

**The stable oxygen isotope signal
of the calcareous-walled dinoflagellate *Thoracosphaera heimii*
as a new proxy for sea-surface temperature**

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Für meine liebe Oma

Ich bin nicht bis hierher gelangt, weil ich davon träumte oder darüber nachdachte,
sondern weil ich meinen Weg gegangen bin.

ESTÉE LAUDER

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Summary

Palaeoceanographic and palaeoclimatic studies are often based on information derived from stable oxygen and carbon isotope measurements on planktonic microfossils. The stable oxygen isotope composition of planktonic foraminifera shells provide a well-established tool to reconstruct past sea surface temperatures (SST). The interpretation of stable oxygen isotope values as a temperature proxy is complicated by several factors such as metabolic, biological and kinetic effects. For instance, the production of the calcareous material might takes place in different depths in the water column, they can show ontogenic induced variability, can bear symbionts and can be influenced by the carbonate ion concentration of seawater.

Culture experiments on the calcareous-walled dinoflagellate *Thoracosphaera heimii* also documented a clear relationship between its oxygen isotope composition and temperature. The high potential of the oxygen isotope composition of *T. heimii* as a palaeotemperature proxy is supported by several advantages over other calcareous species such as foraminifera and coccolithophores. *T. heimii* has a broad geographic distribution, lives in a stable position within the water column, is present in geological records since the Late Cretaceous and is more resistant against dissolution compared to other plankton groups. It additionally does not bear symbionts and do not show any ontogenetic effects due to its short life time of about one to three days. Surface sediment samples in the Atlantic Ocean revealed that *T. heimii* forms a useful tool for temperature reconstructions of the deeper parts of the upper photic zone. This study is the first to test the applicability of the stable oxygen isotope composition of *T. heimii* as a new proxy for sea surface temperature in a down-core analysis.

In order to interpret the isotope signal of *T. heimii* recorded in sediments it is important to investigate its recent seasonal and spatial distribution pattern and its calcification depth habitat in relation to environmental parameters like temperature, chlorophyll-*a* concentrations and salinity. Water samples off NW Africa and off Tanzania reveal highest abundances in the upper water column at or just above the deep chlorophyll-*a* maximum (DCM). In these areas, seasonal shifts of the position of the Intertropical Convergence Zone (ITCZ) induce changes in surface circulation patterns and upwelling intensity. Besides nutrient concentration and temperature, also turbulence and the associated light availability appear to be the main controlling factors for the cyst distribution of *T. heimii*. Off Cape Blanc, cyst production is constant due to year-round

upwelling. Off Tanzania, highest cyst concentrations are observed in the north due to low turbulence and high light penetration during the NE monsoon.

To test the usability of the stable oxygen isotopic signal of *T. heimii*, we apply this new proxy in a downcore study covering the last 45 ka within the upwelling region off Cape Blanc (NW Africa) and compare it to other well-established proxies like the planktonic foraminifera *Globigerinoides ruber* (pink) and *Globigerina bulloides* and the Mg/Ca ratio of *G. ruber* (pink). All temperature proxies carried out comparable conditions in glacial and Holocene times. The isotopic composition of *T. heimii* and the temperature reconstructions based on the equation for inorganic carbon deliver comparable results to those obtained from *G. ruber* (pink) isotopes. Both species reflect the same depth habitat in the upper 50 m of the water column. The slight discrepancy in the Mg/Ca ratios of *G. ruber* (pink) can be explained by different seasonality since *G. ruber* (pink) is supposed to reflect a summer signal. Changes between glacial and interglacial intervals have been especially focused on. Here, the same applies to the relatively low temperatures reconstructions of *T. heimii* between 15 to 8 ka BP that could be explained by differences in its ecology with *G. ruber* (pink) indicating upwelling relaxation conditions whereas *T. heimii* reflects a year-round signal. The slightly lower isotopic values during the last glacial and colder temperatures observed in *G. bulloides* can be related to a deeper habitat between 0 to 75 m and its highest abundances during the upwelling season.

Past and future scenarios show changes in seawater pH in relation to surface water CO₂ concentrations. For instance, during glacial periods the oceans had higher pH than today. Differences in seawater pH are related to changes in oxygen isotope fractionation between water and calcium carbonate. Culture experiments on *T. heimii* reveal a negative linear relationship between pH and stable oxygen isotopes that might be explained by a higher affinity for the isotopically lighter HCO₃⁻. In contrast to planktonic foraminifera, *T. heimii* does not show kinetic fractionation since no correlation between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ can be found. In the future, the relationship between pH and oxygen isotopes has to be taken into account while calculating past sea surface temperatures.

The present study shows that the stable oxygen isotope signal of *T. heimii* constitutes a promising new proxy for the reconstruction of past sea surface temperature. Detailed studies on both, the ecology and physiology of *T. heimii* improve the accuracy of future palaeotemperature reconstructions.

Zusammenfassung

Paläozeanographische und paläoklimatologische Rekonstruktionen basieren oftmals auf stabilen Sauerstoff- und Karbonatisotopenmessungen an planktischen Mikrofossilien. Als Anzeiger für die Abschätzung von Paläotemperaturen haben sich planktische Foraminiferen bewährt. Die Interpretation der stabilen Sauerstoffisotopenwerte als ein Temperaturanzeiger kann durch den Einfluß von metabolische, biologische und kinetische Effekten beeinträchtigt werden. Beispielsweise kann die Produktion ihrer Kalkschalen in verschiedenen Wassertiefen stattfinden, sie können entwicklungsbedingte Variationen zeigen, Symbionten beherbergen und durch die Karbonationenkonzentration des Seewassers beeinflusst werden.

Kulturrexperimente an dem kalkig-wandigen Dinoflagellaten *Thoracosphaera heimii* zeigten ebenfalls eine klare Relation zwischen der Sauerstoffisotopenzusammensetzung und der Temperatur. Das hohe Potential der Sauerstoffisotopenkonzentration von *T. heimii* als ein Anzeiger für Paläotemperaturen wird durch ihre vielen Vorteile gegenüber anderen kalkigen Arten wie Foraminiferen und Coccolithophoriden bekräftigt. *T. heimii* zeigte eine breite geographische Verteilung, lebt in einer stabilen Position in der Wassersäule, tritt in geologischen Aufzeichnungen seit der Späten Kreide auf und ist widerstandsfähiger gegen Lösung als andere planktische Organismengruppen. Zusätzlich beherbergen sie keine Symbionten und zeigt durch ihren kurzen Lebenszyklus von ein bis drei Tagen keine entwicklungspezifischen Effekte. Oberflächensedimentproben im Atlantischen Ozean belegen, daß sie ein nützliches Hilfsmittel für die Temperaturrekonstruktion der unteren photischen Zone darstellen. In dieser Studie wird erstmals die Anwendbarkeit von stabilen Sauerstoffisotopen von *T. heimii* als ein neuer Anzeiger für Oberflächenwassertemperaturen in einem Sedimentkern getestet.

Um eine exakte Interpretation ihres Isotopensignals zu erlangen, sind detaillierte Informationen über ihre heutige saisonale und räumliche Verbreitung sowie ihre Lebenstiefe im Vergleich mit Umweltparametern wie Temperatur, Chlorophyll-*a* Gehalt und Salinität notwendig. Wasserproben vor NW Afrika und vor Tansania zeigten höchste Vorkommen in der oberen Wassersäule im oder kurz über dem Tiefen Chlorophyll-*a* Maximum. In diesen Gebieten führen Bewegungen der Intertropische Konvergenzzone (ITCZ) zu Änderungen in der Oberflächenwasserzirkulation und der Auftriebsintensität. Neben hohen Nährstoffkonzentrationen und der Temperatur sind Turbulenzen und die dazugehörige Verfügbarkeit von Licht die Hauptfaktoren, die die

Zystenverteilung von *T. heimii* kontrollieren. Vor Cape Blanc bleibt die Zystenproduktion durch das ganzjährige Auftriebsgeschehen konstant. Vor Tansania wurden aufgrund von wenig Turbulenzen und höhere Lichtintensität die höchste Zystenkonzentrationen im Norden beobachtet.

Um die Anwendbarkeit des stabilen Isotopensignals von *T. heimii* zu überprüfen, wurde dieser neue Anzeiger in einer Kernstudie, die die letzten 45 ka umfaßt, in der Auftriebsregion vor Cape Blanc (NW Afrika) getestet und mit anderen etablierten Anzeigern wie den planktischen Foraminiferen *Globigerinoides ruber* (pink) und *Globigerina bulloides* und den Mg/Ca Raten von *G. ruber* (pink) verglichen. Alle untersuchten Temperaturanzeiger zeigten vergleichbare Bedingungen während der letzten Eiszeit und des Holozäns an. Die Isotopenzusammensetzung von *T. heimii* und die Temperatur-Rekonstruktionen basierend auf der Gleichung für anorganischen Kohlenstoff liefern vergleichbare Ergebnisse wie die der Isotopen von *G. ruber* (pink). Beide scheinen dasselbe Tiefenhabitat innerhalb der oberen 50 m in der Wassersäule wiederzuspiegeln. Der geringe Unterschied zwischen den Mg/Ca Raten von *G. ruber* (pink) kann durch Unterschied in der Saisonalität erklärt werden, da *G. ruber* (pink) vermutlich ein Sommersignal widerspiegelt. Im Besonderen wurde die Aufmerksamkeit auf die Änderungen zwischen dem Glazial-Interglazial Intervall gelegt. Dasselbe gilt für die vergleichsweise niedrigen Temperaturen von *T. heimii* zwischen 15 bis 8 ka BP, die ebenfalls durch Unterschiede in der Ökologie beider Arten erklärt werden können. Während *G. ruber* (pink) Zeiten der Auftriebsrelaxion anzeigt, spiegelt *T. heimii* ein ganzjähriges Auftriebssignal wider. Der geringe Unterschied in der Isotopenzusammensetzung während des letzten Glazials und die kälteren Temperaturen von *G. bulloides* können mit unterschiedlichen Tiefenhabitaten zwischen 0 bis 75 m und ihrem häufigsten Vorkommen während der Auftriebszeit erklärt werden.

Rekonstruktionen der Vergangenheit und Zukunftsszenarien haben Änderungen im pH-Wert des Meerwassers im Bezug auf Oberflächenwasser CO₂ Konzentrationen aufgezeigt. Beispielsweise war der pH Wert während der letzten Eiszeit höher als heute. Änderungen im pH-Wert im Meerwasser sind mit Änderungen in der Sauerstoffisotopenfraktion zwischen Wasser und Kalziumkarbonat verbunden. Kulturexperimente an *T. heimii* decken einen negativ linearen Zusammenhang zwischen pH und stabilen Sauerstoffisotopen auf, der durch die höhere Affinität für das isotopisch leichtere HCO₃⁻ erklärt werden kann. Im Gegensatz zu planktischen Foraminiferen zeigt *T. heimii* keine kinetische Fraktionierung, weil keine Korrelation zwischen $\delta^{18}\text{O}_c$ –

$\delta^{18}\text{O}_w$ und $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ gefunden werden konnte. In zukünftigen Oberflächenwasserberechnungen muß der Bezug zwischen pH und Sauerstoffisotopen einbezogen werden.

Die aktuelle Studie zeigt, daß das stabile Sauerstoffisotopensignal von *T. heimii* einen hoffnungsvollen neuen Anzeiger für die Rekonstruktion von vergangenen Oberflächenwassertemperaturen darstellt. Detaillierte Studien der Ökologie und Physiologie von *T. heimii* steigern die Genauigkeit von zukünftigen Paläotemperatur Rekonstruktionen.

Chapter 1

Introduction

1.1 The mirror of the past provides an image for the future

Today, rapid global warming is a fact and is one of the most discussed global problems. In order to forecast future climate changes, it is essential to be able to understand the present day climate mechanisms as well as accurately reconstruct the climate of the past. In the Earth history, climate change is a common occurrence but the rapid warming of about 0.74 °C within the last 100 years is an exception in global history (IPCC report 2007). In 2050, scientists expect a rise in temperature of about 1.8 – 4 °C (Chiew *et al.*, 2003).

The world ocean has a large influence on the climate since 71 % of the Earth's surface is covered by water and controls the redistribution of heat and the absorption and release of greenhouse gases (Karl and Trenberth, 2003). Africa is one of the most vulnerable continents to climate change and climate variability. The climate of the continent is controlled by complex maritime and terrestrial interactions. Climate warming is expected to severely influence the hydrological cycle through changes in runoff, hydrology and sea-level rise (IPCC report 2007). It is assumed that the expansion of deserts and droughts will lead to famines and an increase in disease rates.

Climate forecasts require a precise understanding of past climatic, oceanographic and environmental changes that are often based on marine microfossil assemblages preserved in the sedimentary records of the oceans. For instance, the oxygen isotope composition of its shells represent an important tools for palaeoceanographic reconstructions (Fischer and Wefer, 1999 and references therein). Although most current proxies can provide detailed information on palaeoclimate, they contain several biological, ecological and physiological uncertainties that complicate the interpretation of their signals. In contrast, the calcareous-walled dinoflagellate *Thoracosphaera heimii* has several advantages over other proxies since it is geographically widespread, bears no symbionts, lives in a distinct part of the water column with no vertical movements and is extremely resistant against calcite dissolution (Zonneveld *et al.*, 2000; Vink *et al.*, 2002; Baumann, 2003). We therefore established the stable oxygen isotope composition of the calcareous dinoflagellate *Thoracosphaera*

heimii as a proxy for palaeoenvironmental reconstructions to reconstruct sea surface temperatures.

1.2 Dinoflagellates

1.2.1 Survey of biology and life strategies of dinoflagellates

Dinoflagellates are unicellular eukaryotic primary producers occurring in all aquatic environments (e.g. Evitt, 1985; Taylor and Pollinger, 1987; Matthiesen *et al.*, 2005) and are found in all climatic zones (e.g. Stover *et al.*, 1996; Chiew *et al.*, 2003; Maret and Zonneveld, 2003). Among the 2000 known marine species a huge variety of feeding strategies can be observed that include phototrophic, auxotrophic, mixotrophic, parasitic, symbiotic or heterotrophic strategies (e.g. Dale, 1983; Gaines and Elbrächter, 1987; Schnepf and Elbrächter, 1999). Since a considerable part of the dinoflagellates are photoautotrophic, they form an important part of the marine primary production (e.g. Parsons *et al.*, 1984).

Their size commonly ranges between 20 to 200 μm . Dinoflagellates typically occur as biflagellated motile cells with two flagellae inserted, one mid-ventrally and one transverse flagellum. With the aid of these two flagellae they can migrate vertically in spiral motion through the water column (Taylor and Pollinger, 1987). However, dinoflagellates generally live in the upper water column with a diel migration restricted to several metres (Anderson, 1985; Kamykowski *et al.*, 1998; Zonneveld, 2004). Nevertheless, their small size result in a Reynolds number smaller than 1 ($\text{Re} = (D \cdot V \cdot \rho) / \mu$; D = length of the moving object, V = velocity, ρ = density and μ = viscosity of the surrounding medium) that enables them to swim over relatively large distances. Therefore, they live in a quite stable position of the water column (Zonneveld, 2004). Turbulences are unfavorable for the development of dinoflagellates since it hampers the build-up of a standing stock in the photic zone (Wendler *et al.*, 2002a, b, Vink, 2004).

Their complex life cycle involves sexual and asexual reproduction with motile vegetative cells and non-motile cysts, temporary cysts, resting cysts and digestion cysts (for details see Dale, 1986; Fensome *et al.*, 1993). Many uncertainties still remain about the physical and chemical processes that underlie cyst formation. Encystment can be triggered by the nutrient depletion of nitrate and phosphate especially (e.g. Anderson *et al.*, 1984; Anderson and Lindquist, 1985; Blanco, 1995; Olli and Anderson, 2002). In

contrast, long-term field studies suggested maximum cyst formation during or just after periods of maximal vegetative cell division with non-depleted nutrient concentrations (e.g. Ishikawa and Taniguchi, 1996; Montresor *et al.*, 1998). Excystment can be triggered by several factors such as temperature, light availability, oxygen concentration and endogenous rhythms (e.g. Dale, 1983; Binder and Anderson, 1990; Kremp and Anderson, 2000). It is generally thought that the majority of cysts found fossilized within the sediments are produced during the sexual life cycle of dinoflagellates. Since this thesis mainly focuses on the calcareous dinoflagellate *Thoracosphaera heimii*, which exhibits a vegetative life cycle and asexual reproduction (refer to 1.2.2), the above mentioned life cycle is not described in detail.

Several dinoflagellates are able to produce cysts of calcareous-, siliceous- and organic-walled material. Calcareous dinoflagellates are characterised by the incorporation of calcite in at least one layer of the cyst wall. Sediment trap studies in the tropics and subtropics have shown that calcareous dinoflagellate cysts often dominate the total dinoflagellate cyst flux to the sea floor (Dale, 1992a; Höll *et al.*, 1998; Montresor *et al.*, 1998).

Their first appearance in the fossil record goes back to the Early Triassic with a major increase in dinocyst diversity at the end of the Triassic (Janofske, 1992). More than 200 fossil and about 30 modern calcareous dinoflagellate species are known (Streng *et al.*, 2004; Elbrächter *et al.*, 2008;). Since they react to long- and short-term, global and local changes, they are a useful proxy for palaeoclimatological and palaeoenvironmental studies (e.g. Vink, 2001; Esper *et al.*, 2004; Meier, 2004; Zonneveld *et al.*, 2005 and references therein).

1.2.2 Applications of the calcareous-walled dinoflagellate

Thoracosphaera heimii

Calcareous dinoflagellate cysts have been used in (palaeo-) ecological studies to explore their distribution patterns and their relationship to environmental parameters. The calcareous-walled dinoflagellate *Thoracosphaera heimii* (Kamptner, 1927) is well suited for palaeoenvironmental reconstructions since it is by far the most abundant species in sediments (Höll *et al.*, 1998) and seems to be relatively resistant against dissolution (Zonneveld *et al.*, 2000; Vink *et al.*, 2002; Baumann, 2003). Surface sediments and water samples were investigated in the Atlantic Ocean (e.g. Höll *et al.*, 1998; Höll *et al.*, 1999; Karwath *et al.*, 2000a; Karwath *et al.*, 2000b; Vink *et al.*, 2000;

Zonneveld *et al.*, 2000; Vink *et al.*, 2002; Richter *et al.*, 2007), the Arabian Sea (Wendler *et al.*, 2002b) and the Mediterranean Sea (Meier and Willems, 2003). Preliminary culture studies on the elemental composition of *T. heimii* revealed a characteristic fractionation and partitioning systematic of Ca isotopes and Sr/Ca, Mg/Ca and U/Ca ratios with the Sr/Ca having a good potential as a temperature proxy (Gussone *et al.*, *subm.*).

The stable oxygen isotopic signal of *T. heimii* was recently used for palaeotemperature reconstructions in surface sediment samples in the Atlantic Ocean (Zonneveld, 2004). This species forms a suitable candidate for palaeoreconstructions since it is found in sediments since the Late Cretaceous (e.g. Hildebrand-Habel and Willems, 2000; Streng *et al.*, 2004). Due to its small size (9 to 27 μm), it is quite easily isolated into a monospecific assemblage from marine sediments (Kamptner, 1967; Fütterer, 1977). Recent studies of its geographical distribution in modern sediment have shown that it has a broad geographic distribution and can be observed from sub-polar to tropic environments with the highest diversity and abundance in subtropical areas and from inner neritic to oceanic environments (e.g. Zonneveld *et al.*, 1999; Esper, 2000; Zonneveld *et al.*, 2000; Wendler *et al.*, 2002a; Meier and Willems, 2003; Vink, 2004). Growth experiments indicated that it has a broad temperature tolerance between 14 to 27 °C (Karwath *et al.*, 2000a). It is suggested that *T. heimii* preferentially lives in the photic zone around the thermocline (Karwath *et al.*, 2000b; Vink *et al.*, 2003). For different regions, various depth habitats were evaluated in terms of water column stability, nutrients and temperature in order to better constrain the preferential environment of *T. heimii* (e.g. Karwath *et al.*, 2000b; Wendler *et al.*, 2002b). In chapter 3 this issue is discussed in more detail.

In contrast to other calcareous-walled dinoflagellates, *T. heimii* reproduces asexually and spends most of its life cycle in a dominant vegetative-coccoid life-stage, which is not a resting stage (Fig. 1 (a)). After a cell hatches from the calcareous shell (b), it divides (c) and forms aplanospores either directly (e) or via the production of planospores (d). The aplanospores start to calcify (f). With a reproduction time every 1 – 2 days it has much higher turn-over rates than other resting cyst forming species (e.g. Tangen *et al.*, 1982; Dale, 1992b).

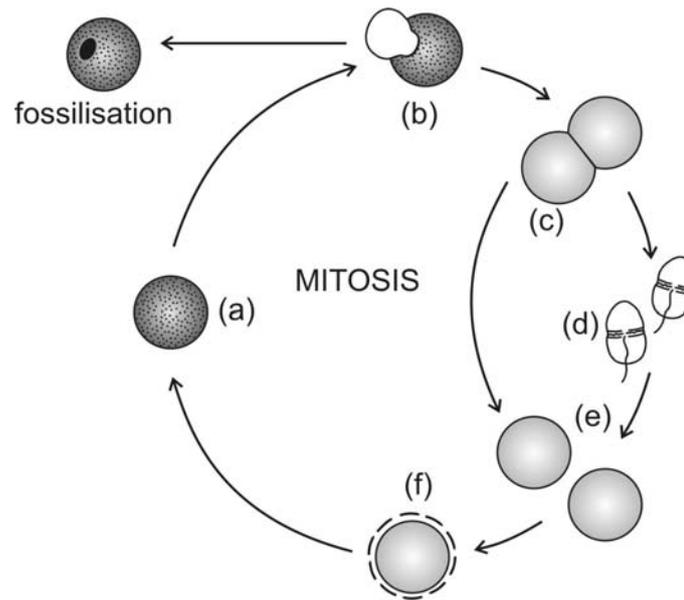


Fig. 1. Life cycle of *Thoracosphaera heimii* (modified after Vink, 2000; Meier, 2007). (a) vegetative cyst. (b) cell hatches. (c) cell division. (d) aplanospores. (e) planospores. (f) calcification.

1.3 Stable oxygen isotopes

The element oxygen forms 21 % of the Earth atmosphere by volume and is the most abundant element by mass in our biosphere, air, water and land. It occurs as three stable isotopes containing different numbers of neutrons. They are found in nature in differing amounts: $\delta^{16}\text{O} = 99.76\%$, $\delta^{17}\text{O} = 0.04\%$, $\delta^{18}\text{O} = 0.20\%$. The oxygen isotopic composition is expressed as $\delta^{18}\text{O}$:

$$\delta^{18}\text{O}(\text{‰}) = \left[\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}} - \left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}} \right] \cdot 1000$$

Stable isotopes are usually measured using a mass-spectrometer. To determine oxygen isotope ratios, $\delta^{18}\text{O}/^{16}\text{O}$ ratios are compared to the known $\delta^{18}\text{O}/^{16}\text{O}$ ratio of a standard. Two standards are referred to V-PDB (Cretaceous belemnite formation at Peedee in South Carolina, USA) was used for carbonate samples and for water samples SMOW (Standard Mean Ocean Water; Craig, 1961) or more recently V-SMOW (Vienna Standard Mean Ocean Water; (Gonfiantini, 1978; Coplent, 1996) was used for water samples. To convert V-SMOW to V-PDB the following equation is used:

$$\delta^{18}\text{O}(\text{‰ V-PDB}) = 0.99973 * \delta^{18}\text{O}(\text{‰ V-SMOW}) - 0.27\text{‰} \text{ (Hut, 1987)}$$

1.3.1 Fractionation in the hydrological cycle

Isotope fractionation that occurs during chemical reactions or physical processes (e.g. diffusion, precipitation) results in either an enrichment of lighter isotopes (more negative values) or an enrichment of heavier isotopes (more positive values). Two kinds of isotope fractionation occur. Equilibrium isotope fractionation is defined as the partial separation of isotopes between substances during isotopic exchange reactions (Broecker and Maier-Reimer, 1992; Lynch-Stieglitz *et al.*, 1995). A non-equilibrium effect describes an unidirectional process (e.g. evaporation, photosynthesis).

Isotope fractionation is linked to the hydrological cycle (Fig. 2). The difference between $\delta^{18}\text{O}$ of the atmosphere and seawater is defined as the Dole effect. Since $\delta^{18}\text{O}$ is heavier than $\delta^{16}\text{O}$, water vapour evaporating from the sea surface is depleted of heavy isotopes relative to sea water. Precipitation leads to an enrichment of heavy isotopes. Isotope fractionation that occurs during condensation in a moist air mass and leads to lighter isotopes enrichment is called Rayleigh distillation (Rayleigh, 1902). Several other factors influence isotope fractionation such as latitude, height, continentality, temperature, freshwater input, sea ice melting and freezing and mixing between water masses (e.g. Paul *et al.*, 1999).

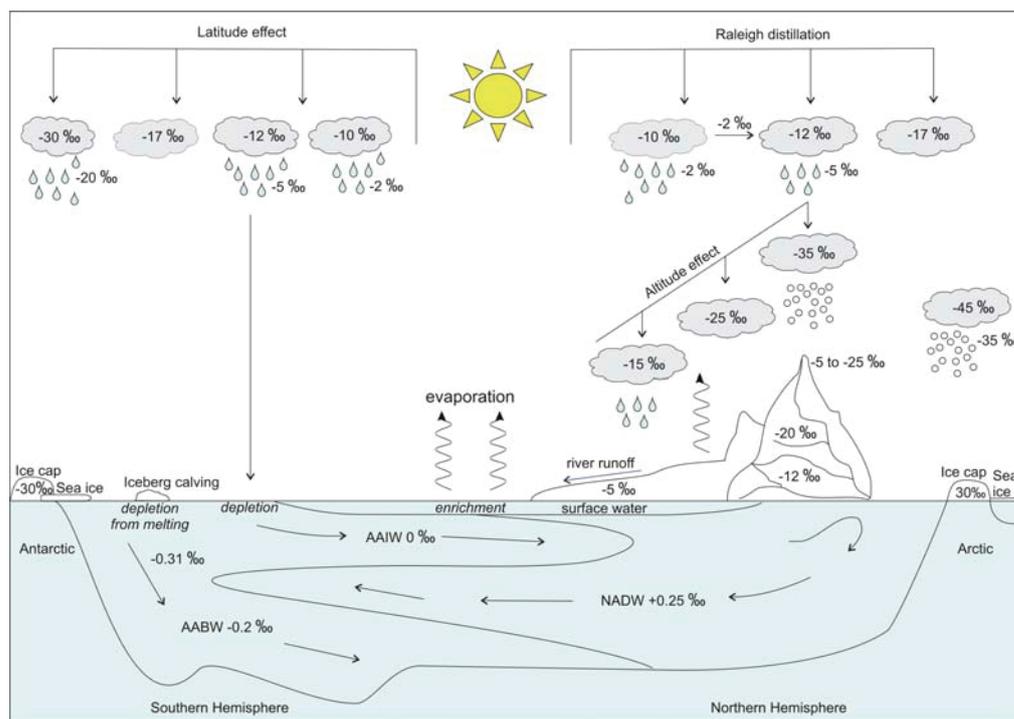


Fig. 2. Schematic overview of the global $\delta^{18}\text{O}$ cycle (modified after Paul *et al.*, 1999).

1.3.2 Palaeotemperature equation and disequilibrium effects

Sea surface temperature (SST) is the most important environmental variable for the Earth's climate system since it is the lower boundary that drives circulation in the atmosphere, generates wind and weather and influences evaporation and precipitation patterns (Henderson, 2002). Many different organisms like planktonic and benthic foraminifera, coccolithophores and corals have been used to determine past sea surface temperatures (for further details see the review paper of (Wefer *et al.*, 1999). Early proxies such as stable oxygen and carbon isotopes have been complemented by an increasing number of new proxies, such as the stable oxygen isotopes and Mg/Ca of planktonic foraminifera, Sr/Ca of corals, U_{37}^k (alkenone saturation index) of coccolithophores and Tex_{86} based on the glycerol dialkyl glycerol tetraethers (GDGTs) of the aquatic microbe Crenarchaeota (for a detailed review see Henderson, 2002; Schouten *et al.*, 2002). Among these proxies, stable oxygen isotope measurements on planktonic organisms have become a standard tool in reconstructing palaeotemperature of upper water temperatures since the pioneer work of Urey, 1947; McCrea, 1950 and Epstein, 1953. Due to the fact that this proxy is influenced by both changes in temperature and seawater chemistry, it has to be corrected for seawater (Emiliani, 1955). The calculation of temperature from oxygen isotopes is based on the quadratic equation:

$$T (^{\circ}\text{C}) = a + b (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) + c * (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})^2$$

which is the standard form used in palaeoceanographic studies. The term “a” is temperature when $\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$ is 0, “b” is the slope and “c” is the second-order term for curvature. Commonly used temperature equations are given in (Bemis and Spero, 1998). Deriving temperature from $\delta^{18}\text{O}$ is complicated due to possible spatial and temporal variations in the determination of $\delta^{18}\text{O}_{\text{water}}$ (e.g. salinity and global ice volume; Spero *et al.*, 1997; Zeebe, 1999; Bickert, 2000; Mulitza *et al.*, 2003). During the last glacial periods a large volume of ocean water was deposited as ice on the continents and in the ocean, resulting in higher $\delta^{18}\text{O}_w$ and salinity values (ice volume effect; Mook *et al.*, 1974). The exact effect on the $\delta^{18}\text{O}_w$ of this phenomenon is however not known. In addition to these uncertainties, several other processes like biological, kinetic and metabolic (or vital) processes can cause deviations of the isotopic composition of calcareous parts of organisms from equilibrium with respect to seawater. These main

effects include the effects of different depth habitats, vertical migration of the organisms throughout the water column, ontogenetic effects, changing carbonate ion concentration $[\text{CO}_3^{2-}]$ of the ambient seawater, ontogenetic, symbiotic and species-specific vital effects (for a detailed summary see Rohling and Cooke 1999 and references therein). For instance, the symbionts-bearing foraminifera *Orbulina universa* shows decreasing $\delta^{18}\text{O}$ values with increasing light irradiance (e.g. Spero and Lea, 1993; Bijma *et al.*, 1999). The planktonic foraminifera *Globigerina bulloides* calcifies at depth as a juvenile and migrates to shallower waters as an adult which leads to chamber-dependent effects (Spero and Lea, 1996; Bemis and Spero, 1998). Consequently, it is complicated to interpret the oxygen isotope signal of the commonly used planktonic foraminifera. Therefore, several studies tested the usability of other organisms like corals, coccolithophores, bivalves and pteropods to get a more accurate SST calculation based on isotopes (e.g. Margolis *et al.*, 1975; Anderson, 1983; Dudley, 1986; Fabry and Deuser, 1992; Klein *et al.*, 1996). Corals are restricted to specific sites only and bear symbionts that again lead to disequilibrium effects (e.g. McConnaughey, 1989). Coccolithophores are difficult to separate monospecifically due to their small size and they also show quite a large number of vital effects probably related to the fact that their coccoliths are produced in a membrane-bounded intracellular space called the coccolith vesicle (Young *et al.*, 1999; Stoll *et al.*, 2001; Stoll and Ziveri, 2002). Due to their solubility molluscs occur often discontinuously in sediments limiting their usability (Titschak, 2006). Studies on pteropods showed that they are easily dissolved, show diel migration within the water column and are produced only over several months of the year that yields a more seasonal signal (Fischer, 1999). Some of the problems demonstrated by these proxies can be solved by using the calcareous dinoflagellate *T. heimii* since it does not bear symbionts, lives at a relatively stable position of the water column with no vertical movements and is relatively resistant against dissolution (Zonneveld, 2004; Zonneveld *et al.*, 2007). In comparison to other calcareous dinoflagellate species *T. heimii* can be easily separated out of the sediment due to its comparatively small size (Zonneveld, 2004). The first studies on *T. heimii* indicated that its stable oxygen isotopes can be used to reconstruct past sea surface temperatures (Friedrich and Meier, 2003; Zonneveld, 2004; Friedrich and Meier, 2006; Zonneveld *et al.*, 2007). For a reliable interpretation of the $\delta^{18}\text{O}$ signal, it is important to know at which depth its signal originates. The limited information available on the depth habitat of *T. heimii* gives no clear indication of the relationship between its maximum

abundance in comparison to environmental parameters in the upper water column (see chapter 3). In order to optimise the temperature calculation, it is important to determine possible metabolic and kinetic effects on the fractionation process of the stable oxygen isotope composition. For instance, detailed information about possible fractionation differences at changing pH of seawater are required (chapter 4).

1.4 Investigation areas

1.4.1 Characteristics of oceanic boundary currents

The boundary currents of the ocean can be divided into western boundary currents (WBC) characterised by downwelling and eastern boundary currents (EBC) characterised by upwelling. Subtropical EBCs flow equatorwards and bring cold water from higher to lower latitudes. Two major examples, the upwelling region off NW Africa and the downwelling region off Tanzania area are focus of this study.

Coastal upwelling occurs where trade winds blow alongshore and the Coriolis-force induced Ekman transport pull surface waters offshore within a divergent horizontal flow (Fig. 3a). The deficit waters are replaced by central water masses that well up onto the shelf. Upwelled waters are characterised by a shallow thermocline, relatively low temperatures and comparatively high nutrient values indicated by high chlorophyll concentrations (e.g. Nelson and Hutchings, 1983; Nykjaer and Van Camp, 1994; Hernandez-Guerra and Nykjaer, 1997; Shaffer *et al.*, 1999; Van Camp *et al.*, 1991; Blanco *et al.*; Hagen, 2001). Depending on the coast morphology at pronounced capes upwelled water can be transported far offshore within filaments and eddies.

In contrast to the EBCs, WBCs transport warm waters from the tropics poleward. Downwelling occurs where Ekman transport moves surface waters towards

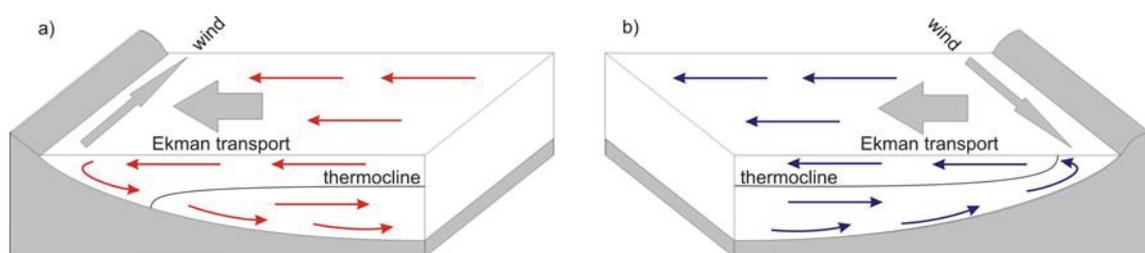


Fig. 3. Scheme of wind driven coastal (a) downwelling, (b) upwelling (modified after Shanks and Brink, 2005)

the coast (Fig. 3b). The water masses pile up onshore and sink down. Downwelled waters are characterised by a deeper thermocline, relatively warm temperatures and comparatively low nutrient contents denoted by low chlorophyll concentrations (McClanahan, 1988). Upwelling and downwelling form a continuous loop rotation throughout the ocean. They play a key role in palaeoceanographic studies because they are linked to major oceanic processes such as the formation of current patterns, the mixing of water masses and wind stress (e.g. Berger and Wefer, 2002).

1.4.2 Comparison of the NW African upwelling region to the Tanzanian downwelling

In chapters 2 and 3 a detailed description of oceanographic and climatological settings off NW Africa and in the western Indian Ocean are given. Here, the focus is taken on the relationship between the two monsoon systems and their dependence on the shift of the ITCZ over Africa.

The most important atmospheric feature over Africa is the seasonal latitudinal shift of the Intertropical Convergence Zone (ITCZ) from about 40 °N to about 45 °S (e.g. Gasse, 2000). Seasonal changes in insolation and local air pressure lead to a northward shift of the ITCZ in boreal summer (Fig. 4b) and to a more southern location in boreal winter (Fig. 4a). It separates the northern and southern Hadley cells and designated the boundary where northern and southern trade winds meet (Stuut *et al.*, 2005). The migration of the ITCZ affects seasonal precipitation patterns across the African continent leading to greater distinctions between wet and dry seasons (McClanahan, 1988). The greatest amount of rainfall occurs during the SW monsoon when the southeast trade winds cross the equator north-eastwards (Ramage, 1971). Accordingly, shifts in trade wind persistence and strength lead to changes in upwelling with latitude. Off NW Africa, the upwelling cell is shifted to the south between 12 – 20 °N in boreal winter and to the north between 25 – 32 °N in boreal summer (Nykjaer and Van Camp, 1994; Santos *et al.*, 2005; Fig. 4). Therefore, upwelling is persistent year-round between 20 – 25 °N (Mittelstaedt, 1991; Hernandez-Guerra and Nykjaer, 1997). In contrast, off Tanzania, downwelling occurs throughout the year and is associated with relatively low nutrient concentrations (Bell, 1972; McClanahan, 1988). During the SW monsoon downwelling is strongest leading to a thickening of nutrient-deficient waters.

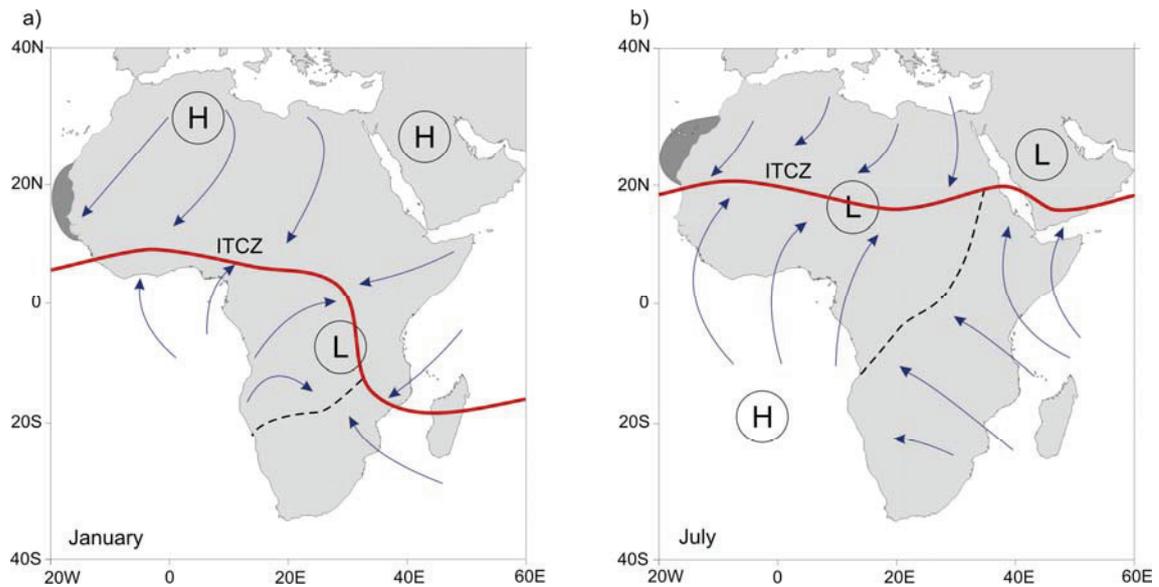


Fig. 4. Prevailing winds and location of the Intertropical Convergence Zone (ITCZ) over Africa in (a) January, (b) July. Upwelling area shaded in grey (modified after (Nicholson, 1996)).

1.5 Late Quaternary climatic and oceanographic changes

To evaluate a new proxy is it important to choose a well documented time period. Climate changes in the Late Quaternary have been investigated in many studies and discussed in detail in and off Africa (e.g. Rognon, 1977; Sarnthein *et al.*, 1981; deMenocal, 2000; Swezey, 2001 and references therein).

Warm and humid conditions were correlated with interglacial times whereas cold and dry conditions equate with glacial climates. These climate changes are linked to changes in Earth's orbital parameters (e.g. Hays *et al.*, 1976; Imbrie, 1982; Berger and Keir, 1984). Changes in insolation are caused by fluctuations in the Earth's orbital eccentricity, obliquity and precession which have periods of 100, 41, 23 ka respectively and are known as the Milankovitch Cycles (Milankovitch, 1920; Berger *et al.*, 1978; Imbrie *et al.*, 1993, Ruddiman, 2001). These cycles affect global and regional climates by changing insolation and thus influencing seasonality as well as ice sheet melting and building. Sub-Milankovitch cycles indicate rapid climate oscillations at millennial scales like Heinrich events (H), Dansgaard-Oeschger cycles (D-O) and the Younger Dryas (YD) cooling event (e.g. Dansgaard, 1985; Heinrich, 1988; Bond, 1992; Broecker *et al.*, 1992; Vidal *et al.*, 1997; Alley and Clark, 1999). D-O cycles are depicted in Greenland ice cores as periods of abrupt warming (interstadials) with temperature increases up to 8 °C within 40 years followed by gradual cooling (stadials) lasting

several centuries (Bond *et al.*, 1999; Alley, 2000). In contrast, Hs are periods of rapid temperature decrease in cold stadials that were observed in the North Atlantic have a global effect (Heinrich, 1988; Voelker and workshop participants, 2002), Fig. 5). They anomalously occur in the sediment record alongside ice-rafted debris layers every 7 to 10 ka BP (Hemming, 2004). They are thought to be related to large pieces of icebergs that detached from the Laurentide ice sheet and to disturbances in the thermohaline circulation (MacAyeal, 1993; Sarnthein *et al.*, 2000; Rahmstorf, 2002). Such large breaking events might have lead to a sudden discharge of freshwater and thus produced lower salinity and density values of the surface water between 45 °N to 55 °N (e.g. Broecker, 1986; Rahmstorf, 2002; McManus *et al.*, 2004). Consequently, the production of North Atlantic Deep Water (NADW) would have been reduced and the THC would have been interrupted.

Hs are supposed to correlate to variability in hydrological patterns such as the shift of the ITCZ and thus the monsoon system (Schulz *et al.*, 1998; Wang *et al.*, 2001; Broecker, 2003). Phases of desertification in North Africa are suggested to be caused by a southward shift of the ITCZ during glacial times (Mulitza *et al.*, 2008; Tjallingii *et al.*, 2008; Itambie *et al.*, 2009). In contrast, during the African Humid Period (AHP) between about 9 to 6 ka BP a shift of the ITCZ more to the north is thought to have led to an increase in precipitation over North Africa and accordingly to a green Sahara and lake level rises (Claussen *et al.*, 1999; deMenocal, 2000; Gasse, 2000 Fig. 5). The onset of the AHP was already induced by 14.5 ka BP. At this time the Bølling/Allerød warm period (BA) marked the termination of the last glacial period (Grafenstein *et al.*, 1999; Brauer *et al.*, 2000; Zolitzschka *et al.*, 2000; Yu and Eichner, 2001; Weaver *et al.*, 2003). The BA was interrupted by the relatively short cold YD (approximately 12.9 to 11.5 ka BP) which was a response to reduced THC caused by freshwater input from North America and Lake Agassiz (Broecker, 2006).

For the future, a number of climate models suggested human-induced large ice sheet melting with the consequence of a reduction or even a shutdown of the THC that would have profound implications for climate change (Manabe and Stouffer, 1993; Stocker and Schmittner, 1997; Clark *et al.*, 2002) and references therein, IPCC report, 2007). Although uncertainties still remain regarding if and how much the THC will be weakened, a recent study in the North Atlantic (at 25 °N) already suggests a decline in the THC of about 30 % between 1957 and 2004 (Bryden *et al.*, 2005). Due to the

complexity of the process further studies need to be carried with the goal of a better understanding of the past and future climatic processes.

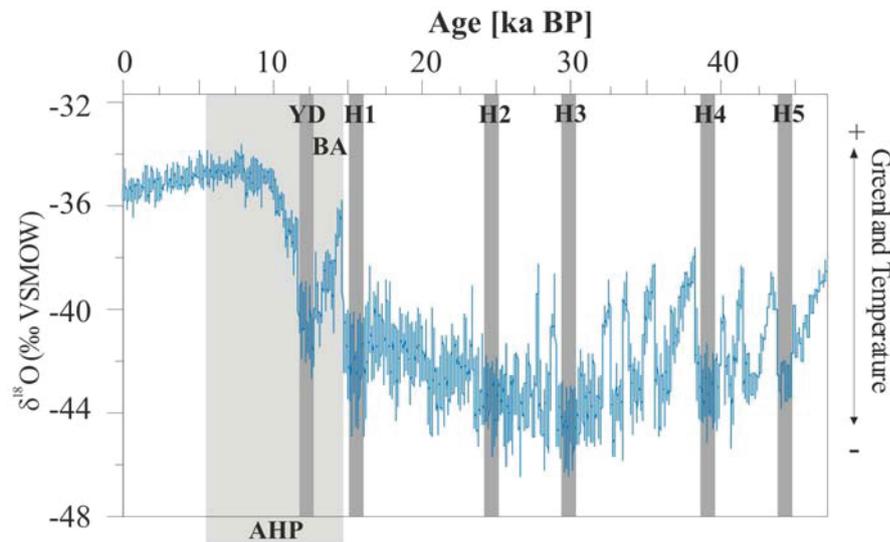


Fig. 5. Stable isotope stratigraphy ($\delta^{18}\text{O}$) over the last 55 ka of the North Greenland Ice Core Project (NGRIP; 75.10 °N and 42.32 °W; NGRIP-members, 2004) showing the Heinrich Events (H), the Bølling/Allerød (BA) and the Younger Dryas (YD) (modified after Holzwarth, 2009).

1.6 Objectives and overview

The main objective of this thesis is to establish the calcareous dinoflagellate *Thoracosphaera heimii* as a proxy for sea surface temperature (SST) and to obtain more information about its ecology and physiology. Therefore, this study comprises the following geological and biological approaches (Fig. 6):

- sediment core analyses to investigate its stable oxygen isotope signal in the Late Quaternary in comparison to well established proxies (chapter 2)
- survey of its horizontal and vertical distribution in the upper water column in relation to physical environmental parameters such as temperature, salinity and chlorophyll-*a* (chapter 3)
- laboratory experiments to determine the influence of different pH of seawater on its isotope composition (chapter 4)

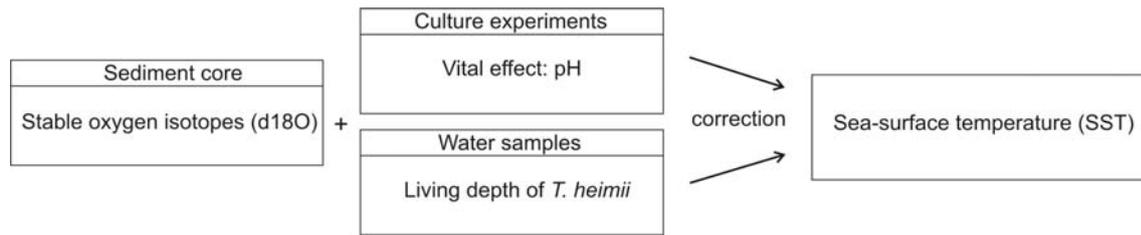


Fig. 6. Overview of the different studies and methods on *Thoracosphaera heimii*.

The outcomes of this project are presented in three manuscripts that correspond to chapter 2, 3 and 4 of this thesis.

Manuscript 1 - *Stable oxygen isotopes of the calcareous-walled dinoflagellate Thoracosphaera heimii as a proxy for mixed layer temperatures*

This study investigated the applicability of the new proxy in a time series analysis. For this purpose stable oxygen isotope analyses were carried out on core GeoB 8507-3 off Cape Blanc to examine Late Quaternary sediments. Our results were compared to other well established proxies like the planktonic foraminifera *Globigerina bulloides* and *Globigerinoides ruber* (pink), and the Mg/Ca ratio of *G. ruber* (pink). Stable oxygen isotope values of *T. heimii* coincide with those of *G. ruber* (pink). Reconstructed temperatures lie within the same range as the Mg/Ca values of *G. ruber* (pink). However, open questions on the ecology and biology of *T. heimii* still remain and are necessary to answer in order for a better interpretation of its stable oxygen isotope signal.

Manuscript 2 - *Calcification depth of Thoracosphaera heimii; implications for palaeoceanographic reconstructions*

We examined the horizontal and vertical distribution patterns of *T. heimii* within the upper 10 to 200 m of the water column off the coasts of NW Africa, Portugal and Tanzania in relation to temperature, salinity and chlorophyll-*a* concentrations. This survey was conducted to determine which depth *T. heimii* inhabits and subsequently out of which depth its oxygen isotope signal is originating. Highest cell counts have been observed at or just above the deep chlorophyll maximum depth. Highest cyst

concentrations have been found in regions with low turbulence and high nutrient concentrations.

Manuscript 3 – *Influence of pH on the $\delta^{18}\text{O}$ signal of the calcareous-walled dinoflagellate Thoracosphaera heimii*

Culture experiments have been carried out to determine the effects of different pH values on the stable oxygen isotope signal of *T. heimii*. A negative linear relationship between pH and has been observed $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$. This indicates a preferential uptake of HCO_3^- due to a decreasing HCO_3^- concentration with increasing pH. No correlation between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ has been found suggesting that *T. heimii* does not show kinetic effects.

The results of this study provides a more accurate calculated palaeo sea surface temperature (SST) of *T. heimii* since during the last glacial large changes in pH comparad to the last interglacial can lead to an underestimation of SST.

The results presented in chapters 3 and 4 are critically important to interpreting the stable oxygen isotope signal discussed in chapter 2. Together, they provide the basis for the determination of *T. heimii*'s role as a proxy for palaeoenvironmental reconstructions.

1.7 Material and methods

In chapters 2, 3 and 4 materials and methods examined in this thesis are described in detail. However, some methods are only cited from literature and will be described in the following section in more detail.

1.7.1 Separation of *T. heimii*

Marine sediment core GeoB 8507-3 was recovered off Cape Blanc at approximately 2411 m water depth (19°29' N, 18°06' W) and sampled every 5 cm. A widely used tool for the reconstructions of palaeoceanography and palaeoclimate on sediment cores are isotope compositions of foraminifera. They are isolated from sediment by monospecific picking. *T. heimii* is too small to be picked since $3 * 10^4$ individual shells have to be selected for mass spectrometry measurements (Zonneveld, 2004). Therefore, we purified them from the samples by using the density-size method developed. Since

T. heimii can be easily dissolved by deionized water. Therefore, we used tap water throughout the entire cleaning process. About 0.3 – 1.3 g of material was dissolved and homogenised ultrasonically for about half a minute (Sonorex RK 100, 35 kHz frequency). Samples were sieved through a 20 µm steel sieve into a 3000 ml glass beaker to remove particles bigger than *T. heimii*. Five 500 ml glass beakers were filled with 300 ml of water each and 200 ml aliquots of the sample. After 10 min of settling the upper 400 ml of the mixture was carefully decanted using a water jet pump to remove particles that are lighter than *T. heimii*. The residual 100 ml was collected into a glass beaker. To remove particles heavier than *T. heimii* 100 ml of the sample was added to 400 ml of water and settled for 30 s. The material was then decanted into a glass beaker and checked under a polarized light microscope with a gypsum plate. The settling and the decanting step were repeated until the residue contained less than 15 % calcite particles other than *T. heimii*. The purified samples were filtered through a polycarbonate filter and oven-dried for 24 h at 60 °C. Stable isotope measurements were performed with a mass spectrometer as described in detail in chapter 2. A schematic presentation of the density/size method is shown in Fig. 7. The advantage of this method is that a large amount of cysts and samples can be separated in a relatively short time period.

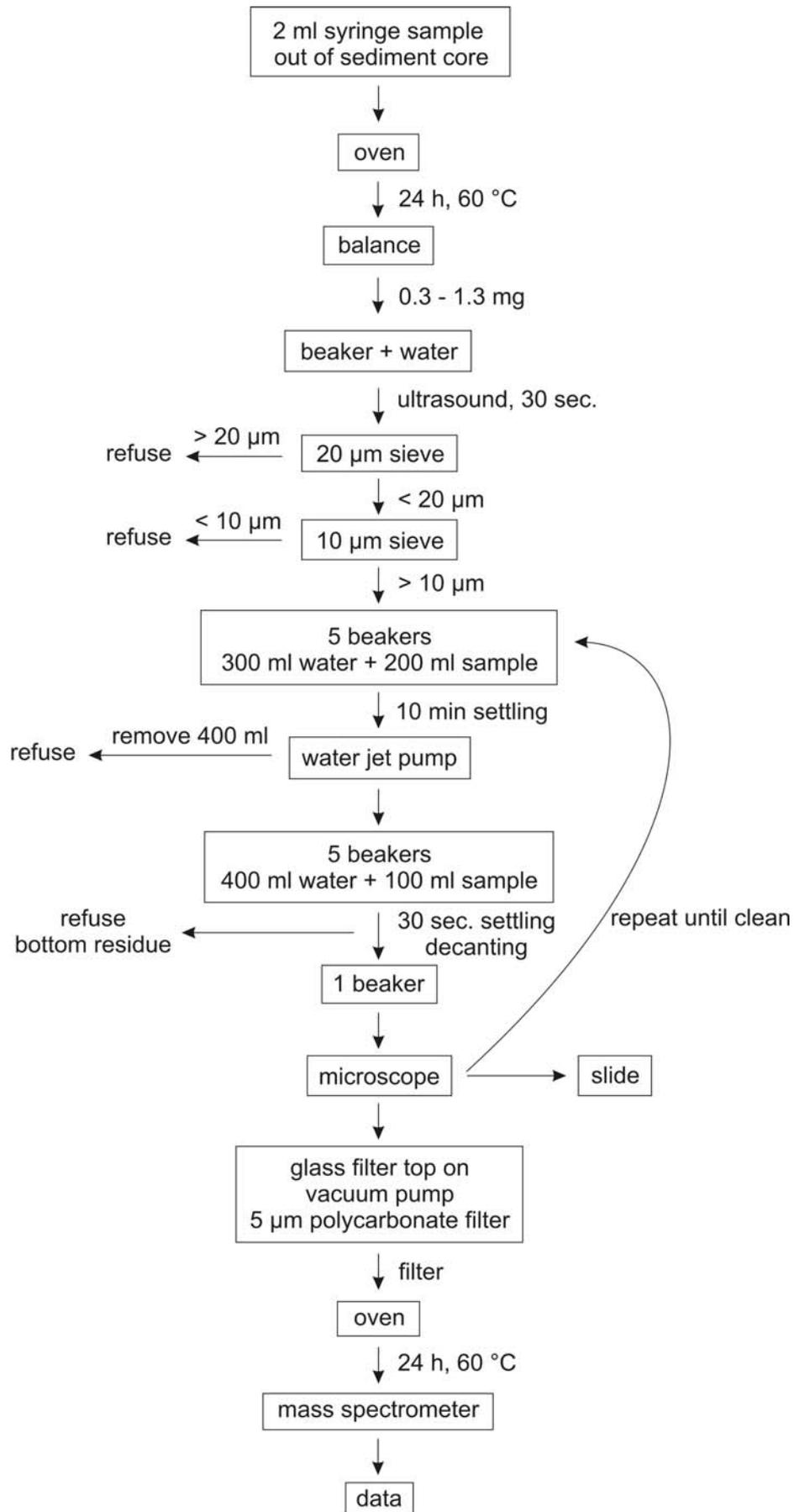


Figure 7. Schematic presentation of the density/size method.

1.7.2 Onboard filtration method

Each samples retrieved with the CTD/Rosette was contained within a 10 l NISKINTM bottle. The sample was pre-filtered through a 100 μm mesh sieve (DIN 4188) into a 10 l bucket (Fig. 8). Samples were then filtered through a 5 μm polycarbonate filters (diameter 50 mm) using a vacuum pump system. Overflowing water was discarded. Filters were oven dried for 24 h at 60 $^{\circ}\text{C}$.

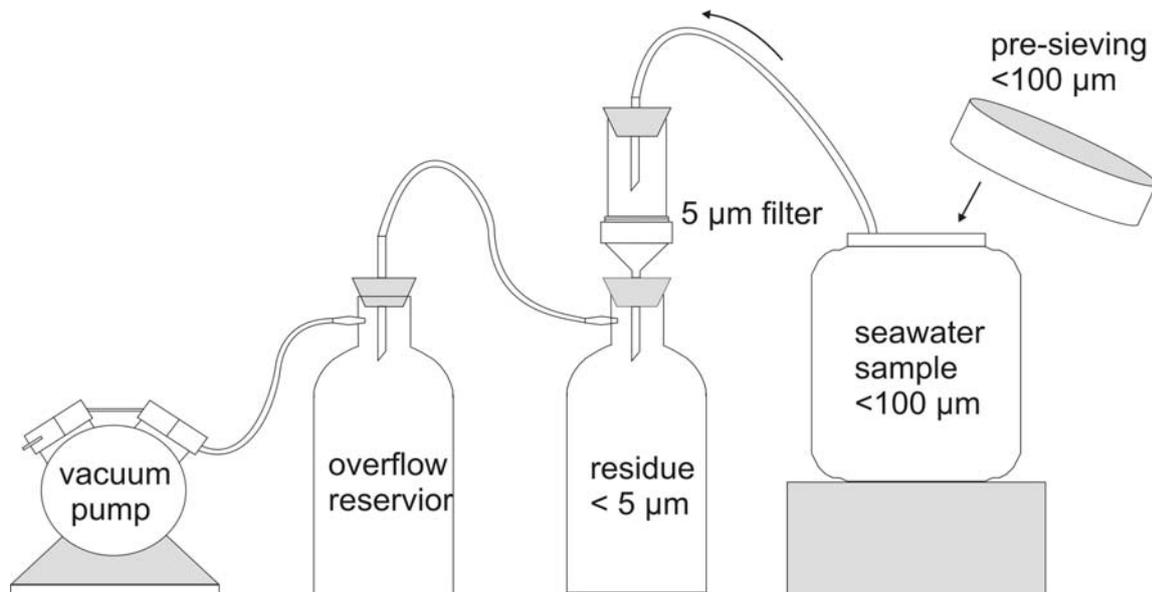


Fig. 8. Vacuum pump filtration unit (modified after Karwath, 2000).

1.7.3 Experimental set-up of the culture experiment

The temperature related growth curve of *Thoracosphaera heimii* strain *148 was investigated by culturing them at 22 $^{\circ}\text{C}$ in a 50 ml Eppendorf flask containing 20 ml of K-medium with seawater. Growth of a culture within a constant volume of stable medium is described by a sigmoid growth curve and can be divided into four phases (Winslow and Walker, 1939; Monod, 1942; Sorokin, 1973). In the lag phase, the cells adapt to the medium. In this phase the growth rate is increasing, unless a net growth is absent. During the exponential growth phase the mass of cells doubles over each of the successive time intervals. Within the declining phase, growth rate is increasing, and reaches a stable concentration of cell mass per unit volume of cell suspension within the stationary phase. Therefore, samples have to be taken within the exponential growth phase because the growth rate is constant and cells are well adapted to the surrounding

medium. Growth rates were determined by calculating cell counts per volume unit of culture media (here per ml).

We developed a new method to investigate the influence of pH changes in seawater on the isotopic composition of *T. heimii*. Due to the complexity of the culture experiment, a schematic set-up is given (Fig. 9). Details on the different measurements are described in chapter 4.

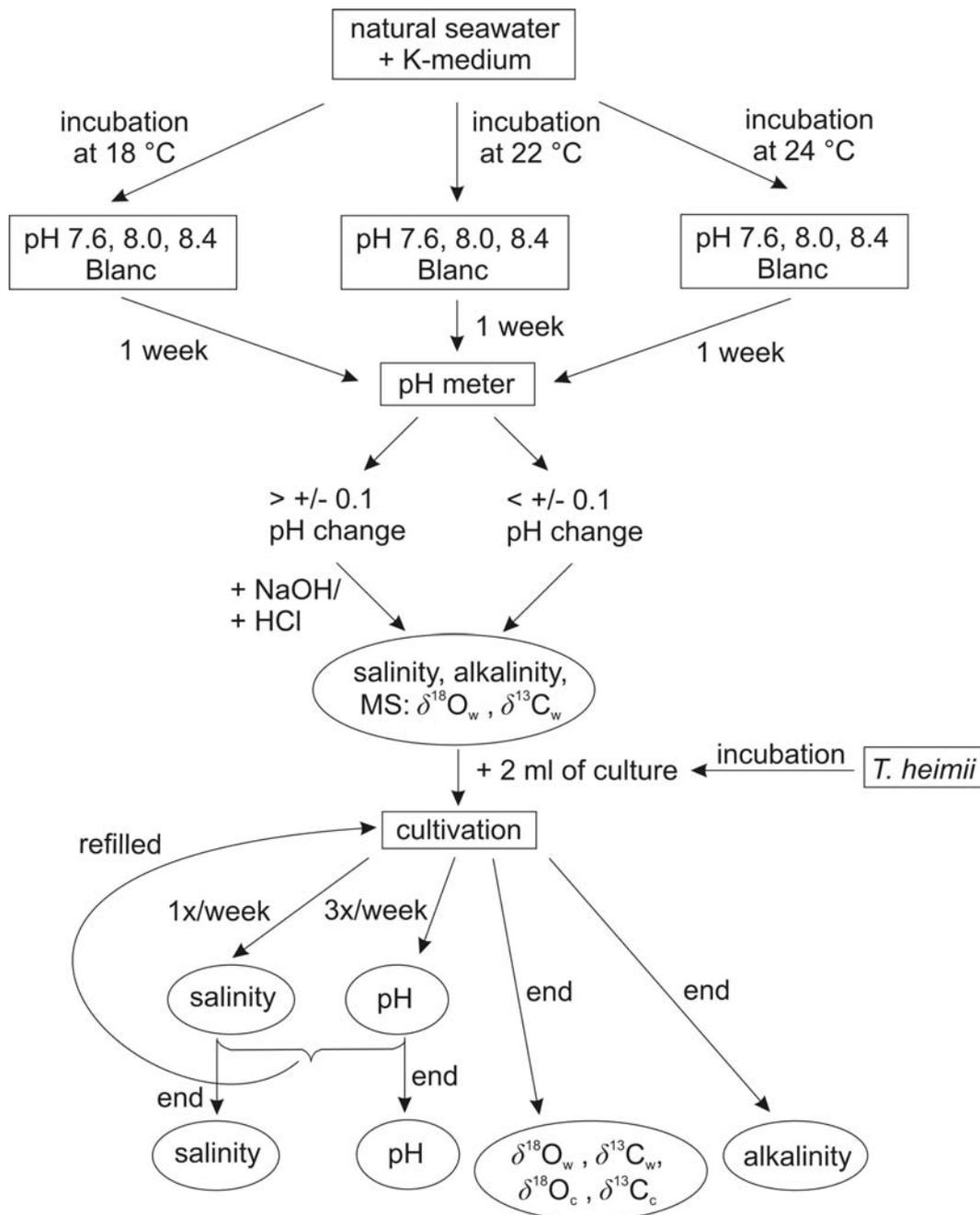


Fig. 9. Flow diagram of the experimental setup of the pH experiment. Circles indicate measured parameters.

1.8 References

- Alley, R.B., Clark, P.U., 1999. The deglaciation of the northern hemisphere: A global perspective. *Annual Review Earth Planetary Science* 27, 149-182.
- Alley, R.B., 2000. Ice-core evidence of abrupt climate changes. *Proceedings of the National Academy of Science* 97, 1331-1334.
- Anderson, T.F., Steinmetz, J.C., 1983. Stable isotopes in calcareous nannofossils: potential application to deep-sea paleoenvironmental reconstructions during the Quaternary. In: Meulenkamp, J.E. (Ed.), *Reconstruction of marine paleoenvironment. Micropaleontological Bulletin*, Utrecht, pp. 189-204.
- Anderson, D.M., Lindquist, N.L., 1985. Time-course measurements of phosphorus depletion and cyst formation in the dinoflagellate *Gonyaulax tamarensis* Lebour. *Journal of Experimental Marine Biology and Ecology* 86 (1), 1-13.
- Anderson, D.M., Kulis, D.M., Binder, B.J., 1984. Sexuality and cyst formation in the dinoflagellate *Gonyaulax tamarensis*: cyst yield in batch cultures *Journal of Phycology* 20 (3), 418-425.
- Anderson, D.M., Stolzenbach, K.D., 1985. Selective retention of two dinoflagellates in a well-mixed estuarine embayment: The importance of diel vertical migration and surface avoidance. *Marine Ecology. Progress Series* 25, 39-50.
- Baumann, K.-H., Böckel, B., Donner, B., Gerhardt, S., Henrich, R., Vink, A., Volbers, A., Willems, H., Zonneveld, K.A.F., 2003. Contribution of calcareous plankton groups to the carbonate budget of South Atlantic surface sediments. In: Wefer, G., Mulitza, S., Ratmeyer, V. (Ed.), *The South Atlantic in the late Quaternary: Reconstruction of material budgets and current systems*. Springer-Verlag, Berlin Heidelberg New York Tokyo.
- Bell, B.E., 1972. Marine fisheries. In: Morgan, W.T.W. (Ed.), *East Africa: its people and resources*. Oxford University Press, London, pp. 243-254.
- Bemis, B.E., Spero, H.J., 1998. Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations. *Paleoceanography* 13 (2), 150-160.
- Berger, A., 1978. Long-Term Variations of Daily Insolation and Quaternary Climatic Changes. *Journal of the Atmospheric Sciences* 35 (12), 2362-2367.
- Berger, W.H., Keir, R.S., 1984. Glacial-Holocene changes in atmospheric CO₂ and deep-sea record. *Geophysical Monograph Series* 29, 337-351.
- Berger, W.H., Wefer, G., 2002. On the reconstruction of upwelling history: Namibia upwelling in context. *Marine Geology* 180, 3-28.
- Bickert, T., 2000. Influences of geochemical processes on stable isotope distribution in marine sediments. In: Schulz, H.D., Zabel, M. (Eds.), *Marine Geochemistry*. Springer, Berlin, pp. 309-333.
- Bijma, J., Spero, H.J., Lea, D.W., 1999. Reassessing Foraminiferal Stable Isotope Geochemistry: Impact of the Oceanic Carbonate System (Experimental Results). Springer-Verlag, Berlin Heidelberg.
- Binder, B.J., Anderson, D.M., 1990. Biochemical composition and metabolic activity of *Scrippsiella trochoidea* (Dinophyceae) resting cysts *Journal of Phycology* 26 (2), 289-298.
- Blanco, J., 1995. Cyst production in four species of neritic dinoflagellates. *J. Plankton Res.* 17 (1), 165-182.

- Blanco, J.L., Thomas, A.C., Carr, M.E., Strub, P.T., 2001. Seasonal climatology of hydrographic conditions in the upwelling region off northern Chile. *J. Geophys. Res.* 106.
- Bond, G., Heinrich, H., Broecker, W., Labeyrie, L., McManus, J., Andrews, J., Sylvain, H., Jantschik, R., Clasen, S., Simet, C., Tedesco, K., Klas, M., Bonani, G., Ivy, S., 1992. Evidence for massive discharge of icebergs into the North Atlantic ocean during the last glacial period. *Nature* 360, 245-249.
- Bond, G., Showers, W., Elliot, M., MEvans, M., Lotti, R., Hajdas, I., Bonani, G., Johnson, S., 1999. The North Atlantic's 1-2 kyr climate rhythm: relation to Heinrich events, Dansgaard-Oeschger cycles and the little ice age. In: Clark, P.U., Webb, R.S., Keigwin, L.D. (Eds.), *Mechanisms of global change at millennial time scales*. Geophysical Monograph, American Geophysical Union, Washington DC, pp. 59-76.
- Brauer, A., Günter, C., Johnsen, S.J., Negendank, J.F.W., 2000. Land-ice teleconnections of cold climatic periods during the last Glacial/Interglacial transition. *Climate Dynamics* 16, 229-239.
- Broecker, W.S., 1986. Oxygen isotope constraints on surface temperatures. *Quaternary Research* 26, 121-134.
- Broecker, W.S., Maier-Reimer, E., 1992. The influence of air and sea exchange on the carbon isotope distribution in the sea. *Global Biogeochemical Cycles* 6 (315-320).
- Broecker, W.S., Bond, G., Klas, M., Clark, E., McManus, J., 1992. Origin of the northern Atlantic's Heinrich events. *Climate Dynamics* 6, 265-273.
- Broecker, W.S., 2003. Does the trigger for abrupt climate changes reside in the ocean or in the atmosphere? *Science* 300, 1519-1522.
- Broecker, W.S., 2006. Was the Younger Dryas triggered by a flood? *Science* 312 (5777), 1146-1148.
- Bryden, H.L., Longworth, H.R., Cunningham, S.A., 2005. Slowing of the Atlantic meridional overturning circulation at 25[deg][thinsp]N. *Nature* 438 (7068), 655-657.
- Chiew, F.H.S., Harrold, T.I., Siriwardena, L., Jones, R.N., Srikanthan, R., 2003. Simulation of climate change impact on runoff using rainfall scenarios that consider daily patterns of change in GCMs, Congress on Modelling and Simulation (MODSIM 2003). International Congress on modelling and simulation, Townsville 1 (154-159), available from <http://mssanz.org.au/modsim03/modsim2003.html>.
- Clark, P.U., Pisias, N.G., Stocker, T.F., Weaver, A.J., 2002. The role of the thermohaline circulation in abrupt climate change. *Nature* 415 (6874), 863-869.
- Claussen, M., Kubatzki, C., Brovkin, V., Ganopolski, A., Hoelzmann, P., Pachur, H.J., 1999. Simulation of an abrupt change in Saharan vegetation in the mid-Holocene. *Geophysical Research Letters* 24 (14), 2037-2040.
- Coplen, T.B., 1996. New guidelines for reporting stable hydrogen, carbon, and oxygen isotope-ratio data. *Geochimica et cosmochimica acta* 60 (17), 3359-3360
- Dale, B., 1983. Dinoflagellate resting cysts: "benthic plankton". In: Fryxell, G.A. (Ed.), *Survival strategies of the algae*, Cambridge University Press, pp. 69-136.
- Dale, B., 1986. Life cycle strategies of oceanic dinoflagellates. *Unesco technical papers in marine science*.

- Dale, B., 1992a. Dinoflagellate contribution to the open ocean sediment flux. In: Dale, B., Dale, A. (Ed.), *Dinoflagellate contribution to the Deep Sea*. Woods Hole Oceanographic Institution, Woods Hole.
- Dale, B., 1992b. Thoracosphaerids: Pelagic fluxes. In: Honjo, S. (Ed.), *Dinoflagellate contribution to the Deep Sea*. Woods Hole Oceanographic Institution, Woods Hole.
- Dansgaard, W., 1985. Greenland ice core records. *Palaeogeography, Palaeoclimatology, Palaeoecology* 50, 185-187.
- deMenocal, P., Ortiz, J., Guilderson, T., Sarntheim, M., 2000. Coherent high- and low-Latitude climate variability during the Holocene warm period. *Science* 288, 2198-2202.
- Dudley, W.C., Blackwelder P., Brand, L., Duplessy, J.-C., 1986. Stable isotopic composition of coccoliths. *Marine Micropaleontology* 10, 1-8.
- Elbrächter, M., Gottschling, M., Hildebrand-Habel, T., Keupp, H., Kohring, R., Lewis, J., Meier, S.K.J., Montresor, M., Streng, M., Versteegh, G.J.M., Willems, H., Zonneveld, K.A.F., 2008. Establishing an Agenda for Calcareous Dinoflagellate Research (Thoracosphaeraceae, Dinophyceae) including a nomenclatural synopsis of generic names. *Taxon* 57, 1289-1303.
- Emiliani, C., 1955. Pleistocene Temperatures. *The Journal of Geology* 63 (6), 538-578.
- Epstein, S., Buchsbaum, R., Lowenstam, H.A., Urey, H.C., 1953. Revised carbonate-water isotopic composition of coccoliths. *Marine Micropaleontology* 10 (1-8).
- Esper, O., Zonneveld, K.A.F., Höll, C., Karwath, B., Kuhlmann, H., Schneider, R.R., Vink, A., Weisshlo, I., Willems, H., 2000. Reconstruction of palaeoceanographic conditions in the South Atlantic Ocean at the last two Terminations based on calcareous dinoflagellate cysts. *International Journal of Earth Sciences* 88 (4), 680-693.
- Esper, O., Versteegh, G.J.M., Zonneveld, K.A.F., Willems, H., 2004. A palynological reconstruction of the Agulhas Retroflexion (South Atlantic Ocean) during the Late Quaternary. *Global and Planetary Change* 41 (1), 31-62.
- Evitt, W.R., 1985. Sporopollenin dinoflagellate cysts: Their morphology and interpretation. *American Association of Stratigraphic Palynologists Foundation, Dallas*, 333 pp..
- Fabry, V.J., Deuser, W.G., 1992. Seasonal changes in the isotopic composition and sinking fluxes of euthecosmatous pteropod shells in the Saragossa Sea. *Paleoceanography* 7, 195-213.
- Fensome, R.A., Taylor, F.J.R., Norris, G., Sarjeant, W.A.S., Wharton, D.I., Williams, G.L., 1993. *A Classification of Modern and Fossil Dinoflagellates*. *Micropaleontology Special Publication*, 7 (Sheridan Press, Hanover, NH), 351 pp.
- Fischer, G., Wefer, G., 1999. *Use of proxies in paleoceanography - Examples from the South Atlantic*. Springer-Verlag, Berlin, Heidelberg.
- Fischer, G., Kalberer, M., Donner, B., Wefer, G., 1999. Stable isotopes of pteropod shells as recorders of sub-surface water conditions, comparison to the record of *G. ruber* and measured values. In: Fischer, G., Wefer, G. (Ed.), *Use of Proxies in Oceanography*. Berlin, Springer.
- Friedrich, O., Meier, S.K.J., 2003. Stable isotopic indication for the cyst formation depth of Campanian/Maastrichtian calcareous dinoflagellates. *Micropaleontology* 49 (4), 375-380.
- Friedrich, O., Meier, K.J.S., 2006. Suitability of stable oxygen and carbon isotopes of calcareous dinoflagellate cysts for paleoceanographic studies: evidence from the Campanian/Maastrichtian cooling phase. *Palaeogeography, Palaeoclimatology, Palaeoecology* 239 (3-4), 456-469.

- Fütterer, D., 1977. Distribution of calcareous dinoflagellates in Cenozoic sediments of Site 366, Eastern North Atlantic. In: Lancelot, Y., Seibold, E. et al. (Ed.), DSDP: Initial Reports XLI, pp. 709-737.
- Gaines, G., Elbrächter, M., 1987. Heterotrophic nutrition In: Taylor, F.J.R. (Ed.), The biology of dinoflagellates. Blackwell.
- Gasse, F., 2000. Hydrological changes in the African tropics since the Last Glacial Maximum. *Quaternary Science Reviews* 19, 189-211.
- Gonfiantini, R., 1978. Standards for stable isotope measurements in natural compounds. *Nature* 271 (5645), 534-536.
- Grafenstein, U.v., Erlenkeuser, H., Brauer, A., Jouzel, J., Johnsen, S.J., 1999. A Mid-European Decadal Isotope-Climature Record from 15,500 to 5000 Years B.P. *Science* 284 (5420), 1654-1657.
- Gussone, N., Zonneveld, K.A.F., Kuhnert, H., subm. Minor element and Ca isotope composition of calcareous dinoflagellate cysts of cultured *Thoracosphaera heimii*. *Earth and Planetary Science Letters*.
- Hagen, E., 2001. Northwest African upwelling scenario. *Oceanologica Acta* 24 (Supplement), S113-S128.
- Hays, J.D., Imbrie, J., Shackleton, N.J., 1976. Variations in the earth's orbit: Pacemaker of the Ice Ages. *Science* 194, 1121-1132.
- Heinrich, H., 1988. Origin and consequences of cyclic ice rafting in the northeast Atlantic Ocean during the past 130,000 years. *Quaternary Research* 29, 142-152.
- Hemming, S.R., 2004. Heinrich Events: massive Late Pleistocene detritus layers of the North Atlantic and their global climate imprint. *Review of Geophysics* 42, doi:10.1029/2003RG000128.
- Henderson, G.M., 2002. New oceanic proxies for paleoclimate. *Earth and Planetary Science Letters* 203 (1), 1-13.
- Hernandez-Guerra, A., Nykjaer, L., 1997. Sea surface temperature variability off north-west Africa: 1981-1989. *International journal of remote sensing* 18 (12), 2539-2558.
- Hildebrand-Habel, T., Willems, H., 2000. Distribution of calcareous dinoflagellates from the Maastrichtian to early Miocene of DSDP Site 357 (Rio Grande Rise, western South Atlantic Ocean). *Int Journ Earth Sciences* 88, 694-707.
- Höll, C., Zonneveld, K.A.F., Willems, H., 1998. On the ecology of calcareous dinoflagellates: The Quaternary eastern equatorial Atlantic. *Marine Micropaleontology* 33 (1-2), 1-25.
- Höll, C., Karwath, B., Rühlemann, C., Zonneveld, K.A.F., Willems, H., 1999. Palaeoenvironmental information gained from calcareous dinoflagellates: The late Quaternary eastern and western tropical Atlantic Ocean in comparison. *Palaeogeography, Palaeoclimatology, Palaeoecology* 146 (18), 147-164.
- Holzwarth, U., 2009. Characterization of West African upwelling areas based on organic-walled dinoflagellate cysts and their implication in the fossil record, Ph.D. Thesis, University of Bremen.
- Imbrie, J., 1982. Astronomical theory of the Pleistocene ice ages: A brief historical review. *Icarus* 50 (2-3), 408-422.
- Imbrie, J., Berger, A., Boyle, E.A., Clemens, S.C., Duffy, A., Howard, W.R., Kukla, G., Kutzbach, J., Martinson, D.G., McIntyre, A.C., Mix, A.C., Molino, B., Morley, J.J., Peterson, L.C., Pisias,

- W.L., Prell, W.L., Raymo, M.E., Shackleton, N.J., Toggweiler, J.R., 1993. On the structure and origin of major glaciation cycles: 2. The 100,000-year cycle. *Paleoceanography* 8 (6), 699-735.
- IPCC, 2007, *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Ishikawa, A., Taniguchi, A., 1996. Contribution of benthic cysts to the population dynamics of *Scripsiella* spp. (Dinophyceae) in Onagawa Bay, northeast Japan. *Marine Ecology Progress Series* 140, 169-178.
- Itambie, C.A., van Dobeneck, T., Mulitza, S., Bickert, T., Heslop, D., 2009. Millennial-scale North West African droughts related to Heinrich events and Dansgaard/Oeschger cycles: Evidence in marine sediments from offshore Senegal. *Paleoceanography* 24, P1205.
- Janofske, D., 1992. Kalkiges Nannoplankton, insbesondere kalkige Dinoflagellate-Zysten der alpinen Ober-Trias: Taxonomie, Biostratigraphie und Bedeutung für die Phylogenie der Peridinales. *Berliner Geowiss. Abh. E* (4), 1-93.
- Kamptner, E., 1927. Beitrag zur Kenntnis adriatischer Coccolithophoriden. *Archiv für Protistenkunde* 48, 173-184.
- Kamptner, E., 1967. Kalkflagellaten-Skelettreste aus Tiefseeschlamm des Südatlantischen Ozeans. *Annalen des Naturhistorischen Museums Wien* 66, 117-198.
- Kamykowski, D., Milligan, A.J., Reed, R.E., 1998. Relationships between geotaxis/phototaxis and diel vertical migration in autotrophic dinoflagellates. *Journal of Plankton Research* 20, 1781-1796.
- Karl, T.R., Trenberth, K.E., 2003. Modern global climate change. *Science* 302, 1719-1723.
- Karwath, B., Janofske, C., Tietjen, F., Willems, H., 2000a. Temperature effects on growth and cell size in the marine calcareous dinoflagellate *Thoracosphaera heimii*. *Marine Micropaleontology* 39 (1), 43-51.
- Karwath, B., Janofske, D., Willems, H., 2000b. Spatial distribution of the calcareous dinoflagellate *Thoracosphaera heimii* in the upper water column of the tropical and equatorial Atlantic. *International Journal of Earth Sciences* 88 (4), 668-679.
- Klein, R.T., Lohmann, K.C., Thayer, C.W., 1996. Bivalve skeletons record sea-surface temperature and $\delta^{18}\text{O}$ via Mg/Ca and $^{18}\text{O}/^{16}\text{O}$ ratios. *Geology* 24, 415-418.
- Kremp, A., Anderson, D.M., 2000. Factors regulating germination of resting cysts of the spring bloom dinoflagellate *Scripsiella hangoei* from the northern Baltic Sea. *J. Plankton Res.* 22 (7), 1311-1327.
- Lynch-Stieglitz, J., Stocker, T.F., Broecker, W.S., Fairbanks, R.G., 1995. The influence of air-sea gas exchange on the isotopic composition of oceanic carbon: observation and modelling. *Global Biogeochemical Cycles* 9, 653-665.
- MacAyeal, D.R., 1993. Binge/Purge oscillations of the Laurentide Ice-Sheet as a cause of the North-Atlantic Heinrich Events. *Paleoceanography* 8, 775-784.
- Manabe, S., Stouffer, R.J., 1993. Century-scale effects of increased atmospheric CO_2 on the ocean atmosphere

- system. *Nature* 364, 215-218.
- Maret, F., Zonneveld, K.A.F., 2003. Atlas of modern organic-walled dinoflagellate cyst distribution. *Review of Palaeobotany and Palynology* 125, 1-200.
- Margolis, S.V., Kroopnick, P.M., Goodney, D.E., Dudley, W.C., Mahoney, M.E., 1975. Oxygen and carbon isotopes from calcareous nannofossils as paleoceanographic indicators. *Science* 189, 555-557.
- Matthiesen, J., de Vernal, A., Head, M.J., Okolodkov, Y.B., Zonneveld, K.A.F., Harland, R., 2005. Modern organic-walled dinoflagellate cysts in Arctic marine environments and their (paleo) environmental significance. *Paläontologische Zeitschrift* 73, 3-51.
- McClanahan, T.R., 1988. Seasonality in East Africa's coastal waters. *Marine Ecology - Progress Series* 44, 191-199.
- McConnaughey, T., 1989. ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochimica et Cosmochimica Acta* 53 (1), 151-162.
- McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *The journal of chemical physics* 18 (6), 849-857.
- McManus, J.F., Francois, R., Gherardi, J.-M., Keigwin, L.D., Brown-Leger, S., 2004. Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes. *Nature* 428, 834-837.
- Meier, K.J.S., Willems, H., 2003. Calcareous dinoflagellate cysts in surface sediments from the Mediterranean Sea: distribution patterns and influence of main environmental gradients. *Marine Micropaleontology* 48, 321-354.
- Meier, K.J.S., Höll, C., Willems, H., 2004. Effect of temperature on culture growth and cyst production in the calcareous dinoflagellates *Calciodinellum albatrosianum*, *Leonella granifera* and *Pernambugia tuberosa*. *2004* 50 (1), 93-106.
- Meier, K.J.S., Young, J.R., Kirsch, M., Feist-Burkhardt, S., 2007. Evolution of different life-cycle strategies in oceanic calcareous dinoflagellates. *European Journal of Phycology* 42 (1), 81-89.
- Milankovitch, M., 1920. *Theorie mathématique des phénomènes thermiques produits par la radiation solaire*. Gauthier-Villars, Paris.
- Mittelstaedt, E., 1991. The ocean boundary along the northwest African coast: Circulation and oceanographic properties at the sea surface. *Progress in Oceanography* 26 (4), 307-355.
- Monod, J., 1942. *La Croissance des cultures bactériennes*. Hermann et Cie Paris, France.
- Montresor, M., Zingone, A., Sarno, D., 1998. Dinoflagellate cyst production at a coastal Mediterranean site. *J. Plankton Res.* 20 (12), 2291-2312.
- Mook, W.G., Bommerson, J.C., Staverman, W.H., 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth and Planetary Science Letters* 22 (2), 169-176.
- Mulitza, S., Fischer, G., Paul, A., Pätzold, J., Rühlemann, C., Zegel, M., 2003. Field calibration of the oxygen isotope composition of planktic foraminifera. In: Wefer, G., Mulitza, S., Ratmeyer, V. (Eds.), *The South Atlantic in the Late Quaternary - reconstruction of material budgets and current systems*. Springer, Berlin.

- Mulitza, S., Prange, M., Stuut, J.B., Zabel, M., von Dobeneck, T., Itambie, C.A., Nizou, J., Schulz, M., Wefer, G., 2008. Sahel Megadrought triggered by glacial slowdowns of Atlantic meridional overturning. *Paleoceanography* 23, PA4206.
- Nelson, G., Hutchings, L., 1983. The Benguela upwelling area. *Progress In Oceanography* 12 (3), 333-356.
- Nicholson, S.E., 1996. A review of climate dynamics and climate variability in eastern Africa. In: Johnson, T.C., Odada, E. (Eds.), *The Limnology, Climatology and Paleoclimatology of the East African Lakes*. Gordon & Breach, pp. 25-56.
- Nykjaer, L., Van Camp, L., 1994. Seasonal and interannual variability of coastal upwelling along northwest Africa and Portugal from 1981 to 1991. *Journal of Geophysical Research* 99 (C7) (14), 197-214, 207.
- Olli, K., Anderson, D.M., 2002. High encystment success of the dinoflagellate *Scrippsiella lachrymosa* in culture experiments *Journal of Phycology* 38 (1), 145-156.
- Parsons, T.R., Takahashi, M., Hargrave, B., 1984. *Biological oceanographic processes*. Pergamon Press, Oxford, p. 330 pp.
- Paul, A., Mulitza, S., Pätzold, J., Wolff, T., 1999. Simulation of oxygen isotopes in a global ocean model. In: Fischer, G., Wefer, G. (Ed.), *Use of proxies in Paleoceanography: Examples from the South Atlantic*. Springer, Berlin Heidelberg, pp. 655-686.
- Rahmstorf, S., 2002. Ocean circulation and climate during the past 120,000 years. *Nature* 419 (6903), 207-214.
- Ramage, C.S., 1971. *Monsoon Meteorology*. Academic Press, San Diego, CA.
- Rayleigh, L., 1902. On the distillation of binary mixtures. *Philos. Mag. (6th series)* 4, 521.
- Richter, D., Vink, A., Zonneveld, K.A.F., Kuhlmann, H., Willems, H., 2007. Calcareous dinoflagellate cyst distributions in surface sediments from upwelling areas off NW Africa, and their relationships with environmental parameters of the upper water column. *Marine Microbiology* 63, 201-228.
- Rognon, P., Williams, M.A.J., 1977. Late Quaternary climatic changes in Australia and North Africa: a preliminary interpretation. *Palaeoceanography, Palaeoclimatology, Palaeoecology* 21, 285-327.
- Rohling, E.J. and Cooke, S., 1999. Stable oxygen and carbon isotopes in foraminiferal carbonate shells. In: Sen Gupta, B.K. (Editor), *Modern Foraminifera*. Kluwer Acad., Norwell, Mass., pp. 239-258.
- Ruddiman, W.F., 2001. *Earth's climate past and future*. Freeman, New York.
- Santos, M.A., Kazmin, A.S., Peliz, A., 2005. Decadal changes in the Canary upwelling system related by satellite observations: Their impact on productivity. *Journal of Marine Research* 63, 359-379.
- Sarnthein, M., Tetzlaff, G., Koopmann, B., Wolter, K., Pflaumann, U., 1981. Glacial and interglacial wind regimes over the eastern subtropical Atlantic and North-West Africa. *Nature* 293 (5829), 193-196.
- Sarnthein, M., Statterger, K., Dreger, D., Erlenkeuser, H., Grootes, R., Haupt, B., Jung, S., Kiefer, T., Kuhnt, W., Pflaumann, U., Schäfer-Neth, C., Schulz, H.D., Schulz, M., Seidov, D., Simstich, J., Van Kreveld, S., Vogelsang, E., Völker, A., Weinelt, M., 2000. Fundamental modes and abrupt changes in North Atlantic circulation and climate over the last 60 ky - Concepts reconstruction and numerical modeling. In: Schäfer, P., Ritzau, W., Schlüter, M., Thiede, J. (Eds.), *the Northern North Atlantic: A changing environment*. Springer, Berlin, pp. 365-410.

- Schnepf, E., Elbrächter, M., 1999. Dinophyte chloroplasts and phylogeny - A review. *Grana* 38, 81-97.
- Schouten, S., Hopmans, E.C., Schefuß, E., Sinninghe-Damsté, J.S., 2002. Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures? *Earth and Planetary Science Letters* 204 (1-2), 265-274.
- Schulz, H., von Rad, U., Erlenkeuser, H., 1998. Correlation between Arabian Sea and Greenland climate oscillations of the past 110,000 years. *Nature* 393, 54-57.
- Shaffer, G., Hormazabal, S., Pizarro, O., Salinas, S., 1999. Seasonal and interannual variability of currents and temperature off central Chile. *Journal of Geophysical Research* 104 (C12), 29,951-919,961.
- Shanks, A.L., Brink, L., 2005. Upwelling, downwelling, and cross-shelf transport of bivalve larvae: test of a hypothesis. *Marine Ecology Progress Series* 302, 1-12.
- Sorokin, C., 1973. Dry weight, packed cell volume and optical density. In: Stein, J.R. (Ed.), *Handbook of phycological methods*, Cambridge University Press, pp. 321-343.
- Spero, H.J., Lea, D.W., 1993. Intraspecific stable isotope variability in the planktic foraminifera *Globigerinoides sacculifer*: Results from laboratory experiments. *Marine Micropaleontology* 22, 221-234.
- Spero, H.J., Lea, D.W., 1996. Experimental determination of stable isotope variability in *Globigerina bulloides*: implications for paleoceanographic reconstructions. 28, 231-246.
- Spero, H.J., Bijma, J., Lea, D.W., Bemis, B.E., 1997. Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. *Nature* 390, 497-500.
- Stocker, T.F., Schmittner, A., 1997. Influence of CO₂ emission rates on the stability of the thermohaline circulation. *Nature* 388, 862-865.
- Stoll, H.M., Encinar, J.R., Alonso, J.I.G., Rosenthal, Y., Probert, I., Klaas, C., 2001. A first look at palaeotemperature prospects from Mg in coccolith carbonate: cleaning techniques and cultural measurements. *Geochemistry Geophysics Geosystems*, 2 pp..
- Stoll, H.M., Ziveri, P., 2002. Separation of monospecific and restricted coccolith assemblages from sediments using differential settling velocity. *Marine Micropaleontology* 46, 209-221.
- Stover, L.E., Brinkhuis, H., Damassa, S.P., Verteuil, L., Helby, R.J., Monteil, E., Partridge, A., Powell, A.J., Riding, J.B., Smelror, M., Williams, G.L., 1996. Mesozoic-Tertiary dinoflagellates, acritarchs and prasinophytes. In: Jansonius, J., McGregor, D.C. (Ed.), *Palynology: principles and applications*. American Association of Stratigraphic Palynologists Foundation, Dallas, pp. pp. 641-750.
- Streng, M., Hildebrand-Habel, T., Willems, H., 2004. A proposed classification of archeopyle types in calcareous dinoflagellate cysts. *Journal of Paleontology* 78 (3), 456-483
- Stuut, J.-B., Zabel, M., Ratmeyer, V., Helmke, P., 2005. Provenance of present-day eolian dust collected off NW-Africa. *Journal of Geophysical Research* 110.
- Swezey, C., 2001. Eolian sediment responses to late Quaternary climate changes: temporal and spatial patterns in the Sahara. *Palaeogeography, Palaeoclimatology, Palaeoecology* 167, 119-155.
- Tangen, K., Brand, L.E., Blackwelder, P.L., Guillard, R.R.L., 1982. *Thoracosphaera heimii* (Lohmann) Kamptner is a dinophyte: observations on its morphology and life cycle. *Marine Micropaleontology* 7, 193-212.

- Taylor, F.J.R., Pollinger, U., 1987. The ecology of dinoflagellates. In: Taylor, F.J.R. (Ed.), *The biology of dinoflagellates*. Blackwell Scientific Publications, Oxford, pp. 398-529.
- Titschak, J., 2006. Sedimentology, facies and diagenesis of warm-temperature carbonates on a tectonically structured island shelf: key studies from Rhodes.
- Tjallingii, R., Claussen, M., Stuut, J.B.W., Fohlmeister, J., Jahn, A., Bickert, T., Lamy, F., Röhl, U., 2008. Coherent high- and low-latitude control of the northwest African hydrological balance. *Nature Geoscience* 1, 635-718.
- Urey, H.C., 1947. The thermodynamic properties of isotopic substances. *J. Chem. Soc.*, 562-581.
- Van Camp, L., Nykjaer, L., Mittelstaedt, E., Schlittenhardt, P., 1991. Upwelling and boundary circulation off Northwest Africa as depicted by infrared and visible satellite observations. *Progress in Oceanography* 26 (4), 357-402.
- Vidal, L., Labeyrie, L., Cortijo, E., Arnold, M., Duplessy, J.C., Michel, E., Becqué, S., van Weering, T.C.E., 1997. Evidence for changes in the North Atlantic Deep Water linked to meltwater surges during the Heinrich events. *Earth and Planetary Science Letters* 146, 13-27.
- Vink, A., 2000. Reconstruction of recent and Late Quaternary surface water masses of the western subtropical Atlantic ocean based on calcareous and organic-walled dinoflagellate cysts, University of Bremen.
- Vink, A., Rühlemann, C., Zonneveld, K.A.F., Mulitza, S., 2001. Shifts in the position of the North Equatorial Current and rapid productivity changes in the western Tropical Atlantic during the last glacial. *Paleoceanography* 16 (5), 479-490.
- Vink, A., Brune, A., Höll, C., Zonneveld, K.A.F., Willems, H., 2002. On the response of calcareous dinoflagellates to oligotrophy and stratification of the upper water column in the equatorial Atlantic Ocean. *Paleogeography, Paleoclimatology, Palaeoecology* 178, 53-66.
- Vink, A., 2004. Calcareous dinoflagellate cysts in South and equatorial Atlantic surface sediments: diversity, distribution, ecology and potential for palaeoenvironmental reconstructions. *Marine Micropaleontology* 50 (1-2), 43-88.
- Vink, A., Zonneveld, K.A.F., Willems, H., 2000. Distributions of calcareous dinoflagellate cysts in surface sediments of the western equatorial Atlantic Ocean, and their potential use in paleoceanography. *Marine Micropaleontology* 38 (2), 149-180.
- Voelker, A.H.L. and workshop participants, 2002. Global distribution of centennial-scale records for Marine Isotope Stage (MIS) 3: a database. *Quaternary Science Reviews* 21, 1185-1212.
- Wang, Y.J., Cheng, H., Edwards, R.L., An, Z.S., Wu, J.Y., Shen, C.-C., Dorale, J.A., 2001. A high-resolution absolute-dated late Pleistocene monsoon record from Hulu Cave, China. *Science* 294, 2345-2348.
- Weaver, A.J., Saenko, O.A., Clark, P.U., Mitrovica, J.X., 2003. Meltwater Pulse 1A from Antarctica as a Trigger of the Bølling-Allerød Warm Interval. *Science* 299 (5613), 1709-1713.
- Wefer, G., Berger, W.H., Bijma, J., Fischer, G., 1999. Clues to Ocean History: a Brief Overview of Proxies. *Use of Proxies in Paleoceanography: Examples from the South Atlantic*, 1-68.
- Wendler, I., Zonneveld, K.A.F., Willems, H., 2002a. Calcareous cyst-producing dinoflagellates: ecology and aspects of cyst preservation in a highly productive oceanic region. In: Clift, P.D., Kroon, D.,

- Gaedicke, C., Craig, J. (Eds.), The tectonic and climatic evolution of the Arabian Sea region. Geological Society, Special Publication, London, pp. 317 - 340.
- Wendler, I., Zonneveld, K.A.F., Willems, H., 2002b. Production of calcareous dinoflagellate cysts in response to monsoon forcing off Somalia: a sediment trap study. *Marine Micropaleontology* 46, 1-11.
- Winslow, C.E.A., Walker, H.H., 1939. The earlier phase of the bacterial culture cycle. *Bacterial. Rev.* 3, 147-186.
- Young, J.R., , Davis, S.A., , Bown, P.R., , Mann, S., 1999. Coccolith Ultrastructure and Biomineralisation. *Journal of Structural Biology* 126, 195-215.
- Yu, Z., Eichner, U., 2001. Three amphi-Atlantic century-scale cold events during the Bølling-Allerød warm period. *Geographie Physique et Quaternaire* 55, 171-179.
- Zeebe, R.E., 1999. An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes. *Geochimica et Cosmochimica Acta* 63 (13/14), 2001-2007.
- Zolitzschka, B., Brauer, A., Negendank, J.F.W., Stockhausen, H., Lang, A., 2000. Annually dated late Weichselian continental paleoclimate record from the Eifel, Germany. *Geology* 28, 783-786.
- Zonneveld, K.A.F., Höll, C., Janofske, D., Karwarth, B., Kerntopf, B., Rühlemann, C., Willems, H., 1999. Calcareous Dinoflagellate Cysts as Paleo-Environmental Tools. In: Fischer, G., Wefer, G. (Ed.), *Use of Proxies in Paleoceanography: Examples from the South Atlantic*. Springer Verlag, Berlin Heidelberg New York, pp. 145-164.
- Zonneveld, K., Brune, A., Willems, H., 2000. Spatial distribution of calcareous dinoflagellate cysts in surface sediments of the Atlantic Ocean between 13°N and 36°S. *Review of Palaeobotany and Palynology* 111, 197-223.
- Zonneveld, K., 2004. Potential use of stable isotope composition of *Thoracosphaera heimii* (Dinophyceae) for upper water column (thermocline) temperature reconstruction. *Marine Micropaleontology* 50 (3-4), 307-317.
- Zonneveld, K., Meier, S., Esper, O., Siggelkow, D., Wendler, I., Willems, H., 2005. The (paleo-)environmental significance of modern calcareous dinoflagellate cysts: a review. *Paläontologische Zeitschrift* 79/1, 61-77.
- Zonneveld, K.A.F., Mackensen, A., Baumann, K.-H., 2007. Stable oxygen isotopes of *Thoracosphaera heimii* (Dinophyceae) in relationship to temperature; a culture experiment. *Marine Micropaleontology* 64 (1-2), 80-90.

Chapter 2
Stable oxygen isotopes of the
calcareous-walled dinoflagellate *Thoracosphaera heimii*
as a proxy for mixed layer temperatures

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Abstract

To date there is an increasing demand to establish detailed reconstructions of upper ocean temperatures of specific layers in the water column such as the deep chlorophyll maximum. Recently, a new promising proxy has been proposed which is based on the stable oxygen isotope signal of the photosynthetic calcareous-walled dinoflagellate species *Thoracosphaera heimii*. Although laboratory and modern day field experiments have documented the potential of this new tool to reconstruct temperatures at the deep chlorophyll maximum (DCM), no information is present about the usability of this tool in pre-modern time intervals. Here, we present the first study that tests the functionality of this new proxy in late glacial to Holocene sediments of the upwelling region off Cape Blanc (NW Africa). For this, we compared *T. heimii* based temperature reconstructions of sediment core GeoB 8507-3 with those of other well-established sea surface temperature SST proxies that use the $\delta^{18}\text{O}$ compositions of the planktonic foraminifera *Globigerina bulloides* and *Globigerinoides ruber* (pink), and the Mg/Ca ratio of *G. ruber* (pink).

We show that the isotopic composition of *T. heimii* and the temperature reconstruction based on the equation for inorganic carbon provides comparable results to those obtained from *G. ruber* (pink) isotopes and Mg/Ca ratios. The recently

proposed palaeotemperature equation of Zonneveld *et al.* (2007), however, provides unrealistic reconstructed temperatures of about 16 °C lower than those estimated based on foraminifera and we suggest that this equation has to be revised. The difference between *T. heimii* and *G. bulloides* isotopic signals and the reconstructions based on the isotopic signal of *G. bulloides* can be subscribed to differences in the ecology of both species, especially with regard to its depth habitat and/or seasonal production in the research area.

All temperature proxies suggest comparable conditions in glacial and Holocene times. A small difference between the temperature registration by *T. heimii* and the other proxies can be explained by differences in seasonal production of the individual species. The relative low temperatures recorded by *T. heimii* about 15 ka to 8 ka BP are interpreted to reflect an increase in duration and/or frequency of the upwelling events in the vicinity of the core site, with an abrupt and strong decrease of upwelling frequency and/or duration during the Younger Dryas.

Keywords: calcareous-walled dinoflagellate cysts, stable oxygen isotopes, upwelling, palaeotemperature, thermocline/deep chlorophyll maximum, NW Africa

2.1 Introduction

The isotopic composition of calcareous microfossils is one of the most important tools in palaeoceanographic and palaeoclimatic studies. To date, there is an increasing need for detailed information on the environmental characteristics of specific layers within the water column, for example the thermocline depth (Jansen *et al.*, 2007). Unfortunately, it is not always trivial to obtain such data, as not all species calcify in a relatively restricted part of the water column. For instance, many planktonic foraminifera migrate between different water layers during their life cycle, resulting in an isotopic signal reflecting the mixed environmental conditions of their depth habitats.

An organism that is generally known to produce fossilisable calcareous cysts within its vegetative life cycle in a relatively restricted part of the upper water column is the phototrophic dinoflagellate *Thoracosphaera heimii* (Lohmann, 1920; Kamptner, 1944). In the equatorial, eastern and southern Atlantic, the presence of this species is restricted to the photic zone with highest abundances at the deep chlorophyll maximum depth (DCM; Karwath, 2000a, b; Vink *et al.*, 2003). The species has a wide modern day

geographic distribution and is present in the fossil record from the Cretaceous onwards (Hildebrand-Habel and Willems, 2000). Since it is easy to isolate the cysts of this species from marine sediment samples, their potential for further use in palaeoceanographic research is high. Recently, a survey of core top samples throughout the South Atlantic Ocean revealed that the isotopic signal *T. heimii* reflects mean annual DCM water temperatures when the palaeotemperature equation of inorganic carbon proposed by Kim and O'Neil (1997) is used (Zonneveld, 2004). Culture experiments confirmed the relationship between the isotope composition of *T. heimii* and temperature but resulted in a palaeotemperature equation that differs markedly from that of the inorganic carbon equation (Zonneveld *et al.*, 2007). Until now, no studies have been carried out in order to test which equation should be preferred. Furthermore, until now this new $\delta^{18}\text{O}$ palaeotemperature proxy has not been tested for its usability to reconstruct past DCM temperatures. Within this study we aim to overcome this lack of information by comparing isotopically derived temperature reconstructions of *T. heimii* to those from other well-established SST proxies such as the stable oxygen isotope composition of the planktonic foraminifera *Globigerina bulloides* (d'Orbigny, 1839) and *Globigerinoides ruber* (pink) (d'Orbigny, 1839) as well as Mg/Ca SST estimates of *G. ruber* (pink). For this we measured $\delta^{18}\text{O}$ of *T. heimii* cysts in a sediment core off NW African which covers the last 45 ka BP (GeoB 8507-3; Schulz *et al.*, 2003). This sediment core is located in an area where detailed information is available about the spatial and seasonal distribution of *T. heimii* in the water column and surface sediments (Karwath *et al.*, 2000b; Siggelkow *et al.*, 2002; 2004; Richter *et al.*, 2007). Temperature calculations have been performed both using the equation for inorganic carbon as proposed by Kim and O'Neil (1997) as well as the recently suggested equation by Zonneveld *et al.* (2007). Differences between the temperature reconstructions are being discussed in the frame of the different ecologies of the individual organisms as well as by comparing the different methodologies.

2.2 Oceanographic setting

The surface current system in the research area is characterised by the Canary Current (CC), which flows southward along the northwest African coast as far as Cape

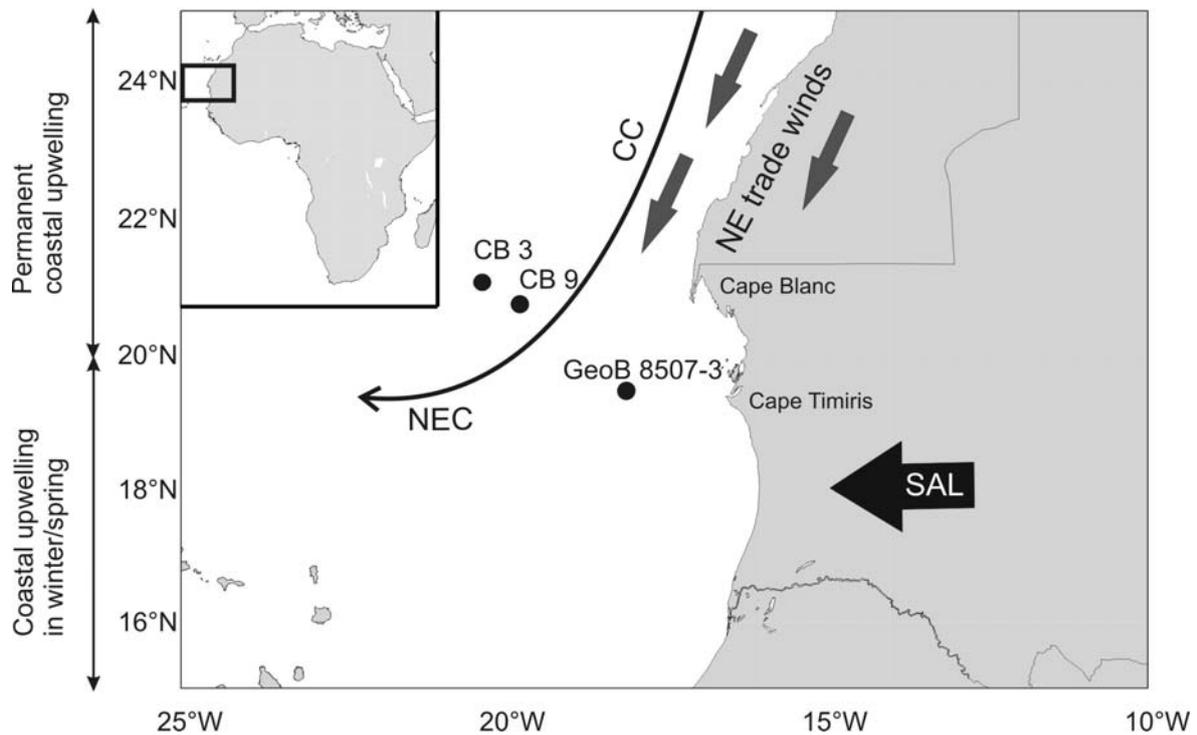


Fig. 1. Map showing the location of core GeoB 8507-3 off Cape Timiris and the sediment traps CB 3 and CB 9 off Cape Blanc (for details see Fig. 6). Thick arrows represent the wind system; thin arrow indicates the main surface water current. CC, Canary Current; SAL, Saharan Air Layer.

Blanc (CB) (Fig. 1). Here, it detaches from the continental slope and continues into the westward-flowing North Equatorial Current (NEC) (Hagen and Schemainda, 1984; Schott *et al.*, 2002). Main transport with peak velocities within the CC and NEC are achieved in late summer (Arnault, 1987; Stramma and Siedler, 1988; Bayev and Polonskiy, 1991; Mittelstaedt, 1991).

The coastal region is characterised by the upwelling of cold, nutrient-rich water which promotes high primary production (Van Camp *et al.*, 1991; Zenk *et al.*, 1991). Strength and persistence of upwelling off northwest Africa show strong regional differences, depending on the intensity of the north-easterly trade winds which, in turn, are strongly related to the position of the Inter Tropical Convergence Zone (ITCZ; Wefer and Fischer, 1993; Hernández-Guerra and Nykjaer, 1997). Upwelling is persistent throughout the year between 20 °N and 25 °N (Barton *et al.*, 1998). South of 20 °N, upwelling is most intense in winter and spring (Fig. 1). The investigated core site colder temperatures in the upper 50 m during winter and spring due to enhanced upwelling and warmer temperatures during summer and autumn (Fig. 2). Upwelling is restricted to a narrow coastal band located about 20 to 30 km offshore

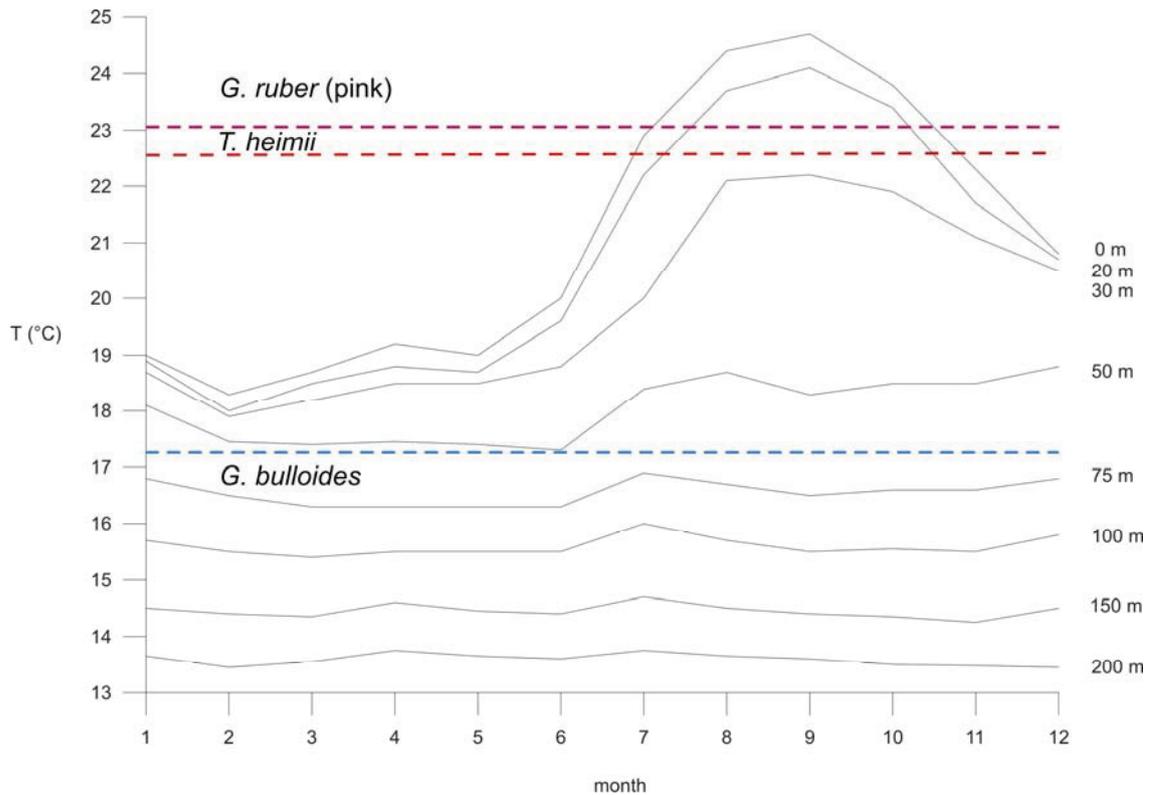


Fig. 2. Modern monthly temperatures for different water depth at the position of GeoB 8507-3. Data were obtained from the World Ocean Atlas 2005 (available at <http://www.nodc.noaa.gov>). Dashed lines indicate mean Holocene temperatures calculated from the oxygen isotopes and Mg/Ca for the different species.

(Mittelstaedt, 1991). However, the relatively cold, nutrient-rich upwelled water can be transported in the form of large filaments and eddies up to 450 km offshore. This results in strong, highly flexible upper ocean temperature gradients on a small regional scale. Within the filaments and eddies, chlorophyll-*a* concentrations can reach values up to 9.0 mg m^{-3} off CB (Van Camp *et al.*, 1991; Gabric *et al.*, 1993). Therefore, enhanced primary production with coastal phytoplankton can be observed far offshore. Within the CC region the mixed layer depth (MLD) varies seasonally from 20 to 50 m (Longhurst, 1995). In the coastal region off Cape Blanc the MLD is relatively flat throughout the year probably due to perennial upwelling activity at this site (Monterey and Levitus, 1997). However, more offshore the MLD is deeper ($\sim 165 \text{ m}$) due to stronger stratification (Morel *et al.*, 1989).

Apart from upwelling, nutrients and trace elements are brought into the region by Saharan dust that is transported by north-easterly trade winds and the African Easterly Jet (e.g. Sarnthein *et al.*, 1981, 1982; Tetzlaff and Peters, 1986).

Subsurface waters in the research area consist of South Atlantic Central Water (SACW) and North Atlantic Central Water (NACW; Mittelstaedt, 1983, 1991; Barton *et al.*, 1998). Compared to NACW, SACW is slightly cooler, less saline, and has higher nutrient concentrations. These subsurface waters form the main source of the upwelled water masses in the region, with NACW-spiced upwelling cells north of 21 °N and SACW-spiced cells south of this latitude (Mittelstaedt, 1989).

2.3 Materials and methods

Gravity core GeoB 8507-3 (19°29' N, 18°06' W; water depth 2411 m; core length 1000 cm) was obtained during the RV Meteor cruise M 58-1 in April/May 2003 (Schulz *et al.*, 2003; Fig. 1). It comprises the Holocene and Marine Isotope Stage (MIS) 2 and 3 (Fig.3, Table 1). It is located on the levee structures of the Cape Timiris canyon off the Mauritanian coast. The upper 810 cm of the core were sampled at regular 5 cm depth intervals for the stable oxygen isotope analyses of both *Thoracosphaera heimii* (Fig. 3) and *Globigerina bulloides*, and every 10 cm for *Globigerinoides ruber* (pink). Sediments of three turbidites at 130 – 145 cm, 225 – 245 cm and at 425 cm depth (Wien *et al.*, 2006) have been excluded from the analysis.

T. heimii was isolated from the sediment by using the density/size method according to Zonneveld (2004). Depending on the cyst concentration, 0.3 – 1.3 g of sediment was dried, weighted and sieved through a 20 µm and a 10 µm precision sieve (Storck-Veco, mesh 417, 403). Density separation was carried out on the fraction between 10 and 20 µm. Cyst concentration was estimated by light microscopy. If the material contained more than 15 % calcite particles other than *T. heimii*, the density separation was repeated.

Stable oxygen isotopes of *T. heimii*, *G. bulloides* and *G. ruber* (pink) were measured at the Center for Marine Environmental Sciences (MARUM), University Bremen, with a Finnigan MAT 251 mass spectrometer coupled to an automated carbonate preparation device (Kiel II) and calibrated with the NIST 19 international standard. Stable isotope values are given in δ-notation versus VPDB (Vienna Pee Dee Belemnite; Table 2). The precision of the measurements at 1σ based on repeated analyses of an internal laboratory standard (Solnhofen limestone) over a one-year period was better than ±0.08 ‰ for oxygen isotopes.

Table 1. AMS-14C ages and calendar ages for core GeoB 8507-3

Lab. code	Sample depth (cm)	Foraminiferal species	AMS- ¹⁴ C age (yr BP)	Cal. age BP	1 σ cal. age range ^b (relative area)
KIA35304*	10	<i>G. bulloides</i>	925±35	460 ⁺	407-512 (1.0)
KIA33752*	85	<i>G. bulloides</i>	8070±70	8440 ⁺	8354-8524 (1.0)
KIA35303*	155	<i>G. bulloides</i>	11,530±90	12,970 ⁺	12,883-13,045 (1.0)
KIA32644*	175	<i>G. bulloides</i>	12,110±80	13,450 ⁺	13,339-13,567 (1.0)
KIA32645*	355	<i>G. bulloides</i>	17,120±140	19,650 ⁺	19,563-19,738 (0.56)
				19,810 ⁺	19,740-19,880 (0.44)
KIA32646*	565	<i>G. bulloides</i>	25,710+360/-340	30,310 ^a	29,829-30,791

*Measured at the Leibniz-Labor, University of Kiel, Germany

⁺14C ages were calibrated using CALIB 5.0.1 (Stuiver and Reimer, 1993) and the marine 04.14c dataset (Hughen *et al.*, 2004) assuming a conservative surface water reservoir age of 500±50 years (deMenocal *et al.*, 2000); $\Delta R = 100 \pm 50$ years (ΔR = deviation from the average global reservoir age of 400 years)

^a14C age was calibrated using the Fairbanks0107 calibration data set (Fairbanks *et al.*, 2005) assuming a conservative surface water reservoir age of 500±50 years (deMenocal *et al.*, 2000)

^b1 σ encloses 68.3% of the probability distribution (Stuiver *et al.*, 1998)

Calcification temperatures for *T. heimii* based on *T. heimii* isotope data were calculated by using the palaeotemperature equation for inorganic carbon of Kim and O'Neill (1997) (eq. 1) and a recently published, specific palaeo-equation for *T. heimii* by Zonneveld *et al.* (2007) (eq. 2):

$$T (^{\circ}\text{C}) = 16.1 - 4.64 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w - \delta^{18}\text{O}_{ice}) + 0.09 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w - \delta^{18}\text{O}_{ice})^2 \text{ (eq. 1)}$$

$$T (^{\circ}\text{C}) = -6.827 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w - \delta^{18}\text{O}_{ice}) - 3.906, \text{ pH } 8.0 \text{ (eq. 2)}$$

For *G. bulloides* and *G. ruber* (pink), we used the temperature: $\delta^{18}\text{O}$ relationship from surface waters according to Mulitza *et al.* (2003). This has been corrected by subtracting the ice-volume according to Waelbroeck *et al.* (2002). A constant $\delta^{18}\text{O}_w$ value of about 0.59 ‰ was assumed throughout the investigated time interval

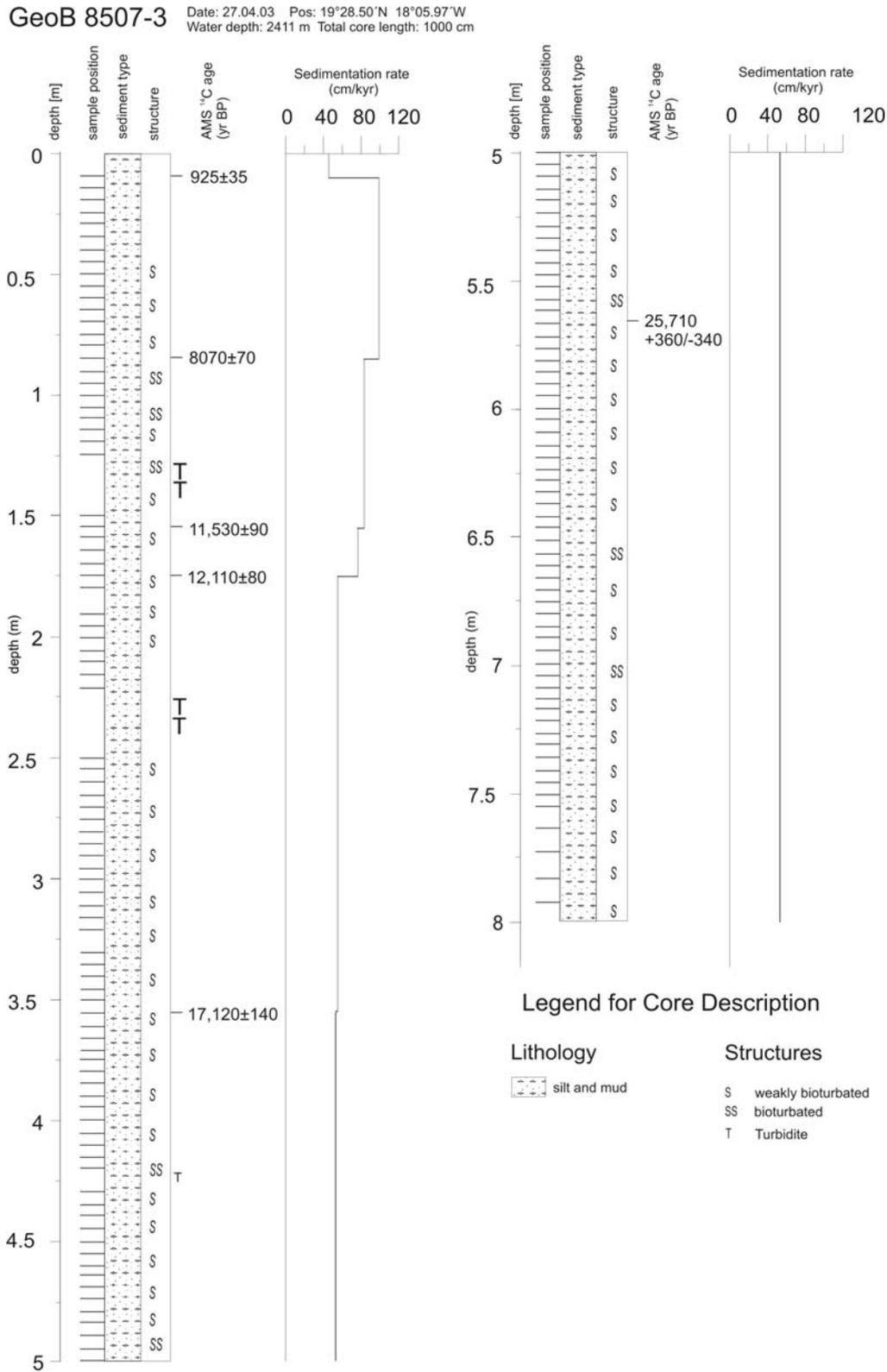


Fig. 3. Lithologic column of gravity core GeoB 8507-3 (modified after Schulz *et al.*, 2003) including sample positions (*T. heimii*) and sedimentation rates. Calibrated ages BP are shown on the right of each column.

(converted to PDB; Pierre *et al.*, 1994). We assume a stable modern sea surface salinity / $\delta^{18}\text{O}$ relationship through the investigated time interval as is proposed by Rohling and Bigg (1998).

For Mg/Ca analyses, about 30 - 40 specimens of *G. ruber* (pink) were picked out of the 250 - 355 μm fraction. Foraminiferal tests were cleaned in successive steps following the cleaning protocol developed by Barker *et al.* (2003). After dissolving the foraminiferal test, solutions were centrifuged for 10 min at 6000 rpm. Mg/Ca ratios were measured on a Perkin Elmer Optima 3300R Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) at the Department of Geosciences, University of Bremen. Instrumental precision was

Table 2. Stable oxygen and carbon isotope values of *Thoracosphaera heimii* and the purification index including the main components of the residual ~15 % other calcareous material.

GeoB 8507 depth [cm]	<i>T. heimii</i> $\delta^{18}\text{O}$	<i>T. heimii</i> $\delta^{13}\text{C}$	Purification (% <i>T. heimii</i> of total particles)	Rest	GeoB 8507 depth [cm]	<i>T. heimii</i> $\delta^{18}\text{O}$	<i>T. heimii</i> $\delta^{13}\text{C}$	Purification (% <i>T. heimii</i> of total particles)	Rest	GeoB 8507 depth [cm]	<i>T. heimii</i> $\delta^{18}\text{O}$	<i>T. heimii</i> $\delta^{13}\text{C}$	Purification (% <i>T. heimii</i> of total particles)	Rest
10	-0.78	-1.26	<85	C	300	-0.12	0.33	>85	other	565	0.47	0.18	85	C
15	-0.84	-0.69	>85	other	305	0.27	0.46	>85	other	570	0.25	0.34	<85	other
20	-0.39	-0.61	>85	other	310	0.23	0.26	>85	F	575	0.56	0.18	85	C
25	-0.67	-0.50	<85	C	315	0.70	0.40	<85	C	580	0.09	0.44	>85	other
30	-1.11	-1.02	>85	other	320	0.24	0.48	>85	F	585	0.18	0.21	85	C
35	-0.65	-0.80	>85	C	330	0.23	0.49	>85	other	590	0.00	0.42	>85	other
40	-1.05	-0.91	>85	other	335	0.49		>85	other	595	0.42	0.34	85	C
45	-0.69	-0.73	>85	C	340	0.12	0.43	>85	other	600	-0.02	0.42	>85	other
50	-0.82	-0.70	>85	other	345	0.68	0.51	>85	F	605	0.27	0.25	85	C
55	-0.76	-1.00	<85	F	350	0.16	0.43	>85	F	610	-0.06	0.10	<85	other
60	-0.65	-0.68	>85	other	355	0.53	0.61	>85	other	615	0.34	0.05	85	C
65	-0.52	-0.96	>85	F	365	0.56	0.43	>85	C	620	-0.09	0.21	<85	other
70	-0.57	-0.38	>85	other	370	0.21	0.62	>85	other	625	0.32	-0.04	85	C
75	-0.64	-0.85	>85	F	375	0.26		>85	other	630	0.07	0.10	<85	other
80	-0.24	-0.27	<85	other	380	-0.08	0.54	>85	other	635	0.33	-0.02	85	other
85	-0.04	-0.14	>85	F	385	0.32	0.31	>85	C	640	0.14	0.14	>85	other
90	-0.24	-0.21	>85	other	390	-0.13	0.47	>85	other	645	0.44	-0.28	85	C
95	0.27	0.27	<85	other	395	0.37	0.33	>85	C	650	0.09	-0.01	>85	other
100	-0.86	-0.94	>85	F	400	0.10	0.52	>85	F	655	0.36	0.19	85	C
105	0.22	0.14	>85	other	405	0.36	0.34	>85	FC	660	0.12	0.17	>85	other
110	0.25	0.37	>85	other	410	0.67	0.52	<85	other	665	0.40	0.19	>85	C
115	0.03	-0.11	>85	F	415	0.75	0.38	>85	C	670	-0.07	0.14	>85	other
120	0.20	0.13	>85	other	435	0.55	0.56	>85	other	675	0.59	0.02	85	C
125	0.22	0.08	>85	other	440	0.32	0.52	>85	other	680	0.04	0.17	>85	other
150	-0.50	0.04	>85	other	445	0.73		>85	other	685	-0.18	0.22	>85	C
155	-0.32	-0.09	>85	other	450	0.16	0.53	>85	other	690	0.08	0.14	>85	other
160	-1.06	-0.23	>85	other	455	0.81		>85	C	695	0.33	-0.09	85	other
165	-0.65	-0.75	>85	C	460	0.03	0.66	<85	other	700	0.07	0.07	>85	other
170	-0.16	-0.54	>85	F	465	0.49	0.42	<85	C	705	0.11	-0.03	85	other
175	0.41	-0.13	>85	C	470	0.06	0.59	>85	other	710	0.07	-0.27	<85	other
180	0.61	-0.08	>85	other	475	0.68	0.35	>85	other	715	0.33	0.15	85	other
190	0.64		>85	other	480	0.08	0.60	<85	other	720	-0.14	-0.22	>85	other
195	0.53	0.32	>85	F	485	0.61	0.23	>85	C	725	0.48	0.14	85	other
200	0.81	0.21	>85	other	490	0.05	0.56	>85	other	730	0.06	0.07	>85	other
205	0.45	0.56	<85	FC	495	0.44	0.39	>85	C	735	0.52	0.10	85	other
210	0.25	0.29	>85	other	500	0.01	0.46	>85	other	740	0.15	-0.03	>85	other
215	0.54	0.31	>85	C	505	0.72	0.29	>85	C	745	0.30	-0.18	85	other
220	0.16	0.29	>85	F	510	-0.10	0.45	>85	other	750	0.09	-0.24	>85	other
250	0.05	0.35	>85	other	515	0.60	0.24	>85	C	755	0.30	0.18	85	other
255	0.52	0.23	<85	other	520	0.11	0.34	<85	other	760	0.22	0.31	>85	other
260	0.06	0.31	>85	gran	525	0.47	0.17	>85	C	765	0.23	0.27	85	other
265	0.39	0.24	>85	other	530	0.24	0.42	<85	other	770	0.22	0.23	>85	other
270	0.26	0.42	>85	other	535	0.39	0.12	>85	C	780	-0.04	0.13	<85	other
275	0.75	0.46	<85	other	540	0.08	0.29	<85	other	790	0.11	0.26	>85	other
280	0.26	0.61	>85	other	545	0.31	0.15	>85	C	800	0.13		>85	other
285	0.35	0.62	<85	other	550	0.07	0.28	>85	other	810	0.21		>85	other
290	0.04	0.57	<85	gran	555	0.57	0.29	>85	C					
295	0.29	0.27	>85	other	560	0.13	0.22	<85	other					

determined after an external in-house standard that was run after every five samples. The relative standard deviation of the external standard was ± 0.09 %. The analytical precision for the samples is ± 0.22 %. Mg/Ca ratios were converted to SST by means of the species-specific calibration for *G. ruber* (pink) (size fraction 250 - 350 μm) developed by Anand *et al.* (2003).

The age model of core GeoB 8507-3 is based on six AMS ^{14}C measurements that have been carried out on *G. bulloides* (Leibniz-Laboratory for Radiometric Dating and Stable Isotope Research, University of Kiel, Germany; Table 1). We converted the AMS ^{14}C ages into calendar ages according to the method described by Fairbanks *et al.* (2005) and using the Calib 5.0.1 software (Stuiver *et al.*, 2005) with an adjustment of 500 ± 50 years for surface water reservoir age (deMenocal *et al.*, 2000a).

2.4 Results

The radiocarbon age model shown in Table 1 indicates highest sedimentation rates during the Holocene at site GeoB8507-3 (Fig. 3).

The oxygen isotope curve of *Thoracosphaera heimii* shows a clear glacial-interglacial transition of about 1 ‰, which is comparable to that of the planktonic foraminifera *Globigerina bulloides* and *Globigerinoides ruber* (pink) (Fig. 4). Isotope values of *T. heimii* are positive during glacial times with a shift to negative values at about 13.5 ka BP. A distinct interval with relative strong negative values can be observed during the Younger Dryas (YD) (~13 – 11.5 ka). In glacial sediments the isotope values of *T. heimii* are comparable to those of *G. ruber* (pink). During the deglaciation the two records diverge resulting in somewhat higher values of *T. heimii* during the Holocene (Fig. 4). Compared to *G. bulloides*, glacial stable oxygen isotope values of *T. heimii* are about 1 ‰ higher. During the Holocene the difference between the signals of *T. heimii* and *G. bulloides* is slightly smaller.

Calculated temperatures based on the palaeotemperature equation for inorganic calcite (Kim and O'Neil, 1997) for *T. heimii* result in temperatures of about 20 – 22.5°C (Fig. 5b). No clear shift in temperature can be observed related to the glacial-interglacial transition. Temperatures reconstructions based on the isotope signal of *T. heimii* using the equation of Zonneveld *et al.* (2007) are much lower and lie around 4 °C (Fig. 5a). SST values reconstructed based the equation of inorganic calcite are

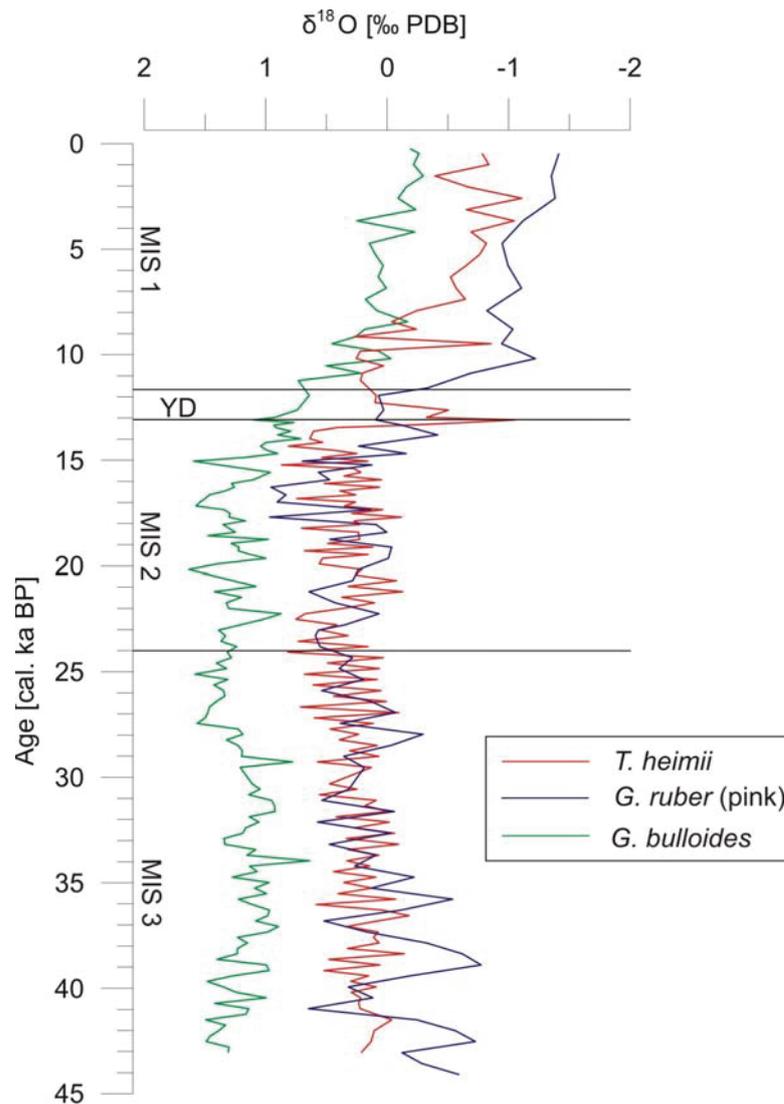


Fig. 4. Stable oxygen isotope ($\delta^{18}\text{O}$) records of *Thoracosphaera heimii* (solid line), *Globigerinoides ruber* (pink) (dashed line) and *Globigerina bulloides* (dotted line) of core GeoB 8507-3.

within the same range as those based on the oxygen isotope and Mg/Ca signal of *G. ruber* (pink). However, the oxygen isotope based signal of *G. ruber* (pink) provides slightly lower temperature values in the glacial interval compared to the *T. heimii* signal whereas the Mg/Ca based reconstruction give slightly higher SST values during MIS 3. In contrast, throughout the Holocene, all reconstructions give comparable results (Fig. 5b). Between 15 and 8 ka BP the reconstructions based on *T. heimii* and *G. ruber* show a discrepancy with *T. heimii* registering lower temperatures between 15 - 13.5 ka BP and 12 - 8 ka BP and higher temperatures during the YD between 13.5 – 12 ka BP.

Temperature reconstructions based on oxygen isotope values of *G. bulloides* are about 5 °C lower throughout the record than those reconstructed from *T. heimii* and *G. ruber*

(pink). Comparable to the signals described above no large shift in temperature can be observed related to the glacial-interglacial transition

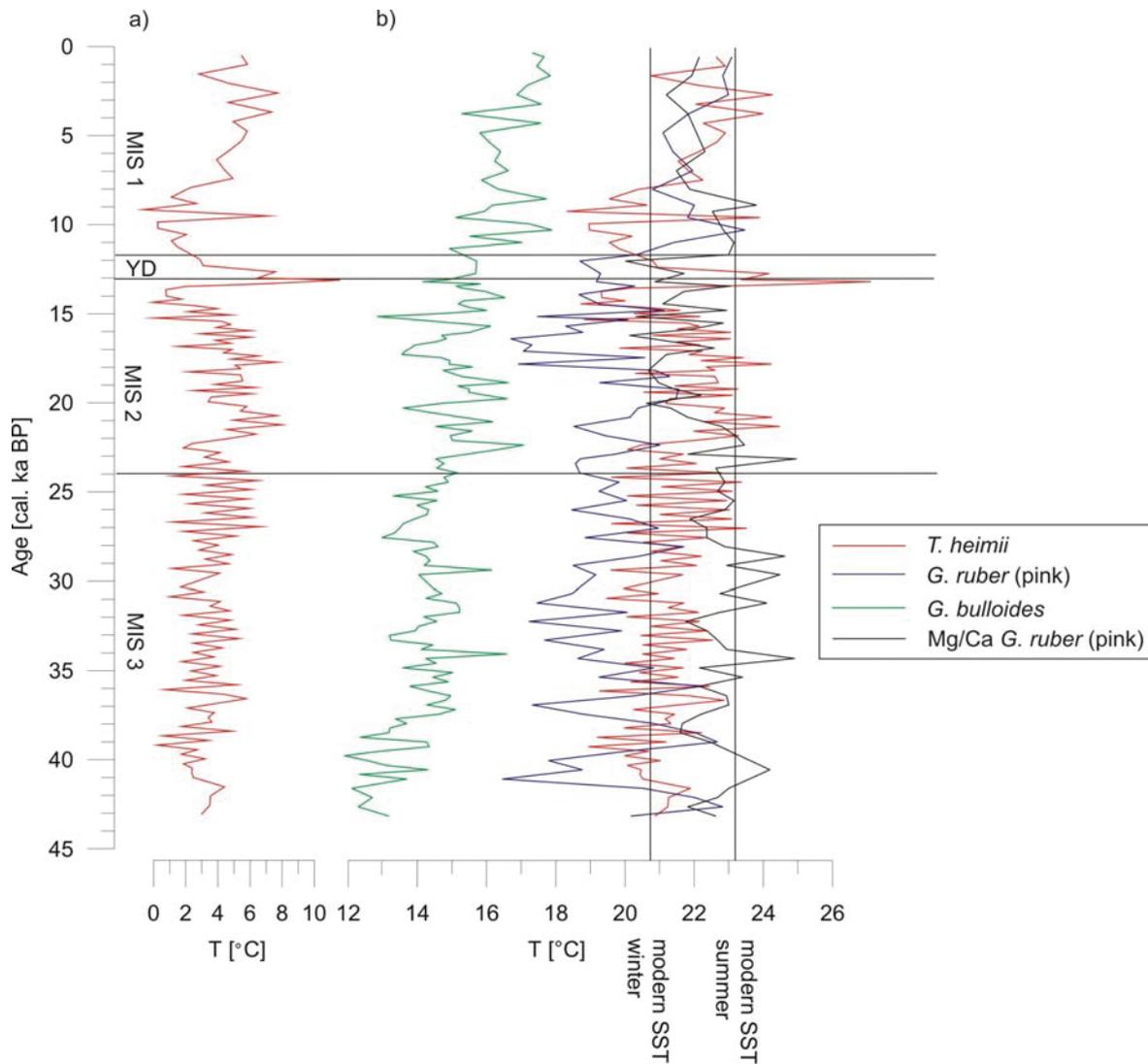


Fig. 5. Calculated calcification temperatures of *T. heimii* (solid lines) using the palaeotemperature equation (a) of Zonneveld *et al.* (2007) and (b) for inorganic calcite of Kim and O'Neill (1997) compared to the calculated temperatures of *G. ruber* (pink) (dashed line) and *G. bulloides* (dotted line) using the equation of Mulitza *et al.* (2003) and to the Mg/Ca ratio of *G. ruber* (pink) (dashed/dotted line). Modern SST in winter and summer as derived from the World Ocean Atlas 2005 are indicated (Locarnini *et al.*, 2006).

2.5. Discussion

Before evaluating the temperature signals based on the calcareous dinoflagellate *Thoracosphaera heimii* and the two planktonic foraminifera it is necessary to determine whether post depositional alteration processes such as calcite dissolution might have changed the $\delta^{18}\text{O}$ signal. Compared to other calcite producing organisms, cysts of *T. heimii* are relatively robust against dissolution (Vink *et al.*, 2000; Vink 2004). Species-specific carbonate dissolution could therefore result in different isotope signals as carbonate dissolution can shift the stable oxygen isotope signal towards heavier values (Lohmann, 1995). In the Atlantic the upper boundary of the present-day lysocline is situated at about 4500 m and during the Pleistocene at about 3800 m (Bickert and Wefer, 1996). However, core GeoB 8507-3 is sampled at 2411 m water depth and is located well above the modern lysocline. We therefore assume that carbonate dissolution did not affect our signal. As our core is located in a high productivity area, dissolution through the bacterial degradation of organic matter might have affected the fossil content. So far, effects of this process on the preservation of *T. heimii* has only been documented in the eastern Arabian Sea where the occurrence of a strong oxygen minimum zone in combination with extreme high year round primary production in upper waters resulted in enhanced preservation of *T. heimii* within the oxygen minimum zone (Wendler *et al.*, 2002a). Within the research area, no preservation differences of *T. heimii* could be observed in relationship to differential upper ocean production and the presence of an oxygen minimum zone (Richter *et al.*, 2007). We therefore assume that species-specific dissolution did not affect our results.

The pilot study of Zonneveld (2004) on South-Atlantic surface samples showed that the purity of the samples is of crucial importance with “dirty” samples containing many other calcareous particles providing strong scatter in isotopic values of *T. heimii*. Within this study the scatter of the *T. heimii* measurements lie within the same range as the isotopic measurements of both planktonic foraminifera species and is even slightly smaller than that recorded for *Globigerinoides ruber* (pink). We observe $\delta^{13}\text{C}$ values, which are lower than average values known for planktonic foraminifera and coccolithophores but are characteristic for *T. heimii* (Friedrich and Meier, 2003; Zonneveld, 2004; Zonneveld *et al.*, 2007, Table 2). We therefore assume that contamination did not severely affect our signal and that the isotopic composition of *T. heimii* reflects upper ocean conditions.

We observe a strong difference between palaeotemperature reconstructions based on the isotopic composition of *T. heimii* according to the equation as given in Zonneveld *et al.* (2007) and the inorganic calcite equation of Kim and O'Neil (1997). The equation of Zonneveld *et al.* (2007) provides temperatures around 4 °C which correspond to water column conditions at over 1500 m depth (Fig. 2). As *T. heimii* is known to be produced in the upper water column, this reconstruction is quite unrealistic. Our isotopic values are in range of those measured for *T. heimii* shells extracted from South Atlantic surface sediments (Zonneveld, 2004). Applying the equation of Zonneveld *et al.* (2007) for this latter dataset would provide unrealistic temperature reconstructions as well. We therefore suggest that the palaeotemperature equation as provided by Zonneveld *et al.* (2007) is not correct. Within the study of Zonneveld *et al.* (2007), physical conditions within the culture medium did not remain completely constant throughout the experiment. If this has a larger effect on the isotopic conditions than previously thought the palaeotemperature equation of Zonneveld *et al.* (2007) has to be revised. Future experiments are required to confirm this suggestion.

With exception of a short interval during the YD, the isotopic signal of *T. heimii* and the temperature reconstruction based on inorganic calcite, lie within the same range as those of *G. ruber* (pink). This might be the result of comparable ecological characteristics of these species. Both species are considered to reproduce within the upper part of the water column. *G. ruber* (pink) is characteristically present in water depths above the thermocline between about 0 and 50 m (Hemleben *et al.*, 1989; Peeters *et al.*, 2002; Anand *et al.*, 2003; Tedesco *et al.*, 2006). Seawater samples taken off Cape Blanc during January/February 1997 document freshly produced cysts of *T. heimii* in the complete upper 100 m of the water column. Highest abundances are, however, found at slightly lower depths as *G. ruber* (pink) with maximal concentrations at the DCM at about 50 m (Karwath *et al.*, 2000a, b). This is supported by the mean Holocene temperatures as reconstructed in this study which correspond to present day surface water conditions for *G. ruber* (pink) and subsurface water conditions for *T. heimii* (Fig. 2, 5).

We observe an offset between the isotope values and temperature reconstructions of *Globigerina bulloides* compared to that of *T. heimii*. *G. bulloides* is generally been found to be characteristically formed at intermediate water depths between 25 and 75 m (Hemleben *et al.*, 1989, Peeters *et al.*, 2002). The reconstructed mean Holocene temperatures of *G. bulloides* are lower than those reconstructed for

T. heimii and *G. ruber* (pink) and reflect modern day conditions at the sample site that prevail around 75 m (Fig. 2). The different isotopic values and temperature reconstructions can therefore well be the result of the different depth habitats of the studied species. Another possibility could be that *T. heimii* and *G. ruber* (pink) are being produced in different seasons as *G. bulloides*. *G. bulloides* is known to be a typical upwelling indicator that can be found in relatively cold, nutrient-rich waters (e.g. Prell and Curry, 1981; Ganssen and Sarnthein, 1983; Thiede, 1983; Thunell *et al.*, 1983; Hebbeln *et al.*, 2000). In the Arabian Sea and within the Canary Islands region, highest shell fluxes can be observed during the upwelling season (Bé, 1960; Fairbanks and Wiebe, 1980; Sautter and Thunell, 1991; Peeters *et al.*, 2002; Mulitza *et al.*, 2004). Off Cape Blanc, *G. bulloides* is more abundant in the cold upwelling season in winter and spring. On the other hand, *G. ruber* (pink) is generally considered to reflect a summer signal related to warmer surface water temperatures (Ganssen und Sarnthein, 1983; Fischer *et al.*, 1996; Waelbroeck *et al.*, 2005). Such conditions are in the research area characteristic for times of upwelling relaxation. This is in good agreement with the mean Holocene palaeotemperature reconstruction that provides reconstructed temperatures that are more or less consistent with modern temperature values of the upper water column characteristic for the upwelling relaxation season (Fig. 6). Sediment trap surveys show that within the Arabian Sea, *T. heimii* cysts are produced throughout the year but with enhanced cyst fluxes just after the termination of the SW monsoon, when upper ocean temperatures are higher compared to upwelling conditions (Gibson, 2000; Wendler *et al.*, 2002b). In the research area, the *T. heimii* flux can not be related to a certain season or to certain characteristic upper ocean temperatures as sediment trap surveys document a production of cyst throughout the year. Furthermore, the mean Holocene temperature reconstruction gives values that are characteristic mean annual temperatures of the upper 50 m of the water column (Fig. 2). We therefore assume that within the region the isotopic composition of *T. heimii* reflects mean annual temperatures of the upper water layer. This is supported by the South Atlantic surface sediment study that also documents the isotopic signal of *T. heimii* reflecting mean annual temperatures. The observation that temperatures reconstructed by *G. bulloides* are lower than those reconstructed based on *G. ruber* (pink) and *T. heimii* could therefore, next to the differential depth habitat of the investigated species, well be the result of the differential seasonal production of the species with *G. bulloides* reflecting

upwelling conditions, *G. ruber* (pink), upwelling relaxation conditions and *T. heimii* mean annual conditions.

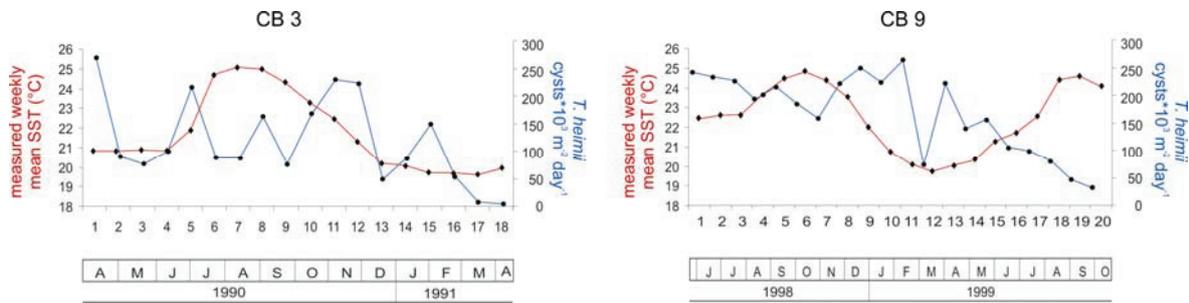


Fig. 6. Time series fluxes of *T. heimii* (cysts x $10^3 \text{ m}^{-2} \text{ day}^{-1}$) compared to the measured, weekly mean sea surface temperature in Cape Blanc sediment trap CB 3 (from April 1990 to April 1991) and CB 9 (from June 1998 to October 1999) (modified after Siggelkow *et al.*, 2002, 2004). CB 3 was deployed at a water depth of 730 m and CB 9 at a depth of 541 m.

Palaeotemperature reconstructions based on the Mg/Ca ratio of *G. ruber* (pink) are higher than those of *T. heimii* in the lower part of the record whereas the isotopically based palaeotemperature reconstructions are lower than those of *T. heimii* in glacial times. This indicates that there are methodological discrepancies between the both methods. A questionable factor within the palaeotemperature reconstruction, based on stable isotope, forms the estimation of the $\delta^{18}\text{O}_w$. This value is dependent on several factors such as the amount of ice-volume on the poles. Although we corrected for the ice-volume effect only, there are a couple of uncertainties that makes it difficult to determine all other factors. We can further safely assume that the further we go back in time, the larger the error of the $\delta^{18}\text{O}_w$ value will be. It is therefore quite logical that the largest discrepancy between the two records can be observed in MIS 3.

None of our palaeotemperature reconstructions based on planktonic foraminifera and the calcareous dinoflagellate document a clear difference of upper ocean temperatures between glacial and Holocene times. This suggests that upper ocean conditions were comparable in these two periods. This is conform to previous palaeotemperature reconstructions in the same area based on alkenones that also indicate small temperature changes maximal 1 - 3 °C across the glacial-interglacial transition (Elderfield and Ganssen, 2000, Ternois *et al.*, 2000; Zhao *et al.*, 2000). However, records from nearby regions based on alkenones such as the CLIMAP curves off Cape Blanc, suggest changes between modern and LGM temperatures from up to

10 °C (Henderiks and Bollmann, 2004 and references therein). As elucidated in the oceanography part, the oceanographic conditions in the upper water column change remarkably on a small geographical distance within the research area, for instance as results of the locally defined tracks of the upwelling filaments. It is therefore logical that records from nearby sites reflect a different history of local oceanographical conditions. We therefore compared the *T. heimii* signal to results of other proxies of the same core.

A discrepancy between the temperature reconstructions based on *G. ruber* (pink) and *T. heimii* can be observed during the YD and the beginning of the Holocene. As discussed before, *T. heimii* reflects mean annual temperatures rather than the conditions of a certain season. When the upper ocean temperature conditions during upwelling and upwelling-relaxation would remain similar, but a change in duration of these seasons or the frequency of upwelling events would take place, this should be reflected in the isotopic signal of *T. heimii* but not in the signals based on *G. bulloides* and *G. ruber* (pink). For the studied time interval this would result in a reconstruction of relatively stable duration and/or frequency of upwelling events during the glacial period followed by an increase in duration and/or frequency of the upwelling events at about 15 ka reflected by the relative low temperatures registered by *T. heimii*. The sudden high temperatures reflected by *T. heimii* in the YD suggest a strong decrease in duration of the upwelling season or a decrease in amount of upwelling filaments crossing the core site. This suggestion is supported by information coming from alkenone and planktonic foraminifera based temperature reconstructions from sites close to the core position (Martinez *et al.*, 1999; Haslett and Smart, 2006). These studies suggest that enhanced upwelling occurred as results of an intensification of the trade wind system during the African Humid Period (AHP) and/or the transition from MIS 2-MIS 1 and weaker upwelling during the YD. However, this is in contrast to the work of deMenocal *et al.* (2000b) and Romero *et al.* (2008) which assume less upwelling due to weaker trade winds intensity during the Bølling-Allerød (B/A) and the Holocene and enhanced upwelling during the YD. However, when studying the high resolution record as given in Romero *et al.* (2008) high variability in the $\delta^{18}\text{O}$ values of *G. bulloides* and the alkenone-based temperatures can be observed. Although not discussed in the text, these records show an increase in temperature during the YD that is in consistence with our results. Future high spatial and temporal resolution studies are therefore required to shed light into this discrepancy.

Our results subscribe the high potential of the use of the stable oxygen isotope signal of *T. heimii* to reconstruct mean annual upper ocean temperatures and elucidate the possibility to obtain information about seasonal changes in temperature history in a research area when this tool will be used in a multi proxy study.

2.6 Conclusion

This study documents the first down-core palaeotemperature reconstruction based on the oxygen isotope composition of *Thoracosphaera heimii*. There is no indication that carbonate dissolution or contamination did affect our signal.

The glacial-interglacial variability in the oxygen isotope record of *T. heimii* is comparable to that of the planktonic foraminifera *Globigerina bulloides* and *Globigerinoides ruber* (pink). Isotope values most closely resemble those of *G. ruber* (pink) and are about 1 ‰ higher than *G. bulloides* in glacial times.

Reconstructed palaeotemperatures of *T. heimii* based on the equation for inorganic calcite of Kim and O'Neill (1997) lie within the same range as the oxygen isotopic and Mg/Ca based palaeotemperature reconstructions of *G. ruber* (pink). The use of the palaeotemperature equation of Zonneveld *et al.* (2007) provides temperatures of about 16 °C lower than those reconstructed for the region suggesting that this equation might need to be revised.

The higher temperature reconstructions based on *T. heimii* and *G. ruber* (pink) compared to *G. bulloides* can be explained to be the result of their depth habitat with *T. heimii* and *G. ruber* (pink) being characteristically formed in the upper water column whereas *G. bulloides* built its shells in more deeper waters. Furthermore, whereas *T. heimii* is known to be produced throughout the year in the research area, the present-day production of *G. bulloides* takes place during the upwelling season when temperatures are reduced.

The slight discrepancy between temperature reconstructions based on stable oxygen isotopes and Mg/Ca of *G. ruber* (pink) can be explained by methodological differences. The difference in temperature reconstructions of *T. heimii* and *G. ruber* (pink) between 15 ka BP and 8 ka BP can be explained by differences in their ecology with *G. ruber* (pink) reflecting upwelling relaxation conditions whereas the *T. heimii* signal provides mean annual temperatures.

None of the records presented here shows a large difference between glacial and interglacial temperatures which is in good agreement with records that lie within the close vicinity of the core site.

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2.8 References

- Anand, P., Elderfield, H., Conte, M.H., 2003. Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series. *Palaeoceanography* 18 (2), 1050.
- Arnault, S., 1987. Tropical Atlantic geostrophic currents and ship drifts. *Journal of Geophysical Research* 92 (C5), 5076-5088.
- Barker, S., Greaves, M., Elderfield, H., 2003. A study of cleaning procedures used for foraminiferal Mg/Ca palaeothermometry. *Geochemistry Geophysics Geosystems* 4, 8407.
- Barton, E.D., Aristegui, J., Tett, P., Cantón, M., Garcia-Braun, J., Hernández-León, S., Nykjaer, L., Almeida, C., Almunia, J., Ballesteros, S., Basterretxea, G., Escáñez, J., Garcia-Weill, L., Hernández-Guerra, A., López-Laatzén, F., Molina, R., Montero, M.F., Navarro-Pérez, E., Rodríguez, J.M., van Lenning, K., Vélez, H., Wild, K., 1998. The transition zone of the Canary Current upwelling region. *Progress in Oceanography* 41 (4), 455-504.
- Bayev, S.A., Polonskiy, A.B., 1991. Seasonal variability of the equatorial countercurrent and the north equatorial current in the central tropical Atlantic. *Oceanology* 31, 155-159.
- Bé, A.W.H., 1960. Ecology of recent planktonic foraminifera: part 2 – bathymetric and seasonal distributions in the Sargasso Sea off Bermuda. *Micropalaeontology* 6, 373-392.
- Bickert, T., Wefer, G., 1996. Late Quaternary deep water circulation in the South Atlantic: Reconstruction from carbonate dissolution and benthic stable isotopes. In: Wefer, G. (Ed.), *The South Atlantic: Present and Past Circulation*, Springer-Verlag, New York, 599-620.
- deMenocal, P.B., Ortiz, J., Guilderson, T., Sarnthein, M., 2000a. Coherent high- and low-Latitude climate variability during the Holocene warm period. *Science* 288, 2198-2202.
- deMenocal, P.B., Ortiz, J., Guilderson, T., Adkins, J., Sarnthein, M., Baker, L., Yarusinski, M., 2000b. Abrupt onset and termination of the African humid period: rapid climate responses to gradual insolation forcing. *Quaternary Science Reviews* 19, 347-361.
- Elderfield, H., Ganssen, G., 2000. Past temperature and $\delta^{18}\text{O}$ of surface ocean water inferred from foraminiferal Mg/Ca ratios. *Nature* 405, 442-445.
- Fairbanks, R.G., Wiebe, P.H., 1980. Foraminifera and chlorophyll maximum: vertical distribution, seasonal succession and palaeoceanographic significance. *Science* 26 (4464), 1524-1526.
- Fairbanks, R.G., Mortlock, R.A., Chiu, T.-C., Cao, L., Kaplan, A., Guilderson, T.P., Fairbanks, T.W., Bloom, A.L., 2005. Marine radiocarbon calibration curve spanning 0 to 50,000 Years B.P. based on paired $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and ^{14}C dates on pristine corals. *Quaternary Science Reviews* 24, 1781-1796.
- Fischer, G., Donner, B., Ratmayer, V., Davenport, R., Wefer, G., 1996. Distinct year-to-year flux variations off Cape Blanc during 1988-1991: relation to ^{18}O -deduced sea surface temperatures and trade winds. *Journal of Marine Research* 54, 73-98.
- Fraile, I., 2008. Modelling the spatial and temporal distribution of planktonic foraminifera. Ph.D. thesis, University of Bremen, 91-118.
- Friedrich, O. and Meier, S.K.J., 2003. Stable isotopic indication for the cyst formation depth of Campanian/Maastrichtian calcareous dinoflagellates. *Micropaleontology*, 49(4): 375-380.

- Gabric, A. J., Garcia, L., Van Camp, L., Nykjær, L., Eifler, W., Schrimpf, W., 1993 Offshore export of shelf production in the Cap Blanc (Mauritanian) filament as described from coastal zone colour scanner imagery. *Journal of Geophysical Research* 98, 4697-4712.
- Ganssen, G., Sarnthein, M., 1983. Stable isotope composition of foraminifers: the surface and bottom water record of coastal upwelling. In: Suess, E., Thiede, J., (Eds.), *Coastal upwelling: Its sedimentary record, Part A*. Plenum Press, New York, 99-121.
- Gibson, C. H., 2000. Laboratory and ocean studies of phytoplankton response to fossil turbulence. *Dynamics of Atmospheres and oceans* 31, 295-306.
- Hagen, E., Schemainda, R., 1984. Der Guineadom im ostatlantischen Stromsystem. *Beiträge zur Meereskunde* 51, 5-27.
- Hagen, E., Schemainda, R., 1984. Der Guineadom im ostatlantischen Stromsystem. *Beiträge zur Meereskunde* 51, 5-27.
- Haslett, S.K., Smart, C.W., 2006. Late Quaternary upwelling off tropical NW Africa: new micropaleontological evidence from ODP Hole 658 C. *Journal of Quaternary Science* 21 (3), 259-269.
- Hebbeln, D., Marchant, M., Freudenthal, T., Wefer, G., 2000. Surface sediment distribution along the Chilean continental slope related to upwelling and productivity. *Marine Geology* 164 (3-4), 119-137.
- Hemleben, C., Spindler, M., Anderson, O.R., 1989. *Modern planktonic foraminifera*. New York, Springer.
- Hernández-Guerra, A., Nykjaer, L., 1997. Sea-surface temperature variability off north-west Africa: 1981-1989. *International Journal of Remote Sensing* 18 (12), 2539-2558.
- Henderiks, J., Bollmann, J., 2004. The *Geophyrocapsa* sea surface palaeothermometer put to the test: comparison with alkenone and foraminifera proxies off NW Africa. *Marine Micropaleontology* 50 (3-4), 161-184.
- Hildebrand-Habel, T., Willems, H., 2000. Distribution of calcareous dinoflagellates from the Maastrichtian to middle Eocene of the western South Atlantic Ocean. *International Journal of Earth Sciences* 88, 694-707.
- Hughen, K., Baille, M., Bard, E., Beck, J., Bertrand, C., Blackwell, P., Buck, C., Burr, G., Cutler, K., Damon, P., Edwards, R., Fairbanks, R., Friedrich, M., Guilderson, T., Kromer, B., McCormac, F., Manning, S., Bronk-Ramsey, C., Reimer, P., Remmele, S., Southon, J., Stuiver, M., Talamo, S., Taylor, F., der Plicht, J.v., Weyhenmeyer, C., 2004. Marine 04: Marine radiocarbon age calibration, 26-0 ka BP. *Radiocarbon* 46 (3), 1059-1086.
- Jansen, E., Overpeck, J., Briffa, K.R., Duplessy, J.-C., Joos, F., Masson-Delmotte, V., Olago, D.O., Otto-Bliesner, B., Peltier, W.R., Rahmstorf, S., Ramesh, R., Raynaud, D., Rind, D., Solomina, O., Villalba, R., and Zhang, D., 2007. Palaeoclimate. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., and Miller, H.L. (Eds), *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK, 434-497.

- Karwath, B., 2000a. Ecological studies on living and fossil calcareous dinoflagellates of the equatorial and tropical Atlantic Ocean. Ph.D. thesis, Berichte Fachbereich Geowissenschaften Universität Bremen No. 152, 66-92.
- Karwath, B., Janofske, D., Willems, H., 2000b. Spatial distribution of the calcareous dinoflagellate *Thoracosphaera heimii* in the upper water column of the tropical and equatorial Atlantic. *International Journal of Earth Sciences* 88, 668–679.
- Kim, S.-T., O’Neil, J.R., 1997. Equilibrium and non-equilibrium oxygen isotope effects in synthetic carbonates. *Geochimica et Cosmochimica Acta* 61, 3461-3475.
- Locarnini, R. A., Mishonov, A. V., Antonov, J. I., Boyer, T. P. and Garcia, H. E., 2006. World Ocean Atlas 2005, Volume 1: Temperature. Levitus, S., (Ed.), NOAA Atlas NESDIS 61, U.S. Government Printing Office, Washington, D.C., 182 pp.
- Lohmann, G.P., 1995. A model for variation in the chemistry of planktonic foraminifera due to secondary calcification and selective dissolution. *Palaeoceanography*, 10 (3), 445-457.
- Longhurst, A., 1995. Seasonal cycles of pelagic production and consumption. *Progress in Oceanography* 36, 77-167.
- Martinez, P., Bertrand, P., Shimmield, G.B., Cochrane, K., Jorissen, F.J., Foster, J., Dignan, M., 1999. Upwelling intensity and ocean productivity changes off Cape Blanc (northwest Africa) during the last 70.000 years: geochemical and micropaleontological evidence. *Marine Geology* 158, 57-74.
- Mittelstaedt, E., 1983. The upwelling area off northwest Africa – a description of phenomena related to coastal upwelling. *Progress in Oceanography* 12, 307-331.
- Mittelstaedt, E., 1989. The subsurface circulation along the Moroccan slope. In: Neshyba, S.J., Mooers, C.N.K., Smith, R.L., Barber, R.T., (Eds.), Poleward flows along eastern Ocean boundaries. Springer, Berlin, 96-109.
- Mittelstaedt, E., 1991. The ocean boundary along the northwest African coast: circulation and oceanographic properties at the sea surface. *Progress in Oceanography* 26 (4), 307-355.
- Monterey, G., Levitus, S., 1997. Seasonal variability of mixed layer depth for the world ocean NOAA atlas Nesdis 14, US Government Printing Office, Washington DC, 96.
- Morel, A., Berthon, J.-F., 1989. Surface pigments, algal biomass profiles, and potential production of the euphotic layer: Relationships reinvestigated in view of remote-sensing applications. *Limnol. Oceanogr* 34 (8), 1545-1562.
- Mulitza, S., Boltovskoy, D., Donner, B., Meggers, H., Paul, A., Wefer, G., 2003. Temperature: $\delta^{18}\text{O}$ relationship of planktonic foraminifera collected from surface waters. *Palaeogeography, Palaeoclimatology, Palaeoecology* 202, 143-152.
- Mulitza, S., Donner, B., Fischer, G., Paul, A., Pätzold, J., Rühlemann, C., Segl, M., 2004. The South Atlantic oxygen isotope record of planktic foraminifera. In: Wefer, G., Mulitza, S., Ratmeyer, V. (Eds.) *The South Atlantic in the Late Quaternary: Reconstruction of Material Budgets and Current Systems*, Springer, 121-142.
- Peeters, F. J. C., Brummer, G.-J.A., Ganssen, G., 2002. The effect of upwelling on the distribution and stable isotope composition of *Globigerina bulloides* and *Globigerinoides ruber* (planktic foraminifera) in modern surface waters of the NW Arabian Sea. *Global and Planetary Change* 34, 269-291.

- Pierre, C., Vangriesheim, A., Laube-Lenfant, E., 1994. Variability of water masses and of organic production-regeneration systems as related to eutrophic, mesotrophic and oligotrophic conditions in the northeast Atlantic ocean. *Journal of Marine Systems* 5, 159-170.
- Prell, W.L., Curry, W.B., 1981. Faunal and isotopic indices of monsoonal upwelling: Western Arabian Sea, *Oceanologica Acta* 4, 91-98.
- Richter, D., Vink, A., Zonneveld, K.A.F., Kuhlmann, H., Willems, H., 2007. Calcareous dinoflagellate cyst distribution in surface sediments from upwelling areas off NW Africa, and their relationship with environmental parameters of the upper water column. *Marine Micropalaeontology* 63, 201–228.
- Rohling, E.J., Bigg, G.R., 1998. Palaeosalinity and $\delta^{18}\text{O}$: A critical assessment. *Journal of Geophysical Research* 103 (C1), 1307-1318.
- Romero, O.E., Kim, J.-H., Donner, B., 2008. Submillennial-to-millennial variability of diatom production off Mauritania, NW Africa, during the last glacial cycle. *Paleoceanography* 23, doi: 10.1029/2008PA001601.
- Sarnthein, M., Thiede, J., Pflaumann, U., Erlenkeuser, H., Fütterer, D., Koopmann, B., Lange, H., Seibold, E., 1982. Atmospheric and oceanic circulation patterns off Northwest Africa during the past 25 million years. In: von Rad, U., Hinz, K., Sarnthein, M., Seibold, E. (Eds.), *Geology of the Northwest African Continental Margin*. Springer-Verlag, Berlin, Heidelberg, 545-604.
- Sarnthein, M., Tetzlaff, G., Koopmann, B., Wolter, K., Pflaumann, U., 1981. Glacial and interglacial wind regimes over the eastern subtropical Atlantic and North-West Africa. *Nature* 293, 193-196.
- Sautter, L. R., Thunell, R. C., 1991. Seasonal variability in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of planktonic foraminifera from an upwelling environment; Sediment trap results from the San Pedro Basin, Southern California. *Paleoceanography* 6 (3), 307-34.
- Schott, F.A., Brandt, P., Hamann, M., Fischer, J., Stramma, L., 2002. On the boundary flow off Brazil at 5-10°S and its connection to the interior tropical Atlantic, *Geophysical Research Letters* 29 (17), 1840.
- Schulz, H.D., Ait Cahtou, M., Antobreh, A.A., Enneking, K., Esper, O., Fabian, K., Geogiopoulou, A., Gerriets, A., Hanebuth, T., Henrich, R., Holz, C., Kastanja, M.M., Klöcker, R., Knefelkamp, B., Kölling, M., Krammer, R., Krastel, S., Pannike, S., Richter, F., Schäfer, R., Schnieders, L., Siggelkow, D., Sonnabend, H., Spilker, S., Steinbach, A., Truscheit, T., Wien, K., Wynn, R.B., Zühlsdorff, L., 2003. Report and preliminary results of Meteor Cruise M 58/1, Dakar - Las Palmas, 15.04. - 12.05.2003, Berichte, Fachbereich Geowissenschaften, Universität Bremen, No. 215.
- Siggelkow, D., Vink, A., Willems, H., 2002. Calcareous dinoflagellate cyst production, vertical transport and preservation off Cape Blanc during 1990: a sediment trap study. *Journal of Nannoplankton Research* 24, 160.
- Siggelkow, D., Zonneveld, A., Willems, H., 2004. Calcareous dinoflagellate cyst production linked to upwelling and lithogenic influx off Cape Blanc (NW Africa). *Journal of Nannoplankton Research* 26, 97.
- Stramma, L., Siedler, G., 1988. Seasonal changes in the North Atlantic subtropical gyre. *Journal of Geophysical Research* 93, 8111-8118.

- Stuiver, M., Reimer, P.J., Bard, E., Beck, J.W., Burr, G.S., Hughen, K.A., Kromer, B., McCormac, F.G., v. d. Plicht, J., and Spurk, M., 1998. INTCAL98 Radiocarbon age calibration 24,000 - 0 cal BP. *Radiocarbon* 40, 1041-1083.
- Stuiver, M., Reimer, P.J., Reimer, R., 2005. Calib Radiocarbon Calibration (<http://calib.qub.ac.uk/calib/>).
- Tedesco, K., Thunell, R., Astor, Y., Muller-Karger, F., 2006. The oxygen isotope composition of planktonic foraminifera from the Cariaco Basin, Venezuela: Seasonal and interannual variations. *Marine Micropalaeontology* 62, 180-193.
- Ternois, Y., Sicre, M.-A., Paterne, M., 2000. Climatic changes along the northwestern African continental margin over the last 30 kyrs. *Geophysical Research Letters* 27, 133-136.
- Tetzlaff, G., Peters, M., 1986. Deep-Sea sediments in the eastern equatorial Atlantic off the African coast and meteorological flow patterns over the Sahel. *Geologische Rundschau* 75 (1), 71-79.
- Thiede, J., 1983. Palaeogeography and palaeobathymetry: Quantitative reconstructions of ocean basins. *Tidal Friction and the Earth's Rotation II*. Brosche and Sündermann, Springer-Verlag, Berlin Heidelberg, 229-239.
- Thunell, R. C., W. B. Curry, Honjo, S., 1983. Seasonal variation in the flux of planktonic foraminifera: time series sediment trap results from the Panama Basin. *Earth and Planetary Science Letters* 64, 44-55.
- Van Camp, L., Nykjær, L., Mittelstaedt, E., Schlittenhardt, P., 1991. Upwelling and boundary circulation off Northwest Africa as depicted by infrared and visible satellite observations. *Progress in Oceanography* 26 (4), 3557-402.
- Vink, A., Zonneveld, K.A.F., Willems, H., 2000. Distributions of calcareous dinoflagellate cysts in surface sediments of the western equatorial Atlantic Ocean, and their potential use in palaeoceanography. *Marine Micropalaeontology* 38 (2), 149-180.
- Vink, A., Baumann, K.-H., Böckel, B., Esper, O., Kinkel, H., Volbers, A., Willems, H., Zonneveld, K.A.F., 2003. Coccolithophorid and dinoflagellate synecology in the South and Equatorial Atlantic; improving the palaeoecological significance of phytoplanktonic microfossils. In: Wefer, G., Mulitza, S., Ratmeyer, V., (Eds.), *The South Atlantic in the Late Quaternary – reconstruction of material budgets and Current Systems*. Springer, Berlin, 101-120.
- Vink, A., 2004. Calcareous dinoflagellate cysts in South and equatorial Atlantic surface sediments: diversity, distribution, ecology and potential for palaeoenvironmental reconstructions. *Marine Micropalaeontology* 50 (1-2), 43-88.
- Waelbroeck, C., Labeyrie, L., Michel, E., Duplessy, J.C., McManus, J.F., Lambeck, K., Balbon, E., Labracherie, M., 2002. Sea-level and deep water temperature changes derived from benthic foraminifera isotopic records. *Quaternary Science Reviews* 21, 295-305.
- Waelbroeck, C., Mulitza, S., Spero, H., Dokken, T., Kiefer, T., Cortijo, E., 2005. A global compilation of late Holocene planktonic foraminiferal $\delta^{18}\text{O}$ relationship between surface water temperature and $\delta^{18}\text{O}$. *Quaternary Science Reviews* 24, 853-868.
- Wefer, G., Fischer, G., 1993. Seasonal patterns of vertical particle flux in equatorial and coastal upwelling areas of the eastern Atlantic. *Deep-Sea Research* 40 (8), 1613-1645.
- Wendler, I., Zonneveld, K.A.F., Willems, H., 2002a. Calcareous cyst-producing dinoflagellates: ecology and aspects of cyst preservation in a highly productive ocean region. In: Clift, P.D., Kroon, D.,

- Gedicke, C., Craig, J. (Eds.), The Tectonic and Climatic Evolution of the Arabian Sea Region. Geological Society London Special Publications, vol. 195. London, 317-340.
- Wendler, I, Zonneveld, K.A.F., Willems, H., 2002b. Production of calcareous dinoflagellate cysts in response to monsoon forcing off Somalia: A sediment trap study. *Marine Micropalaeontology* 46, 1-11.
- Wien, K., Holz, C., Kölling, M., Schulz, H., 2006. Age models for pelagites and turbidites from the Cape Timiris Canyon off Mauritania. *Marine and Petroleum Geology* 23, 337-352.
- Zenk, W., Klein, B., Schröder, M., 1991. Cape Verde Frontal Zone. *Deep-Sea Reserach. Part A. Oceanographic Research papers* (38) 1, 505-530, Sup. 1, 1-2.
- Zhao, M., Eglinton, G., Haslett, S.K., Jordan, R.W., Sarnthein, M., Zhang, Z., 2000. Marine and terrestrial biomarker records for the last 35,000 years at ODP site 658C off NW Africa. *Marine Geochemistry* 31, 919-930.
- Zonneveld, K.A.F., 2004. Potential use of stable oxygen isotope composition of *Thoracosphaera heimii* for upper water column (thermocline) temperature reconstruction. *Marine Micropalaeontology* 50, 307-317.
- Zonneveld, K.A.F., Mackensen, A., Baumann, K.-H., 2007. Stable oxygen isotopes of *Thoracosphaera heimii* (Dinophyceae) in relationship to temperature; a culture experiment. *Marine Micropalaeontology* 64 (1-2), 80-90.

Chapter 3

Calcification depth of *Thoracosphaera heimii*; implications for palaeoceanographic reconstructions

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Abstract

For an optimal use of the stable oxygen isotopic signal and elemental composition of the calcareous photosynthetic dinoflagellate *Thoracosphaera heimii* in palaeoceanographic studies it is essential to gain detailed information about its depth habitat. To obtain this information we studied the vertical and horizontal distribution patterns of the photosynthetic dinoflagellate *T. heimii* in upper waters along three transects: an inshore-offshore gradient off Cape Blanc (CB), a south-north transect from CB to the Portuguese coast and a north-south transect off Tanzania. We compared cyst concentrations of living cells with concentrations of chlorophyll-*a*, salinity and with temperature at the sampling depth. To obtain insight in the seasonal variability the CB transect has been sampled at three different times of the year.

Living *T. heimii* cysts are found in the upper 160 m of the water column with highest concentrations in or just above the deep chlorophyll maximum. No significant correlation on the 95 % confidence interval between the cyst concentrations and the studied environmental parameters can be observed.

In both the Atlantic and Indian Ocean highest *T. heimii* were observed in regions where the upper water masses are not or only sporadically influenced by strong turbulences and contain relatively high nutrient concentrations. Low concentrations are found in areas with unstable upper water layers in the vicinity of active upwelling cells and river plumes.

The seasonal cyst production of *T. heimii* can be negatively related to the presence of upwelling filaments crossing sampling sites. Our study suggests that turbulence of the upper water masses is a major environmental factor influencing *T. heimii* production.

Keywords: Calcareous-walled dinoflagellates; calcification depth; deep chlorophyll maximum; NW Africa; Tanzania

3.1 Introduction

Recent studies show that the isotopic and elemental composition of the vegetative calcareous cysts of the photosynthetic dinoflagellate *Thoracosphaera heimii* can be used for the reconstruction of past upper ocean physical conditions such as sea surface temperatures (Gussone *et al.*, 2004; Zonneveld, 2004; Zonneveld *et al.*, 2007; Gussone *et al.*, *subm.*; Kohn *et al.*, *subm.*). For a sound interpretation of *T. heimii* based on isotope and elemental records, it is essential to have detailed information about the calcification depth and environmental requirements of *T. heimii*. Pilot studies carried out in the equatorial Atlantic Ocean suggest that *T. heimii* calcifies in the deeper part of the upper water column notably at the thermocline depth (Karwath *et al.*, 2000a). Since thermocline depth often co-varies with the position of the deep chlorophyll-*a* maximum (DCM) in these regions it has been suggested that the sedimentary isotope and elemental signal preserved by fossilized cysts might reflect the physical conditions of the DCM. However, the study of (Karwath *et al.*, 2000a) provides no direct information about the relationship between the position of the DCM and the living habitat of *T. heimii* or about the relationship between cyst calcification and physical conditions at the calcification depth. Furthermore, it documents the distribution of *T. heimii* from a restricted area based on a few data points only. Within this study, we intent to enhance this information and test if the generalisations made in previous studies about the calcification depth of *T. heimii* are correct. For this, we studied the *T. heimii* concentration in water samples from different water depths collected along an offshore-inshore transect off NW Africa in three different seasons, along a transect from Cape Blanc to the Portuguese Coast and along a transect off Tanzania. We compare the concentrations of full and empty cysts with the physical environmental parameters temperature, salinity and chlorophyll-*a* at the sampling depth as registered by CTD profiles.

3.2 Oceanographic settings

3.2.1 East Atlantic Ocean (off Cape Blanc – off Portugal)

The surface currents off the Portuguese coast are characterised by the Portugal Current (PC) that flowing southwards from about 46 °N to 36 °N between about 10 °W to 24 °W (Fig. 1). The PC is mainly supplied by the intergyre zone between the North Atlantic Current (NAC) and the Azores Current (AC) (Pollard *et al.*, 1996; Pérez *et al.*, 2001). Trade wind induced upwelling of cooler nutrient-rich water from depths about 100 to 300 m occur in summer from late May to early October (Smyth *et al.*, 2001). Particularly of Cabo da Roca filaments of upwelled water can extend up to 100 km offshore (Coelho *et al.*, 2002; Huthnance *et al.*, 2002). During the summer the open ocean is very oligotrophic (Peliz and Fiúza, 1999). In winter downwelling occurs due to southern winds leading to a convergence of warmer, oligotrophic water towards the

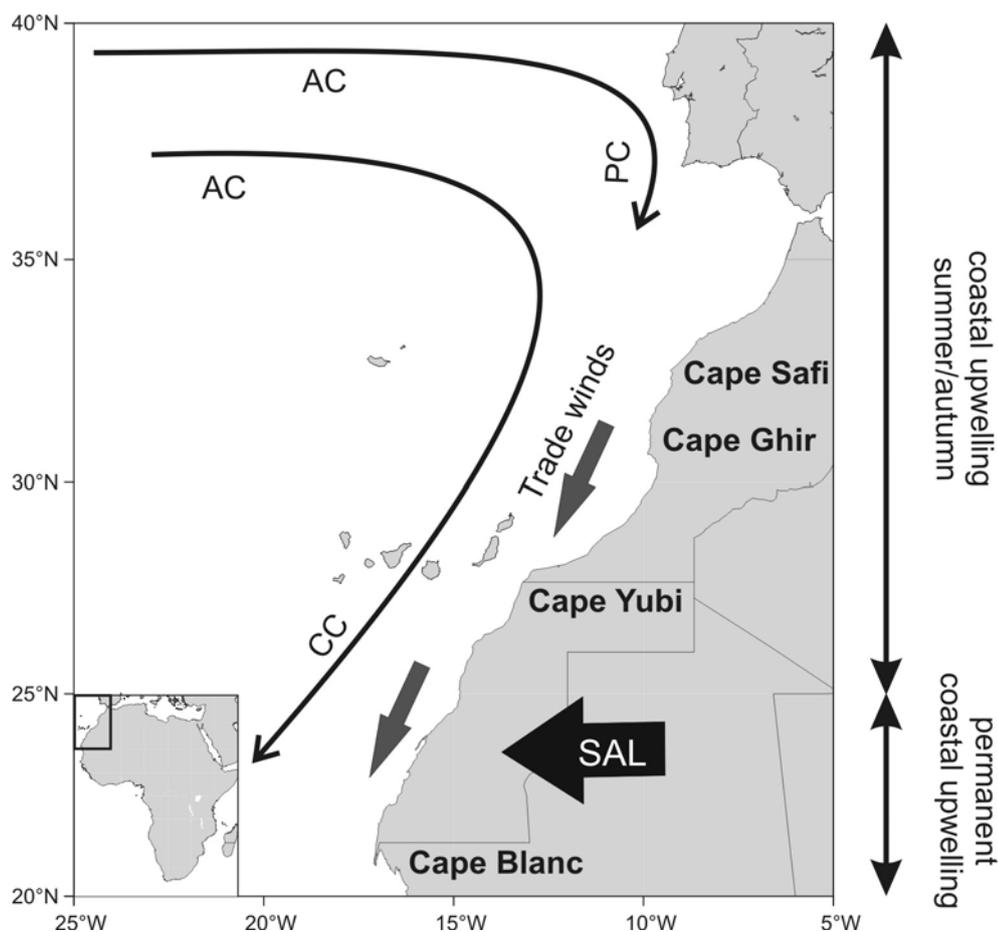


Fig. 1. Map showing the hydrographic and atmospheric settings off NW Africa. Thick arrows represent the wind system; thin arrows indicate the main surface water currents. AC, Azores Current; PC, Portuguese Current; CC, Canary Current; SAL Saharan Air Layer.

coast (Huthnance *et al.*, 2002). The PC is underlain by the North Atlantic Central Water (NACW; 100 – 600 m) and between 600 and 1500 m by the Mediterranean Outflow Water (MOW) (Schönfeld, 1997).

Further south, the PC continues as the southward flowing Canary Current (CC). Off Cape Blanc (CB) the CC detaches from the continental slope and forms the westward-flowing North Equatorial Current (NEC; Hagen and Schemainda, 1984; Schott *et al.*, 2002). The CC is underlain by the NACW and the South Atlantic Central Water (SACW; 200 – 400 m; Mittelstaedt, 1983, 1991; Barton *et al.*, 1998). Compared to the SACW, the NACW is slightly warmer, contains higher salinity and lower nutrient concentrations. The north-east trade winds that blow parallel to the coast lead to upwelling of these nutrient-rich waters promoting high primary productivity. Strength and persistence of upwelling show strong regional differences, depending on the meridional shift of the Intertropical Convergence Zone (ITCZ; Wefer and Fischer, 1993; Hernandez-Guerra and Nykjaer, 1997). Upwelling is persistent throughout the year between 20 °N and 25 °N whereas south of 20 °N upwelling is most intense in winter and spring. North of 25 °N coastal upwelling is predominant in summer and early fall. Upwelling is restricted to a narrow coastal band located about 20 to 30 km offshore. However, at pronounced capes (Cape Blanc, Cape Yubi and Cape Ghir) upwelled water can be transported in the form of large filaments and eddies up to 450 km offshore (Van Camp *et al.*, 1991; Nykjaer and Van Camp, 1994; Hagen, 2001). Off CB upwelling is persistent year-round with highest intensity in winter and spring when nutrient-rich SACW is the source of the upwelled water. Within the filaments high chlorophyll-*a* concentrations of up to 9.0 mg m⁻³ can be observed (Gabric *et al.*, 1993). At offshore regions that are not influenced by filaments chlorophyll-*a* values range from 0 - 1 mg/m⁻³ (Meggers *et al.*, 2002).

Apart from upwelling, terrigenous material from the land is transported into the area by either aeolian dust or by river discharge resulting in an enhancement of the bioproductivity in the upper waters. The majority of the Sahara and Sahel dust is transported into the region between 16 °N and 21 °N in the form of dust storms forced by the north-east trade winds and the African Easterly Jet (AEJ) (e.g. Sarnthein *et al.*, 1981; Sarnthein and Thiede, 1982; Tetzlaff and Peters, 1986).

3.2.2 Tanzania

The East African Indian Ocean is influenced by a strong monsoonal system. From June to October (SW monsoon) the air pressure contrast between the Tibetan plateaus and the south-eastern Indian Ocean region results in the development of a strong north-north-eastward blowing low level jet (Newell, 1959; Fig. 2a). In boreal winter (NE monsoon) the pressure difference reverses, leading to low level south-south-westward blowing winds and to a southward shift of the Inter-Tropical Convergence Zone (ITCZ; Fig. 2b). The SW monsoon is characterised by high cloud cover, rain, decreased temperature ($\sim 25^{\circ}\text{C}$) and irradiance values (McClanahan, 1988). During the NE monsoon both wind and surface circulation patterns are reversed, leading to high temperatures ($>30^{\circ}\text{C}$), low wind speed and calmer sea in the research area (Qasim, 1982; Schott, 1983, 1990; Smith *et al.*, 1991; Lugomela *et al.*, 2001; Lugomela *et al.*, 2002).

Surface waters of the research area are formed by the South Equatorial Current (SEC) that passes the northern part of Madagascar and splits into the south going Mozambique Current (MC) and the northward flowing East African Coastal Current (EACC)

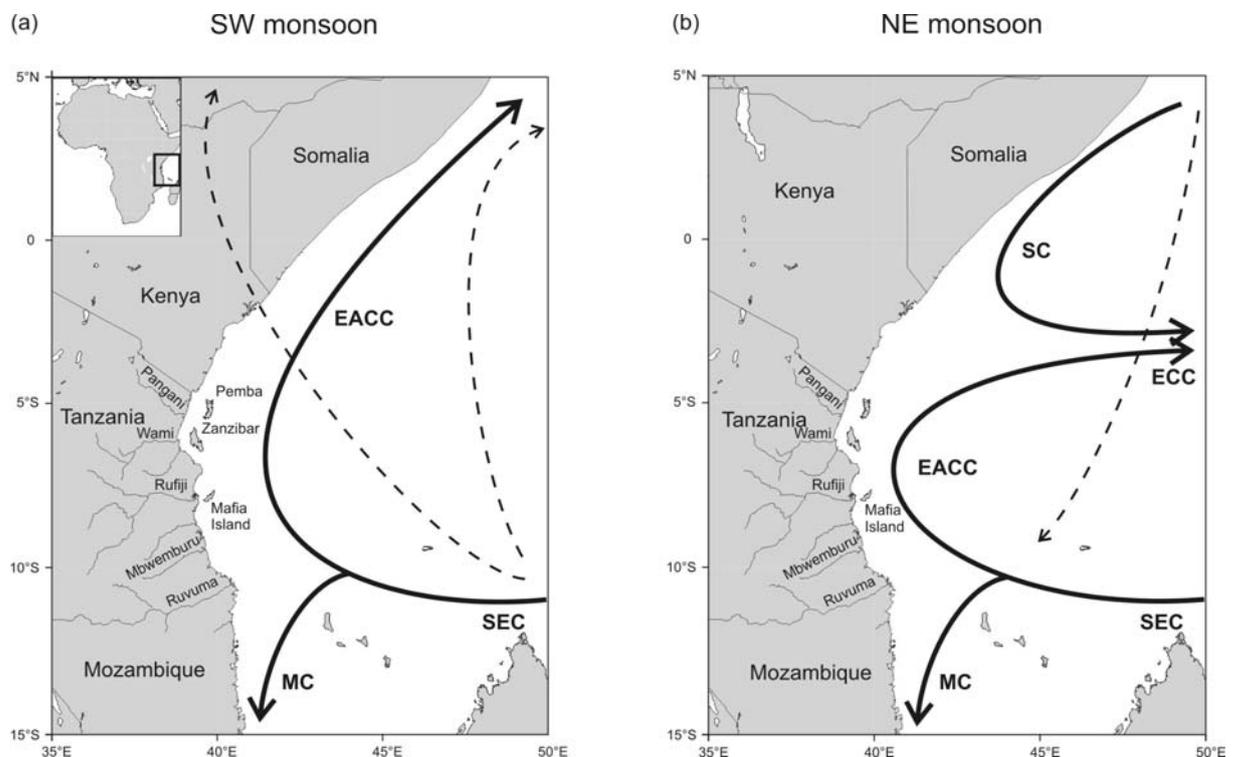


Fig. 2. Surface current patterns (arrows) and wind directions (dashed arrows) during the (a) SW and (b) the NE monsoons in the East African region. SC, Somali Current; EACC, East African Coastal Current; SEC, South Equatorial Current; MC, Mozambique Current; ECC, Equatorial Counter Current.

(EACC; Fig. 2a, b). During the SW monsoon the EACC flows northwards and cold, nutrient-rich waters are upwelled (Fig. 2a). The water column is strongly mixed and the thermocline is deepened (Morgans, 1962; Newell, 1957; Newell, 1959; Iversen, 1984). During the NE monsoon the EACC detaches the coast near 3 °S and forms together with the southward flowing Somali Current (SC) the Equatorial Countercurrent (ECC; Swallow *et al.*, 1991; Fig. 2b). During this time downwelling occurs. In contrast to the situation in the SW monsoon the water column is now more stable and the thermocline is shallower (e.g. Bryceson, 1977; Kithaka *et al.*, 1996; Kronkamp *et al.*, 1997; Paula *et al.*, 1998).

Two rainy seasons can be observed with “long” and heavy rains between March to May and the “short rain” between October and December (Oelfke Clark *et al.*, 2003). Five big rivers (Pangani, Wami, Rufiji, Mbwemburu and Ruvuma) and numerous minor rivers drain into the research area (Fig. 2a, b). Rufiji River and Ruvuma River are the largest rivers off Tanzania. River discharge is dependent on the inland rainfall leading to higher discharges after the inland rain season in may (McClanahan, 1988). Salinity is lowest at the onset of the SW monsoon when river discharge is at a minimum.

There are numbers of large and small islands and reefs along the coast. The large islands include Zanzibar (Unguja and Pemba) and Mafia Island (Fig. 2a, b). The continental shelf extends about 4 km offshore with exceptions in the vicinity of the Pemba and Mafia Islands where the shelf extends only 80 m (Francis and Bryceson, 2001). Between the coast and Zanzibar the Pemba Channel is situated with depths of about 900 m.

In contrast to NW Africa, nutrient concentrations off Tanzania are much lower. In the research area, highest chlorophyll-*a* concentrations are found during the NE monsoon and rainy seasons due to a shallower thermocline and a more stable water column (e.g. Bryceson, 1977; Kithaka *et al.*, 1996; Kronkamp *et al.*, 1997; Paula *et al.*, 1998).

3.3 Materials and methods

Seawater samples were collected along an inshore-offshore and north-south transect during three cruises off NW Africa with the RV Poseidon (P 344-1) from October/November 2006, RV M.S. Merian (MSM 4/4B) March 2007 and RV Poseidon

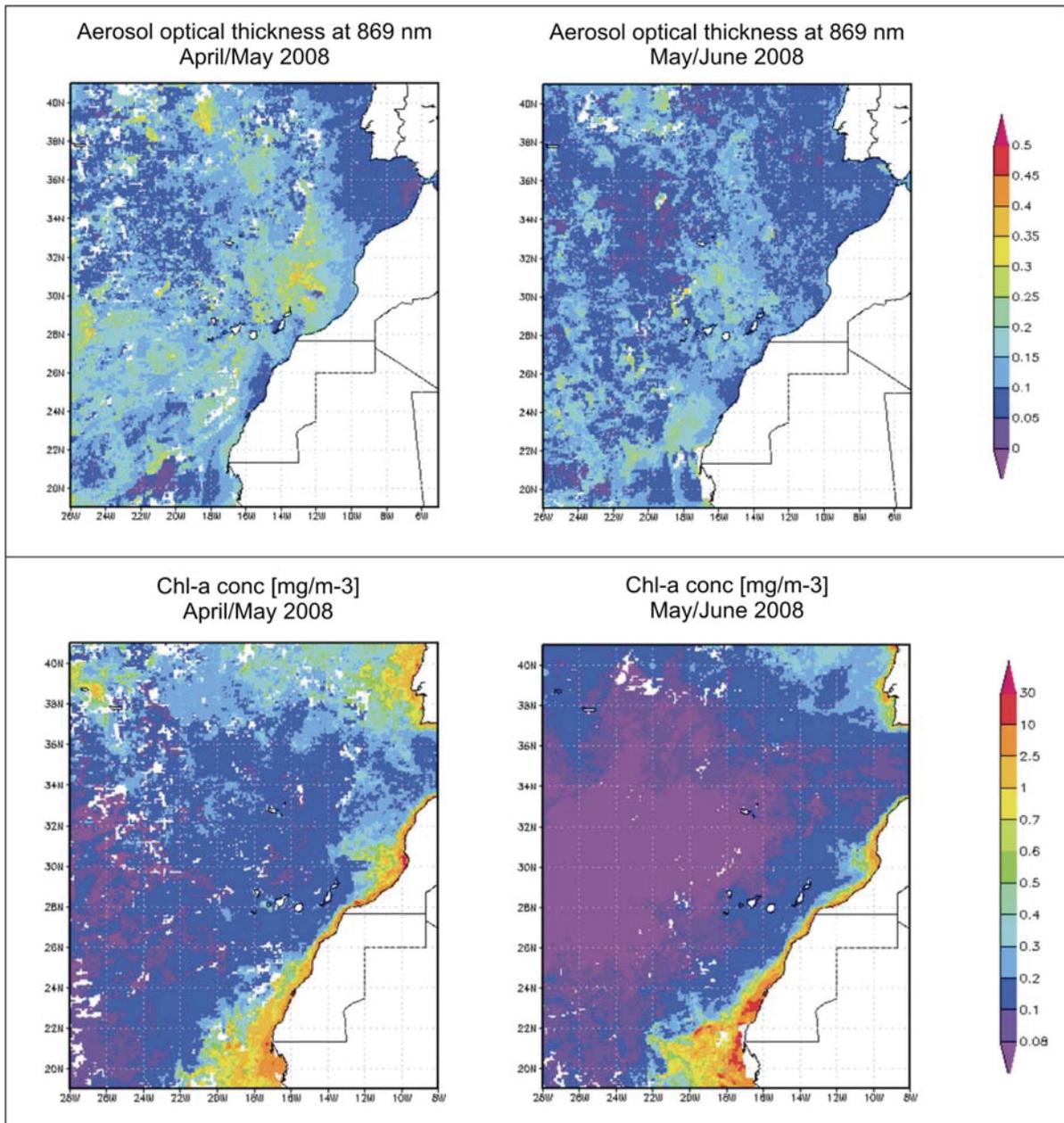


Fig 3. (a) Chlorophyll-*a* concentrations [mg/m³] in April/May and May/June 2008 off NW Africa and the Portuguese coast. (b) Aqua aerosol optical thickness at 869 nm in April/May and May/June 2008 off NW Africa and the Portuguese coast. Generated by Giovanni (NASA).

(P 366-1 + P 366-2) May 2008. During cruise P 344-1 no samples deeper than 50 m were taken due to logistic problems.

Satellite images of the region document moderate coastal upwelling in November 2006 and March 2007. In May/June 2008 large upwelling filaments passed the sample region. Just previous to the sample cruise P366-1 and P366-2 enhanced amount of Sahara dust was transported into the region north of the Canary Islands, as

reflected by enhanced aerosol thickness (Fig. 3). No indication of enhanced post-cruise dust input into the region is observed in 2006 and 2007.

South Indian Ocean samples have been collected along several inshore-offshore transects along the coast off Somalia with the RV Meteor (M 75-2) in February 2008. Previous to the cruise heavy rains over southern Tanzania lead to large river input off the Ruvuma River (Pätzold *et al.*, *subm.*).

Samples have been collected using a CTD/Rosette combination containing 18 x 10 l NISKIN™ bottles and a SBE19+ CTD that has been expanded by an additional oxygen and chlorophyll-*a* sensor.

Details on sampling intervals, sample depths and volume are given in Appendix 1. Data were recorded and processed using the SBE 5.37 software.

10 l to 50 l of seawater was pre-filtered through 75 µm and a 20 µm stainless steel sieves. Additionally the material was filtered through a 10-µm polycarbonate filter (diameter 50 mm) using a vacuum pump system. The residues of the 10 - 20 µm fraction was oven-dried overnight at 60 °C and stored in small petri-dishes until further treatment.

For further treatment the dried residue was brought into suspension in tap water. To remove soot from the ships engine and small dust particles the suspension was thoroughly sieved again with 20 µm and 10 µm stainless-steel sieves. Water volume was reduced by centrifuging (3600 r/min/5 min) and the material was transferred to eppendorf cups. A fixed volume was embedded in glycerine gelatine on an object glass for light microscopic analysis. Whole slides were counted under polarised light. Depending on the amount of material one to three (all) slides per sample were analyzed. Care has been taken to distinguish between cells with cell content (full) and cells without cell content (empty).

We extrapolated our counts to a standardized volume of 100 l of sea water. To test the relationship between the absolute values of the measured environmental parameters a linear regression has been performed using the statistical package SPSS. An ANOVA table of the relationships is given in Table 1. To determine potential relationship between full and empty shells and environmental parameters, redundancy analyses (RDA) were carried out on the dataset of NW and SE Africa using the statistical package CANOCO for Windows version 4.02 (ter Braak and Smilauer, 2002). The choice for using RDA for the current datasets was based on the outcome of initial

detrended correspondence analyses (DCA) that documented a linear type of ecological responses for both datasets.

Regression variables	Model	R	R ²
Temp-Th (full)	linear	0.1367	0.0187
Depth-Th (full)	linear	0.0510	0.0026
Sal-Th (full)	linear	0.0600	0.0036
O ₂ -Th (full)	linear	0.0173	0.0003
Chl-Th (full)	linear	0.0520	0.0027
Temp-Th (empty)	linear	0.0700	0.0049
Depth-Th (empty)	linear	0.1338	0.0179
Sal-Th (empty)	linear	0.1480	0.0219
O ₂ -Th (empty)	linear	0.1077	0.0116
Chl-Th (empty)	linear	0.1192	0.0142
Temp-Th (total)	linear	0.0529	0.0028
Depth-Th (total)	linear	0.0490	0.0024
Sal-Th (total)	linear	0.1158	0.0134
O ₂ -Th (total)	linear	0.0812	0.0066
Chl-Th (total)	linear	0.1072	0.0115

Tab 1. Linear regression analyses between *Thoracosphaera heimii* (Th full, empty and sum) and environmental parameters (temp-temperature, depth, sal-salinity, O₂-oxygen, Chl-chlorophyll-*a*, NO₃-nitrate, PO₄-phosphate, Si-silicate).

3.4 Results

Thoracosphaera heimii is observed in all investigated areas and seasons (Figs. 4 - 8).

3.4.1 NW Africa

Along the inshore-offshore gradient off Cape Blanc (CB) highest abundances of full and empty *Thoracosphaera heimii* cysts are observed at the most offshore sites whereas, lowest concentrations are registered at the innermost stations (Figs. 4 - 6). A trend from decreasing chlorophyll-*a* concentrations (mean of entire depth profile – mdp) along the inshore-offshore

The presence of large upwelling filaments in May 2008 is documented by satellite images of the regions (Fig. 3). Temperature and salinity are comparable during the different seasons (Figs. 4 - 6).

Along the transect from CB to the Portuguese Coast, highest concentrations of *T. heimii* (mdp) are observed just right north of the Canary Islands (13031, 13032; Fig. 7). South of the Canary Islands (13024, 13030), off Cape Ghir (13033) and off Cape

Safi (13034) nearly no full shells were found, although, a relatively large number of empty shells was observed. Further north to the Portuguese Coast full shells are nearly absent and the concentrations of empty shells are decreasing. Chlorophyll-*a* values (mdp) are relative high south of the Canary Islands and much lower north of these islands. Off the Portuguese coast relatively high chlorophyll-*a* concentrations are observed because of

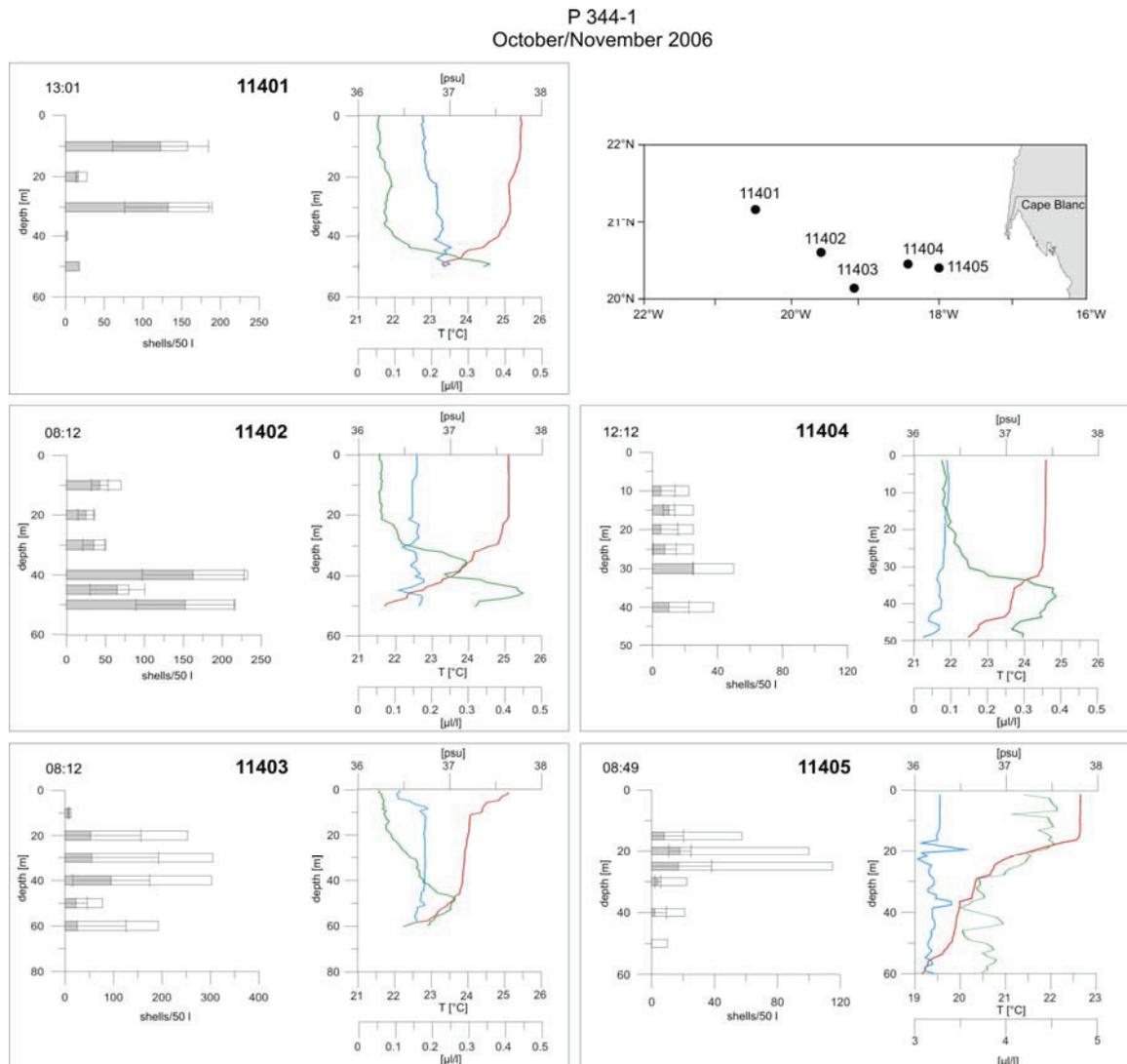


Fig. 4. Vertical distribution of *Thoracosphaera heimii*, cruise P344-1, October/November 2006 and measured CTD data (temperature, salinity and chlorophyll-*a*). Open bars show empty shells, black bars show full shells. Arrows indicate arithmetic mean of total *T. heimii* content of the entire depth profile. Temperature: red line. Salinity: blue line. Chlorophyll-*a*: green line.

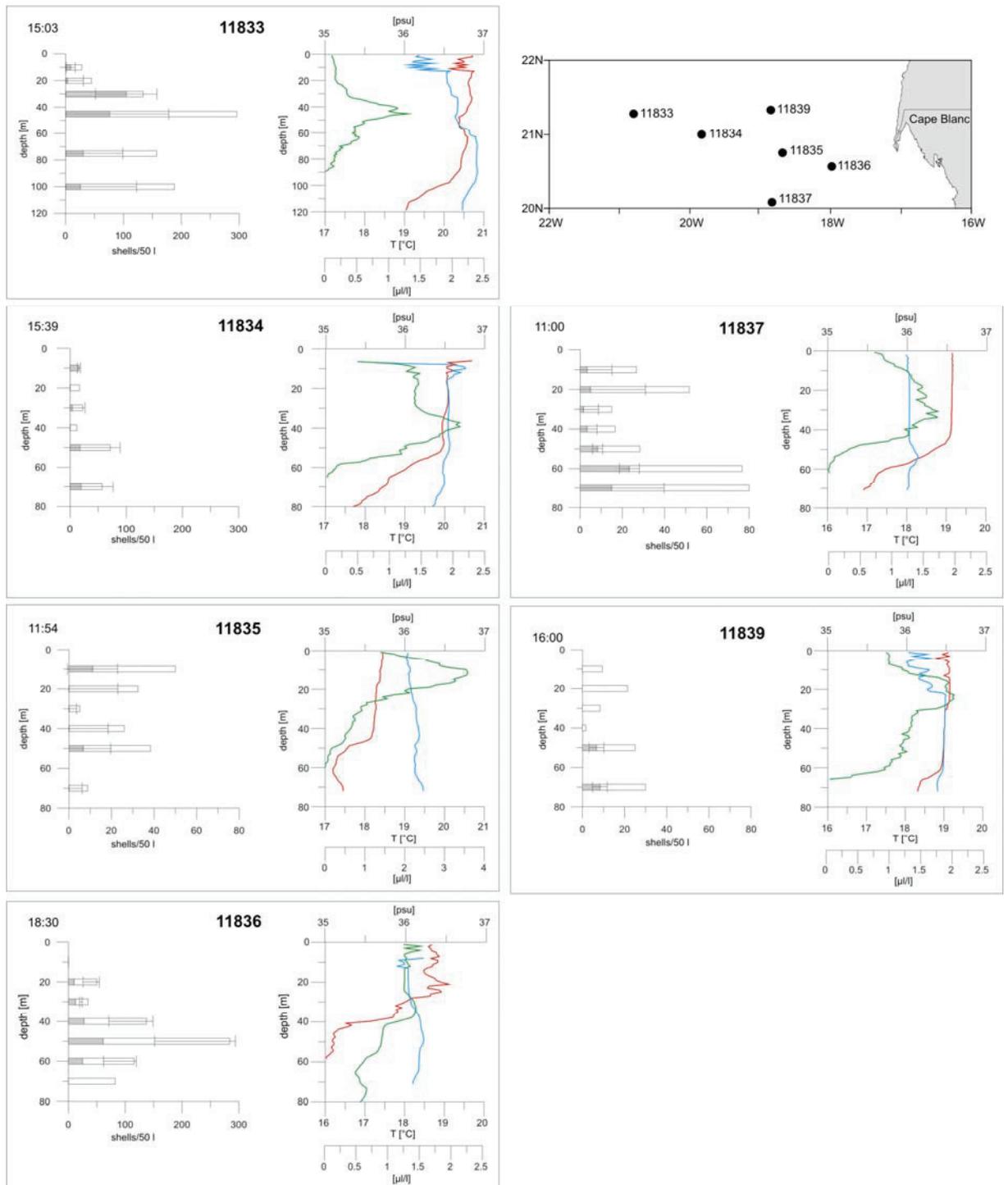
MSM4/4B
March 2007

Fig. 5. Vertical distribution of *Thoracosphaera heimii*, cruise MSM4/4B, March 2007 and measured CTD data (temperature, salinity and chlorophyll-*a*). Open bars show empty shells, black bars show full shells. Arrows indicate arithmetic mean of total *T. heimii* content of the entire depth profile. Temperature: red line. Salinity: blue line. Chlorophyll-*a*: green line.

P366-1
May 2008

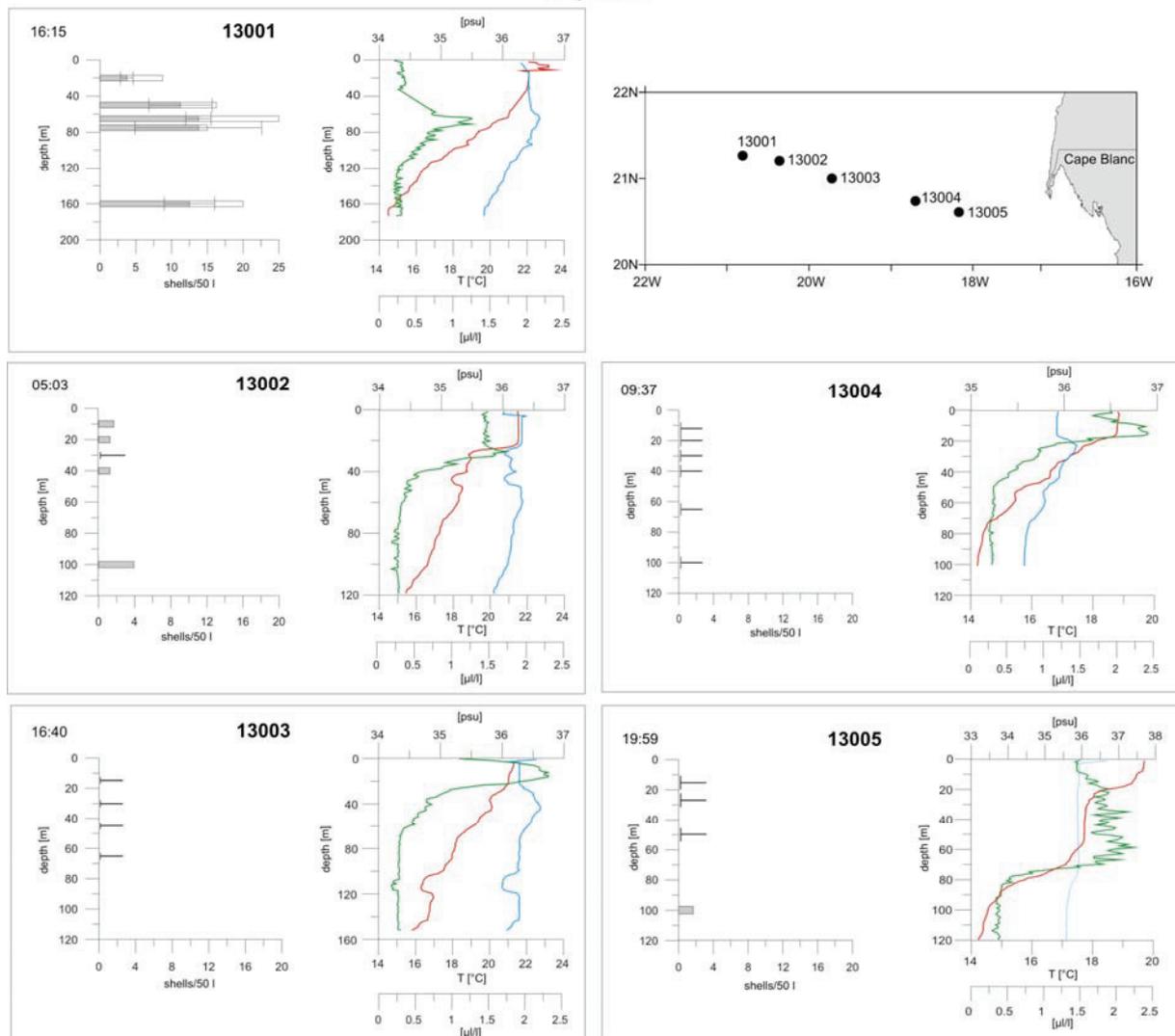
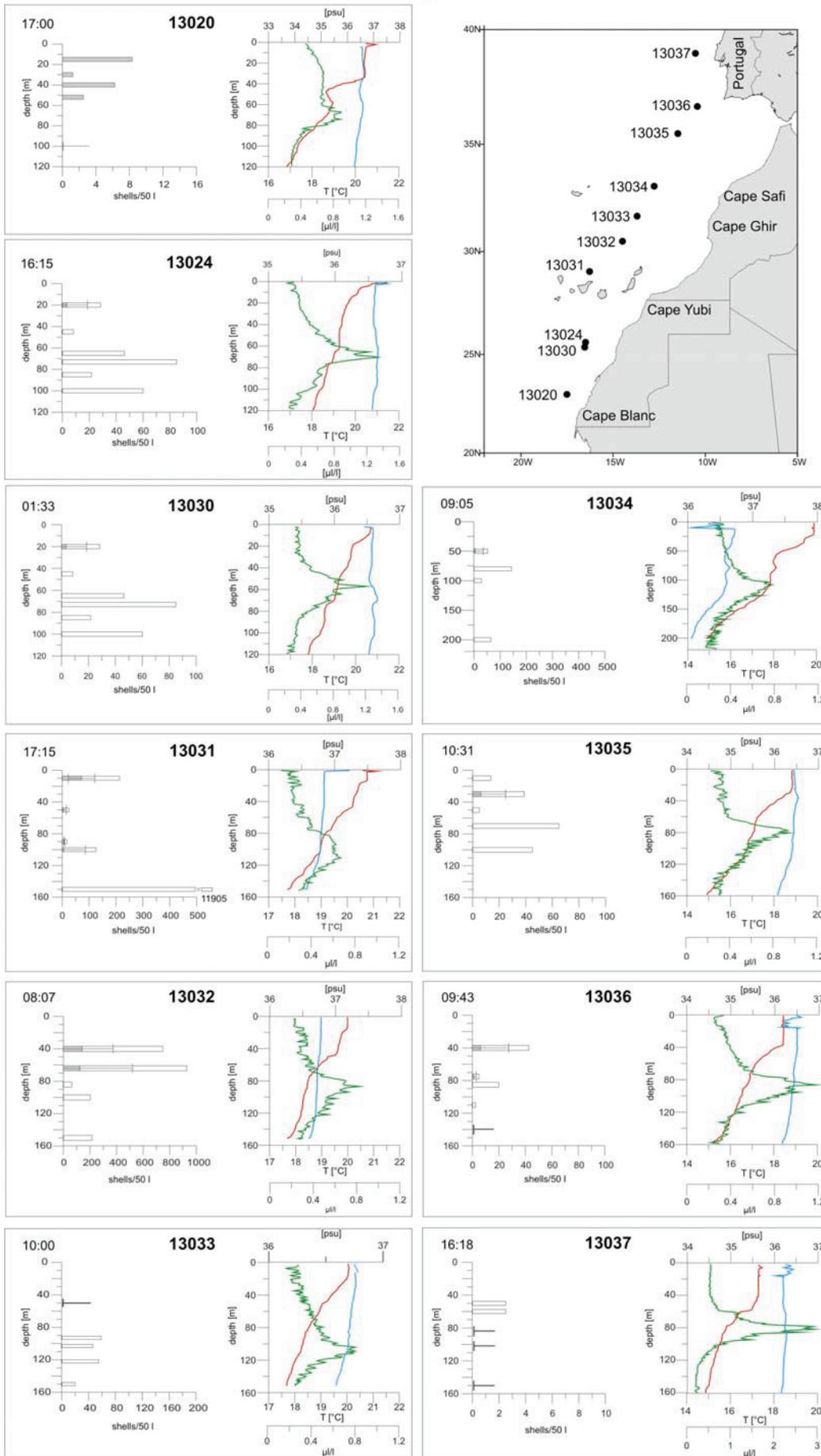


Fig. 6. Vertical distribution of *Thoracosphaera heimii*, cruise P366-1 off Cape Blanc, May 2008 and measured CTD data (temperature, salinity and chlorophyll-*a*). Open bars show empty shells, black bars show full shells. Arrows indicate arithmetic mean of total *T. heimii* content of the entire depth profile. Temperature: red line. Salinity: blue line. Chlorophyll-*a*: green line.

Fig. 7. Vertical distribution of *Thoracosphaera heimii*, cruise P366-1 north off Cape Blanc and P366-2, May 2008 and measured CTD data (temperature, salinity and chlorophyll-*a*). Open bars show empty shells, black bars show full shells. Arrows indicate arithmetic mean of total *T. heimii* content of the entire depth profile. Temperature: red line. Salinity: blue line. Chlorophyll-*a*: green line.

P366-1/2
May 2008



M75-2
February 2008

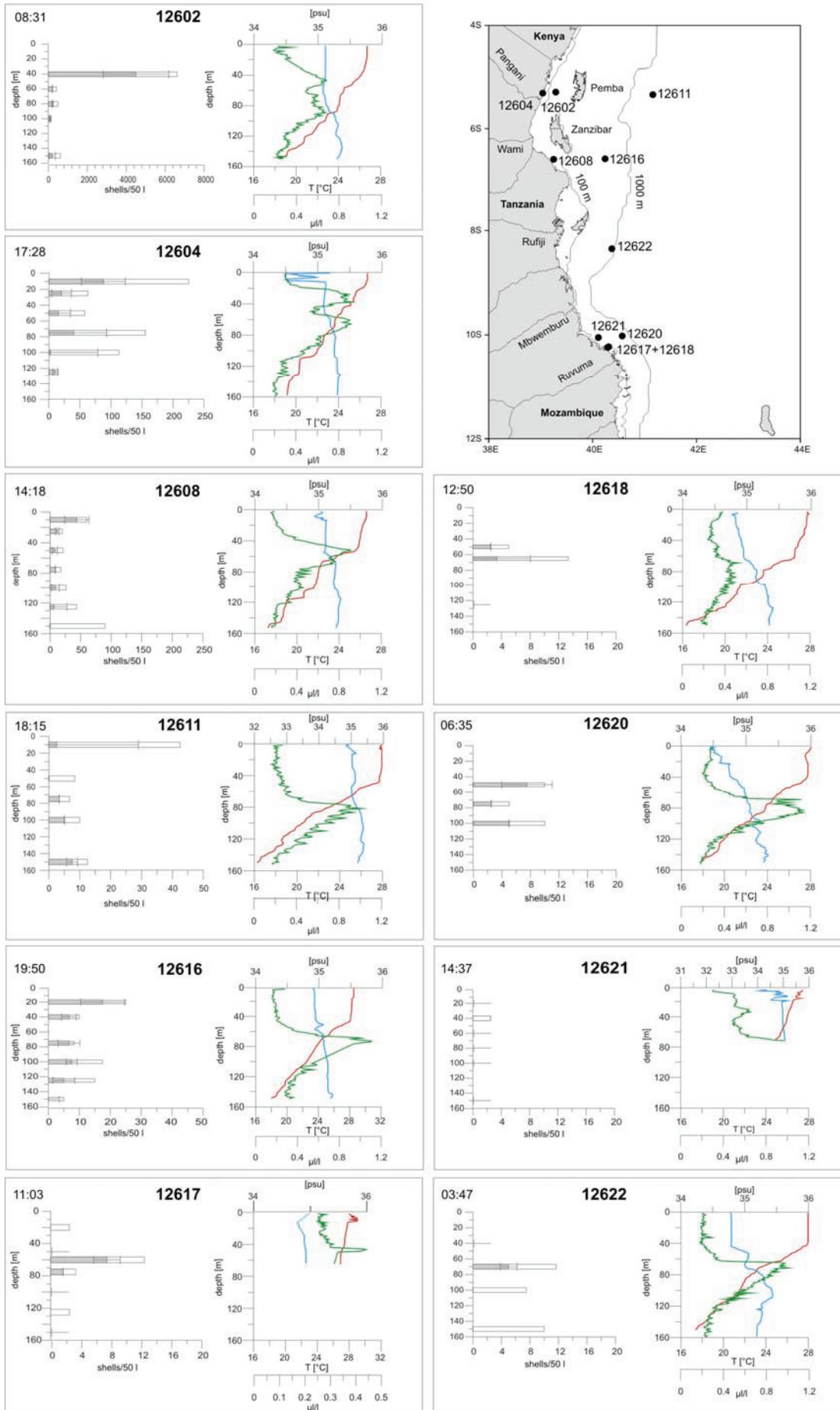


Fig. 8. Vertical distribution of *Thoracosphaera heimii*, cruise M75-2, February 2008 and measured CTD data (temperature, salinity and chlorophyll-*a*). Open bars show empty shells, black bars show full shells. Arrows indicate arithmetic mean of total *T. heimii* content of the entire depth profile. Temperature: red line. Salinity: blue line. Chlorophyll-*a*: green line.

the vicinity of the coastal upwelling. On the south-north gradient from CB to the Portuguese Coast mean temperatures are decreasing and salinity is lowest at the northernmost station.

3.4.2 SE Africa

Off Tanzania a north-south gradient is found with highest abundances of *Thoracosphaera heimii* (mdp) in the northern part of the region (Fig. 8). High concentrations of *T. heimii* are observed in the Pemba channel (samples GeoB 12602, 12604, 12608). Lowest concentrations are registered in the vicinity of the Ruvuma river outflow.

Chlorophyll-*a* concentrations are quite low (0.2 to 1.2 $\mu\text{l/l}$) throughout the whole area. Sea surface temperatures are relative to the Atlantic sites high throughout the region. Salinity concentrations were constant except from GeoB 12617 off the Ruvuma River mouth. Here, salinity concentrations were relatively low due to the large river plume.

3.4.3 Vertical distribution of *Thoracosphaera heimii* in relation to environmental parameters

Cysts with cell content (full cysts) can be recorded between 0 to 160 m with highest concentrations in the upper 100 m. No significant correlation between full cyst concentrations and absolute values of chlorophyll-*a*, temperature and salinity (95 % confidence interval) has been found (see Appendix 1).

At the majority of the sites the maximum concentrations of full shells can be observed within and immediately above the DCM. Maximum abundances of empty cells are generally observed below the position of the DCM. The vertical distribution of empty and full cysts is similar during day and night time.

3.5 Discussion

Within our study we distinguish between “empty” and “full” cells. Cysts that contain cell content (full cells) represent the living planktonic stage in the life cycle of *Thoracosphaera heimii*. Culture and sediment trap studies indicate that new cysts are produced about once a day in a process that takes one to a few hours (e.g. Inouye and Pienar, 1983; Wendler *et al.*, 2002b). During this process, a cyst hatches through a predefined opening, remains shortly in a motile planktonic stage to become quickly immobile during the formation of a new calcareous wall. Although the ability of diel migration up to some tenths of metres is well known for several dinoflagellate species, the motile stage of *T. heimii* is only active from three minute to a few hours (Anderson, 1985; Liebermann *et al.*, 1994; Kamykowski *et al.*, 1998). We can therefore assume that *T. heimii* is able to move vertically over a short distance only (Inouye and Pienar, 1983). As result of the fast reproduction cycle the presence of full cysts in the water column reflects the calcification depth of *T. heimii* or cysts that have been transported over small distances only.

Empty cysts, might represent either recently departed cysts or are already moved to deeper water layers. Although there is only little known about the sinking rates of *T. heimii*, sediment trap studies of the Cape Blanc upwelling area suggest that its sinking rates are quite fast of about 139 m/d (Vink, 2004). This is in the range of the sinking velocities of diatom and coccolithophore based phytoplankton aggregates and “slower” faecal pellets that are much faster than marine snow that can remain in suspension in the water column for longer time intervals (e.g. Ploug *et al.*, 2008; Fischer and Karakas, 2009). We therefore assume that the majority of the empty cysts observed in our water samples have been transported.

3.5.1 Lateral distribution

Although *Thoracosphaera heimii* cysts are observed in all studied sites their concentrations vary remarkably. Lowest *T. heimii* concentrations are found in regions characterised by high total bioproductivity reflected by high chlorophyll-*a* concentrations in the upwelling influenced regions off Portugal, off Cape Blanc (CB) and near the Ruvuma river outlet. These regions are characterised by high nutrient concentrations. First studies on the ecology of calcareous dinoflagellate cysts suggested *T. heimii* to be characteristically produced in high amounts in regions with reduced

productivity, probably related to relatively stratified conditions of the upper water column (Höll *et al.*, 1998; Höll *et al.*, 1999). However, later work showed that stratification and the presence of a well developed thermocline are more important than oligotrophy (e.g. Vink, 2004 and references therein; Richter *et al.*, 2007). Within our research area the trophic state of the upper waters strongly co-varies to the presence of turbulence. Whereas, off Portugal and off Cape Blanc this is related to the presence of coastal upwelling, in the Indian Ocean it is related to the presence of river plumes.

Along the CB transect and near Portugal we observe highest cyst concentrations in the more offshore regions outside the direct upwelling cells. Here, the water column is more stable but nutrient concentrations are relatively high throughout the year (Wendler *et al.*, 2002a; Wendler *et al.*, 2002b; Richter *et al.*, 2007). Lowest cyst concentrations were observed in the vicinity of active upwelling cells where turbulence is strong. This is in agreement with detailed surveys of the distribution of *T. heimii* in surface sediments off NW Africa show highest sedimental cyst concentrations just outside the regions of active upwelling (Richter *et al.*, 2007). Off Tanzania, highest concentrations of *T. heimii* are observed in the north of the research area in the Pemba channel. Here, the current velocity of the EACC is low and the residence time of the water in the shallower parts is high. The offshore islands (Zanzibar and Pemba) protect the Pemba channel resulting in a stable upper water column (Bryceson, 1977). In the south, lowest cyst concentrations are found south of 8 °S especial in the Ruvuma River and Rufiji River plumes. In this area the surface current velocity was high at sampling times and off the Ruvuma River a large freshwater plume with major suspension load was present as result from strong rainfalls over southern Tanzania that had taken place just previous to the sampling cruise. The strong current velocities and the presence of the plume forced a rather turbulent upper water layer with a remarkable low light penetration depth. We assume that both factors might have hampered cyst production of *T. heimii*. A negative relationship between the presence of river drainage water and cyst accumulation of *T. heimii* is also known from the Amazon River area where extreme low concentrations of *T. heimii* cysts are observed in upper sediments below the discharge plume and highest abundances in the more oceanic region beyond the influence of the river (Vink *et al.*, 2000). We therefore that turbulence in combination with light penetration might be the most important environmental factor negatively influencing the cyst production of *T. heimii*.

However, turbulences and light appear not to be the most important steering factor in all studied regions as we observe low *T. heimii* concentrations in waters off Tanzania in the north-east of our research area (GeoB 12611, 12616, 12622). Here, the open ocean waters characterise the upper water column and turbulence is very low. Temperatures are very high at these sites. Culture experiments and field studies have documented that *T. heimii* tolerates a broad temperature range between about 13 and 28 °C (e.g. Karwath *et al.*, 2000a; Zonneveld *et al.*, 2000; Vink, 2004). The high temperatures around 28 °C in surface waters off Tanzania lie near the upper limit of the temperature tolerance observed in culture experiments (Fig. 8). We therefore assume that temperature might have been the limiting factor influencing *T. heimii* production in this local region. At all other studied sites temperature values are in the tolerance range of *T. heimii* and there is no significant relationship between the concentrations of full cysts and temperature (Fig. 4 – 7, Appendix 1).

The same holds for salinity. Our CTD data reveal the salinity varies between 35.7 to 36.9 psu off NW Africa and off Portugal, and 34.4 to 35.4 psu off Tanzania (Figs. 4 - 8). Culture and field studies reveal that *T. heimii* tolerates a range of 33.8 – 37.5 psu (Karwath *et al.*, 2000a; Karwath *et al.*, 2000b; Vink, 2004). Our salinity data lie within this range and we therefore assume that within our study salinity was not a major factor influencing *T. heimii* production.

The highest cyst concentrations we observe in this study are found in the upper waters of the region just north of the Canary Islands (CI). This latter area is not influenced by upwelling resulting in a stable water column throughout the year. Nutrient and trace elements are brought into this area by frequently occurring dust storms that transport large amount of Saharan Dust into the region. Satellite derived information about the aerosol thickness reveals that an event of enhanced dust input occurred in this area just previous to the water sampling (Fig. 3). We therefore assume that this event might have enhanced nutrient- and trace element input improving the conditions for *T. heimii* production. Sea-water samples south of the CI and north of the CB region (between ~ 22 °N – 28 °N) exhibit much lower concentrations of full shells than off CB although relatively large numbers of empty shells can be observed (Figs. 4 - 7). North of about 25 °N upwelling has a seasonal character whereas year round upwelling can be found south of this latitude. Our samples were taken in May at the end of the non-upwelling period where chlorophyll-*a* and nutrient concentrations are low (Fig. 3).

3.5.2 Seasonal distribution

In Cape Blanc (CB) area, only a small seasonal difference in cyst distribution in the different sample seasons can be observed (Figs. 4 - 7). Compared to November 2006 and March 2007 slightly lower concentrations are observed in May 2008. In May 2008 a large upwelling filament covers the sample region whereas in the other sample intervals upwelling had a more coastal character (Fig. 3). Assuming turbulence being a major steering parameter, the less stable conditions in upwelling filaments might explain these observations. Our findings are in agreement with results of recent sediment trap studies off CB that show only a slight seasonal difference in *Thoracosphaera heimii* production with somewhat lower cyst production at times of enhanced upwelling (Richter, 2009). However, a sediment trap study from the Arabian Sea documents a much stronger seasonal signal between the SW-monsoon upwelling period and the non-upwelling interval (Wendler *et al.*, 2002a; Wendler *et al.*, 2002b). Here highest accumulation rates of *T. heimii* were found at the end of the SW monsoon when active upwelling is terminating. At this time period nutrient concentrations in the upper water column are relatively high but turbulence is low. This indicates that the seasonal production of *T. heimii* is region dependent.

3.5.3 Vertical distribution

Thoracosphaera heimii is abundant throughout the entire upper water column especially above 100 m depth. With some exceptions no full cysts are observed at depths below 130 m. In most samples, we observe highest full *T. heimii* cysts in or immediately above the deep chlorophyll-*a* maximum (DCM) (Figs. 4 - 8). This confirms the suggestions made in earlier that highest abundances of *T. heimii* might be linked to the position of the DCM (Karwath *et al.*, 2000c; Vink *et al.*, 2003; Zonneveld, 2004). We observed this relationship in both, the Atlantic Ocean in different seasons as well as in the Indian Ocean. We therefore assume that this is a general character of *T. heimii*.

Culture experiments show that *T. heimii* tolerates low irradiances under 1 % PAR and can withstand long phases without having light (Karwath, 2000). Therefore, it has been suggested that it might migrate in line with the diurnal movement of the 1 % PAR boundary. Our data do not show any significant correlation between time of the

day and depth habitat. We therefore assume that *T. heimii* is produced at a stable position in the water column throughout the day.

3.5.4 Implications for palaeoceanographic reconstructions based on isotopic or elemental signals

Our study documents that *Thoracosphaera heimii* is likely to be produced in a restricted part of the upper water column not showing diurnal vertical migrations. This implies that the isotopic and elemental compositions of fossil cysts will reflect environmental conditions of this water layer at times of deposition. This together with the fact that *T. heimii* is an photosynthetic organism, is produced in a short time interval, has a broad geographical distribution and can relatively easily be isolated from the surrounding sediments gives the use of this species advantage over several conventional used proxies where ontogenetic aspects, the presence of symbionts, vertical migration, a restricted geographic distribution etc. might hamper its usability. The observation that within the Cape Blanc region cyst production is more or less equal throughout the year suggest that in this region the isotopic and elemental composition reflect mean annual conditions. More information about the seasonal production of *T. heimii* in other regions is required to obtain information if this is the case in these other regions as well.

3.6. Conclusions

Thoracosphaera heimii is produced in the upper water column at all studied sites. Highest concentrations are found in regions where upper waters are characterised by low turbulence and high nutrient concentrations. Turbulence and related to that light penetration are the major environmental factors influencing the cyst production in the research areas. In the northerneast part off Tanzania high upper ocean temperatures might hamper cyst production. At the majority of the studied sites *T. heimii* is produced at or just above the deep chlorophyll maximum depth suggesting this to be the living depth of the species.

In the Cape Blanc region cyst production is generally constant throughout the year indicating that the isotopic and elemental compositions of fossilized associations in this region reflect mean annual conditions.

3.7 Acknowledgements

Thanks are given to Monika Kodrans-Nsiah and Ilham Bouimetarhan, as well as all cruise participants and the crews of P 344-1, MSM4/4B, M75-2, P366-1 and P366-2 for recovering the investigated water samples. The manuscript benefitted from helpful comments of Marum working group A9. We also thank all members of the working group of Historical Geology and Palaeontology (University of Bremen) for their general assistance and openness to discussions. The images and data used in this study were acquired using the GES-DISC Interactive Online Visualization and Analysis Infrastructure (Giovanni) as part of the NASA's Goddard Earth Sciences (GES) Data and Information Services Center (DISC). This research was funded through DFG-Research Center / Excellence Cluster „The Ocean in the Earth System“. This is contribution unknown yet.

3.8 Appendix

Appendix 1. Water samples of all cruises and environmental data. Local time: begin of sampling, sampling time approximately 35 min.

Sample	Date	Depth [m]	Lat (N)	Lon (W)	Start CTD local time	Volume sampled [l]	Th empty (shells/50l)	Th full (shells/50l)	Sum	Temp [°C]	Sal [psu]	O2 [ml/l]	Chl [µl/l]	Time [UTC]
P344														
11401-8	23.10.2006	10	21°16.50	20°48.50	13:15	20	35	123	158	25.44	36.71	3.12	0.05	13:15
11401-8		20			13:15	20	13	15	28	25.17	36.78	3.15	0.09	
11401-8		30			13:15	20	53	133	185	25.15	36.87	3.21	0.08	
11401-8		40			13:15	20	0	3	3	24.82	36.88	3.29	0.10	
11401-8		50			13:15	20	0	18	18	23.39	36.92	3.24	0.34	
11402-2	24.10.2006	10	20°59.59	19°59.59	08:12	20	28	43	70	25.10	36.59	4.70	0.06	08:12
11402-2		20			08:12	20	10	25	35	25.10	36.58	4.72	0.07	
11402-2		30			08:12	20	15	35	50	24.52	36.47	4.73	0.15	
11402-2		40			08:12	20	70	163	233	23.53	36.62	4.80	0.25	
11402-2		45			08:12	20	15	65	80	22.38	36.53	4.62	0.45	
11402-2		50			08:12	20	63	153	215	21.69	36.65	4.16	0.32	
11403-2	25.10.2006	10	20°14.05	19°14.55	08:12	20	5	8	13	24.10	36.70	4.85	0.07	08:12
11403-2		20			08:12	20	200	53	253	24.01	36.71	4.95	0.09	
11403-2		30			08:12	20	250	55	305	23.93	36.73	4.89	0.14	
11403-2		40			08:12	20	208	95	303	23.87	36.73	4.86	0.18	
11403-2		50			08:12	20	55	23	78	23.46	36.72	4.77	0.25	
11403-2		60			08:12	20	168	25	193	21.97	36.57	4.41	0.17	
11404-4	26.10.2006	10	20°45.20	18°42.15	12:12	20	18	5	23	24.57	36.36	4.69	0.08	12:12
11404-4		15			12:12	20	15	10	25	24.55	36.34	4.66	0.09	
11404-4		20			12:12	20	20	5	25	24.52	36.32	4.61	0.13	
11404-4		25			12:12	20	18	8	25	24.41	36.28	4.69	0.19	
11404-4		30			12:12	10	25	25	50	23.69	36.27	4.58	0.39	
11404-4		40			12:12	20	28	10	38	21.45	36.08	4.10	0.21	
11405-2	28.10.2006	15	20°39.55	18°00.28	12:12	20	38	20	58	22.21	36.07	4.52	0.37	08:49
11405-2		20			08:49	20	55	45	100	20.75	36.18	4.15	0.28	
11405-2		25			08:49	20	73	43	115	20.33	36.21	3.70	0.21	
11405-2		30			08:49	20	13	10	23	20.26	36.23	3.76	0.17	
11405-2		40			08:49	19	16	5	21	19.83	36.18	3.55	0.30	
11405-2		50			08:49	20	10	0	10	19.15	36.22	3.72	0.33	

Appendix 1. (continued)

Sample	Date	Depth [m]	Lat (N)	Lon (W)	Start CTD local time	Volume sampled [l]	Th empty (shells/50l)	Th full (shells/50l)	Sum	Temp [°C]	Sal [psu]	O2 [ml/l]	Chl [µl/l]	Time [UTC]
MSM4														
11833-2	23.03.2007	10	21°17.2	20°48.2	15:03	30	19	8	28	20.53	36.07	3.47	0.16	15:03
11833-2		20			15:03	30	41	3	44	20.63	36.54	4.94	0.17	
11833-2		30			15:03	30	29	104	133	20.65	36.59	4.88	0.34	
11833-2		45			15:03	20	220	76	296	20.53	36.66	4.80	1.30	
11833-2		75			15:03	30	127	30	157	20.48	36.91	4.40	0.15	
11833-2		100			15:03	30	163	25	188	19.91	36.86	4.14	0.00	
11834-1	23.03.2007	10	20°59.9	19°50.0	15:39	30	12	16	28	20.07	36.76	3.51	1.33	15:39
11834-1		20			15:39	30	24	0	24	20.07	36.54	4.97	1.41	
11834-1		30			15:39	30	36	4	40	20.05	36.55	5.04	1.47	
11834-1		40			15:39	30	17	0	17	19.94	36.54	5.10	2.00	
11834-1		50			15:39	30	119	18	136	19.94	36.56	4.99	1.27	
11834-1		70			15:39	30	100	19	119	18.44	36.47	3.67	0.00	
11835-3	25.03.2007	10	20°44.9	18°41.7	11:54	30	28	11	39	18.41	36.07	4.01	2.88	11:54
11835-3		20			11:54	30	33	0	33	18.29	36.10	3.57	3.42	
11835-3		30			11:54	35	5	0	5	18.28	36.06	4.80	2.15	
11835-3		40			11:54	25	26	0	26	18.23	36.10	4.79	1.21	
11835-3		50			11:54	30	25	7	32	17.28	36.11	4.03	0.00	
11835-3		70			11:54	30	9	0	9	17.47	36.25	3.65	0.00	
11836-1	25.03.2007	10	20°34.7	17°58.8	18:30	20	0	0	0	18.07	30.19	3.56	1.78	18:30
11836-1		20			18:30	20	30	10	40	17.99	36.04	4.76	1.83	
11836-1		30			18:30	20	9	13	22	18.24	36.18	4.62	1.28	
11836-1		40			18:30	20	83	28	110	17.78	36.20	4.33	0.72	
11836-1		50			18:30	20	162	61	223	17.41	36.18	3.86	0.12	
11836-1		60			18:30	20	66	25	91	16.97	36.13	3.62	0.01	
11836-1		70			18:30	10	83	0	83	16.87	36.14	3.32	0.00	
11837-2	26.03.2007	10	20°04.9	18°50.0	11:00	30	20	3	23	19.13	31.23	3.30	1.31	11:00
11837-2		20			11:00	30	42	5	47	19.13	36.02	4.69	1.38	
11837-2		30			11:00	30	12	2	13	19.13	36.02	4.69	1.26	
11837-2		40			11:00	30	10	3	13	18.91	36.01	4.55	0.87	
11837-2		50			11:00	30	12	8	20	18.37	36.12	2.92	0.11	
11837-2		60			11:00	30	30	23	53	17.13	36.02	1.61	0.01	
11837-2		70			11:00	30	50	15	65	16.91	36.00	1.45	0.00	
11839-1	27.03.2007	10	21°20.0	18°50.5	16:00	37	9	0	9	19.18	36.49	4.95	1.52	16:00
11839-1		20			16:00	35	21	0	21	19.15	36.49	5.18	2.10	
11839-1		30			16:00	30	8	0	8	19.03	36.49	5.08	1.54	
11839-1		40			16:00	30	2	0	2	19.01	36.48	5.01	1.36	
11839-1		50			16:00	30	12	7	18	18.98	36.47	4.97	1.16	
11839-1		70			16:00	30	13	8	22	18.35	36.39	4.11	0.00	

Calcification depth of *T. heimii*

Appendix 1. (continued)

Sample	Date	Depth [m]	Lat (N)	Lon (W)	Start CTD local time	Volume sampled [l]	Th empty (shells/50l)	Th full (shells/50l)	Sum	Temp [°C]	Sal [psu]	O2 [ml/l]	Chl [µl/l]	Time [UTC]
P366-1														
13001-2	05.05.2008	20	21°16.51	20°48.38	16:15	40	5	4	9	22.08	36.42	4.93	0.30	16:15
13001-2		50			16:15	40	5	11	16	21.17	36.46	4.98	0.64	
13001-2		65			16:15	40	11	14	25	20.73	36.60	4.98	1.20	
13001-2		75			16:15	40	1	14	15	19.93	36.52	4.42	0.91	
13001-2		160			16:15	20	8	13	25	14.89	35.77	1.53	0.22	
13002-3	07.05.2008	10	21°12.69	20°21.87	05:03	30	0	2	2	21.52	36.31	5.08	1.47	05:03
13002-3		20			05:03	40	0	1	1	21.51	36.31	5.12	1.51	
13002-3		30			05:03	40	0	0	0	18.87	36.07	4.72	1.55	
13002-3		40			05:03	40	0	1	1	18.75	36.21	3.96	0.58	
13002-3		100			05:03	10	0	4	10	16.61	36.08	1.81	0.26	
13003-1	07.05.2008	15	20°59.99	19°43.01	16:40	50	0	0	0	21.06	36.28	5.39	2.26	16:40
13003-1		30			16:40	50	0	0	0	20.45	36.49	5.16	0.95	
13003-1		45			16:40	40	0	0	0	20.09	36.61	4.82	0.64	
13003-1		65			16:40	40	0	0	0	18.67	36.34	4.12	0.33	
13004-4		12	20°44.50	18°42.20	09:37	40	0	0	0	18.79	35.92	5.27	2.27	09:37
13004-4	09.05.2008	20			09:37	40	0	0	0	18.10	36.07	4.40	1.65	
13004-4		30			09:37	40	0	0	0	17.23	36.06	3.09	0.92	
13004-4		40			09:37	30	0	0	0	16.60	35.95	2.78	0.56	
13004-4		65			09:37	20	0	0	0	15.20	35.76	1.35	0.31	
13004-4		100			09:37	10	0	0	0	14.22	35.57	1.02	0.28	
13005-2	09.05.2008	15	20°36.39	18°10.11	19:59	40	0	0	0	19.09	35.90	4.83	1.75	19:59
13005-2		27			19:59	40	0	0	0	17.45	35.89	3.44	1.85	
13005-2		50			19:59	30	0	0	0	16.45	35.90	1.66	1.71	
13005-2		100			19:59	30	0	2	2	14.54	35.59	1.15	0.39	
13020-1	13.05.2008	15	22°59.96	17°30.07	17:00	30	8	8	16	20.43	36.57	5.04	0.61	17:00
13020-1		30			17:00	40	1	1	2	20.44	36.63	5.02	0.83	
13020-1		40			17:00	40	1	6	7	19.37	36.50	4.87	0.95	
13020-1		52			17:00	40	20	3	23	18.74	36.48	4.55	0.56	
13020-1		100			17:00	20	0	0	0	17.35	36.34	3.06	0.18	
13024-4	15.05.2008	20	25°36.07	16°29.43	16:15	30	25	3	28	19.64	36.59	5.20	0.36	16:15
13024-4		45			16:15	30	8	0	8	19.24	36.60	5.27	0.62	
13024-4		65			16:15	40	46	0	46	19.04	36.64	5.22	0.94	
13024-4		73			16:15	30	85	0	85	18.92	36.63	5.17	1.12	
13024-4		85			16:15	30	22	0	22	18.66	36.63	4.91	0.81	
13024-4		100			16:15	20	60	0	60	18.39	36.60	4.77	0.51	
13030-2	17.05.2008	35	25°21.61	16°32.29	22:59	40	24	15	39	19.68	36.57	5.18	0.41	22:59
13030-2		55			22:59	40	29	13	42	19.20	36.56	5.22	0.67	
13030-2		67			22:59	40	25	8	33	19.05	36.65	5.17	0.90	
13030-2		80			22:59	40	29	4	33	18.58	36.58	5.04	0.70	
13030-2		100			22:59	20	260	60	320	18.38	36.61	4.89	0.43	

Appendix 1. (continued)

Sample	Date	Depth [m]	Lat (N)	Lon (W)	Start CTD local time	Volume sampled [l]	Th empty (shells/50l)	Th full (shells/50l)	Sum	Temp [°C]	Sal [psu]	O2 [ml/l]	Chl [µl/l]	Time [UTC]
P366-2														
13031-2	22.05.2008	10	29°03.00	16°16.90	17:15	30	142	72	213	20.76	36.85	5.01	0.21	17:15
13031-2		50			17:15	40	19	6	25	20.03	36.83	5.14	0.33	
13031-2		90			17:15	40	10	8	18	19.03	36.79	5.14	0.60	
13031-2		100			17:15	40	120	6	126	18.98	36.79	5.14	0.61	
13032-1	23.05.2008	150			17:15	20	5953	0	5953					
13032-1		40	30°29.44	14°29.21	08:07	40	471	139	610	19.63	36.77	5.11	0.28	08:07
13032-1		64			08:07	30	683	123	807	18.83	36.73	5.19	0.41	
13032-1		84			08:07	40	64	0	64	18.45	36.72	5.14	0.68	
13032-1		100			08:07	40	203	0	203	18.31	36.71	5.07	0.52	
13032-1		150			08:07	10	215	0	215	17.78	36.61	4.96	0.30	
13033-2	24.05.2008	50	31°39.99	13°41.75	10:00	40	0	0	0	19.09	36.73	5.25	0.37	10:00
13033-2		93			10:00	40	59	0	59	18.36	36.70	5.19	0.56	
13033-2		103			10:00	40	46	0	46	18.28	36.69	5.16	0.76	
13033-2		122			10:00	40	55	0	55	17.99	36.65	5.04	0.51	
13033-2		150			10:00	10	20	0	20	17.70	36.59	5.00	0.26	
13034-1	25.05.2008	50	33°05.55	12°46.20	09:05	40	48	5	53	18.42	36.59	5.28	0.37	09:05
13034-1		80			09:05	40	143	0	143	18.10	36.64	5.21	0.46	
13034-1		100			09:05	40	29	0	29	17.86	36.60	5.18	0.78	
13034-1		117			09:05	40	4	0	4	17.64	36.56	5.07	0.69	
13034-1		200			09:05	20	65	0	65	14.91	36.06	4.64	0.27	
13035-2	26.05.2008	10	35°29.04	11°29.16	10:31	40	14	0	14	18.82	36.29	3.67	0.33	10:31
13035-2		30			10:31	40	33	6	39	18.70	36.49	5.08	0.36	
13035-2		50			10:31	40	5	0	5	17.66	36.47	5.39	0.39	
13035-2		70			10:31	40	65	0	65	17.13	36.43	5.32	0.65	
13035-2		100			10:31	20	45	0	45	16.78	36.41	5.25	0.57	
13036-1	27.05.2008	40	36°41.00	10°25.57	09:43	40	36	6	43	18.12	36.51	5.28	0.39	09:43
13036-1		75			09:43	40	4	1	5	16.91	36.43	5.41	0.66	
13036-1		85			09:43	40	20	0	20	16.80	36.44	5.34	1.05	
13036-1		110			09:43	40	3	0	3	16.34	36.36	5.19	0.61	
13036-1		140			09:43	10	0	0	0	15.78	36.28	5.07	0.35	
13037-2	28.05.2008	50	38°59.65	10°31.51	16:18	40	3	0	3	17.11	36.16	5.45	0.61	16:18
13037-2		60			16:18	40	3	0	3	16.55	36.20	5.51	0.81	
13037-2		84			16:18	40	0	0	0	15.76	36.22	5.51	2.23	
13037-2		102			16:18	40	0	0	0	15.46	36.21	5.31	0.62	
13037-2		150			16:18	20	0	0	0	15.03	36.16	5.20	0.19	

Calcification depth of *T. heimii*

Appendix 1. (continued)

Sample	Date	Depth [m]	Lat (S)	Lon (E)	Start CTD local time	Volume sampled [l]	Th empty (shells/50l)	Th full (shells/50l)	Sum	Temp [°C]	Sal [psu]	O2 [ml/l]	Chl [µl/l]	Time [UTC]
M75-2														
12602-1	10.02.2008	40	5.29.90	39.29.188	08:31	20	2120	4500	6620					05:31
12602-1		60			08:31	20	206	206	412	24.51	35.08	4.74	0.49	
12602-1		80			08:31	20	269	217	486	24.04	35.13	4.68	0.56	
12602-1		100			08:31	20	46	92	138	22.72	35.28	4.20	0.50	
12602-1		150			08:31	10	418	209	627	18.35	35.29	3.26	0.25	
12604-1	10.02.2008	10	5.31.10	39.04.388	17:28	20	138	88	225	26.71	34.49	3.09	0.31	14:28
12604-1		25			17:28	20	43	20	63	25.69	35.11	4.58	0.79	
12604-1		50			17:28	20	43	15	58	24.32	35.10	4.67	0.58	
12604-1		75			17:28	10	115	40	155	23.19	35.24	4.52	0.80	
12604-1		100			17:28	20	110	3	113	22.03	35.26	3.91	0.48	
12604-1		125			17:28	20	5	10	15	20.32	35.30	3.50	0.28	
12608-3	10.02.2008	10	6.59.56	39.25.982	14:18	25	16	44	60	26.67	35.19	2.42	0.19	11:18
12608-3		25			14:18	25	8	12	20	26.25	35.11	4.56	0.25	
12608-3		50			14:18	25	14	8	22	25.76	35.11	4.59	0.82	
12608-3		75			14:18	22.5	9	9	18	22.26	35.27	4.04	0.51	
12608-3		100			14:18	22.5	18	9	27	21.78	35.26	3.80	0.42	
12608-3		125			14:18	15	37	7	43	19.01	35.33	3.34	0.21	
12608-3		150			14:18	5	90	0	90	17.57	35.30	3.18	0.18	
12611-4	12.02.2008	10	5.33.91	41.15.831	21:15	20	40	3	43	27.95	34.46	2.79	0.20	18:15
12611-4		50			21:15	30	8	0	8	27.25	35.08	4.49	0.24	
12611-4		75			21:15	30	3	3	7	23.81	35.10	4.62	0.72	
12611-4		100			21:15	30	5	5	10	20.50	35.34	3.56	0.65	
12611-4		150			21:15	20	5	8	13	16.26	35.21	2.84	0.17	
12616-2	16.02.2008	20	6.58.72	40.23.752	19:50	20	8	18	25	28.29	34.93	4.38	0.20	16:50
12616-2		40			19:50	30	3	7	10	28.13	34.95	4.40	0.22	
12616-2		75			19:50	30	2	7	8	24.78	35.03	4.57	0.70	
12616-2		100			19:50	20	10	8	18	22.37	35.14	3.61	0.65	
12616-2		125			19:50	20	10	5	15	18.76	35.15	2.35	0.34	
12616-2		150			19:50	10	5	0	5	17.31	35.17	2.28	0.28	
12617-3	19.02.2008	50	10.22.64	40.30.735	11:03	20	3	8	10	26.95	34.92	4.48	0.33	08:03
12617-3		75			11:03	20	3	3	5					
12617-3		100			11:03	20	5	5	10					
12618-2	19.02.2008	20	10.24.069	40.29.047	12:50	20	3	0	3	27.67	34.83	4.42	0.26	09:50
12618-2		50			12:50	30	0	0	0	26.64	34.94	4.47	0.33	
12618-2		60			12:50	20	5	8	13	26.55	34.95	4.48	0.31	
12618-2		75			12:50	30	2	2	3	24.37	35.10	4.40	0.43	
12618-2		100			12:50	30	0	0	0	21.40	35.28	3.77	0.43	
12618-2		125			12:50	20	3	0	3	20.08	35.35	3.68	0.29	
12618-2		150			12:50	10	0	0	0	16.31	35.35	3.52	0.22	
12620-4	20.02.2008	20	10.01.909	40.57.392	06:35	20	0	0	0	27.68	34.61	3.75	0.25	03:35
12620-4		40			06:35	20	3	0	3	27.69	34.77	4.45	0.22	
12620-4		60			06:35	20	0	0	0	25.24	34.98	4.63	0.44	
12620-4		80			06:35	30	0	0	0	23.82	35.06	4.33	1.08	
12620-4		100			06:35	20	0	0	0	21.88	35.18	3.78	0.60	
12620-4		150			06:35	10	0	0	0	17.76	35.27	2.90	0.18	
12621-2	21.02.2008	50	10.05.491	40.11.392	14:37	20	3	3	5	25.81	34.99	4.54	0.50	11:37
12621-2		65			14:37	30	10	3	13	25.30	35.04	4.58	0.64	
12621-2		125			14:37	20	0	0	0					
12622-1	22.02.2008	40	08.34.720	40.36.545	03:47	20	0	0	0	27.94	34.79	4.41	0.19	00:47
12622-1		70			03:47	30	7	5	12	23.55	35.01	4.04	0.93	
12622-1		100			03:47	20	8	0	8	21.48	35.43	4.06	0.60	
12622-1		150			03:47	10	10	0	10	17.35	35.19	2.64	0.24	

3.9 References

- Anderson, D.M., Stolzenbach, K.D., 1985. Selective retention of two dinoflagellates in a well-mixed estuarine embayment: The importance of diel vertical migration and surface avoidance. *Marine Ecology. Progress Series* 25, 39-50.
- Barton, E.D., Aristegui, J., Tett, P., Cantón, M., García-Braun, J., Hernández-León, S., Nykjaer, L., Almeida, C., Almunia, J., Ballesteros, S., Basterretxea, G., Escánez, J., García-Weill, L., Hernández-Guerra, A., López-Laatzén, F., Molina, R., Montero, M.F., Navarro-Pérez, E., Rodríguez, J.M., van Lenning, K., Vélez, H., Wild, K., 1998. The transition zone of the Canary Current upwelling region. *Progress in Oceanography* 41 (4), 455-504.
- Bryceson, I., 1977. An ecological study of phytoplankton of the coastal waters of Dar es Salaam. University of Dar es Salaam, Dar es Salaam, Zanzibar.
- Coelho, H.S., Neves, R.J.J., White, M., Leitão, P.C., Santos, A.J., 2002. A model for ocean circulation on the Iberian coast. *Journal of Marine Systems* 32 (1-3), 153-179.
- Fischer, G., Karakas, G., 2009. Sinking rates and ballast composition of particles in the Atlantic Ocean: implications for the organic carbon fluxes to the deep ocean. *Biogeosciences* 6, 85-102.
- Francis, J., Bryceson, I., 2001. Tanzanian coastal and marine resources: Some examples illustrating questions of sustainable use, IUCN, Gland, Switzerland.
- Gabric, A.J., Garcia, L., Van Camp, L., Nykjaer, L., Eifler, W., Schrimpf, W., 1993. Offshore export of shelf production in the Cap Blanc (Mauretania) giant filament as derived from coastal zone colour scanner imagery. *Journal of Geophysical Research* 98 (C3), 4697-4712.
- Gussone, N., Eisenhauer, A., Tiedemann, R., Haug, G.H., Heuser, A., Bock, B., Nägler, T.F., Müller, A., 2004. Reconstruction of Caribbean Sea surface temperature and salinity fluctuations in response to the Pliocene closure of the Central American Gateway and radiative forcing, using $[\delta]^{44}\text{Ca}$, $[\delta]^{18}\text{O}$ and Mg/Ca ratios. *Earth and Planetary Science Letters* 227 (3-4), 201-214.
- Gussone, N., Zonneveld, K.A.F., Kuhnert, H., subm. Minor element and Ca isotope composition of calcareous dinoflagellate cysts of cultured *Thoracosphaera heimii*. *Earth and planetary science letters*.
- Hagen, E., 2001. Northwest African upwelling scenario. *Oceanologica Acta* 24 (Supplement), S113-S128.
- Hagen, E., Schemainda, R., 1984. Der Guineadom im ostatlantischen Stromsystem. *Beiträge zur Meereskunde* 51, 5-27.
- Hernandez-Guerra, A., Nykjaer, L., 1997. Sea surface temperature variability off north-west Africa: 1981-1989. *International journal of remote sensing* 18 (12), 2539-2558.
- Höll, C., Karwath, B., Rühlemann, C., Zonneveld, K.A.F., Willems, H., 1999. Palaeoenvironmental information gained from calcareous dinoflagellates: The late Quaternary eastern and western tropical Atlantic Ocean in comparison. *Palaeogeography, Palaeoclimatology, Palaeoecology* 146 (18), 147-164.
- Höll, C., Zonneveld, K.A.F., Willems, H., 1998. On the ecology of calcareous dinoflagellates: The Quaternary eastern equatorial Atlantic. *Marine Micropaleontology* 33 (1-2), 1-25.

- Huthnance, J.M., Van Aken, H.M., White, M., Barton, E.D., Le Cann, B., Coelho, E.F., Fanjul, E.A., Miller, P., Vitorino, J., 2002. Ocean margin exchange-water flux estimates. *Journal of Marine Systems* 32 (1-3), 107-137.
- Inouye, I., Pienar, R.N., 1983. Observations on the life cycle and microanatomie of *Thoracosphaera heimii* (Dinophyceae) with special reference to its systematic position. *South African Journal of Botany* 2, 63-75.
- Iversen, S.A., 1984. Kenyan marine resources in water deeper than 10 m investigated by R/V Dr Fridtjof Nansen. In: Iversen, S.A., Myklevoll, S. (Ed.), *Proceedings of the North-Kenya seminar to review the marine fish stocks and fisheries in Kenya*. Institute of Marine research, Bergen, Norway, pp. 33-60.
- Kamykowski, D., Milligan, A.J., Reed, R.E., 1998. Relationships between geotaxis/phototaxis and diel vertical migration in autotrophic dinoflagellates. *Journal of Plankton Research* 20, 1781-1796.
- Karwath, B., Janofske, D., Willems, H., 2000a. Spatial distribution of the calcareous dinoflagellate *Thoracosphaera heimii* in the upper water column of the tropical and equatorial Atlantic. *International Journal of Earth Sciences* 88 (4), 668-679.
- Karwath, B., Janofske, C., Tietjen, F., Willems, H., 2000b. Temperature effects on growth and cell size in the marine calcareous dinoflagellate *Thoracosphaera heimii*. *Marine Micropaleontology* 39 (1), 43-51.
- Karwath, B., 2000c. Ecological studies on living and fossil calcareous dinoflagellates of the equatorial and tropical Atlantic Ocean. Fachbereich Geowissenschaften der Universität Bremen, Bremen.
- Kitheka, J.U., Ohowa, B.O., Mwashote, B.M., Shimibira, W.S., Mwaluma, J.M., Kazungu, J.M., 1996. Water circulation dynamics, water column nutrients and plankton productivity in a well-flushed tropical bay in Kenya. *J. Sea Res.* 35 (4), 257-268.
- Kohn, M., Steinke, S., Baumann, K.-H., Donner, B., Meggers, H., Zonnveld, K.A.F., subm. Stable oxygen isotopes of the calcareous-walled dinoflagellate *Thoracosphaera heimii* as a proxy for mixed layer temperatures. *Palaeogeography, Palaeoclimatology, Palaeoecology*.
- Kronkamp, J., De Bie, M., Goosen, N., Peene, J., Van Rijswijk, P., Sankie, J., Duineveld, G.C.A., 1997. Primary production by phytoplankton along the Kenyan coast during the SE monsoon and November intermonsoon 1992, and the occurrence of *Trichodesmium*. *Deep Sea Research Part II: Topical Studies in Oceanography* 44 (6-7), 1195-1212.
- Liebermann, O.S., Shilo, M., van Rijn, J., 1994. The physiological ecology of a freshwater dinoflagellate bloom population: vertical migration, nitrogen limitation, and nutrient uptake kinetics. *Journal of Phycology* 30, 964-971.
- Lugomela, C., Lyimo, T.J., Bryceson, I., Semesi, A.K., Bergman, B., 2002. *Trichodesmium* in coastal waters of Tanzania: diversity, seasonality, nitrogen and carbon fixation. *Hydrobiologica* 477, 1-13.
- Lugomela, C., Wallberg, P., Nielsen, T.G., 2001. Plankton composition and cycling of carbon during the rainy season in a tropical coastal ecosystem, Zanzibar, Tanzania. *Journal of Plankton Research* 23 (10), 1121-1136.
- McClanahan, T.R., 1988. Seasonality in East Africa's coastal waters. *Marine Ecology - Progress Series* 44, 191-199.

- Meggers, H., Freudenthal, T., Nave, S., Targarona, J., Abrantes, F., Helmke, P., 2002. Assessment of geochemical and micropaleontological sedimentary parameters as proxies of surface water properties in the Canary Islands region. *Deep-Sea Research II: Tropical studies in Oceanography* 49 (17), 3631-3654.
- Mittelstaedt, E., 1983. The upwelling area off Northwest Africa - a description of phenomena related to coast upwelling. *Progress in Oceanography* 12 (3), 307-331.
- Mittelstaedt, E., 1991. The ocean boundary along the northwest African coast: Circulation and oceanographic properties at the sea surface. *Progress in Oceanography* 26 (4), 307-355.
- Morgans, J.F.C., 1962. Ecological aspects of demersal tropical fishes off East Africa. *Nature* 193, 86-87.
- Newell, B.S., 1957. A preliminary survey of the hydrography of the British East African coastal waters. *Fish. Publ. London* 9, 1-21.
- Newell, B.S., 1959. The hydrography of the British East African coastal waters. Part II. Colonial Office Fishery Publication 12 H.M.S.O. London, pp. 18.
- Nykjaer, L., Van Camp, L., 1994. Seasonal and interannual variability of coastal upwelling along northwest Africa and Portugal from 1981 to 1991. *Journal of Geophysical Research* 99 (C7) (14), 197-214, 207.
- Oelfke Clark, C., Webster, P.J., Cole, J.E., 2003. Interdecadal variability of the relationship between the Indian Ocean zonal mode and East African coastal rainfall anomalies. *Journal of Climate* 16 (3), 548-554.
- Pätzold, J., Bartholomä, A., Baumann, K.-H., Bouimetarhan, I., Kreuzmann, C., Flemming, B., Groeneveld, J., Hathorne, E., Hüttich, D., Keil, H., Klages, J., Klann, M., Krastel-Gudegast, S., Köhl, B., Kuhlmann, H., Meyer, M., Mulitza, S., Muzuka, A., Niedermeyer, E., Nizou, J., Nyandwi, N., Ochsenhirt, W.-T., Schlömer, A., Schöttke, L., Schulz, M., Shaghude, Y., Stolz, K., Vogel, S., Wilsenack, M., subm. Western Indian Ocean Climate and Sedimentation (WINOCS) PaläoIndik, Part 3, R/V METEOR Cruise No. 75, Leg 2, Dar es Salaam – Dar es Salaam (Tanzania). Meteor-Berichte, Leitstelle Meteor, Universität Hamburg.
- Paula, J., Pinto, I., Guembe, I., Monteiro, S., Gove, D., Guerreiro, J., 1998. Seasonal cycle of planktonic communities at Inhaca Island, southern Mozambique. *Journal of Plankton Research* 20 (11), 2165-2178.
- Peliz, A.J., Fiúza, A.F.G., 1999. Temporal and spatial variability of CZCS-derived phytoplankton pigment concentrations of the western Iberian Peninsula. *International journal of remote sensing* 20 (7), 1363-1403.
- Pérez, F.F., Castro, C.G., Álvarez-Salgado, X.A., Ríos, A.F., 2001. Coupling between the Iberian basin - scale circulation and the Portugal boundary current system: a chemical study. *Deep Sea Research Part I: Oceanographic Research Papers* 48 (6), 1519-1533.
- Ploug, H., Iversen, M.H., Koski, M., Buitenhuis, E.T., 2008. Production, oxygen respiration rates, and sinking velocity of copepod fecal pellets: Direct measurements of ballasting by opal and calcite. *LIMNOL. OCEANOGR.* 53, 469-476.
- Pollard, R.T., Griffiths, M.J., Cunningham, S.A., Read, J.F., Pérez, F.F., Ríos, A.F., 1996. Vivaldi 1991 - A study of the formation, circulation and ventilation of Eastern North Atlantic Central water. *Progress in Oceanography* 37 (2), 167-172.

- Qasim, S.Z., 1982. Oceanography of the northern Arabian Sea. Deep-Sea Research, Part A. Oceanographic Research Papers 29 (9A), 1041-1068.
- Richter, D., 2009. Characteristics of calcareous dinoflagellate cyst assemblages in a major upwelling region (NW Africa) - Spatial distribution, fluxes and ecology. Ph.D. Thesis, University of Bremen.
- Richter, D., Vink, A., Zonneveld, K.A.F., Kuhlmann, H., Willems, H., 2007. Calcareous dinoflagellate cyst distributions in surface sediments from upwelling areas off NW Africa, and their relationships with environmental parameters of the upper water column. Marine Microbiology 63, 201-228.
- Sarnthein, M., Tetzlaff, G., Koopmann, B., Wolter, K., Pflaumann, U., 1981. Glacial and interglacial wind regimes over the eastern subtropical Atlantic and North-West Africa. Nature 293 (5829), 193-196.
- Sarnthein, M., Thiede, J., 1982. In: von Rad, U. (Ed.), Geology of the Northwest African continental margin. Springer, Berlin, p. Kap. 24 + 25.
- Schönfeld, J., 1997. The impact of the Mediterranean Outflow Water (MOW) on benthic foraminiferal assemblages and surface sediments at the southern Portuguese continental margin. Marine Micropaleontology 29 (3), 211-236.
- Schott, F.A., 1983. Monsoon response of the Somali Current and associated upwelling. Progress in Oceanography 12 (3), 357-381.
- Schott, F.A., 1990. The Somali current at the equator: annual cycle of currents and transports in the upper 1000 m and connection to neighbouring latitudes. Deep Sea Research Part A. Oceanographic Research Papers 37 (12), 1825-1848.
- Schott, F.A., Brandt, P., Hamann, M., Fischer, J., Stramma, L., 2002. On the boundary flow off Brazil at 5-10°S and its connection to the interior tropical Atlantic. Geophysical Research Letters 29 (17), 1840, doi: 1810.1029/2002GM14786.
- Smith, S.I., Banse, K., Cochran, K.J., Codispoti, L.A., Ducklow, H.W., Luther, M.E., Olson, D.B., Peterson, W.T., Prell, W.L., Surgi, N., Swallow, J.C., Wishner, K. (Eds.), 1991. U.S. JGOFS: Arabian Seas process study. Woods Hole Oceanographic Institution, Woods Hole, Massachusetts.
- Smyth, T.J., Miller, P.I., Groom, S.B., Lavender, S.J., 2001. Remote sensing of sea surface temperature and chlorophyll during Lagrangian experiments at the Iberian margin. Progress in Oceanography 51 (2-4), 269-281.
- Swallow, J.C., Schott, F., Fieux, M., 1991. Structure and transport of the East African Coastal current. Journal of Geophysical Research 96 (C12), 22,245-222,257.
- ter Braak, C.J.F., Smilauer, P., 2002. CANOCO Reference Manual and CanoDraw for Windows User's Guide: Software for Canonical Community Ordination (version 4.5). Microcomputer Power (Ithaca NY, USA), 500 pp.
- Tetzlaff, G., Peters, M., 1986. Deep-sea sediments in the eastern equatorial Atlantic off the African coast and meteorological flow patterns over the Sahel International Journal of Earth Sciences 75 (1), 71-79.
- Van Camp, L., Nykjaer, L., Mittelstaedt, E., Schlittenhardt, P., 1991. Upwelling and boundary circulation off Northwest Africa as depicted by infrared and visible satellite observations. Progress in Oceanography 26 (4), 357-402.

- Vink, A., 2004. Calcareous dinoflagellate cysts in South and equatorial Atlantic surface sediments: diversity, distribution, ecology and potential for palaeoenvironmental reconstructions. *Marine Micropaleontology* 50 (1-2), 43-88.
- Vink, A., Baumann, K.-H., Böckel, B., Esper, O., Kinkel, H., Volbers, A., Willems, H., Zonneveld, K.A.F., 2003. Coccolithophorid and dinoflagellate synecology in the South and Equatorial Atlantic: Improving the paleoecological significance of phytoplanktonic microfossils. In: Wefer, G., Mulitza, S., Ratmeyer, V. (Eds.), *The South Atlantic in the Late Quaternary: Reconstructions of material budgets and current systems*. Springer-Verlag, Berlin Heidelberg New York, pp. 101-120.
- Vink, A., Zonneveld, K.A.F., Willems, H., 2000. Distributions of calcareous dinoflagellate cysts in surface sediments of the western equatorial Atlantic Ocean, and their potential use in paleoceanography. *Marine Micropaleontology* 38 (2), 149-180.
- Wefer, G., Fischer, G., 1993. Seasonal patterns of vertical particle flux in equatorial and coastal upwelling areas of the eastern Atlantic. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 40 (8), 1613-1645.
- Wendler, I., Zonnefeld, K.A.F., Willems, H., 2002a. Calcareous cyst-producing dinoflagellates: ecology and aspects of cyst preservation in a highly productive oceanic region. In: Clift, P.D., Kroon, D., Gaedicke, C., Craig, J. (Eds.), *The tectonic and climatic evolution of the Arabian Sea region*. Geological Society, Special Publication, London, pp. 317 - 340.
- Wendler, I., Zonnefeld, K.A.F., Willems, H., 2002b. Production of calcareous dinoflagellate cysts in response to monsoon forcing off Somalia: a sediment trap study. *Marine Micropaleontology* 46, 1-11.
- Zonneveld, K., 2004. Potential use of stable isotope composition of *Thoracosphaera heimii* (Dinophyceae) for upper water column (thermocline) temperature reconstruction. *Marine Micropaleontology* 50 (3-4), 307-317.
- Zonneveld, K., Brune, A., Willems, H., 2000. Spatial distribution of calcareous dinoflagellate cysts in surface sediments of the Atlantic Ocean between 13°N and 36°S. *Review of Palaeobotany and Palynology* 111, 197-223.
- Zonneveld, K.A.F., Mackensen, A., Baumann, K.-H., 2007. Stable oxygen isotopes of *Thoracosphaera heimii* (Dinophyceae) in relationship to temperature; a culture experiment. *Marine Micropaleontology* 64 (1-2), 80-90.

Chapter 4

Influence of pH on the $\delta^{18}\text{O}$ signal of the calcareous-walled dinoflagellate *Thoracosphaera heimii*

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Abstract

The relationship between the pH of ambient seawater and the stable oxygen isotope composition of the calcareous-walled dinoflagellate *Thoracosphaera* has been established in a culture experiment to obtain more information on possible vital effects. *T. heimii* was cultured under three different pH values at three different temperatures. The stable oxygen isotope composition of *T. heimii* relates negatively to pH according to the relationship $y = -4.4985 * x + 33.4$. This can be explained by the preferential uptake of HCO_3^- due to different equilibrium fractionations of carbonate species with respect to seawater.

No significant correlation between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ was observed. We therefore exclude that *T. heimii* shows kinetic effects as a result of fast calcite precipitation. However, based on the relatively light oxygen and carbon isotope values in comparison to other calcareous organisms, we suggest that *T. heimii* uses respirative carbon as part of its carbon source for calcite precipitation.

The results of this study improve palaeo sea surface temperature (SST) estimates especially during the last glacial maximum where large changes in pH compared to the last interglacial can lead to an underestimation of SST.

Keywords: pH; $\delta^{18}\text{O}$; $\delta^{13}\text{C}$; ocean acidification, kinetic effect, vital effect

4.1 Introduction

Stable oxygen isotopes of calcareous microfossils are an important tool for palaeoceanographic reconstructions (for a review see e.g. Emiliani, 1966; Wefer and Berger, 1991). Culture experiments of living foraminifera showed that seawater carbonate chemistry can considerably affect the oxygen and carbon isotopic signal of biogenic carbonates (for a review see Rohling and Cooke, 1999). Stable oxygen isotope measurements on planktonic foraminifera suggested a major effect of seawater pH on the stable oxygen isotope fractionation between water and calcium carbonate indicating a negative linear relationship (e.g. Spero *et al.*, 1997; Zeebe, 1999; Zeebe, 2001; Rollion-Bard *et al.*, 2003). In foraminifera a strong correlation between oxygen and carbon isotopes was observed suggesting kinetic fractionation during hydration and hydroxylation of CO_2 (McConnaughey, 1989).

During the last decades it became obvious that pH of the ambient seawater can have a major influence on $\delta^{18}\text{O}$ of calcite forming organisms and the resulting isotopic palaeotemperature estimates. (McCrea, 1950) (Spero *et al.*, 1997; Zeebe, 2001; Rollion-Bard *et al.*, 2003). This observation has consequences for the interpretation of the stable oxygen isotope signal as a proxy for palaeotemperature. For instance, higher pH values during the last glacial maximum would result in ^{18}O depleted shells and were hitherto interpreted as higher sea surface temperatures (Sanyal *et al.*, 1995). A good pH proxy is required to obtain more information about the past ocean.

Recently, the stable oxygen isotope composition of the phytoplanktonic calcareous-walled dinoflagellate *Thoracosphaera heimii* has been proposed as a new proxy for sea surface temperatures (Zonneveld, 2004; Zonneveld *et al.*, 2007; Kohn *et al.*, *subm.*). Culture studies suggested an inverse pH effect with heavier oxygen isotope values at higher pH values (Zonneveld *et al.*, 2007). This relationship has been explained by an increase in carbon anhydrase (CA) efficiency with increasing pH (Berman-Frank *et al.*, 1995; Nimer *et al.*, 1999).

Within this study we test the relationship between pH and $\delta^{18}\text{O}$ measured on *T. heimii* and determine the relationship between pH and $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$, and between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ by culturing them at three different temperatures, three different pH values and constant light conditions. We want to figure out possible kinetic and physiological effects of *T. heimii* as well as differences between foraminifera and *T. heimii*.

4.2 Material and Methods

In 1998 strain *148 of *Thoracosphaera heimii* was isolated from the South Atlantic Ocean during Meteor cruise M41/4 at station GeoB 4910-1 (02°19'S/08°04'E). Unicellular cultures have been established in a 50 ml Erlenmeyer flask. The medium consists of seawater collected in 2007 off NW Africa during Merian cruise MSM 4/4B and 20 ml of culture medium (K-medium 35 %; (Keller and Guillard, 1985; Keller *et al.*, 1997). The flask was incubated at 18 °C and a 12:12 h light and dark cycle. Light in the incubator was provided by cool white fluorescent tubes.

The exponential growth phase of *T. heimii* was determined by cultivating strain *148 in a 50 ml Erlenmeyer flask containing 20 ml of K-medium without trisma buffer at 22 °C. Over a 25-day period, sub-sampling occurred twice a week (Table 1). Forty μ l

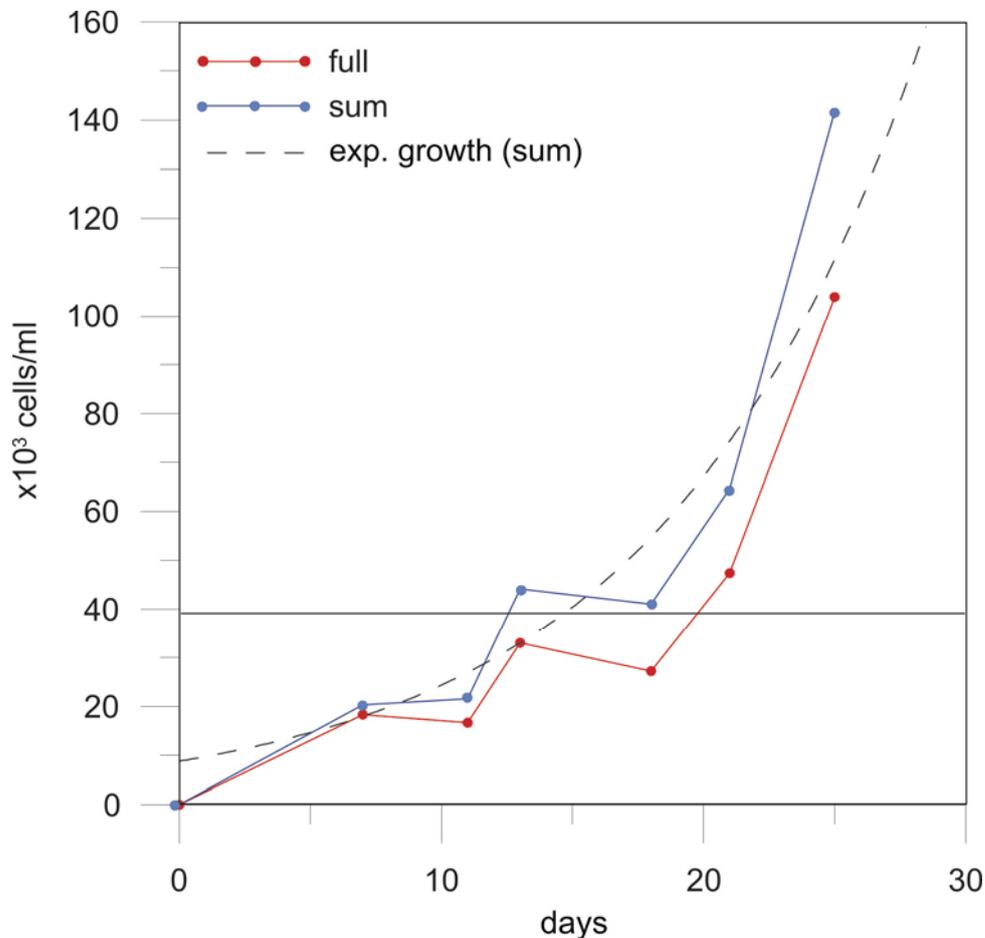


Fig. 1. Calibration curve to investigate exponential growth curve of *Thoracosphaera heimii*. Blue dots indicate full shells. Red dots show the sum of full and empty shells. Blue line represents the exponential growth rates of full shells. Red line represents the exponential growth rates the sum of shells.

a)	Sample number	Temp [°C]	Date	<i>T. heimii</i>	<i>T. heimii</i>
				full/ml	empty/ml
Growth curve					
	pH 1	22	23.10.2008	0.0519	0.0153
	pH 3	22	30.10.2008	18300	2000
	pH 4	22	03.11.2008	16650	4900
	pH 5	22	05.11.2008	33000	11200
	pH 7	22	10.11.2008	27200	13800
	pH 8	22	13.11.2008	47400	17200
b)	pH 9	22	17.11.2008	104000	37800
Growth experiment					
	pH 8.0, 1	18	End	13900	7400
	pH 8.0, 2	18	End	18950	10100
	pH 8.0, 3	18	End	8700	3100
		22	Start	0.0503	0.0125
	pH 7.75-1	22	End	19500	4700
	pH 7.75-2	22	End	18800	14400
	pH 7.75-3	22	End	20100	6700
	pH 8.0-1	22	End	35600	9600
	pH 8.0-2	22	End	58000	18800
	pH 8.0-3	22	End	41700	9400
	pH 8.4-1	22	End	6800	1500
	pH 8.4-2	22	End	10800	3200
	pH 8.4-3	22	End	19700	2500
		24	Start	0.0756	0.0622
	pH 7.62-1	24	End	17600	4000
	pH 7.62-2	24	End	75100	7700
	pH 7.62-3	24	End	76000	6100
	pH 8.04-1	24	End	91100	10600
	pH 8.04-2	24	End	116000	16500
	pH 8.42-1	24	End	7900	2600
	pH 8.42-2	24	End	86600	6400
	pH 8.42-3	24	End	44700	2500

Table 1. a) Shell counts for calibration curve at 22 °C. b) Shell counts for growth experiment at each pH and temperature. Start indicates cell counts at the beginning of the experiment. End indicates cell counts at the end of the experiment.

of the homogenised medium was transferred to a slide, embedded in glycerine jelly and sealed air-tightly with paraffin wax. Entire slides were counted with a light microscope (20x magnification) for their cyst content of full (living) and total (sum) shells (Fig. 1).

For the culture experiment K-medium without buffer solution was prepared and bubble-free filled into 1200 ml Erlenmeyer flasks with air-tightly sealing caps. Bottles were filled up to the brim that there was no air between water and the cap. The pH values were adjusted with NaOH (40 %) and HCl (10 %) to 7.6, 8.0 and 8.4 (NBS). The relatively restricted pH-range between 7.6 and 8.4 has been chosen since *T. heimii* lives

in the open ocean where changes in pH are small (e.g. Tangen *et al.*, 1982; Vink *et al.*, 2000).

The pH-adjusted medium was transferred bubble-free to four one litre bottles for each pH. These bottles were placed air-tight in three incubators and temperature was kept constant at 18 °C, 22 °C and 24 °C. The pH was measured three times a week and readjusted with NaOH (40 %) and HCl (10 %) when a change of more than 0.1 occurred. Total alkalinity (TA) was determined in duplicate by potentiometric titration and calculated from linear Gran Plots (Gran, 1952). Salinity was kept stable at 36.7 psu. Stable oxygen of the medium was measured with a Finnigan MAT 251 mass spectrometer coupled to an automated carbonate preparation device (Kiel II) and calibrated via NIST 19 international standard to the VPDB (Vienna Pee Dee Belemnite) scale at the MARUM, Bremen. Dissolved inorganic carbon (DIC) was extracted from seawater with phosphoric acid in an automatic preparation line (Finnigan Gasbench I), coupled online with a Finnigan MAT 252 mass spectrometer to determine $\delta^{13}\text{C}/\delta^{12}\text{C}$ ratios. All samples were run in duplicate. Results are reported in δ -notation relative to the VPDB-scale with an external reproducibility of $\pm 0.03\%$ at 1 σ .

Two ml of the source culture was transferred into nine bottles; three at each pH. One bottle of each pH remained culture free (blanc). Salinity was kept constant by sealing the bottles with air-tightly closing caps preventing evaporation. Salinity was measured once a week at 10 a.m. and pH was measured three times a week. At 18 °C the experiment was stopped after 28 days, at 22 °C after 18 days and at 24 °C after 33 days.

After terminating the experiments the content of each bottle was filtered using a 5 μm polycarbonate filter to separate the calcareous dinoflagellates from the medium. The filters were oven dried at 60 °C. The residual medium was transferred to 20 ml brown glass bottles to measure $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of seawater (Table 2). Bottles for $\delta^{13}\text{C}$ measurements were poisoned with HgCl and closed air-tightly with wax. TA was measured in duplicate at the beginning and at the end of the incubation time. The carbonate system was calculated from TA, pH, phosphate, temperature and salinity using the program CO2Sys (Lewis and Wallace, 1998; Appendix 1). Equilibrium constants of (Mehrbach *et al.*, 1973) refitted by (Dickson, 1987) were chosen.

18°C						
pH-value	pH (end)	Sample no.	$^{13}\text{C}/^{12}\text{C}$	$\delta^{13}\text{C}_w$	$^{18}\text{O}/^{16}\text{O}$	$\delta^{18}\text{O}_w$
pH7 62	7.72	1	0.39		-0.20	1.31
pH7 62	7.8	2	2.77	4.64	-0.52	1.41
pH7 62	7.86	3	2.97	2.42	-0.78	1.44
pH7 62	7.65 blanc			-2.08		1.30
pH8 04	7.98	1	0.48	-1.67	-1.09	1.40
pH8 04	8.02	2	0.84	2.2	-1.64	1.39
pH8 04	7.92	3	0.17	0.96	-1.34	1.07
pH8 04	7.97 blanc			-6.08		1.41
pH8 42	8.27	1	-7.92	0.78	-2.95	1.38
pH8 42	8.41	2	-3.75	5.56	-3.05	1.32
pH8 42	8.43	3	-4.92	5.54	-3.14	1.23
pH8 42	8.12 blanc			-1.3		1.36
22°C						
PH7.75	7.86	1	1.54	2.06	-0.79	1.036
PH7.75	7.91	2	2.12	3.04	-0.97	1.001
PH7.75	7.91	3	1.68	2.99	-1.02	1.002
PH7.75	7.71 blanc			-2.3		0.846
PH8.0	8.05	1	-0.05	1.23	-1.09	1.153
PH8.0	8.02	2	-0.05	3.03	-1.14	1.128
PH8.0	8.05	3	0.21	2.81		1.048
PH8.0	7.84 blanc			-2.8		0.954
PH8.4	8.28	1	-8.00	-1.34	-2.60	1.032
PH8.4	8.34	2	-6.49	0.23	-3.12	1.089
PH8.4	8.35	3	-7.11	-0.18	-3.12	1.065
PH8.4	8.18 blanc			-3.19		1.069
24°C						
pH7.6	7.47	1		-4.73		0.98
pH7.6	7.44	2				1.01
pH7.6	7.97	3	-0.97	4.83	-2.38	0.29
pH7.6	7.96 blanc			-5.3		0.89
pH8.0	7.82	1	-1.29	-1.8	-1.05	0.86
pH8.0	7.94	2	-1.25	5.17	-1.25	0.47
pH8.0	8.24	3		2.45		0.68
pH8.0	8.1 blanc			-3.51		0.81
pH8.4	8.26	1	-7.69	-2.35	-3.46	0.29
pH8.4	8.35	2	-9.12	-2.84	-3.17	0.93
pH8.4	8.32	3	-8.59	-2.81	-3.43	0.97
pH8.4	8.3 blanc			-3.83		0.87

Table 2. Stable oxygen and carbon isotope values of *Thoracosphaera heimii* and of seawater.

4.3 Results

After 15 days at 22 °C the culture growth rate enter the exponential phase passing a threshold value of about 40.000 cells/ml/t, indicating the cultures (Fig. 1). *T. heimii* grows at all investigated temperatures and pH values but nevertheless at different

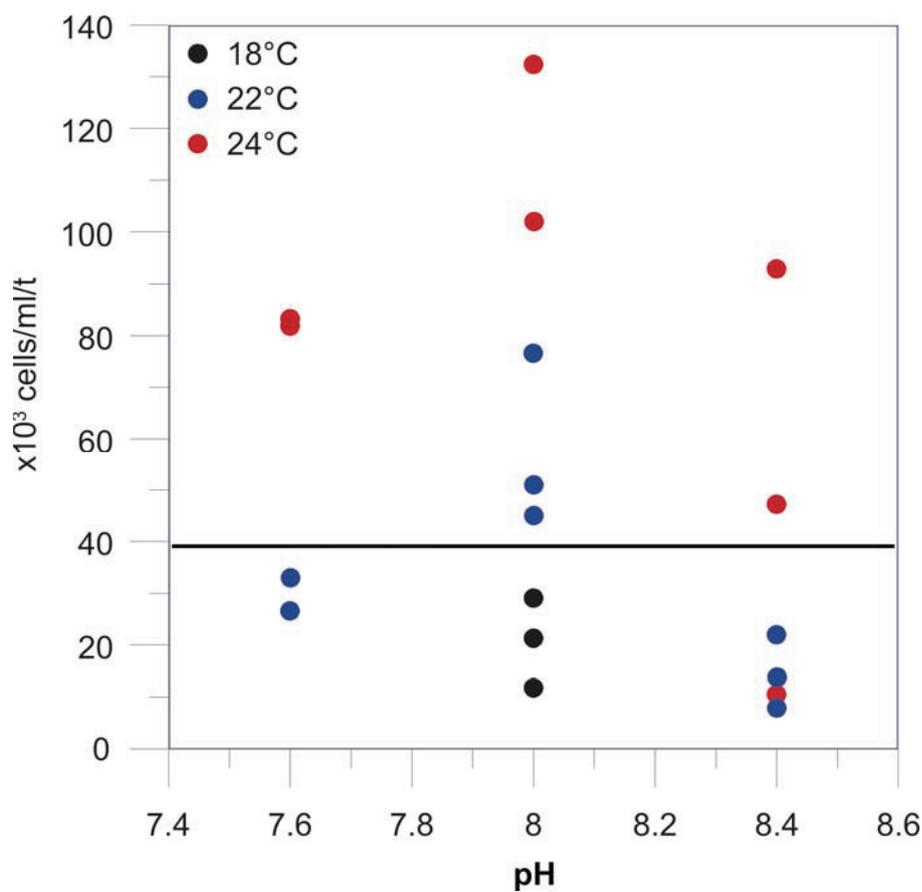


Fig. 2. Final yield at each temperature and each pH. Dots represent 18 °C. Triangles show 22 °C. Diamonds indicate 24 °C. No data on pH 7.6 and 8.4 at 18 °C are available.

growth rates (Table 1). Highest final yield is observed at 24 °C (Fig. 2). Growth rates are lowest at pH 8.4. No data are available on growth rates at pH 7.6 and 8.4 at 18 °C.

Total alkalinity (TA) values demonstrate that CO₂ did not become depleted during the experiment (Appendix 1). The values of TA, HCO₃⁻, CO₃²⁻ and CO₂ decrease with increasing growth rates. All alkalinity values remain at the basic level comparable to that of the blanc experiment when low growth rates are observed.

A negative linear relationship between pH and $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ is observed according to the equation $y = -4.4985 * x + 33.34$ ($R^2 = 0.9251$; Fig. 3). No significant relationship between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ is observed ($R^2 = 0.4452$; Fig. 4). Relatively negative $\delta^{13}\text{C}$ values are observed.

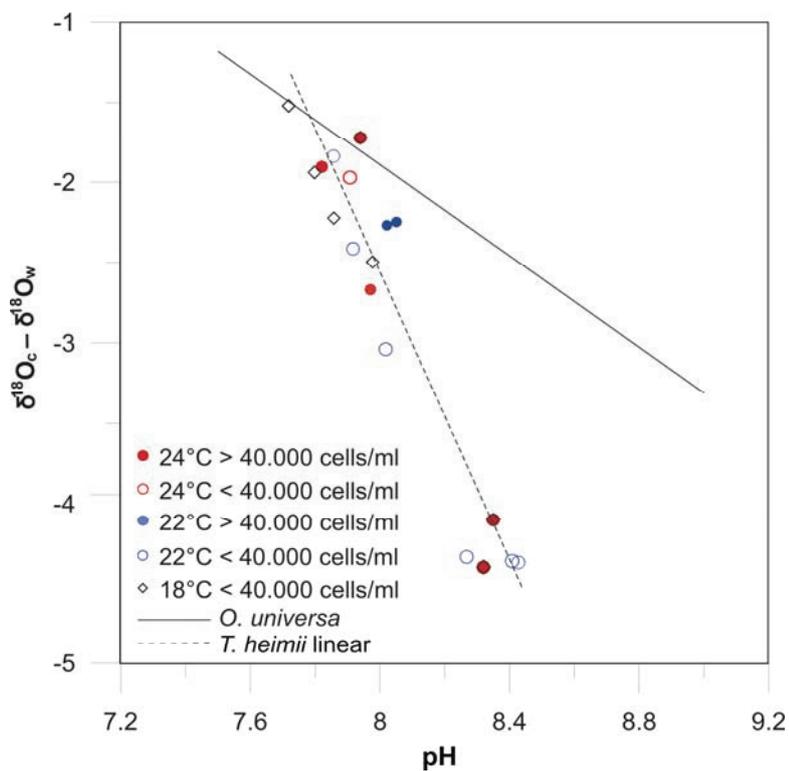


Fig. 3 Relationship between pH and $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ of *Thoracosphaera heimii* for all temperatures of the culture medium. Linear relationship between pH and $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ of *Orbulina universa* (slope -1.42‰ per pH unit; after Zeebe, 1999).

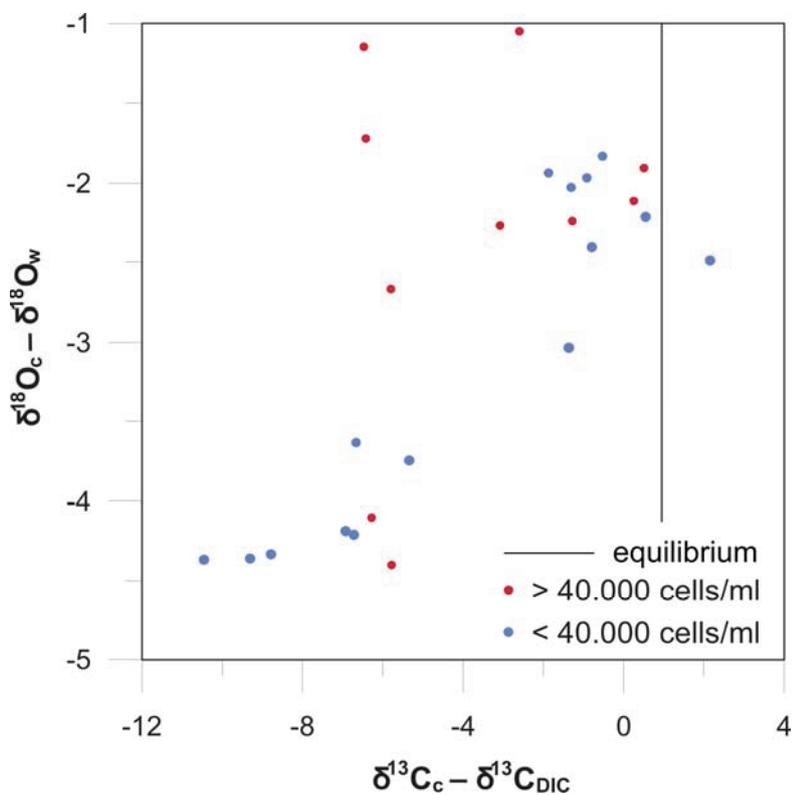


Fig. 4. Relationship between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_w$ of *Thoracosphaera heimii*. Equilibrium ^{13}C values of inorganic calcite are according to Romanek *et al.* (1992).

4.4 Discussion

Under the culture conditions of this experiment the exponential growth phase started after 13 days at 22 °C roughly when cell numbers exceeded 40.000 cells/ml/t (Fig. 1). The exponential growth rate increases with an increasing culture volume and higher nutrient and element concentrations. All samples at 18 °C and at 22 °C with pH 7.6 and 8.4 and one sample at 24 °C with pH 8.4 stayed below a final yield of 40.000 cells/ml/t (Fig. 2). It is therefore not clear if the above given strains had reached the exponential growth phase at the time of the harvest. However, *Thoracosphaera heimii* reproduces asexually within 1 to 2 days and it can therefore be assumed that at the end of the experiment the harvested cells were well adapted to the culture conditions (e.g. Tangen *et al.*, 1982; Inouye and Pienar, 1983; Wendler *et al.*, 2002). Nevertheless, the results of these strains have been considered carefully in the rest of the paper.

Growth rates of *T. heimii* were extremely low at pH 8.4 (Fig. 2). At this pH we also observed precipitation in all culture vessels at the end of the experiment. High pH can affect the solubility of both macro- and micronutrients (Hansen *et al.*, 2007). Trace metals such as Zn, Fe, Co or Cu tend to form hydroxides at higher pH which are less soluble in seawater. We assume that the precipitation of some trace elements might have limited the trace elemental availability for *T. heimii* and consequently might have reduced growth rates.

We found a negative linear relationship between pH and $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ (Fig. 3). Our results contrast earlier findings of Zonneveld *et al.* (2007) who observed a positive relationship between pH and $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$. They explain this with the presence of an external (periplasmatic) carbon anhydrase (eCA) at higher pH that might become increasingly efficient. The carbonic anhydrase (CA) is an enzyme that catalyses the conversion of CO_2 to HCO_3^- (Badger and Price, 1994). In several dinoflagellate species an internal carbon anhydrase (iCA) and an eCA has been demonstrated (e.g. Berman-Frank *et al.*, 1995; Nimer *et al.*, 1997, 1999; Dason *et al.*, 2004). A possible explanation for these contrasting results could be that the physical conditions within the culture medium in the experiment of Zonneveld *et al.* (2007) did not remain completely constant. If culture medium carbon concentrations become depleted, calcite precipitation may have had an organism's internal carbon source. Then, the internal pH concentrations would have influenced the calcification processes rather than the medium pH. Within our experiment the culture medium remained constant.

For *T. heimii* we observed an extremely strong decrease of $\delta^{18}\text{O}$ in relationship to increasing pH values with a slope of -4.4985 ‰ per pH unit independent if final harvest is above or below the boundary of 40.000 cells/ml/t (Fig. 3). Our findings correspond to previous observations in other organism groups. Culture experiments on corals and planktonic foraminifera demonstrated that seawater pH has a major effect on the stable oxygen isotope fractionation with increasing $\delta^{18}\text{O}$ values at decreasing pH values (Spero *et al.*, 1997; Zeebe *et al.*, 1999; Zeebe, 2001; Fig. 3). Studies on symbiotic corals also indicated a negative relationship between pH and $\delta^{18}\text{O}$ with higher $\delta^{18}\text{O}$ values at lower pH values (Rollion-Bard *et al.*, 2003). These studies showed that different carbonate species $S = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ have different equilibrium fractionations with respect to seawater. With increasing pH a solution containing a mixture of these carbonate species will contain relatively higher concentrations of CO_3^{2-} and lower concentrations of HCO_3^- . The mechanisms seen in foraminifera is explained by HCO_3^- being isotopically lighter than CO_3^{2-} (Spero *et al.*, 1997; Bijma *et al.*, 1999; Zeebe, 1999; Zeebe, 2001). In the planktonic foraminifera *Orbulina universa* the average slope of $\delta^{18}\text{O}$ vs pH is -1.42 ‰ per pH unit at 22 °C (Zeebe, 2001). For some dinoflagellate species it is known that they primarily and/or selectively uptake CO_2 as inorganic carbon source (e.g. Nimer *et al.*, 1999; Dason *et al.*, 2004). Although other species preferentially uptake HCO_3^- (Rost *et al.*, 2006). In a few species bicarbonate even contributes to more than 80 % of the photosynthetic carbon fixation. Since HCO_3^- is isotopically lighter we assume that *T. heimii* preferably uptakes HCO_3^- .

No significant linear relationship can be observed between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ (Fig. 4). This is in line with previous studies on the isotopic composition of *T. heimii* (Friedrich and Meier, 2003; Zonneveld *et al.*, 2007) but contrasts with the strong co-variance between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ in non-symbiotic corals and foraminifera (McConnaughey, 1989; Spero *et al.*, 1997). A positive linear correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is explained by a kinetic effect on isotopic fractionation during carbonate precipitation (e.g. McConnaughey, 1989; Adkins *et al.*, 2003; McConnaughey, 2003). If the precipitation of carbonate is faster than the hydration and hydroxylation of carbon dioxide then this results in the depletion of ^{13}C and ^{18}O due to faster hydration of ^{12}C and ^{16}O . Our observation that $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ of *T. heimii* are not linearly related suggest that no kinetic isotope fractionation occurs during hydration and hydroxylation of CO_2 .

Consistent with previous observations on the stable isotopic composition of *T. heimii*, its $\delta^{13}\text{C}$ values are extremely low compared to other calcite forming marine organisms, which generally have values near the equilibrium with seawater ($\sim +1$ ‰; Goodeny *et al.*, 1980; Romanek *et al.*, 1992; Friedrich and Meier, 2003; Zonneveld, 2004; Zonneveld *et al.*, 2007). Such negative values can be explained by fractionation during photosynthesis where a strong isotope fractionation of carbon occurs by Ribulose-1,5-biphosphate carboxylase-oxygenase (RuBisCo) (e.g. McConnaughey *et al.*, 1997; Ziveri *et al.*, 2003; Zonneveld *et al.*, 2007, Rost *et al.*, 2008). RuBisCo is an enzyme that catalyses the fixation of CO_2 during photosynthesis but it is not optimal efficient since it has a high susceptibility to a competing reaction with O_2 . The extremely low carbon isotope values of *T. heimii* in our data confirms the suggestion of Zonneveld *et al.* (2007) that *T. heimii* at least partly might use respired carbon as source for calcite precipitation.

Our investigations showed a linear relationship between pH and stable oxygen isotopes of *T. heimii*. This may indicate that seawater pH has a major effect on isotopic palaeotemperature estimations and has to be taken into account when using palaeotemperature equations. In the past the oceanic pH varied, for instance, with a change of about 0.3 ± 0.1 pH units between the last glacial maximum and the Holocene periods (Sanyal *et al.*, 1995). Consequently, changes in pH would have lead to a depletion of ^{18}O in *T. heimii* and to an underestimation of sea surface temperatures during the last glacial maximum.

4.5 Conclusion

Within this study, a detailed understanding of the kinetic fractionation mechanisms and physiological processes of *Thoracosphaera heimii* were obtained.

In contrast to planktonic foraminifera, no correlation between $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ and $\delta^{13}\text{C}_c - \delta^{13}\text{C}_{\text{DIC}}$ was found. Therefore, we assume that kinetic effects do not influence the isotopic fractionation during the calcification process of *T. heimii*. The extremely negative carbon isotope values suggest that *T. heimii* partly respire carbon as a source for calcite precipitation.

The documented negative relationship between pH and stable oxygen isotopes of *T. heimii* is in line with earlier findings on other calcareous organisms like corals and foraminifera. Although the slope between pH and $\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$ is different, we expect the same physiological mechanisms to be used in these species. Oxygen isotopes

respond to changes in pH through relative fractionation of dissolved carbonate species so that with increasing pH the concentration of HCO_3^- decreases. As shown in previous studies, some dinoflagellate species preferentially uptake HCO_3^- . Since HCO_3^- is isotopically lighter, we assume that *T. heimii* also preferably takes up HCO_3^- .

Large changes in pH during the last glacial maximum compared to the last interglacial might have led to underestimation of past sea surface temperatures based on *T. heimii* reconstructions due to a depletion of its $\delta^{18}\text{O}$ signal. This study helps us to get a better interpretation of the stable oxygen isotope signal of *T. heimii* in past sediments and suggests *T. heimii* as a proxy for pH.

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4.7 Appendix

Appendix 1. Calculated total concentration of all dissolved bicarbonate species and total alkalinity of the growth medium before and after the experiment.

Sample	T [°C]	Salinity [psu]	pH (NBS)	TA [mmol/kg SW]	HCO ₃ ⁻ in [mmol/kg SW]	CO ₃ ²⁻ in [mmol/kg SW]	CO ₂ in [mmol/kg SW]
Start 7.62	18	36.4	7.763	2631.64	2332.3	119.4	31.7
Start 7.62	18	36.4	7.767	2636.14	2334.0	120.6	31.4
Start 8.04	18	36.4	7.776	2827.93	2502.0	131.9	33.0
Start 8.04	18	36.4	7.764	2865.02	2543.4	130.5	34.4
Start 8.42	18	36.4	8.446	3280.75	2073.3	511.4	5.8
Start 8.42	18	36.4	8.445	3287.03	2079.2	511.7	5.9
7.62 1_1	18	38.5	7.560	2088.74	1914.6	64.3	40.8
7.62 1_2	18	38.5	7.598	2103.83	1914.9	70.2	37.4
7.62 1_3	18	38.5	7.534	2112.62	1946.0	61.6	44.1
7.62 2_1	18	38.4	7.688	1472.88	1299.4	58.5	20.7
7.62 2_2	18	38.4	7.686	1481.65	1308.1	58.6	20.9
7.62 2_3	18	38.4	7.690	1479.80	1305.1	59.0	20.7
7.62 3_1	18	38.5	7.710	1480.62	1298.5	61.6	19.6
7.62 3_2	18	38.5	7.713	1483.06	1299.7	62.1	19.5
7.62 3_3	18	38.5	7.709	1484.65	1302.6	61.7	19.7
7.62 2 Blanc	18	38.2	7.733	2459.55	2181.9	108.4	31.3
7.62 3 Blanc	18	38.2	7.764	2480.81	2183.6	116.6	29.2
8.04 1_1	18	38.2	7.758	1512.40	1310.9	69.0	17.8
8.04 1_2	18	38.2	7.756	1528.66	1326.4	69.5	18.1
8.04 1_3	18	38.2	7.734	1523.39	1330.0	66.3	19.0
8.04 2_1	18	38.2	7.609	1440.08	1294.3	48.4	24.7
8.04 2_2	18	38.2	7.667	1502.02	1333.9	57.0	22.3
8.04 2_3	18	38.2	7.650	1479.80	1318.9	54.1	22.9
8.04 3_1	18	37.2	7.447	1539.50	1431.1	36.0	40.0
8.04 3_2	18	37.2	7.689	1578.15	1400.4	61.5	22.4
8.04 3_3	18	37.2	7.620	1562.73	1408.6	52.8	26.4
8.04 Blanc_1	18	38.6	7.719	2562.46	2281.0	110.7	33.7
8.04 Blanc_2	18	38.6	7.719	2568.73	2286.7	111.0	33.8
8.04 Blanc_3	18	38.6	7.733	2589.68	2297.8	115.2	32.9
8.42 1_1	18	38.5	8.170	2819.96	2112.4	289.0	11.1
8.42 1_2	18	38.5	8.121	2796.16	2150.8	262.9	12.6
8.42 1_3	18	38.5	8.161	2818.29	2121.9	284.4	11.3
8.42 2_1	18	38.3	8.322	2157.65	1438.1	278.0	5.3
8.42 2_2	18	38.3	8.248	2123.23	1491.1	243.1	6.5
8.42 2_3	18	38.3	8.084	2091.49	1618.1	180.8	10.3
8.42 3_1	18	38.3	8.334	2371.41	1577.8	313.6	5.7
8.42 3_2	18	38.3	8.332	2380.50	1586.7	313.9	5.7
8.42 3_3	18	38.3	8.190	2258.21	1653.4	235.9	8.3
8.42 Blanc_1	18	38.3	7.928	3590.12	3031.4	236.6	27.8
8.42 Blanc_2	18	38.3	7.915	3588.66	3043.9	230.5	28.7
8.42 Blanc_3	18	38.3	7.930	3570.82	3012.6	236.2	27.5
pH7.6-1	24	36.4	7.684	2227.06	1957.5	104.4	28.1
pH7.6-2	24	36.4	7.665	2221.21	1962.1	100.1	29.4
pH7.6-3	24	36.4	7.716	2214.45	1928.7	110.7	25.7
pH8.0-1	24	36.5	7.918	2408.52	1958.2	179.3	16.4
pH8.0-2	24	36.5	7.919	2410.30	1958.8	179.8	16.3
pH8.0-3	24	36.5	7.925	2387.27	1934.4	180.0	15.9
pH8.4-1	24	36.5	8.242	2681.00	1821.4	351.7	7.2
pH8.4-2	24	36.5	8.241	2692.47	1831.0	352.8	7.3
pH8.4-3	24	36.5	8.242	2689.38	1827.4	352.9	7.2
pH7.6-Blanc	24	36.4	7.544	2895.03	2643.1	102.1	52.4
pH7.6-Blanc	24	36.4	7.545	2687.69	2450.1	94.8	48.4
pH7.6-Blanc	24	36.4	7.543	2613.53	2382.2	91.8	47.3
pH7.6-1	24	36.4	7.544	2498.35	2274.8	87.9	45.1
pH7.6-1	24	36.4	7.553	2498.19	2270.6	89.5	44.1
pH7.6-1	24	36.4	7.564	2538.96	2303.2	93.1	43.6
pH7.6-2	24	36.4	7.739	1309.09	1108.0	67.0	14.0
pH7.6-2	24	36.4	7.745	1318.81	1114.4	68.4	13.9
pH7.6-2	24	36.4	7.74	1318.06	1115.6	67.7	14.1
pH7.6-3	24	36.4	7.709	1232.40	1050.2	59.3	14.2
pH7.6-3	24	36.4	7.712	1214.60	1033.2	58.8	13.9
pH7.6-3	24	36.4	7.71	1208.02	1028.0	58.2	13.9
pH8.0-Blanc	24	36.5	7.762	2480.67	2137.4	136.7	25.6
pH8.0-Blanc	24	36.5	7.787	2505.06	2141.9	145.1	24.2
pH8.0-Blanc	24	36.5	7.79	2505.45	2140.1	146.0	24.0
pH8.0-1	24	36.4	7.854	2260.04	1881.5	148.4	18.3
pH8.0-1	24	36.4	7.851	2283.74	1904.1	149.1	18.6

Appendix 1. (continued)

Sample	T [°C]	Salinity [psu]	pH (NBS)	TA [mmol/kgSW]	HCO ₃ ⁻ in [mmol/kgSW]	CO ₃ ²⁻ in [mmol/kgSW]	CO ₂ in [mmol/kgSW]
pH8.0-1	24	36.4	7.861	2258.58	1875.2	150.3	17.9
pH8.0-2	24	36.5	8.057	1358.71	992.3	125.2	6.0
pH8.0-2	24	36.5	8.062	1359.99	990.3	126.3	5.9
pH8.0-2	24	36.5	8.056	1357.68	992.1	124.8	6.0
pH8.0-3	24	36.5	7.9	1587.14	1274.3	112.0	11.1
pH8.0-3	24	36.5	7.9	1569.14	1259.0	110.6	11.0
pH8.0-3	24	36.5	7.902	1566.97	1256.0	110.9	10.9
pH8.4-Blanc	24	36.6	8.173	2770.17	1976.8	326.4	9.2
pH8.4-Blanc	24	36.6	8.174	2795.33	1994.4	330.1	9.2
pH8.4-Blanc	24	36.6	8.176	2807.05	2000.5	332.6	9.2
pH8.4-1	24	36.6	8.278	2571.04	1693.4	356.1	6.2
pH8.4-1	24	36.6	8.277	2591.00	1708.8	358.5	6.2
pH8.4-1	24	36.6	8.276	2587.84	1707.9	357.5	6.3
pH8.4-2	24	36.5	8.24	2602.56	1767.4	339.7	7.0
pH8.4-2	24	36.5	8.239	2647.40	1801.1	345.4	7.2
pH8.4-2	24	36.5	8.237	2610.73	1777.2	339.3	7.1
pH8.4-3	24	36.6	8.199	2673.37	1870.9	328.0	8.2
pH8.4-3	24	36.6	8.197	2659.49	1863.2	325.1	8.2
pH8.4-3	24	36.6	8.202	2637.90	1840.8	324.9	8.0
pH7.75-1	22	36.7	7.742	2299.27	2005.8	114.3	26.2
pH7.75-1	22	36.7	7.776	2425.71	2098.2	129.4	25.3
pH7.75-1	22	36.7	7.756	1457.24	1244.3	73.3	15.7
pH8.0-1	22	36.8	7.932	2452.98	2007.3	177.6	16.9
pH8.0-2	22	36.8	7.937	2452.66	2002.9	179.3	16.7
pH8.0-3	22	36.8	7.937	1764.46	1419.2	127.0	11.8
pH8.4-1	22	36.7	8.25	2734.05	1888.4	346.8	7.6
pH8.4-2	22	36.7	8.244	2736.71	1898.3	343.8	7.8
pH8.4-3	22	36.7	8.234	1773.20	1200.0	212.4	5.0
pH7.75-Blanc	22	36.8	7.69	2239.54	1979.5	100.3	29.1
pH7.75-Blanc	22	36.8	7.692	2245.28	1983.7	101.0	29.0
pH7.75-Blanc	22	36.8	7.698	2253.81	1988.3	102.7	28.7
pH7.75-1	22	36.8	7.792	1505.80	1271.8	81.5	14.8
pH7.75-1	22	36.8	7.792	1528.71	1292.1	82.8	15.0
pH7.75-1	22	36.8	7.811	1746.55	1475.6	98.8	16.4
pH7.75-2	22	36.5	7.788	1380.69	1164.0	73.4	13.7
pH7.75-2	22	36.5	7.78	1376.78	1163.8	72.1	13.9
pH7.75-2	22	36.5	7.778	1370.68	1159.2	71.5	13.9
pH7.75-3	22	36.4	7.773	1404.96	1192.2	72.5	14.5
pH7.75-3	22	36.4	7.77	1403.22	1191.8	72.0	14.6
pH7.75-3	22	36.4	7.769	1400.14	1189.5	71.7	14.6
pH8.0-Blanc	22	36.8	7.986	1506.79	1172.6	117.5	8.7
pH8.0-Blanc	22	36.8	7.987	1508.76	1173.6	117.9	8.7
pH8.0-Blanc	22	36.8	7.972	1620.90	1276.4	123.8	9.8
pH8.0-2	22	36.6	7.961	1552.82	1227.2	115.6	9.7
pH8.0-2	22	36.6	7.966	1571.27	1239.8	118.1	9.7
pH8.0-2	22	36.6	7.961	1545.80	1221.3	115.0	9.6
pH8.0-3	22	36.6	7.967	1568.10	1236.5	118.1	9.6
pH8.0-3	22	36.6	7.966	1562.27	1232.2	117.4	9.6
pH8.0-3	22	36.6	7.966	1541.43	1214.7	115.7	9.5
pH8.4-Blanc	22	36.7	8.182	2758.95	1995.5	313.3	9.5
pH8.4-Blanc	22	36.7	8.18	2753.66	1994.0	311.7	9.5
pH8.4-Blanc	22	36.7	8.178	2779.04	2015.9	313.6	9.6
pH8.4-1	22	36.5	8.283	2532.76	1702.2	335.8	6.4
pH8.4-1	22	36.5	8.279	2521.92	1699.6	332.2	6.4
pH8.4-1	22	36.5	8.281	2525.91	1699.9	333.7	6.4
pH8.4-2	22	36.5	8.315	2328.86	1517.5	322.2	5.3
pH8.4-2	22	36.5	8.313	2335.47	1524.6	322.2	5.3
pH8.4-2	22	36.5	8.309	2330.95	1526.3	319.6	5.4
pH8.4-3	22	36.5	8.34	2448.80	1569.6	353.0	5.2
pH8.4-3	22	36.5	8.335	2436.53	1567.6	348.5	5.2
pH8.4-3	22	36.5	8.338	2451.06	1573.7	352.3	5.2

4.8 References

- Adkins, J.F., Boyle, E.A., Curry, B. and Lutringer, A., 2003. Stable isotopes in deep-sea corals and a new mechanism for "vital effects". *Geochimica et Cosmochimica Acta*, 67(6): 1129-1143.
- Badger, M.R., Price, G.D., 1994. The role of carbonic anhydrase in photosynthesis. *Annu. Rev. Plant Physiol. Plant Mol. Bio.* 45: 369–392.
- Berman-Frank, I., Kaplan, A., Zohary, T. and Dubinsky, Z., 1995. Carbonic anhydrase activity in the bloom-forming dinoflagellate *Peridinium gatunense*. *J. Phycol.*, 31: 906-913.
- Bijma, J., Spero, H.J. and Lea, D.W., 1999. Reassessing Foraminiferal Stable Isotope Geochemistry: Impact of the Oceanic Carbonate System (Experimental Results). *Use of Proxies in Paleoceanography: Examples from the South Atlantic*. Springer-Verlag, Berlin Heidelberg, 489-512 pp.
- Dason, J.S., Huertas, I.E., Colman, B., 2004. Source of inorganic carbon for photosynthesis in two marine dinoflagellates. *Journal of Phycology*, 40:285-292.
- Dickson, A.G., 1981. Instruments and methods - An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Research* 28A (6): 607-623.
- Emiliani, C., 1966. Isotopic paleotemperatures. *Science*, 154: 851-857.
- Friedrich, O. and Meier, S.K.J., 2003. Stable isotopic indication for the cyst formation depth of Campanian/Maastrichtian calcareous dinoflagellates. *Micropaleontology*, 49(4): 375-380.
- Goodeny, D.E., Margolis, S.V., Dudley, W.C., Kroopnick, P. and Williams, D.F., 1980. Oxygen and carbon isotopes of recent calcareous nannofossils as paleoceanographic indicators. *Marine Micropaleontology*, 5: 31-42.
- Gran, G., 1952. Determination of the equivalence point in potentiometric titrations of seawater with hydrochloric acid. *Oceanologica Acta*, 5: 209-218.
- Hansen, P.J., Lundholm, N. and Rost, B., 2007. Growth limitation in marine red-tide dinoflagellates: effects of pH versus inorganic carbon availability. *Marine ecology progress series*, 334: 63-71.
- Intergovernmental Panel on Climate Change (2007) Working Group I Report "The Physical Science Basis". Available at <http://ipcc-wg1.ucar.edu/wg1/wg1-report.html>.
- Inouye, I. and Pienar, R.N., 1983. Observations on the life cycle and microanatomy of *Thoracosphaera heimii* (Dinophyceae) with special reference to its systematic position. *South African Journal of Botany*, 2: 63-75.
- Keller, M.D. and Guillard, R.R.L., 1985. Factors significant to marine dinoflagellate culture. In: D.M. Anderson, A.W. White and D.G. Baden (Editors), *Toxic dinoflagellates*. Elsevier, New York, pp. 113-116.
- Keller, M.D., Selvin, R.C., Claus, W. and Guillard, R.R.L., 1997. Media for the culture of oceanic ultraphytoplankton. *Journal of Phycology*, 123: 633-638.
- Kohn, M., Steinke, S., Baumann, K.-H., Donner, B., Meggers, H., Zonneveld, K.A.F., subm. Stable oxygen isotopes of the calcareous-walled dinoflagellate *Thoracosphaera heimii* as a proxy for mixed layer temperatures. *Palaeogeography, Palaeoclimatology, Palaeoecology*.

- Lewis, E., Wallace, D., 1998. Program developed for CO₂ system calculations. Carbon Dioxide Information Analysis Center, Tennessee.
- McConnaughey, T.A., 1989. ¹³C and ¹⁸O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochimica et Cosmochimica Acta*, 53(1): 151-162.
- McConnaughey, T.A., 2003. Sub-equilibrium oxygen-18 and carbon-13 levels in biological carbonates: carbonate and kinetic models. *Coral Reefs*, 22(4): 316-327.
- McConnaughey, T.A., Burdett, J., Whelan, J.F. and Paull, C.K., 1997. Carbon isotopes in biological carbonates: Respiration and photosynthesis. *Geochimica et Cosmochimica Acta*, 61(3): 611-622.
- McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *The journal of chemical physics*, 18(6): 849-857.
- Mehrbach, C., Culberson, C.H., Hawley, J.E., Pytkowicz, R.M., 1973. Measurement of the Apparent Dissociation Constants of Carbonic Acid in Seawater at Atmospheric Pressure. *Limnology and Oceanography* 18 (6): 897-907.
- Nimer, N.A., Iglasias-Rodriguez, M.D., Merrett, M.J., 1997. Bicarbonate utilisation by marine phytoplankton species. *Journal of Phycology* 33, 625-631.
- Nimer, N.A., Brownlee, C., and Merrett, M.J., 1999. Extracellular Carbonic Anhydrase Facilitates Carbon Dioxide Availability for Photosynthesis in the Marine Dinoflagellate *Prorocentrum micans*. *Plant Physiology*. 120: 105-111.
- Rohling, E.J. and Cooke, S., 1999. Stable oxygen and carbon isotopes in foraminiferal carbonate shells. In: Sen Gupta, B.K. (Editor), *Modern Foraminifera*. Kluwer Acad., Norwell, Mass., pp. 239-258.
- Rollion-Bard, C., Chaussidon, M. and France-Lanord, C., 2003. pH control on oxygen isotopic composition of symbiotic corals. *Earth and Planetary Science Letters*, 215: 275-288.
- Romanek, C.S., Grossman, E.L. and Morse, J.W., 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate. *Geochimica et Cosmochimica Acta*, 56(1): 419-430.
- Rost, B., Richter, K.-U., Riebesell, U., Hansen, P.J., 2006. Inorganic carbon acquisition in red tide dinoflagellates. *Plant, Cell and Environment*, 29: 810-822.
- Rost, B., Zondervan, L., Wolf-Gladrow, D., 2008. Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: Current knowledge, contradictions and
- Sanyal, A., Hemming, N.G., Hanson, G., N. and Broecker, W.S., 1995. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature*, 373: 234-236.
- Spero, H.J., Bijma, J., Lea, D.W. and Bemis, B.E., 1997. Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. *Nature*, 390: 497-500.
- Tangen, K., Brand, L.E., Blackwelder, P.L. and Guillard, R.R.L., 1982. *Thoracosphaera heimii* (Lohmann) Kamptner is a dinophyte: observations on its morphology and life cycle. *Marine Micropaleontology*, 7: 193-212.
- Vink, A., Zonneveld, K.A.F. and Willems, H., 2000. Distributions of calcareous dinoflagellate cysts in surface sediments of the western equatorial Atlantic Ocean, and their potential use in paleoceanography. *Marine Micropaleontology*, 38(2): 149-180.
- Wefer, G. and Berger, W.H., 1991. Isotope paleontology: growth and composition of extant calcareous species. *Marine Geology*, 100: 207-248.

- Wendler, I., Zonnefeld, K.A.F. and Willems, H., 2002. Production of calcareous dinoflagellate cysts in response to monsoon forcing off Somalia: a sediment trap study. *Marine Micropaleontology*, 46: 1-11.
- Zeebe, R.E., 1999. An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes. *Geochimica et Cosmochimica Acta*, 63(13/14): 2001-2007.
- Zeebe, R.E., Bijma, J. and Wolf-Gladrow, D.A., 1999. A diffusion-reaction model of carbon isotope fractionation in foraminifera. *Marine Chemistry*, 64: 199-227.
- Zeebe, R.E., 2001. Seawater pH and isotopic paleotemperatures of Cretaceous oceans. *Palaeogeography, Palaeoecology*, 170: 49-57.
- Ziveri, P., Stoll, H., Probert, I., Klaas, C., Geisen, M., Ganssen, G., Young, J., 2003. Stable isotope "vital effects" in coccolith calcite. *Earth and Planetary Science Letters*, 210: 137-149.
- Zonneveld, K., 2004. Potential use of stable isotope composition of *Thoracosphaera heimii* (Dinophyceae) for upper watercolumn (thermocline) temperature reconstruction. *Marine Micropaleontology*, 50(3-4): 307-317.
- Zonneveld, K.A.F., Mackensen, A. and Baumann, K.-H., 2007. Stable oxygen isotopes of *Thoracosphaera heimii* (Dinophyceae) in relationship to temperature; a culture experiment. *Marine Micropaleontology*, 64(1-2): 80-90.

Chapter 5

Conclusions and perspectives

5.1 Summary and conclusions

This pilot study documents the applicability of the stable oxygen isotope signal of the calcareous-walled dinoflagellate *Thoracosphaera heimii* in a time series analysis to reconstruct sea surface palaeotemperatures.

In this context the question arises:

Why do we need a new proxy?

since we already have several proxies for palaeotemperature calculations. To demonstrate the advantage of our proxy, we compared it to other well-established proxies like planktonic foraminifera.

In order to obtain a better interpretation of the stable oxygen isotope signal of *Thoracosphaera heimii* it is important to determine (a) its seasonal distribution pattern as well as (b) to quantify the depth habitat where it is produced in relation to physical parameters of the water column and (c) to describe a possible pH effect.

- (a) Compared to other temperature proxies like planktonic foraminifera, this new proxy reflects mean annual temperatures since it is produced throughout the year in the research area off Cape Blanc. In contrast, the planktonic foraminifera *Globigerinoides ruber* (pink) is supposed to reflect a summer signal (Ganssen and Sarnthein, 1983; Fischer *et al.*, 1996; Waelbroeck *et al.*, 2005), while *Globigerina bulloides* is a typical upwelling indicator (e.g. Prell and Curry, 1981; Ganssen and Sarnthein, 1983; Thiede, 1983; Thunell *et al.*, 1983; Hebbeln *et al.*, 2000).
- (b) Water samples off NW and SE Africa imply that *T. heimii* is produced in a relatively restricted part of the upper water column at or just above the deep chlorophyll maximum (DCM). Therefore, they live around the same depth as *G. ruber* (pink) with maximal concentrations at the DCM up to about 50 m (Hemleben *et al.*, 1989;

Peeters *et al.*, 2002; Anand, 2003; Tedesco *et al.*, 2006). Therefore, the discrepancy between the oxygen isotope values and subsequent temperature reconstructions for *G. bulloides* and *T. heimii* can be explained by different depth habitats since *G. bulloides* dwells at depths between 25 and 75 m (Hemleben *et al.*, 1989; Peeters *et al.*, 2002).

- (c) Culture experiments revealed a negative linear relationship between pH and $\delta^{18}\text{O}$ of *T. heimii*. Changes in the pH over Earth's history, such as during the last glacial maximum, would lead to an underestimation of sea surface temperature due to a depletion of the $\delta^{18}\text{O}$ signal of *T. heimii* (Sanyal *et al.*, 1995). It is therefore important to correct palaeotemperature estimations for pH.

The determination of where *T. heimii* exactly forms its calcite shells in the water column combined with the knowledge of its seasonal signal permit the development of a more defined temperature signal. More precise corrections for past-pH changes furthermore help to get improve the palaeotemperature estimations. This result in a more precise interpretation of its stable oxygen isotope signal compared to other calcareous species that were formerly used as a proxy for palaeotemperature.

5.2 Future perspectives

Although detailed information on the ecological preferences of *Thoracosphaera heimii* was sought and has since been successfully applied in high-resolution palaeoclimatic reconstructions, further application of these palaeoceanographic reconstructions will benefit from more detailed field and sediment studies covering a broader range of environments from different oceans and oceanic regimes. Although detailed spatial information on cyst distributions are available, these data have to be treated with care until they can be regionally and seasonally related to temperature, water column stability, chlorophyll concentrations, nutrient and light availability (e.g. Höll *et al.*, 1998; Wendler *et al.*, 2002; Vink, 2004; Richter *et al.*, 2007 and references therein). For instance, off Tanzania vertical and horizontal data are only available during the NE monsoon, while data during the SW monsoon are nonexistent. Furthermore, studies on a full sediment core off Tanzania could provide interesting

insights into climatic and oceanographic changes in the Indian Ocean over a longer time scale.

In the present study, the equation of (Kim and O'Neil, 1997) has been used to calculate palaeotemperature from oxygen isotopes. The palaeotemperature equation of *T. heimii* from Zonneveld *et al.* (2007) provides unrealistic temperatures due to changing parameters in the culture experiment. Consequently, a new equation from *T. heimii* has to be developed by culturing them under different temperatures at constant physical conditions in order to get an accurate species-specific temperature equation.

More recent culture experiments determined that Sr/Ca ratios of *T. heimii* might have great potential as a SST proxy (Gussone *et al.*, *subm.*). In future studies, the method of Zonneveld (2004) and Gussone *et al.* (*subm.*) will be combined and modified to use *T. heimii* surface sediment samples for elemental analyses of Sr/Ca and Mg/Ca (S. Dekeyzer, personal communication). In order to efficiently evaluate the two new SST proxies ($\delta^{18}\text{O}$ and Sr/Ca) they will also have to be compared to other well-established SST proxies like foraminifera.

In the future, calcifiers will be especially influenced by elevated pCO_2 leading to a decrease in carbonate ion concentration and thus calcite saturation levels (Rost, 2008). Depending on the species, some will be influenced in a negative way while others will benefit from ocean acidification. For example, species that are only dependent on CO_2 are less competitive under high pH-values. Several studies indicate that calcification will be reduced and that ocean acidification will be an ecological disadvantage for coccolithophores (Riebesell *et al.*, 2000; Zondervan *et al.*, 2002; Sciandra *et al.*, 2003; Delille *et al.*, 2005). To date, it is not clear whether *T. heimii* is only restricted to CO_2 or also uses HCO_3^{2-} as a carbon source (Langer *et al.*, 2006; Zonneveld *et al.*, 2007). In order to figure out the sensitivity of *T. heimii* to future changes in ocean carbonate chemistry further research on its physiology has to be performed.

5.3 References

- Anand, P., Elderfield, H., Conte, M.H., 2003. Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series. *Paleoceanography*, 18(2): 1050.
- Delille, B. et al., 2005. Response of primary production and calcification to changes of pCO_2 during experimental blooms of the coccolithophorid *Emiliania huxleyi*. *Global Biogeochem. Cycles*, 19.
- Fischer, G., Donner, B., Ratmayer, V., Davenpoort, R. and Wefer, G., 1996. Distinct year-to-year flux variations off Cape Blanc during 1988-1991: relation to ^{18}O -deduced sea-surface temperatures and trade winds. *Journal of Marine Research*, 54(73-98).

- Ganssen, G. and Sarnthein, M., 1983. Stable isotope composition of foraminifers: the surface and bottom water record of coastal upwelling. In: E. Suess, Thiede, J. (Editor), Coastal upwelling: Its sedimentary record, Part A., New York, Plenum.
- Gussone, N., Zonneveld, K.A.F., Kuhnert, H., subm. Minor element and Ca isotope composition of calcareous dinoflagellate cysts of cultured *Thoracosphaera heimii*. Earth and planetary science letters.
- Hebbeln, D., Marchant, M., Freudenthal, T. and Wefer, G., 2000. Surface sediment distribution along the Chilean continental slope related to upwelling and productivity. Marine Geology, 164(3-4): 119-137.
- Hemleben, C., Spindler, M. and Anderson, O.R., 1989. Modern planktonic foraminifera. Springer, New York.
- Höll, C., Zonneveld, K.A.F. and Willems, H., 1998. On the ecology of calcareous dinoflagellates: The Quaternary eastern equatorial Atlantic. Marine Micropaleontology, 33(1-2): 1-25.
- Kim, S.-T. and O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochimica et Cosmochimica Acta, 61(16): 3461-3475.
- Langer, G. et al., 2006. Coccolith strontium to calcium ratios in *Emiliana huxleyi*: The dependence on seawater strontium and calcium concentrations. Limnol. Oceanogr., 51(1): 310-320.
- Peeters, F.J.C., Brummer, G.-J.A. and Ganssen, G., 2002. The effect of upwelling on the distribution and stable isotope composition of *Globigerina bulloides* and *Globigerinoides ruber* (planktic foraminifera) in modern surface waters of the NW Arabian Sea. Global and planetary change, 34: 269-291.
- Prell, W.L. and Curry, W.B., 1981. Faunal and isotopic indices of monsoonal upwelling: Western Arabian Sea. Oceanologica Acta, 4: 91-98.
- Richter, D., Vink, A., Zonneveld, K.A.F., Kuhlmann, H., Willems, H., 2007. Calcareous dinoflagellate cyst distributions in surface sediments from upwelling areas off NW Africa, and their relationships with environmental parameters of the upper water column. Marine Microbiology, 63: 201-228.
- Riebesell, U. et al., 2000. Reduced calcification of marine plankton in response to increased atmospheric CO₂. Nature, 407(6802): 364-367.
- Rost, B., Zondervan, I., Wolf-Gladrow, D., 2008. Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions. Marine Ecology Progress Series, 373: 227-237.
- Sanyal, A., Hemming, N.G., Hanson, G., N. and Broecker, W.S., 1995. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. Nature, 373: 234-236.
- Sciandra, A. et al., 2003. Response of coccolithophorid *Emiliana huxleyi* to elevated partial pressure of CO₂ under nitrogen limitation. Marine Ecology Progress Series, 261: 111-122.
- Tedesco, K., Thunell, R., Astor, Y. and Muller-Karger, F., 2006. The oxygen isotope composition of planktonic foraminifera from the Cariaco Basin, Venezuela: Seasonal and interannual variations. Marine Micropaleontology, 62: 180-193.

- Thiede, J., 1983. Palaeogeography and palaeobathymetry: Quantitative reconstructions of ocean basins. Tidal Friction and the Earth's Rotation II. Brosche and Sündermann. Springer-Verlag, Berlin, Heidelberg.
- Thunell, R.C., Curry, W.B. and Honjo, S., 1983. Seasonal variation in the flux of planktonic foraminifera: time series sediment trap results from the Panama Basin. *Earth and Planetary Science Letters*, 64: 44-55.
- Vink, A., 2004. Calcareous dinoflagellate cysts in South and equatorial Atlantic surface sediments: diversity, distribution, ecology and potential for palaeoenvironmental reconstructions. *Marine Micropaleontology*, 50(1-2): 43-88.
- Waelbroeck, C. et al., 2005. A global compilation of late Holocene planktonic foraminiferal $\delta^{18}O$ relationship between surface water temperature and $\delta^{18}O$. *Quaternary Science Reviews*, 24: 853-868.
- Wendler, I., Zonnefeld, K.A.F. and Willems, H., 2002. Production of calcareous dinoflagellate cysts in response to monsoon forcing off Somalia: a sediment trap study. *Marine Micropaleontology*, 46: 1-11.
- Zondervan, I., Rost, B. and Riebesell, U., 2002. Effect of CO₂ concentration on the PIC/POC ratio in the coccolithophore *Emiliana huxleyi* grown under light-limiting conditions and different daylengths. *Journal of Experimental Marine Biology and Ecology*, 272(1): 55-70.
- Zonneveld, K., 2004. Potential use of stable isotope composition of *Thoracosphaera heimii* (Dinophyceae) for upper watercolumn (thermocline) temperature reconstruction. *Marine Micropaleontology*, 50(3-4): 307-317.
- Zonneveld, K.A.F., Mackensen, A. and Baumann, K.-H., 2007. Stable oxygen isotopes of *Thoracosphaera heimii* (Dinophyceae) in relationship to temperature; a culture experiment. *Marine Micropaleontology*, 64(1-2): 80-90.