a lower continental slope core site of Namibia and assessed proxy performance by relating our results to various proxy records. This piece of research might form the basis of a new method that makes quantification of the O<sub>2</sub> content in bottom water possible and we advise more confidence in the use of selective degradation than presently acknowledged.



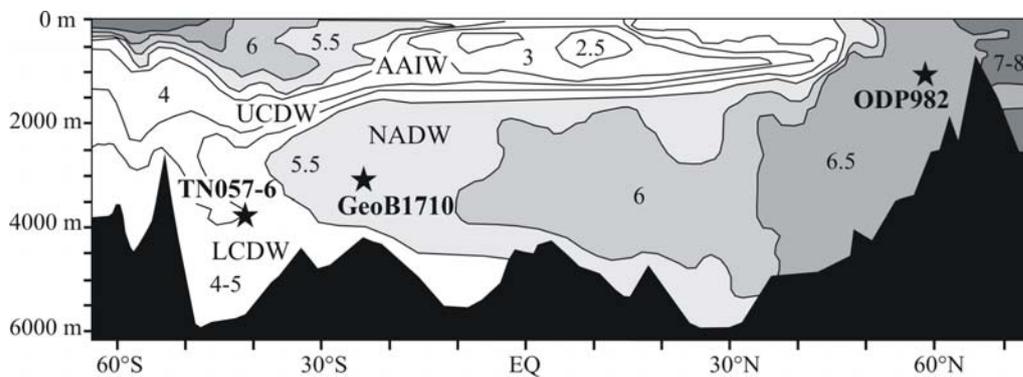
**Figure 5.1.** Core locations and regional hydrography in the BCUS of Namibia. Locations of surface samples (black dots) and gravity core GeoB1710 (asterisk). Surface currents are indicated as black arrows; (BCC) Benguela Coastal Current, (BOC) Benguela Oceanic Current, (SEC) South Equatorial Current (after PETERSON & STRAMMA, 1991). Area of 2003 annual mean bottom water O<sub>2</sub> concentration < 0.5 ml l<sup>-1</sup> is indicated (gray-shaded).

## 5.2. Regional settings

The study area in the northern part of the high-productivity BCUS off southwest Africa stretches adjacent to the Namibian coast between 22°S to 30°S and in its largest offshore extension reaches the Cape Basin at about 8°E, where water depth exceeds 5000 m (Fig. 5.1). The surface hydrography is dominated by the Benguela Current which relates to the eastern boundary current system of the Subtropical Gyre described in detail elsewhere (e.g., PETERSON & STRAMMA, 1991). The northward current is primarily fed by the South Atlantic Current and, to some degree, by the Agulhas Current and sub-Antarctic surface waters. It moves parallel to the shoreline and divides into a coastal and oceanic branch, the latter turning westward at the latitude of the Walvis Ridge to merge with the South Equatorial Current.

The intermediate water masses are represented by South Atlantic Central Water (SACW) and Antarctic Intermediate Water (AAIW) which has its origin at the Antarctic Convergence Zone. SACW is the primary source of thermocline water that feeds the upwelling centres along the Namibian coast, while low saline AAIW occupies depth between 400 and 1200 m (REID, 1989). The modern deep and bottom water characteristic is strongly controlled by the sea floor topography and results from the interaction between southward flowing North Atlantic Deep Water (NADW) and Circumpolar Deep Water (CDW) flowing to the north (REID, 1996). The high-saline and oxygen-rich NADW extends between about 2000 and 4000 m water depth, separating AAIW and upper CDW (UCDW) from lower CDW (LCDW), which fills the Cape Basin from the bottom up to a water depth of 4000 m (REID, 1989; Fig. 5.2).

A number of instructive overviews summarizes the present knowledge on upwelling in the BCUS, and delivers a reliable picture of the main mechanisms influencing productivity dynamics (e.g., SHANNON & NELSON, 1996). For much of the year the prevailing south-easterly trades induce strong upwelling of nutrient-rich SACW that drives high primary production in distinct cells along the continental shelf. South of Lüderitz (~26.5°S) increasing seasonality in wind stress causes stronger relaxation of upwelling intensity during austral summer and early autumn, dividing the BCUS in a northern and southern part. Between 18°S and 34°S, a thermal front coincides with the shelf break. While usually the seaward boundary of upwelled water, this front is penetrated in form of eddies, filaments and plums carrying fertile waters as far as 600 km offshore. In this kind of cold water archipelago, much more extensive than that of the proper coastal upwelling, a substantial portion of net primary production can take place (LUTJEHARMS & STOCKTON, 1987).



**Figure 5.2.** Atlantic Ocean cross-section showing the vertical distribution of dissolved  $O_2$  ( $ml\ l^{-1}$ ) and water masses discussed in the text (source: Ocean Data View). Asterisks show positions of cores relevant to this study.

Inner shelf sediments are dominated by sands with patchy lenses of mud (ROGERS, 1977). These sediments are primarily of Quaternary age with the sands (predominantly quartz) being relict deposits of desert sands transported to the shelf during the last glacial period. On the middle and outer shelf, nannofossil and foraminiferal ooze constitutes the bulk of material accumulating at high rates. Because this region lies within the area of maximum upwelling, the sediments contain up to 80% biogenic constituents ( $CaCO_3$ , opal and organic matter). Highest amounts of organic

carbon (>15%) are recorded in diatomaceous mud-belts on the shelf and in distinct depo-centres (~9%) on the upper continental slope (MOLLENHAUER *et al.*, 2002). The shelf width and depth is variable, and double shelf breaks are common with the outer shelf break at a water depth of about 400 m in large areas. The continental slope is a fairly smooth, gently dipping topographic feature, where slumps or slides do not represent significant transport processes (SUMMERHAYES *et al.*, 1995). Erosion and export of organic matter from the middle and outer shelf to the slope is provoked by cross-shelf circulation and lateral transport of particles in nepheloid layers (INTHORN *et al.*, 2006). Terrigenous material supplied by perennial river discharge and air borne dust from the Namibian desert has little influence on the sediment texture (SHANNON & NELSON 1996) and organic loads of sediments along the margin are predominately of marine origin (FISCHER *et al.*, 1998). In the Recent setting, the northern part of the BCUS has the lowest dissolved oxygen concentration, related to a poor oxygen source in the Angola Basin and the highest marine organic carbon levels. The low oxygenation of South Atlantic Central Water (< 1 ml l<sup>-1</sup>) and the ongoing oxygen consumption during remineralization of organic matter promote the establishment of oxygen minimum zones that impinge the shelf and upper slope (BAILEY 1991), providing a prime setting for natural experiments in selective degradation.

### 5.3. Material and methods

We used the weighted ratio between R-cysts and S-cysts as a proxy of bottom water oxygenation. First, we assessed R-cysts and S-cysts by investigating the relationship between changing bottom water oxygen concentrations and the modern distribution of dinocyst species in surface sediments from the BCUS. We calibrated the derived proxy and used published dinocyst count data from a gravity core retrieved on the lower continental slope of Namibia to infer the bottom water oxygen history for the past 150 kyr. We assessed the proxy performance by relating our results to reconstructions of deep ocean ventilation obtained by different proxies.

#### 5.3.1. Surface and core sediments

The surface sediment data set of dinocyst assemblages was established from forty sites that have been sampled during R/V *Meteor* cruises M20/2, M34/2 (SCHULZ *et al.* 1992, 1996), M34/1 (BLEIL *et al.* 1996), M57/2 (ZABEL *et al.* 2003), M57/3 (BRÜCHERT *et al.* 2005), and R/V *Thomas B. Davie* cruises TBD 268, 273, and 398 (ROGERS, 1977; BREMNER, 1981); see Figure 5.1 for locations. These samples represent oceanographic environments varying from neritic (38 m) to fully oceanic (5102 m) and from eutrophic to oligotrophic. In each case, fifteen stations were located in areas with an modelled mean annual bottom water O<sub>2</sub> content below 0.5 ml l<sup>-1</sup> and above 4 ml l<sup>-1</sup> O<sub>2</sub>, respectively (see detailed description in 5.3.3). The processed material comprised the top centimetre of multi or box-cores, either consisting of diatomaceous mud or calcareous ooze with varying proportions of sand and clay. None of the surface sediments has been dated, but oxygen isotope and AMS <sup>14</sup>C dated gravity cores taken at, or in the vicinity of the sample positions suggest that all were late Holocene (if not modern) in age (LOCHTE & ROMANKEVICH 1998; MOLLENHAUER 2002b). Given the relative stability of late Holocene climatic and oceanographic

conditions we assume that the samples represent present-day dinocyst associations with an acceptable degree of accuracy, aware of the limitations of the available data.

We used gravity core GeoB 1710 (23°25.9'S, 11°41.3'E, 2987 m) for paleoceanographic application, because this site displays changes in deep ocean ventilation as well as the intensity and extension of coastal upwelling during the late Quaternary (e.g., SCHMIEDL & MACKENSEN, 1997; GINGELE & SCHMIEDL, 1999). The core was recovered at the lower Namibian continental slope of the Northern Cape Basin during R/V *Meteor* cruise M20/2 (SCHULZ *et al.*, 1992) ~280 km away from the Namibian coast. The site is currently bathed in oxygen-rich NADW (Fig. 5.2) and located above the calcite lysocline which centres at around 3600 m. Today, slightly enhanced organic matter fluxes are due to its proximity to coastal upwelling and mirrored by typical infaunal species of benthic foraminifera (GINGELE & SCHMIEDL, 1999). The recovered material mainly consisted of bioturbated biogenic mud dominated by planktonic foraminiferal tests and coccoliths with no evidence of turbidities or strong reworking. Carbonate contents were fairly high (40-90%) showing lower values during glacials, while the total organic carbon content exceeds 3% in glacial sections (BICKERT, 1992). We modified the stratigraphy established by BICKERT & WEFER (1999) by correlating the oxygen isotope record for *Cibicides wuellerstorfi* with the benthic 'LR04-stack' of LISIECKI & RAYMO (2005) using the program Analyseries (PAILLARD *et al.*, 1996). The resulting age model of the analyzed section covered the last 150 kyr with sedimentation rates varying between 3.2 and 11.3 cm kyr<sup>-1</sup>. Dinocyst data were taken from ESPER (2001) and comprise 90 samples between core top and 7 m core depth with an average temporal resolution of about 1600 years.

### 5.3.2. Palynological processing

For surface sediments an amount of approximately 1 cm<sup>3</sup> of material was dried overnight at 60°C before dissolution took place in 10% hydrochloric acid in order to remove the carbonate content. Afterwards, they were washed thoroughly, decanted, and subsequently treated with cold 38% hydrofluoric acid to remove silicates. After having stood for two additional days samples were neutralized with 40% potassium hydroxide. Neutralization was essential, as the precision sieve is not resistant to either acids or bases. To avoid dinocyst dissolution care was taken that the solution did not become alkaline at any time. By sieving over a nickel precision sieve (Stork Veco, mesh 570) the size fraction > 20 µm was collected. As most cysts are larger than 20 µm, we assume that very few were lost during the sieving process. The sieved residue was centrifuged (3500 r.p.m. for 8 min) and transferred into a 1.5 ml Eppendorf reaction vessel. After re-centrifugation samples were concentrated to 1 ml. Finally, an aliquot of the homogenized residue, depending on the amount of remaining material, was placed on a microscope slide, embedded in glycerine jelly, and sealed with paraffin wax. At least one whole slide was counted for dinocyst species. Whenever a slide contained fewer than 200 dinocysts, an additional one was counted. Quantitative information on dinocysts in surface sediments was expressed in percent abundance, while accumulation rates (cysts cm<sup>-2</sup> kyr<sup>-1</sup>) of species have been calculated for GeoB 1710 by multiplying the number of cyst g<sup>-1</sup> with the mass accumulation rate.

Dinocysts have been termed according to their cyst names, as application of motile names was insufficient to differentiate them down to species level (for cyst-theca relationships cf. HEAD, 1996). Generic groups designated with 'spp' include species of a similar genus that were not identifiable at species level due to unsuitable orientation, adherence of debris or the inability to spot typical taxonomic features. The group *Brigantedinium* spp. comprises all spherical brown protoperidinioid cysts without processes. The taxonomy used is in accordance to WILLIAMS *et al.*, (1998). Species of the genus *Echinidinium* have been described in ZONNEVELD (1997).

### 5.3.3. Environmental data

Values on annual mean bottom water oxygen concentrations ( $adO_2$ ) were derived from model results gained with a regional implementation of the Modular Ocean Model-31 (MOM-31); Geophysical Fluid Dynamics Laboratory, NOAA Department of Commerce, Princeton, NJ, ([www.gfdl.noaa.gov](http://www.gfdl.noaa.gov)). Theory and concept of MOM-31 are explained elsewhere (PACANOWSKI & GRIFFIES, 1999). The circulation model is coupled with an ecosystem model as described in FENNEL & NEUMANN (2004). Oxygen sources are photosynthesis and exchange with the atmosphere, while consumption is due to respiration and bacterial mineralization of detritus in the sediment and water column. Lateral ventilation by the Ekman compensation current and by the pole-ward undercurrent plays an important role to maintain the permanent oxygen deficit of the shelf water. The horizontal model resolution in the area of investigation is about 8 km and compares with the cross shelf station distance. Simulations were run over five model years for 1999 to 2005. The calculated  $adO_2$  values used in this study correspond to 2003.

Information on total organic carbon contents in surface sediments (TOC) has been gathered from the data archive PANGAEA (LOCHTE & ROMANKEVICH 1998; MOLLENHAUER, 2002a, 2002b), and from literature records (ROGERS, 1977; BREMNER, 1981; CALVERT & PRICE, 1983). The data include 602 locations, of that 83% from stations above 1000 m water depth, resulting in a higher sample density for the shelf and upper slope. Average summer and winter sea surface temperature (SSST, WSST) and salinity (SSSS, WSSS) values, and annual mean sea surface concentrations of phosphate ( $aPO_4$ ) and nitrate ( $aNO_3$ ) were derived from the World Ocean Atlas 2001 Data Set, National Oceanographic Data Center, Silver Springs, MD ([www.nodc.noaa.gov/OC5](http://www.nodc.noaa.gov/OC5)). Upper water column stratification during summer (SSI) and winter (WSI) was indicated by the Brunt-Väisälä frequency [ $N = \sqrt{(9.8\delta D)/(1026\delta z)}$ ], where  $\delta D$  represents the density difference calculated from the temperature and salinity change over  $\delta z$  (in this case 50 m) taking the standard NICMM equation. Seasonal concentrations of chlorophyll *a* (SChl *a*, WChl *a*) for 2001 have been inferred from ocean colour scan images that are available by the SeaWiFS Project, NASA Goddard Space Flight Center, Greenbelt, MD, ([oceancolor.gsfc.nasa.gov/SeaWiFS](http://oceancolor.gsfc.nasa.gov/SeaWiFS)) at a grid size of  $\frac{1}{4}$  degree. In all cases seasonality refers to northern hemisphere summer (Jul - Sep) and winter (Jan - Mar), respectively. Depth was not considered separately within the statistical analyses, because its relationship to species distribution is clearly coincidental with any dependence of other variables on depth. To finally determine a value at each of the 40 sample locations, all environmental variables have been interpolated

horizontally with inverse distance weighting, a mapping method build in Surfer v8, Golden Software, Inc.

**Table 5.1.** Pearson correlation matrix of environmental variables. Pearson's coefficient of correlation in bold ( $p$ -value  $< \pm 0.7$ ) indicate parameter combinations considered in species GAMs.

	adO <sub>2</sub>	TOC	aNO <sub>3</sub>	aPO <sub>4</sub>	SSST	WSST	SSSS	WSSS	SChl <i>a</i>	WChl <i>a</i>	SSI
TOC	<b>-0.62</b>	-	-	-	-	-	-	-	-	-	-
aNO <sub>3</sub>	<b>-0.66</b>	<b>0.51</b>	-	-	-	-	-	-	-	-	-
aPO <sub>4</sub>	<b>-0.69</b>	<b>0.68</b>	0.91	-	-	-	-	-	-	-	-
SSST	0.84	<b>-0.67</b>	-0.78	-0.80	-	-	-	-	-	-	-
WSST	<b>0.65</b>	<b>-0.53</b>	-0.85	-0.81	0.82	-	-	-	-	-	-
SSSS	<b>0.57</b>	<b>-0.36</b>	-0.88	-0.72	0.72	0.83	-	-	-	-	-
WSSS	<b>0.68</b>	<b>-0.53</b>	-0.85	-0.76	0.83	0.84	0.95	-	-	-	-
SChl <i>a</i>	-0.71	<b>0.61</b>	<b>0.55</b>	<b>0.63</b>	-0.77	<b>-0.64</b>	<b>-0.55</b>	-0.75	-	-	-
WChl <i>a</i>	<b>-0.55</b>	<b>0.67</b>	<b>0.38</b>	<b>0.52</b>	<b>-0.64</b>	<b>-0.48</b>	<b>-0.36</b>	<b>-0.56</b>	0.81	-	-
SSI	<b>-0.63</b>	0.37	0.70	<b>0.69</b>	-0.71	<b>-0.58</b>	-0.70	-0.73	<b>0.55</b>	<b>0.32</b>	-
WSI	<b>-0.37</b>	<b>0.25</b>	<b>0.44</b>	<b>0.25</b>	<b>-0.47</b>	<b>-0.46</b>	<b>-0.64</b>	-0.70	<b>0.58</b>	<b>0.44</b>	<b>0.32</b>

#### 5.3.4. Statistical analysis and calibration

We obtained R-cysts and S-cysts by combining explorative and regression analyses. Beforehand, eleven dinocyst species were removed from the surface sediment data set, because they occurred only in three or less samples. The remaining twenty-eight species, accounting for at least 94% of the total assemblage at each station, were retained for statistical analyses (see below). We used relative frequencies instead of concentrations per gram of sediment to circumvent problems due to the extreme data ranges and the unknown sedimentation rates.

First, we explored species relation to the gradient in bottom water oxygen concentration with the help of non-metric multidimensional scaling (N-MDS) (KRUSKAL, 1964) taking the Gower-Index as a measure of between sample dissimilarity. We mapped species scores (weighted averages of site scores expanded to equal variance) nonlinearly onto an ordination space and added information on bottom water oxygen concentration by fitting this variable as a vector indicating the direction of most rapid change. Species displaying a clear positive respond to increasing bottom water oxygen concentration were referred to as R-cysts. We deemed species with a negative respond as potentially sensitive and considered them for further regression analyses to assure sound selection of S-cysts.

For each potential S-cyst we calculated Generalized Additive Models (GAMs) (HASTIE & TIBSHIRANI, 1990) separately, considering single as well as all combinations of two and three environmental parameters as predictor variables. As strong correlations between predictor variables will lead to abnormally high coefficients and standard errors (NETER *et al.* 1989), we only considered combinations of parameters with Pearson correlations  $< \pm 0.7$  (Table. 5.1). GAMs allowed for the exploration of species response to the considered environmental gradients on the basis of non-parametric smoothing functions (i.e. regression splines). We applied angular-transformation to achieve normal distribution of species data and obtained the best GAM for each

species using AIC (Akaike Information Criterion) as selection criterion (SAKAMOTO *et al.*, 1986). On the base of modelling results we computed the weighted ratio of R-cysts and S-cysts referred to as bottom water oxygen index [BWOI = R/(R+S)] and calibrated the derived proxy by describing its non-linear relationship to the available bottom water oxygen data. We used R (R CORE DEVELOPMENT TEAM, 2005), a programming environment for data analysis and graphics, for all statistical computations.

**Table 5.2.** Site information and proxies used in this study

Site	Location	Depth	Proxy data	Reference
GeoB1710	23°25.9'S, 11°41.3'E (NADW)	2987m	BWOI	this study
			%NCW	this study; (after OPPO & FAIRBANKS, 1987)
			R-,S-cysts	this study; ESPER, 2001
			benthic $\delta^{18}\text{O}$ , $\delta^{13}\text{C}$	BICKERT & WEFER, 1996
			CaCO <sub>3</sub>	MÜLLER, 2001
			NADW-fauna	SCHMIEDL & MACKENSEN, 1997
			TOC	BICKERT & WEFER, 1999
			$\delta^{13}\text{C}_{\text{org}}$	KIRST <i>et al.</i> , 1999
GeoB1711	23°18.9'S, 12°22.6'E	1967m	U <sub>K</sub> <sup>37</sup> - SST	BICKERT & WEFER, 1999
			pollen	SHI <i>et al.</i> , 2001
ODP 982	57°30.8'N, 15°52.5'W (upper NADW)	1145m	benthic $\delta^{13}\text{C}$ (NCW end-member)	VENZ <i>et al.</i> , 1999; VENZ <i>et al.</i> , 2002
TN057-6	42° 54.8'S, 8°54'E (60% CDW, 40% NADW)	3751m	benthic $\delta^{13}\text{C}$ (SCW end-member)	HODELL <i>et al.</i> , 2000; VENZ <i>et al.</i> , 2002

### 5.3.5 Assessing dinocyst proxy performance

We applied the derived dinocyst proxy to species count data of core GeoB 1710 and reconstructed the bottom water oxygen history for the last 150 kyr. Therefore, we calculated the downcore oxygen concentrations using the non-linear regression model fitted to the surface sediment dataset. As the main goal of this study was the assessment of dinocyst proxy performance, we related our results to other paleoenvironmental records of core GeoB 1710 and adjacent sites and calculated a quantitative index commonly used to describe the relative proportion of northern component water at a given location after OPPO & FAIRBANKS (1987):

$$\%NCW = \frac{\delta^{13}C_x - \delta^{13}C_{SCW}}{\delta^{13}C_{NCW} - \delta^{13}C_{SCW}} \times 100, \quad (1)$$

where  $\delta^{13}C_{NCW}$  is the carbon isotopic value for Northern Component Water (NCW),  $\delta^{13}C_{SCW}$  is the carbon isotopic value for Southern Component Water (SCW), and  $\delta^{13}C_x$  is the carbon isotopic value of core GeoB1710. We choose ODP site 982 (57°30.8'N, 15°52.5'W, 1145 m) from the Rockall Plateau in the northeast Atlantic as the NCW end-member and piston core TN057-6 (52°54.8'S, 8°54.0'E, 3751 m) from the Agulhas Ridge as the SCW end-member. Stable carbon isotope records for these sites refer to measurements on the benthic foraminifera

*C. wuellerstorfi* and *C. kullenbergi* (VENZ *et al.*, 1999; HOPELL *et al.*, 2000), while GeoB1710 values correspond to measurements on *C. wuellerstorfi* only (BICKERT & WEFER, 1996). Prior to calculating the NCW-index, we modified the existing age models for both end-member cores (VENZ *et al.*, 1999; HOPELL *et al.*, 2000) by adjusting them to the benthic ‘LR04-stack’ of LISIECKI & RAYMO (2005). Information on proxy records and sites that are important to this study are given in Table 5.2.

**Table 5.3.** Species list used in N-MDS.

Species (Peridinioid)	Abbr.	Trophy	Species (Gonyaulacoid)	Abbr.	Trophy
<i>Echinidinium aculeatum</i> *	<i>Eacu</i>	heterotroph	<i>Bitectatodinium tepikiense</i>	<i>Btep</i>	autotroph
<i>Echinidinium delicatum</i> *	<i>Edel</i>	heterotroph	<i>Impagidinium aculeatum</i>	<i>Iacu</i>	autotroph
<i>Echinidinium granulatum</i> *	<i>Egra</i>	heterotroph	<i>Impagidinium paradoxum</i>	<i>Ipar</i>	autotroph
<i>Echinidinium</i> spp. <sup>a</sup>	<i>Espp</i>	heterotroph	<i>Impagidinium patulum</i>	<i>Ipat</i>	autotroph
<i>Echinidinium transparentum</i> *	<i>Etra</i>	heterotroph	<i>Impagidinium plicatum</i>	<i>Ipli</i>	autotroph
cyst of <i>Protoperidinium</i> *	<i>Pame</i>	heterotroph	<i>Impagidinium sphaericum</i>	<i>Isph</i>	autotroph
<i>americanum</i>	<i>Mqua</i>	heterotroph	<i>Impagidinium striolatum</i>	<i>Istr</i>	autotroph
<i>Multispinula quanta</i> *	<i>Pdal</i>	heterotroph	<i>Impagidinium variaseptum</i>	<i>Ivar</i>	autotroph
cyst of <i>Pentapharsodinium dalei</i>	<i>Pkof</i>	autotroph	<i>Nematosphaeropsis</i>	<i>Nlab</i>	autotroph
<i>Polykrikos kofoidii</i>	<i>Tcap</i>	heterotroph	<i>labyrinthus</i>	<i>Pret</i>	autotroph
<i>Trinovantedinium capitatum</i> *	<i>Bspp</i>	heterotroph	<i>Protoceratium reticulatum</i>	<i>Oisr</i>	autotroph
<i>Brigantedinium</i> spp.	<i>Snep</i>	heterotroph	<i>Operculodinium israelianum</i>	<i>Pyxr</i>	autotroph
<i>Selenopemphix nephroides</i> *			<i>Pyxidinospis reticulata</i>	<i>Smir</i>	autotroph
			<i>Spiniferites mirabilis</i>	<i>Spat</i>	autotroph
			<i>Spiniferites patchydermus</i>	<i>Sram</i>	autotroph
			<i>Spiniferites ramosus</i>	<i>Sspp</i>	autotroph
			<i>Spiniferites</i> spp.		

<sup>a</sup>Potential S-cyst candidates considered for individual GAMs.

## 5.4. Results

### 5.4.1. Explorative and regression analyses

After removing the rare species from the data set species list corresponded to 24 taxa (Table 5.3). The computed N-MDS shown in Figure 4.3 revealed a distinct separation of these species with respect to the fitted vector of bottom water oxygen concentration. Most dinocysts belonging to order Gonyaulacales (e.g. of the genus *Impagidinium*) were found to reflect rather well oxygenated settings and were further referred to as R-cysts. In contrast, species of the order Peridiniales (e.g., *Brigantedinium* spp, *Echinidinium* spp) generally showed higher relative abundances at stations characteristic of low bottom water oxygen concentrations. These were considered as potentially sensitive to oxidation and thus subjected to regression analyses separately. Species which showed no obvious relationship to oxygenation were excluded from further analysis.

The results of species regression analysis are illustrated in Table 5.4. From a number of 10 species potentially sensitive to changes in bottom water oxygenation GAM results demonstrated significant relationships ( $p$ -value < 0.05) to  $adO_2$  only for *Brigantedinium* spp, cyst of *Protoperidinium americanum*, *Echinidinium transparentum*, and *Polykrikos kofoidii*. For these dinocysts, the best GAMs selected by lowest AIC explained between about 50 – 87% of deviance

indicating a good representation of species distribution by the fitted models. Hence, we referred these four dinocyst species to as S-cysts. Though, the final GAMs of *Echinidinium* spp and *Multispinula quanta* included adO<sub>2</sub> these species were not associated to S-cysts, because their relationship to bottom water oxygen concentrations was not significant. Among the remaining parameters regarded for regression analysis, only WChl *a* was more often included in the best GAMs than adO<sub>2</sub>, while the parameters SSSS, WSSS, and SChl *a* were never included.

**Table 5.4.** Result of GAMs. Species included in S-cyst end-member category are in bold (adO<sub>2</sub>; *p*-value < 0.05).

Species	adO <sub>2</sub>	TOC	aNO <sub>3</sub>	aPO <sub>4</sub>	SSST	WSST	SSSS	WSSS	SChl <i>a</i>	WChl <i>a</i>	SSI	WSI	AIC	Dev. Expl.
<i>Eacu</i>	-	0.208	-	-	-	-	-	-	-	<0.001	-	<0.001	199.7	80.8%
<i>Edel</i>	-	-	-	0.005	-	-	-	-	-	0.042	0.23	-	179.9	46.4%
<i>Egra</i>	-	-	-	-	0.067	-	-	-	-	0.002	0.017	-	220.2	58.4%
<i>Espp</i>	0.158	0.079	-	0.001	-	-	-	-	-	-	-	-	230.7	69.5%
<b><i>Etra</i></b>	0.002	-	0.059	-	-	-	-	-	-	0.001	-	-	190.3	49.6%
<b><i>Pame</i></b>	<0.001	-	-	-	-	-	-	-	-	<0.001	<0.001	-	163.9	87.0%
<i>Mqua</i>	0.120	-	-	-	-	0.047	-	-	-	<0.001	-	-	201.8	90.2%
<b><i>Pkof</i></b>	0.016	-	-	-	-	-	-	-	-	<0.001	-	<0.001	167.8	79.9%
<i>Tcap</i>	-	<0.001	-	-	-	-	-	-	-	<0.001	-	<0.001	204.3	76.9%
<b><i>Bspp</i></b>	0.012	0.013	<0.001	-	-	-	-	-	-	-	-	-	265.0	78.7%

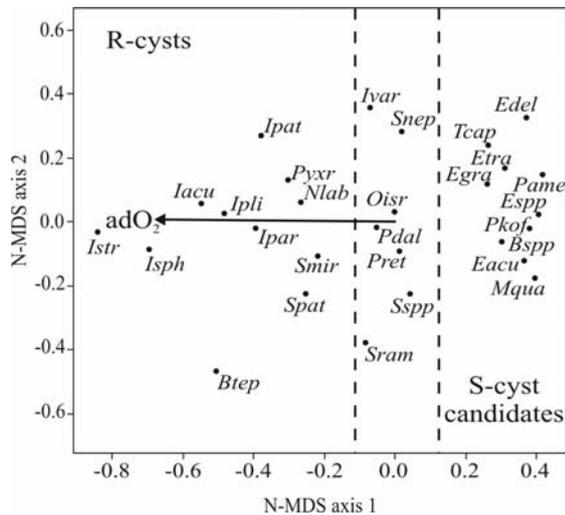
#### 4.4.2. Proxy calibration and application to GeoB 1710

We summed up the relative abundances for R-cysts and S-cysts in order to calculate the BWOI and related it to the available oxygen data. A non-linear (logistic) function  $\{R^2 = 0.78, df = 38, p\text{-value} \ll 0.05, \text{adO}_2 = 5.33 / [1 + 250.63 \exp^{-3.16 \text{BWOI}}]\}$  fitted best the relationship between the BWOI and the bottom water oxygen concentrations (Fig. 5.4). In analogy to growth curves the regression described an initial stage, where the relation was approximately exponential (BWOI < 0.5; adO<sub>2</sub> < 3 ml l<sup>-1</sup>) and a final stage, where the relation approached a maximum (BWOI ~ 0.7; adO<sub>2</sub> ~ 5 ml l<sup>-1</sup>). Upon this calibration, we applied the BWOI to core GeoB 1710, where all dinocyst species referred to as R-cysts and S-cysts were abundant, and reconstructed the bottom water oxygen history at this site for the last 150 kyr (Fig. 5.5).

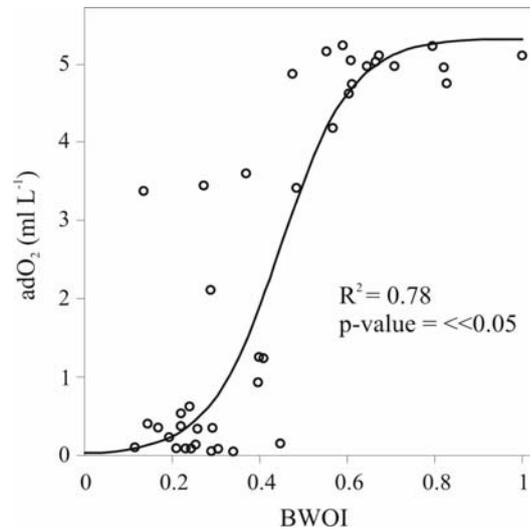
The reconstructed bottom water oxygen concentrations for the late Pleistocene at site GeoB1710 followed a glacial-interglacial pattern. Taking into account the different temporal resolution, peak values were usually in good agreement with the timing of major isotope events as shown by comparison to the δ<sup>18</sup>O record. High values (> 4ml l<sup>-1</sup> O<sub>2</sub>) were generally obtained for isotope stages (IS) 5, 3, and 1. In contrast, low values (< 2 ml l<sup>-1</sup> O<sub>2</sub>) were indicated for IS-6, IS-4, and IS-2. Transitions between cold phases (IS-6, IS-4, IS-2) and warm periods (IS-5, IS-3, IS-1) were characterized by the most profound shifts in calculated oxygen contents showing concentration changes of about 4 ml l<sup>-1</sup> O<sub>2</sub>.

Changes in the relative proportion of NCW at site GeoB1710 were inferred from variations in the Atlantic basin δ<sup>13</sup>C gradient between Site 982 and piston core TN057-6. Compared to bottom water oxygen concentrations calculated from the BWOI, the relative proportion of NCW showed strong fluctuations throughout the entire core interval. Amplitudes ranged between total termination of NCW contribution to the Northern Cape Basin and contributions to deep water as high as 80 to 90% around IS-boundary 2/1 and oxygen isotope

event 5.5, respectively. Though, no clear glacial-interglacial pattern was obvious from the data, relative proportions of NCW higher than 40% were usually observed during time intervals that represent interglacials (IS-5, IS-1) and the warm glacial period of IS-3.



**Figure 5.3.** N-MDS plot of species scores with fitted  $adO_2$  vector. Dashed lines separate resistant dinocysts (R-cysts) and potentially sensitive species referred to as S-cyst candidates. The latter were subjected to GAMs.



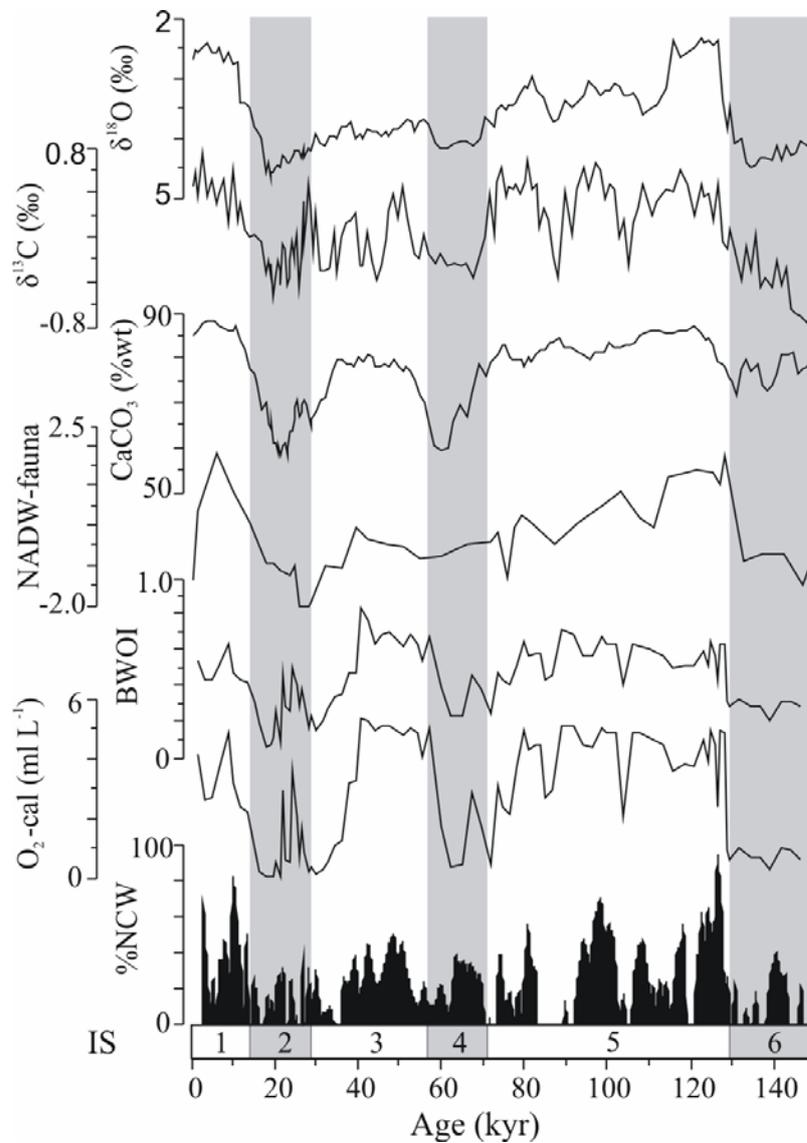
**Figure 5.4.** Non-linear regression model for BWOI calibration.

In addition to the oxygen concentrations calculated from the BWOI, we determined the accumulation rates of R-cysts and S-cysts (Fig. 5.6). Both groups showed a peak (P1) in accumulation during IS-2, slightly enhanced values during IS-6, but lowest rates during IS-5 and the Holocene core section. Differences were most obvious for IS-3, where R-cysts achieved high accumulation rates (P2), while accumulation of S-cyst remained at a low interglacial level. Below, the differences in accumulation of both dinocyst groups and the reconstructed bottom water oxygen history were discussed by comparison to available proxy records.

## 5.5. Discussion

The aim of this study was to use the different resistance of organic-walled dinoflagellate cysts to oxidation to derive a proxy for bottom water oxygen concentrations. We first investigated the modern distribution of dinocyst assemblages in surface sediments of the BCUS, where strong gradients in bottom water oxygen concentrations prevail, to classify oxidation resistant (R-cysts) and sensitive (S-cysts) end-members. Thereupon we calculated a BWOI which was calibrated and applied to a 150 kyr dinocyst record from the lower continental slope of Namibia. The reconstructed deep water oxygen history at this site shows a clear glacial-interglacial signal for the late Pleistocene. However, processes other than selective removal of species possibly influence our interpretation and due to the limited number of samples at our disposal we have to carefully

consider the derivation and interpretation of our proxy before importance is attached to its paleoceanographic performance.



**Figure 5.5.** Proxy records of core GeoB 1710 adjusted to the timescale of LISIECKI & RAYMO (2005). Glacial cold stages (shaded) are periods of lowest calculated bottom water O<sub>2</sub> concentrations (O<sub>2</sub>-cal) indicating reduced advection of NADW and/or stronger influence of LCDW at the core site.

### 5.5.1. Relating dinocysts to bottom water oxygenation

The concept fundamental to our approach contrasts dinocysts that easily degrade in the presence of oxygen and those capable to escape dissolution in oxygenated settings. The results on explorative data analysis of surface sediment assemblages suggest that most peridinioid species belong to the sensitive category, whereas the resistant group exclusively includes gonyaulacoid cyst types (Fig. 5.3). Field and laboratory observations give good reason to use the latter as an oxidation resistant end-member (R-cysts) for BWOI calculation (ZONNEVELD *et al.*, 2001,

HOPKINS & MCCARTHY, 2002). Though these studies also demonstrate high susceptibilities of peridinioid species, we selected sensitive end-members (S-cysts) upon determining the environmental relationships of potential candidates using GAMs. Compared to techniques like correspondence analysis GAMs have the advantage to estimate species response with a non-parametric smoothing function, which is in better agreement with ecological theory (AUSTIN, 2002). The results showed that bottom water oxygenation is among the parameters most often selected in the best models, corroborating its proposed effect on the distribution of peridinioid species (MCCARTHY *et al.*, 2003; **Chapter 2**). However, it also apparent that other factors (e.g., WChl *a*, nutrient content, stratification) exert stronger control on some peridinioid species or that oxygenation of bottom water does not unequivocally explains their distribution (cp. Table 5.4). Species finally included in the S-cyst end-member group are extremely vulnerable to harsh oxidation procedures (HOPKINS & MCCARTHY, 2002) and among the first to vanish during post-depositional oxidation (ZONNEVELD *et al.*, 2001, **Chapter 3**).

Selective dinocyst degradation is a matter of debate in the palynological community and many workers raise objections on its importance in natural settings. It is indisputable that dinocysts possess powerful qualities for the study of marine ecosystems and paleoenvironmental reconstruction (e.g., ESPER *et al.*, 2004; DE VERNAL *et al.*, 2005). However, we refer to the body of evidence that calls upon differences in dinocyst preservation potentials due to chemical disparity of their wall structures (VERSTEEGH & BLOKKER, 2004). For a good reason harsh oxidation procedures are avoided during sample processing, because they tend to destroy many peridinioid species, notably the brown-walled taxa (MARRET, 1993; HOPKINS & MCCARTHY, 2002). In natural settings, selective decay has been qualitatively inferred from turbiditic core layers (ZONNEVELD *et al.*, 2001), and trap studies in the Arabian Sea (ZONNEVELD & BRUMMER, 2000). According to MCCARTHY *et al.* (2003), the offshore increase in the gonyaulacoid/peridinioid ratio commonly observed may primarily result from the selective destruction of peridinioid dinocysts under oxidizing conditions. Critical to our interpretation are redistribution and transport of dinocyst (DALE, 1992). These processes influence the organic carbon distribution in surface sediments of the BCUS (INTHORN *et al.*, 2006). However, in most cases final GAMs do not relate species distribution to the TOC content (Table 5.4), and we only sporadically observe species potentially introduced from different remote sources. Besides, a variety of mechanisms such as faecal pellet transportation (MUDIE *et al.*, 1996) can accelerate the export of dinocysts to bottom sediments and we therefore assume that settling assemblages represent surface water associations with an acceptable degree of accuracy.

A similar end-member approach used by VERSTEEGH & ZONNEVELD (2002) assumes that degradation of S-cysts follows first-order decay, the most widely applied model to describe OM mineralization (HEDGES *et al.*, 1999). The relationship between BWOI and bottom water oxygen concentrations seems to be more complex suggesting a non-linear rate of dinocyst degradation (Fig. 5.4). There are two good reasons for this observation. First, S-cysts constitute only a part of the labile OM and thus degradation may initially depend on the amount and reactivity of other compounds that typically differ in their ease to disassembly, at monomer, polymer or supramolecular scales of organization (EMERSON & HEDGES, 1988). Second, rate constants have

been parameterized as a function of total accumulation rate (MIDDELBURG *et al.*, 1997), organic carbon rain rate (Archer *et al.*, 2002), or the mean age of the sedimentary organic matter (EMERSON, 1985), and therefore may vary between shelf, slope, and abyssal sediments. We suggest that in the initial phase (BWOI < 0.5) S-cyst degradation rate is controlled by the oxygen content, whereat a linear increase in O<sub>2</sub> concentration causes an exponential decrease in S-cysts. Then, above some critical low O<sub>2</sub> level (~ 3 ml l<sup>-1</sup>), dependency becomes controlled by the flux of S-cysts and, ultimately, is independent of O<sub>2</sub> at high concentrations (adO<sub>2</sub> > 5 ml l<sup>-1</sup>).

Our model on the oxic degradation of S-cysts might be more appropriately described by a host of largely unknown processes that characteristically prevail under conditions where O<sub>2</sub> is present. Bottom water O<sub>2</sub> concentration might be only a remote indicator and the potential for oxic degradation of S-cyst is possibly more meaningfully assessed from the time period to oxygen exposure (HARTNETT *et al.*, 1998). Varying accumulation rates, bioturbation, and irrigation, can further modulate the effect (HULTHE *et al.*, 1998; KEIL *et al.*, 2004). However, increases in bottom water oxygen concentration lead on average to elevated gradients across the water-sediment interface, greater O<sub>2</sub> penetration, and hence to more complete degradation of oxygen-sensitive OM within surficial marine sediments (KEIL *et al.*, 1994; MOODLEY *et al.*, 2005). Regarding our application of the BWOI to a core from southeast Atlantic (see below) we assume that the oxygen exposure time is ultimately diffusion controlled and broadly proportional to the concentration of dissolved oxygen in ocean bottom waters (EMERSON, 1985). On a geological timescale it appears that the process of oxic degradation occurs predominantly within the upper few centimetres of the sediment and thus is largely independent of the overall length of the studied core.

#### 5.5.2. Paleoceanographic performance of the BWOI

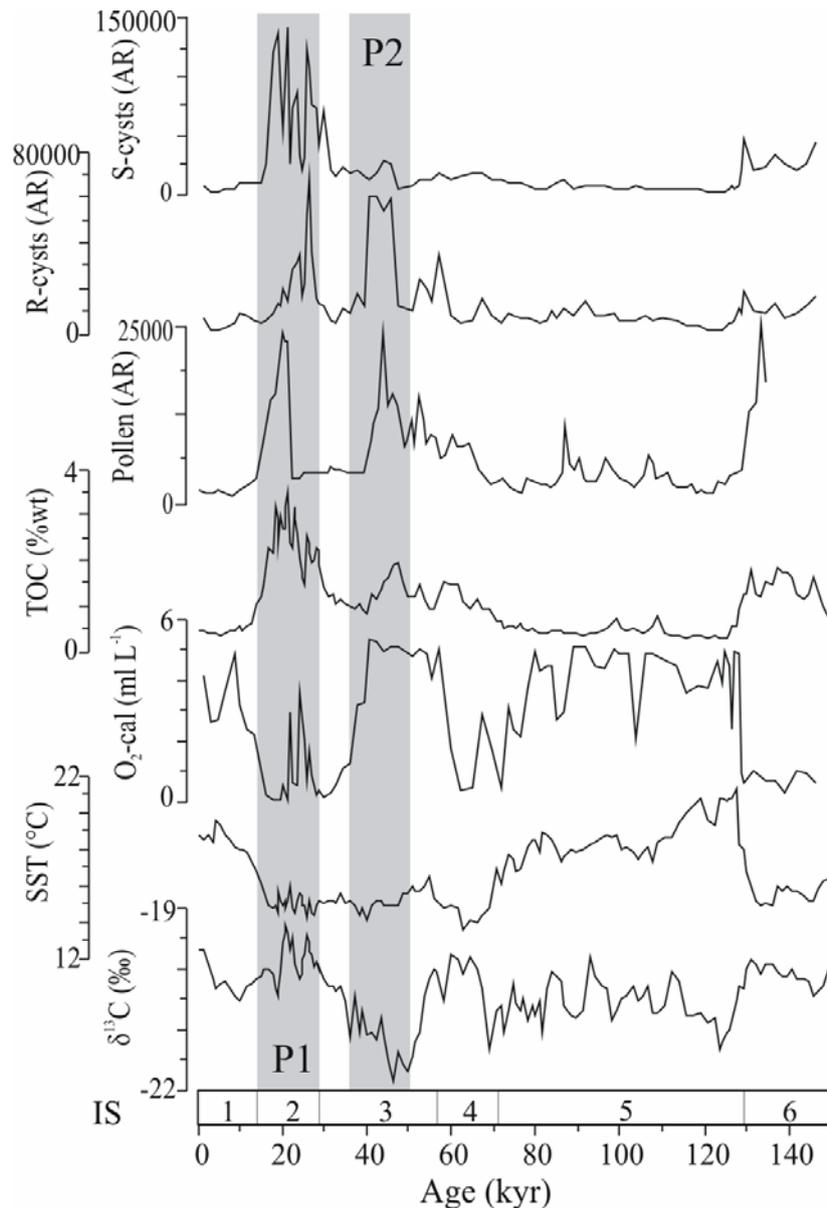
To our knowledge there is no reason why the O<sub>2</sub> concentration of bottom waters cannot be reconstructed from the occurrence of selective dinocyst degradation in marine sediments. To test the performance we related the BWOI to a core from the southwest African continental slope whose late Pleistocene history has been studied by a suit of paleo-proxies. The reconstructed O<sub>2</sub> concentrations for core GeoB 1710 follow the typical glacial-interglacial pattern in benthic δ<sup>18</sup>O (Fig. 5.5) that document the variation in continental ice volume and/or temperature of deep water (LABEYRIE *et al.*, 1987). The drops in O<sub>2</sub> concentration at the close of the relatively warm isotope stages indicate that advection of oxygen-rich deep water into the Cape Basin has ceased dramatically and/or, under reasonable rates of carbon input, dissolved O<sub>2</sub> at core depth has been consumed quickly. The likewise rapid increases at the end of cold stages point to a fast resumption of deep water ventilation in the basin and/or significant decrease in OM flux. Apparently, the transition between preservation and selective degradation of dinocyst under variable bottom water O<sub>2</sub> conditions must have occurred rapidly which is in line with HARTNETT *et al.* (1998), who pointed out that 'oxic effects' are apparent on timescales of decades or less, and thus, need not be slow. The magnitude of change, however, is likely misleading, because the presence of fossilized aerobic benthic organisms in glacially deposited sediment suggests that some flux of O<sub>2</sub> into the Cape Basin has persisted. Hence, it may rather reflect pore water oxygenation in incrementally

depositing surface sediments, which, as pointed out earlier, are assumed to be proportional to dissolved  $O_2$  concentrations in bottom waters (EMERSON, 1985).

At present, the flux of  $O_2$ -rich NADW through low-latitude fracture zones is the main source of oxygen to the eastern basins (METCALF *et al.*, 1964). Although there is no single ocean circulation scenario for the late Pleistocene, numerous studies have demonstrated that NADW was probably still produced during glaciations but generally occupied depth above 2 km (e.g., KEELING & STEPHENS, 2001). Replacement of NADW by relatively  $O_2$ -poor and nutrient-rich LCDW entering the Cape Basin from the south may therefore account for the low  $O_2$  concentrations at site GeoB1710 during cold isotope stages (IS-2, IS-4, IS-6). Estimation of the relative proportion of NCW based on the  $\delta^{13}C$  signal of benthic foraminifera support this suggestion indicating the presence of a low-oxygen water mass of southern origin that might have filled up the basin on the expanse of better ventilated NADW (Fig. 5.5). We interpret these results in terms of changes in the ocean's deep circulation with stronger advection of LCDW into the eastern Atlantic Ocean and reduced advection of  $O_2$ -rich deep water through low-latitude fracture zones at times of an overall decrease in glacial deep water production in the North Atlantic (e.g., LABEYRIE *et al.*, 1987; DUPLESSY *et al.*, 1988; OPPO & FAIRBANKS, 1990). On a more regional scale, our interpretation accords to reconstructions of bottom water composition based  $\delta^{13}C$  (BICKERT & WEFER, 1996) and assemblages of benthic foraminifera (SCHMIEDL & MACKENSEN, 1997) that deduce strongest influence of  $O_2$ -rich NADW for IS-5 and IS-1 (Fig. 5.5). Moreover, studying the clay mineral distribution of core GeoB 1710, GINGELE & SCHMIEDL (1997) found lowest kaolinite/chlorite ratios during glacial cold phases in conjunction with strong smectite crystallinity and concluded that extension of SCW into the Cape Basin possibly blocked way to the flow of NADW. A similar scenario is documented by neodymium isotope ratios from southeast Atlantic sediment cores which tend towards North Atlantic signatures during the warm IS-1 and IS-3, whereas for the full glacial IS-2 and IS-4 they are closer to Pacific Ocean signatures (RUTBERG *et al.*, 2000). Our interpretation are complicated by findings based on Cd/Ca ratios (BOYLE & ROSENTHAL, 1996) and the  $^{231}Pa/^{230}Th$  ratio in late Quaternary sediments from the Atlantic Ocean (YU *et al.*, 1996), both favouring persistent admixture of NADW into CDW during glaci-als.

Of course, the various proxy records at station GeoB 1710 cannot be interpreted straightforward taken at face the proximity to coastal upwelling and accompanied glacial-interglacial variation in productivity induced organic matter input. The pronounced  $\delta^{13}C$  decrease during the Last Glacial Maximum may partly result from an increase in export productivity and subsequent mineralization and/or enhanced isotopic fractionation in a lower pH environment established during organic matter decay (MACKENSEN *et al.*, 1993). On the other hand, CURRY & LOHMANN (1983) assume that  $\delta^{13}C$  records in deep eastern basin cores were equally affected by global causes of  $\delta^{13}C$  variation and that differences seen must reflect changes in the distribution of  $\delta^{13}C$  in the deep ocean. If oxidation of vast amounts of OM occurred under high productivity induced input to the continental slope of Namibia, the excess  $CO_2$  produced would have provoked carbonate dissolution, which then may account for the lower  $CaCO_3$  contents in the glacial deposits. However, the  $CaCO_3$  and  $O_2$  signal core GeoB 1710 are alike and we thus consider it likely that some dissolution in cold stages has been triggered by stronger admixing of  $O_2$ -depleted

and carbonate undersaturated LCDW (Fig. 5.5). This corresponds to carbonate patterns from the Cape Basin and Walvis Ridge which have been attributed to glacial-interglacial variations in NADW production (HODELL *et al.*, 2003) and to the global increase in the  $CO_2$  content of bottom waters in glacial times (SCHMIDT, 1992), respectively. Given the good agreement with the various proxy records presented here, we finally advocate the sensibility of our  $BWOI$  for bottom water  $O_2$  reconstruction and advise the use of dinocysts beyond current fields of application.



**Figure 5.6.** Proxy records of core GeoB 1710 and GeoB 1711 (pollen) plotted on individual age scales adjusted to the timescale of LISIECKI & RAYMO (2005). During P1 high productivity induced input and preservation of OM prevails. During P2 remineralization of labile marine OM under high bottom water  $O_2$  concentrations occurred leaving behind peaks of refractory OM components (R-cysts, pollen).

## 5.6. Perspective and outreach

In several areas closer to the continents where the content of sedimentary OM is high, considerably higher organic carbon loads are reported for glacial times. While this pattern is usually interpreted as the result of glacial-interglacial changes in OM rain rate, it is equally well explained by lower bottom water  $O_2$  contents. WILSON *et al.* (1986), for instance, suggested that organic carbon in glacial sediments of the equatorial Atlantic Ocean was partially degraded after deep-water ventilation had recovered and pore waters became more oxic at the close of glacial conditions. This discussion is fundamental to paleoceanographic studies, because concentration and flux variations of organic carbon in sediment cores are traditionally used to infer changes in marine productivity (e.g., SARNTHEIN *et al.*, 1988), but also continental input, ocean circulation, and water mass properties. In this regard, incorporation of selective dinocyst preservation may solve discrepancies among existing environmental reconstructions in the BCUS (e.g., BICKERT & WEFER, 1999; ABRANTES, 2000; BERGER & WEFER, 2002; ROMERO *et al.*, 2003). For core GeoB 1710, highest accumulation rates of R-cysts relate to minimal sea-surface temperatures and increased wind transported pollen input indicating maximal upwelling and associated high productivity during P1 and P2 (Fig. 5.6). In contrast, peak accumulation rates of S-cysts and maximal organic carbon contents are observed only for P1 suggesting good preservation under low  $O_2$  conditions, and efficient OM decay during P2, at times when bottom water  $O_2$  concentration was high. Evidence in support comes from the stable carbon isotope signal of OM ( $\delta^{13}C_{org}$ ), which indicates that  $^{13}C$ -enriched, refractory terrestrial OM survived 'burn down' during P2 while labile,  $^{13}C$ -depleted material of marine origin was degraded but account for lowest values during P1 when preservation was enhanced. There is as yet no way to prove this hypothesis but we conclude that the records of S-cysts and organic carbon are subjected to diagenetic overprinting and at least are consistent with the assumption that profound changes in the deep water oxygenation accompanied the late Pleistocene climate evolution in the BCUS.

Researchers working on climate archives from ice-cores and marine sediments are aware of the somewhat different questions that are being asked of them in these times of global warming. The role of the ocean within the global carbon cycle is subject of intense focus as the concern grows about the effects of industrial-induced atmospheric  $pCO_2$  increase. It is no longer sufficient to provide evidence on past states in ocean's deep circulation, export productivity, and major element cycling but it is increasingly necessary to quantify the processes that are linked to air-sea  $CO_2$  exchange and carbon storage within the deep-ocean and marine sediments. We know, for instance, that oxygen minimum zones of the global ocean varied in response to climate upheaval with implications for the release of greenhouse gases (ALTABET, 2002) and possible feedbacks on the supposed "positive" effects of fertilization connected to climatic change. We also have realized that mechanisms associated with ocean-atmosphere carbon partition such as biological pumping (BROECKER & HENDERSON, 1998) and chemical stratification (TOGGWEILER, 1999), potentially amplified the small insolation changes on orbital timescales to produce the large and rapid climate swings during glacial-interglacial cycles. These mechanisms call on roughly the same tie between the atmospheric  $pCO_2$  and deep water  $O_2$  concentration change, because they all demand a major reduction in the deep water  $O_2$  content to explain the lower  $pCO_2$  in the glacial atmosphere. There

is as yet no strong message from marine sediments that widespread glacial deep water anoxia existed, but our ability to reconstruct paleo-O<sub>2</sub> changes is not good and we thus have to consider glacial bottom water O<sub>2</sub> contents that were at least considerably lower. Far from being definitive, the relationship between O<sub>2</sub> concentration and the BWOI documented here might form the basis of a new method that makes quantification of the O<sub>2</sub> content in bottom water possible.

To be clear, much work remains to be done and our proposed method should be recognized as a promising but certainly not yet complete attempt. At present a wide range of paleo-proxies, based on different principles and biased by oceanic processes other than circulation or preservation are being developed. By combining these efforts we better document and quantify past climate change. In turn, better estimates will enable to better predict ecosystem changes and global climate in the future.

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## CHAPTER 6

### 6.1. Conclusions

Dinocysts have long been a neglected marine microfossil group for the characterisation and documentation of Neogene to Quaternary climate change. Compared with planktonic and benthic foraminifers, coccolithophores, radiolarians, and diatoms, dinocysts were seldom used for paleoceanographic studies although they are significant primary producers and have an excellent fossil record. Part of this neglect stemmed from the earlier focus of paleoceanography and the Deep Sea Drilling Project on deep-sea carbonate or opaline sediments in temperate and tropical–subtropical ocean basins. However, with the growing concern about impacts of human activity on global climate, attention has turned to the role of carbon transport/storage processes along continental margins (LIU *et al.*, 2000; MOLLENHAUER, 2002; INTORN, 2005) and in high latitude environments (CALDEIRA & DUFFY, 2000; SIGMAN & BOYLE, 2000; SARMIENTO *et al.*, 2004). These zones are significant sources and sinks for atmospheric CO<sub>2</sub>, because the specific rates of productivity, biogeochemical cycling, and sequestration of CO<sub>2</sub> are higher than in other parts of the open oceans. The end result is that it may take only years, as opposed to hundreds of years, for the atmosphere, lithosphere, biosphere, and hydrosphere to interact. Unfortunately, owing to the dynamic and complexity of these systems, their precise roles in the carbon cycle have yet to be quantified with any degree of certainty. In particular, the processes affecting OC burial in sediments and the related CO<sub>2</sub> fixation at a specific time remain largely unconstrained. For instance, in several areas closer to the continents where the content of sedimentary OM is high, considerably higher organic carbon loads are reported for glacial times. While this pattern is usually interpreted as the result of glacial-interglacial changes in OM rain rate, it could be equally well explained by lower bottom water O<sub>2</sub> contents, which in turn would have maintained increased OM preservation. This discussion is fundamental to paleoceanographic studies, as concentration and flux variations of OC in sediment cores are traditionally used to infer changes in the strength of biological pumping but also continental input, ocean circulation, and water mass properties. This thesis was aimed to an understanding of the use of dinocysts as tracers for bioproduction, OM preservation, and deep-ocean ventilation with emphasis on species selective preservation as detected in surface and core sediments. The comprehensive contemplation of the different results obtained in this study and the comparison with geochemical and microfossil paleodata give rise to the major question that motivated the present work:

*Does selective preservation of dinocysts provide a mean to quantify (past) ocean bioproduction?*

Traditional tenets within the palynological community have long been associated with the opinion that there is a close link between POM production in the upper water column and fluxes of dinocysts produced by heterotrophic dinoflagellates (e.g., DALE AND FJELLSÅ, 1004). In contrast, autotrophic dinoflagellates were most often deemed to populate oligotrophic environments what not means that they are not capable of taking advantage of elevated nutrient loads in surface waters, but possibly are just outcompeted by more opportunistic species (e.g., HARLAND, 1983). Based on pioneering studies in the 60's and 70's, this belief prevails largely till now. However, the results of this thesis draw attention to the fact that several dinocysts produced by heterotrophic

dinoflagellates (i.e. S-cysts) suffer from aerobic decay and thus, reflect productivity only in case of excellent preservation. Instead, the compilation of worldwide datasets on dinocyst accumulation rates (**Chapter 1**) suggests that fluxes of some dinocysts produced by autotrophic dinoflagellates (i.e. R-cysts) can be used to assess export production from surface waters without the risk of signal attenuation. This relationship seems to be independent from the environment under consideration and has further been evaluated through the comparison with independent productivity proxies in time series (**Chapter 2 & 5**). The robustness of R-cysts, coupled with the use of precise rate tracers (e.g.,  $^{230}\text{Th}$ ) and proxies of terrigenous OM input (e.g., pollen and spores) may therefore provide an alternative to paleoproductivity studies based on dissolution-susceptible carbonate and opaline microfossils. Nonetheless, an indispensable prerequisite of such studies is a detailed knowledge on the occurrence and distribution of dinocysts in relation to primary production, the  $f$ -ratio (ratio between new and total production), and export production. Moreover, these studies critically need to consider dinocysts production as the result of a complex interaction of a living organism and its environment rather than a “black box” in order to improve proxy calibration.

*Is selective dinocyst preservation a sensitive tool to detect changes in diagenetic conditions?*

The phenomenon of non-steady-state diagenesis is well recognized in open ocean sediments and occurs either due to the deposition of turbidites on pelagic sediments, changes in ocean productivity, or variable fluxes of electron donors and acceptors (e.g., KASTEN *et al.*, 2003). However, the occurrence of oxidized sediment below reducing sediments in many near-shore and continental shelves indicates that non-steady-state diagenesis takes place even in shallow-water regimes. This has not only a meaning for sediment geochemistry and major element cycling but influences the preservational status of several organic biomarkers and calcareous particles. Using the large differences in the preservation potential of R-cysts and S-cysts for calculation of a degradation index ( $kt$ ) based on first-order decay kinetics revealed that selective dinocyst preservation can assess the diagenetic status of sediments (**Chapter 2**). As an independent approach the degradation index reliably recorded the strong variability in the diagenetic overprint of the studied core and thus in degradation/preservation of OC along the glacial-interglacial transition. Besides, the general constraints of TOC as a productivity proxy, this clearly demonstrates that using OC as productivity indicator within these transitional sediment intervals bears a particularly high risk of misleading interpretation. Moreover, since the diagenetic processes are likely the result of changes in sedimentation rate, carbon input and/or increase in bottom water  $\text{O}_2$  content at the onset of interglacial NADW production, studying dinocysts might be a suitable tool to reconstruct paleoceanographic changes. Because it is entirely possible that these processes occurred over large areas of the Atlantic and have not yet achieved a new equilibrium state, important secondary effects of aerobic degradation on carbonate dissolution and atmospheric  $^{14}\text{C}$  have to be expected.

*Is it possible to transform records of dinocysts into estimates of deep-ocean oxygen contents?*

Many of the theories that try to explain the lower  $p\text{CO}_2$  of the atmosphere during full glacial conditions call on roughly the same tie, because they require a major reduction in deep-ocean oxygen contents at the same time. As yet, there is no strong message from marine sediments that widespread anoxia has occurred, but our ability to reconstruct oxygen contents of the ocean's

deepest water is very limited. The distribution of S-cysts in surface sediments of the Benguela Upwelling System has been demonstrated to sensitively reflect changes in bottom water oxygenation (**Chapter 4**). The ecological signals of these species are likely to be smoothed as soon as deposition takes place in an oxygenated environment, where the effect of degradation can be observed due to the distinct non-linear decrease of relative S-cysts abundance with increasing oxygen concentrations. A model of this relationship enabled to derive a bottom water oxygen index which revealed that the late Pleistocene deep-water oxygen history at the lower continental slope of Namibia follows a glacial-interglacial pattern that is consistent with the mode of deep water circulation in the eastern South-Atlantic (**Chapter 5**). Given the good agreement with independent proxies of deep water flow, it seems that the glacial bottom water oxygen content within the Cape Basin was at least considerably lower than today. This information combined with insights on the diagenetic history of the studied core inferred from selective dinocyst preservation places new constraints on the reconstruction of OM production and source as well as on carbonate chemistry.

Comprising it can be suggested that the dinocyst record in marine sediments provides a comprehensive archive for the qualitative and quantitative appreciation of paleoceanographic change. The difference in the preservation potential of R-cysts and S-cysts allows for their use as and indicator of deep-ocean ventilation and enables to separate productivity from OM preservation. Corresponding methods have been proposed and successfully applied in different settings and on different timescales. Dinoflagellates occupy a wide range of marine environments with respect to temperature, sea-ice cover, salinity, and nutrient availability and diversified dinocyst assemblages accordingly can be recovered from high-latitude marine basins and epicontinental seas. The use of dinocysts as tracers for sources and sinks of refractive (particulate) OM, carbon sequestration in marine sediments, and diagenetic mediated mineralization therefore has a high fidelity in high-latitude and shelf-basin carbon budget studies. However, it is not trivial to reconstruct past ocean processes using empirical relations derived from species patterns in the present day ocean. Each one of the methods developed in this work although contributes to our knowledge has limitations and therefore application must be accompanied by thorough testing of the proxy.

## 6.2. Outlook

Major challenges still limit our ability to use proxies to fully understand the past environment. An obvious example is that there are environmental variables for which we have no precise proxy such as salinity, alkalinity, continental weathering, and atmospheric circulation (HENDERSON, 2002). Even for existing proxies, more work is required to ground truth and better understand them. It is tempting, when handed a new tool, to apply it to many paleoclimate questions, but all proxies respond to more than one variable, some of which can be overlooked. An example has been the discovery of changes in foraminiferal  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  with changes in  $[\text{CO}_3^{2-}]$  (SPERO *et al.*, 1997), which forced a reinterpretation of many existing stable isotope records and demonstrates the need to fully understand the controls on a proxy before overusing it. Important with respect to the interpretation of dinocyst records is the ability to adjust for the

skewing associated with the “oxygen effect” on associations being studied. The more accurate the attempted paleoenvironmental interpretation is (e.g., quantitative reconstructions of sea surface temperature or salinity using transfer functions), the more important it is to determine the relative importance of this taphonomic factor. Especially in continental margin settings, where sea level fluctuations and particle re-suspension can result in very different preservational conditions over relatively short time spans, erroneous conclusions may be drawn if the role of oxygen exposure is not considered. Hence, effort needs to be directed to the quantification of selective dinocyst preservation using laboratory and field approaches. First results obtained from incubation experiments seem to be promising (ZONNEVELD, pers. communication), and probably will soon provide a more detailed picture of the degradation kinetics of dinocysts. In this regard, it should be noted that the general idea to use differences in degradation rates is not bound to cysts. Oxygen effect are also evident from lower degradation rates exhibited by recalcitrant macromolecules such as pollen (KEIL *et al.*, 1994), lignin (BENNER *et al.*, 1984), hydrocarbons (ATLAS, 1981), and algaenans (GELIN *et al.*, 1997) under anoxic as compared with oxic conditions. As such, application of degradation models to these markers may elucidate input of terrestrial or fluvial material from adjacent lands as well as carbon transport/storage processes in the ocean.

Another challenge for the future is to support such empirical observations with chemical understanding of the processes that control the proxy. What chemical difference is it, for example, that causes S-cysts to be easier degraded than R-cysts? Such understanding, as well as being a worthwhile scientific goal in its own right, will teach us about the limits in applicability of the proxy, but at the same time may also encourage the use of dinocysts in biomarker studies. Moreover, the high chemical stability of the R-cyst wall material could be useful in assessing how far preferential degradation affects radiocarbon ( $^{14}\text{C}$ ) ages of different organic biomarkers preserved in marine sediment. This is important to gain a fuller understanding of sedimentation processes, delivery mechanisms, and carbon turnover rates (MOLLENHAUER & EGLINTON, 2007).

There are further challenges in extending dinocysts as a proxy to longer timescales, where diagenesis becomes a bigger problem. Because dinocyst have a continuous and relatively diverse record in both the glacial and interglacial intervals, their use as robust indicators for paleoproductivity and OM preservation can be complementary to the data derived from diatoms, foraminifera, coccolithophorids and radiolaria. Ideally, these studies should be accompanied by research on the distribution of dinocyst assemblages in recent sediments along high productive continental margins and in high latitude environments, notably the Southern Ocean, which is presently poorly sampled. Such databases should then serve as a starting point to apply transfer functions for quantitative reconstructions of past sea-surface conditions and bottom water oxygen contents. The urgent need for paleoceanographic data from these regions is twofold. First, at high latitudes, particularly in the Southern Ocean, increased stratification in response to climate change may lead to a more efficient biological export of carbon from surface to deep waters, thereby reducing surface nutrients and carbon. In subtropical and equatorial waters, however, future warming may cause the opposite effect. Increased stratification of the water column may lead to reduced supply of either micro or macronutrients, a shift to N-fixing organisms, and even lower carbon export than occurs today (FALKOWSKI *et al.* 1998).

The future may also see high resolution application of dinocysts in sediment cores from key areas of ocean circulation such as the Indian-to-Atlantic gateway circulation around South Africa. The role of this inter-ocean exchange as a southern source of perturbation for Atlantic meridional overturning circulation (MOC) has been specifically assessed using a realistic representation of fluxes of heat and salt (WEIJER *et al.* 2001), but paleoceanography of the Agulhas system on millennial and sub-millennial timescales is virtually uninvestigated. In this regard, the study of dinocyst associations may enable to trace the important mechanisms that control the opening and closing of this gateway due to their sensitivity to ocean front migration and monsoon strength (ESPER *et al.*, 2004). Moreover, applying transfer functions for salinity, temperature, and bottom water oxygenation may allow for the calculation of inter-ocean transfer of heat and salt and could facilitate the reconstruction of deep ocean ventilation. Together with tracers of deep water advection and particle flux (e.g.,  $^{231}\text{Pa}/^{230}\text{Th}$ ), this approach could refer to a proper quantification of the rate and pace in Atlantic MOC response to transient perturbations of Agulhas warm water transport into the South Atlantic. This may help to trace the millennial to sub-millennial signals from Antarctica across southern latitudes towards the North Atlantic in order to establish a coherent picture of the inter-hemispheric teleconnection.

The results of this thesis should be recognized as a promising but certainly not complete essay. Much work remains to be done. However, the good news for dinocyst research is clear. The last two decades have seen major advances that provided a wealth of new knowledge. Such knowledge is the key to the past, and the past the key to the future.

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