# Quantitative estimation of aerobic diagenetic overprint of palaeoproductivity signals

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**Zusammenfassung**

Artenspezifische aerobe Dekomposition beeinflusst die Aufzeichnungen fossiler organischer Dinoflagellatenzysten (Dinozysten) und somit die auf Dinozysten basierenden Interpretationen über Primärproduktion und ozeanographische Konditionen. Seit der Erkenntnis, dass Dinozysten sowohl empfindlich als auch resistent gegenüber Sauerstoffabbau sein können (insbesondere S- und R-Zysten) zeichnete sich ab, dass R-Zysten weiterhin als zuverlässiger Proxy für Primärproduktion und ozeanographische Konditionen genutzt werden können, während S-Zysten die Möglichkeit bilden die Zersetzung von aeroben organischem Material (OM) und die Sauerstoffkonzentration von früherem Bodenwasser zu quantifizieren. Der Abbau von OM spielt eine Schlüsselrolle im globalen Kohlenstoffkreislauf und dadurch ebenfalls in Bezug auf Klima Veränderungen, und Dinozysten scheinen ein wertvolles Instrument zur Untersuchung diagenetischer Prozesse darzustellen. Dennoch sind viele Fragen betreffend artenspezifische aerobe Degradationen von Dinozysten noch offen.

Um Informationen über die Abbaurate von S-Zysten, die Relation zwischen dem Abbau von S-Zysten und der Sauerstoffkonzentration, sowie über die aerobe Degradation von ausgestorbenen Dinozysten zu erhalten, wurden Studien an quartärem und vor-quartärem Material aus Sedimentkernen sowie entwickelte Belastungs-Experimente (exposure experiments) in der Natur durchgeführt.

Belastungs Experimente im natürlichen Milieu des östlichen Mittelmeeres brachten Informationen über die Abbaurate von S-Zysten. Innerhalb fünfzehn Monatiger Beanspruchung durch sauerstoffhaltiges Wasser nahm die Konzentration der S-Zysten *Brigantedinium* spp. und *Echinidinium granulatum* um 24 - 57% ab. Andere Arten, wie *Nematosphareopsis labyrinthus*, *Echinidinium aculeatum*, *Operculodinium israelianum* und *Impagidinium aculeatum* erfuhren hingegen einen leichten Anstieg ihrer Konzentration, was auf eine Resistenz in Bezug auf aerobe Degradation hinweist. Unsere Ergebnisse zeigen, dass schon kurzzeitige Sauerstoffeinwirkung eine deutliche Veränderung der Dinozysten Vergesellschaftung verursachen kann und damit zu einer Verfälschung des Primärsignals und einer Missinterpretation der

Umweltbedingungen führt. Keine Degradation wurde an S-Zysten gefunden, die anoxischen Wassermassen ausgesetzt waren.

Die Analyse von zwei kurzen Kernen aus dem atlantischen Sektor des Südlichen Ozeans ergab die Kalkulation der Degradationskonstanten (k) der S-Zysten (*Brigantedinium* spp. und *Selenophemphix antarctica*). Die kalkulierte Konstante k nimmt exponential mit dem Steigen der Einwirkungzeit des Sauerstoffes (oxygen exposure time „OET") ab. Dieses unterstützt frühere Ergebnisse, wonach die OM Degradation in Abhängigkeit zu Schwankungen im Gehalt an organischem Material steht. „k" korreliert ebenfalls positiv mit der Sauerstoffkonzentration des Porenwassers, wobei miteinbezogen wird, dass die Degradation nicht nur von der OET und OM Konzentration, sondern auch von den Sauerstofflevels in Boden- und Porenwassern abhängig ist. Sauerstoff scheint bei niedrigen Konzentrationen der limitierende Faktor zu sein, während bei höherer Sauerstoffkonzentration die Verfügbarkeit von unbeständigem OM wichtiger zu sein scheint.

Die Studie der Jura Kimmeridge Clay Formation lieferte Informationen über mögliche selektive Degradation von ausgestorbenen Dinozysten. Viele Arten (z.B. *Circulodinium* spp., *Cyclonephelium* spp., *Sirmiodinium grossi*, *Senoniasphaera jurassica* und *Systematophora* spp.) nehmen in ihrer Häufigkeit während rekonstruierter, postabgelagertert stattgefundener Oxidation des Sedimentes wesentlich schneller ab als andere Arten (zB. *Glossodinium dimorphum* und *Cribroperidinium* sp.1). Die Rekonstruktion von Ablagerungs-/Redoxbedingungen basierte auf miteinander gekoppelten unabhängigen Methoden: Palynofazies Analysen und organische und inorganische chemische Proxies (gesamt-organischer Kohlenstoff „TOC" und entsprechend Fe, Mn, S, Cu, P, Al). Nach unserem Wissen ist es der erste Versuch jurassische aerobe Degradation an Dinozysten *in situ* zu untersuchen und weitere Studien sind nötig um die Rangliste der ausgestorbenen Dinozysten auf Oxidationssensitivität zu etablieren.

Unsere Ergebnisse zeigen, dass sowohl bestehende, als auch ausgestorbene Dinozysten durch artenspezifische aerobe Degradation beeinflusst werden können. Dieses erschwert die Interpretation von fossilen Aufzeichnungen.

Artenspezifische Degradation ist ein schneller Prozess und kann aus diesem Grund in keiner Zeitskala vernachlässigt werden. Die Abhängigkeit der S-Zysten Degradation von der Sauerstoffkonzentration des Porenwassers könnte eine Auswirkung auf die Diskussion des aeroben OM Abbaus haben, mit dem Hinblick dass der Zerfall von OM nicht nur von OET und der Verfügbarkeit von unbeständigem OM, sondern auch von der Sauerstoffkonzentration des Boden- und Porenwassers abhängig ist.

## Abstract

Species-selective aerobic decomposition affects fossil organic-walled dinoflagellate cyst (dinocyst) records and hence dinocyst-based interpretations of primary productivity and oceanographic conditions. However, since the recognition of dinocyst species sensitive and resistant to oxic degradation (S- and R-cysts, respectively) it has become apparent that R-cysts may still serve as reliable productivity and oceanographic conditions proxies. On the other hand S-cysts provide a way to quantify aerobic degradation of organic matter (OM) and past bottom-water $O_2$ concentrations. OM degradation plays a key role in global carbon cycling and is important for global climate change. Therefore dinocysts are a valuable tool for estimating the rate of diagenetic process. Questions concerning species-selective aerobic degradation still remain and will be adressed here.

To obtain information on the rate of S-cyst decomposition, the relationship between S-cyst degradation and $O_2$ concentrations, and the aerobic degradation of extinct dinocyst species, a natural exposure experiment has been conducted and studies of both Quaternary and pre-Quaternary material from sediment cores were executed.

The exposure experiment was conducted in the natural setting of the Eastern Mediterranean. During a 15 month exposure period to oxic water masses, concentrations of S-cysts (*Brigantedinium* spp. and *Echinidinium granulatum*) decreased by 24 to 57%. However, taxa such as *Nematosphaeropsis labyrinthus, Echinidinium aculeatum, Operculodinium israelianum* and *Impagidinium aculeatum* demonstrated a slight increase in concentration, indicating resistance to aerobic degradation. These results show that even short-term exposure to oxygen may cause considerable changes in the dinocyst assemblage and thus overprint the primary signal, leading to misinterpretation of the environmental conditions. No degradation was observed during exposure of S-cysts to anoxic water masses.

Analysis of two short cores from the Atlantic sector of the Southern Ocean permitted calculation of the degradation constant (*k*) for S-cysts (*Brigantedinium* spp. and *Selenophemphix antarctica*). Calculated *k* decreases exponentially

with increasing oxygen exposure time (OET), supporting earlier findings that OM degradation depends on labile organic component concentrations. Constant $k$ also shows a positive correlation with pore-water $O_2$ concentrations, implying that degradation is dependent not only on OET and OM concentration, but also on $O_2$ concentrations in bottom and pore waters. $O_2$ seems to be a limiting factor at lower concentrations, whereas at higher $O_2$ concentrations the availability of labile OM seems to be more important.

A study of the Jurassic Kimmeridge Clay Formation provided information on the selective degradation of extinct dinocyst species. This is the first attempt to investigate aerobic degradation of *in situ* Jurassic dinocysts. Several taxa (i.e. *Circulodinium* spp., *Cyclonephelium* spp., *Sirmiodinium grossi*, *Senoniasphaera jurassica* and *Systematophora* spp.) decrease in abundance during post-depositional oxidation of sediments. Reconstruction of depositional redox conditions was based on coupled independent methods, combining palynofacies analysis with organic and inorganic geochemical proxies (total organic carbon and Fe, Mn, S, Cu, P, Al respectively). Further research is necessary to establish a list of extinct dinocyst species sensitive to oxidation.

These results show that both extant and extinct dinocysts may be affected by species-selective aerobic degradation, making interpretations of fossil records difficult. Species-selective degradation is shown to be a rapid process and therefore cannot be neglected on any time scale. The dependence of S-cyst degradation on pore water $O_2$ concentrations has implications for aerobic OM decomposition, indicating that OM decay is dependent not only on OET and availability of labile OM but also on bottom- and pore-water $O_2$ concentrations.

**CHAPTER 1**

**Introduction**

**1.1. Objectives**

Reconstructions of marine palaeoproductivity are of major interest because primary productivity is linked to the global carbon cycle which, in turn, modulates the $p$CO$_2$ level in the atmosphere and thus affects global climate changes. Such reconstructions are based on proxies dependent on both primary productivity and environmental processes. Organic matter (OM) deposited in marine environments forms the basis for many palaeoceanographic and palaeoclimatic proxies. However, oxidation of sedimentary organic carbon in marine environments may diagenetically overprint the primary signal of the proxies (e.g. Hedges, 1992).

For instance, the total organic carbon (TOC) and its relationship with the sedimentation rate is used to determine palaeoproductivity. This interpretation also depends on the origin of the investigated OM (marine *vs.* terrestrial) and the degree of oxidation during sedimentation (Rullkötter, 2006). Oxidation causes a decrease in TOC, and terrestrial organic matter (OM) is more resistant to degradation than marine OM (Canfield, 1994; Baldock et al., 2004).

Another proxy commonly used for estimation of productivity is the bulk carbonate content. The isotopic and trace element characteristics of carbonate, and the relative concentration of some microfossils may be affected by early diagenetic processes, while some of the sedimentary carbonate is dissolved by CO$_2$ released during oxic decomposition of OM (de Lange et al., 1994). For example, d$^{13}$C of benthic foraminiferal tests provides information on OM flux variations, however it can be extremely depleted when benthic foraminifera incorporate isotopically lighter carbon released from the decomposing OM into their tests (Mackensen et al., 1993; Eberwein and Mackensen, 2006).

The ratio of stable nitrogen isotopes from sediments is a reliable proxy for nutrient and productivity patterns. However, the d$^{15}$N mean values are positively correlated with the water depth and may increase due to the more intense

degradation processes in the overlying oxic water column. Thus relative $d^{15}N$ values in the sediments reflect a primary signal but the absolute values are altered by early diagenesis, making reconstructions of nitrate availability gradients problematic (Zonneveld et al., in prep.).

Barium is a frequently used palaeoproductivity proxy. The rain rates and distribution of Ba in the underlying sediments are determined not only by the ocean productivity, but by seawater sulphate content, age of the water masses and water depth. Additionally, anoxic mobilization and hydrothermal activity may produce relatively high levels of Ba which is unrelated to productivity. Similarly, Mn spikes are often related to the changes in palaeoproductivity but they can also be attributed to sudden changes from suboxic to oxic ocean waters or to early diagenetic mobilization within sediments deposited under non-steady state conditions (de Lange et al., 1994).

Another proxy used to reconstruct past productivity are the organic-walled dinoflagellate cysts (dinocyst). Although regarded as one of the microfossil groups most resistant to degradation, dinocysts also have their limitations. They undergo species-selective aerobic decomposition that leads to changes in the dinocyst concentration and to changes in taxonomic composition of the assemblages. Sensitive dinocysts (S-cysts) are depleted, whereas resistant ones (R-cysts) are enriched (e.g. Zonneveld et al., 1997, 2001; **Chapter 2**). Such overprint of the environmental signal makes palaeoenvironmental interpretation difficult, as has been recognised before (e.g. Reichart and Brinkhuis, 2003; Esper and Zonneveld, 2007; Bockelmann, 2007). Nevertheless, species-selective dinocyst degradation may become a useful interpretative tool rather than a problem. Ever since the method to decouple productivity from preservation was proposed (Versteegh and Zonneveld, 2002), it became apparent that dinocyst interpretations still can yield accurate information on productivity and environmental conditions, and additionally provide information on the rate of OM degradation. Zonneveld at al. (2007) showed that the relationship between the degradation rate and $O_2$ concentration was very significant. This became the basis for development of a new proxy for bottom-water $O_2$ concentration. This proxy utilises the oxygen index proposed

by Verteegh and Zonneveld (2002), and has already been successfully applied to reconstruct past bottom-water $O_2$ concentrations (Bockelmann, 2007). The reasons underlying selective dinocyst degradation are still matter of debate. Also the speed of the degradation process, degradation rates of individual dinocyst species, the relationship between S-cysts degradation and pore-water $O_2$ concentration, and the sensitivity of extinct dinocysts to aerobic decay are unknown. These information are required to improve the application of dinocysts as a proxy and to provide more insight in the OM degradation process and hence in the cycling of organic carbon (OC) and related climatic changes. Furthermore assessing the influence of selective preservation on the original signal is essential for a correct palaeoenvironmental interpretation of the fossil record and, more importantly, for accurate estimation of the OC sink (Zonneveld et al., in prep).

This work explores the limitations of (palaeo-)environmental dinocyst studies to improve interpretation of palaeoproductivity signals, determination of diagenetic overprint rate, and will contribute to the discussion on the factors affecting OM degradation. In **Chapter 2** current knowledge about degradation of dinocysts is summarised and put in the context of overall OM degradation. In the following chapters three major questions are addressed. What is the rate of the dinocyst degradation process? What is the relationship between dinocyst degradation and $O_2$ concentrations? Are the extinct dinocysts prone to selective degradation?

To determine the rate of dinocyst degradation, an experiment in the natural environment was developed. Three different sediment types with known dinocyst associations were exposed to oxic and anoxic conditions. The samples were sealed within dialyse membranes that only allowed for oxygen penetration. Samples were only subject to decay under natural conditions, and changes that occurred in dinocyst assemblages may be linked to aerobic decomposition, since other processes (e.g. transport or primary production) could not influence the samples. This experiment provided the first ever information on the rate at which natural decomposition of the dinocysts occures. These results indicate that even short term exposure to oxic conditions (15 months) may result in a 24

to 57% decrease in the reactive dinocyst concentrations. This is a significant bias on dinocyst assemblages and an overprint of the primary information concerning environmental conditions (**Chapter 3**).



KNOWN

Fact of selective destruction of Quarternary and pre-Quarternary dinocysts during samples preparation.
Fact of species-selective degradation of Quaternary dinocysts in natural environments.
Quarternary dinocyst species resistant and sensitive to aerobic decomposition.
Speed of Quarternary dinocyst decay in laboratory experiments under high oxidant concentrations.
Some factors that affect dinocysts preservation (e.g. $O_2$, dinocyst wall chemistry).
The way, in which species-selective dinocyst decomposition influence dinocyst record interpretation. (**Chapter 2**)

AIMED

Rate of aerobic degradation of Quarternary dinocysts.

Relationship between dinocyst degradation and $O_2$ concentrations.

Information on selective aerobic degradation of pre-Quarternary dinocysts.

APPROACH

Natural experiment

Sediment cores

RESULTS

**Chapter 3**: Quantitative estimation of sensitive dinocysts degradation rates in natural environments.

**Chapter 4**: Assesment of dinocyst degradation level using kt index. Calculation of degradation constant $k$ of S-cysts. Correlation of $k$ with OET, dinocyst concentration, pore water $O_2$ concentrations.

**Chapter 5**: Qualitative information on species-selective decay of extinct dinocysts. Coupling of palynological and geochemical methods for reconstructions of palaeoevnironmental conditions.

*Figure 1.1. Conceptual development of the project.*

Two short cores from the Atlantic sector of the Southern Ocean were studied to obtain information on the relationship between the degradation rates of S-cysts and pore water $O_2$ concentrations. On the basis of the calculated degradation index (kt) it can be concluded that the dinocyst record in both cores were affected by species-selective aerobic degradation. The calculated degradation constant ($k$) of S-cysts displays a strong positive correlation with

pore-water $O_2$ concentrations. Furthermore, dinocyst associations from one of the cores, in which all samples were assumed to be equally affected by early diagenesis, could be interpreted in terms of shifts of the Antarctic Polar Front and maximum sea-ice limit (**Chapter 4**).

To establish whether extinct dinocysts were sensitive to selective degradation, a multidisciplinary study on Late Jurassic sediments was conducted. The redox history of the section was reconstructed independently, based on palynofacies and redox-sensitive/sulphide forming chemical elements (Fe, S, Mn). Information on palaeoproductivity was supplied via analysis of palynofacies and productivity/nutrient-related elements (Ba, Cu, P). The results demonstrate that Jurassic dinocysts also were prone to selective preservation. Additionally palynological and chemical information was generated on the studied section, one of the most important European petroleum source rocks, the Kimmeridge Clay Formation (**Chapter 5**).

Chapter 6 provides a short conclusion.

This work both summarises previously published work and supplies new data on dinocyst/OM degradation. Independent chemical proxies including the major and trace elements (Al, Cr, K, Mg, Ti, Zr, Fe, S, Mn, Ba, Cu, P), TOC, $O_2$ and other palynological proxies (e.g. pollen) were employed to test the dinocyst data.

### 1.2. Organic carbon and preservation

### 1.2.1. Organic carbon cycle

It is estimated that two-thirds of all actively cycling OC is stored on land and the other one-third in the oceans (Hedges et al., 1997). Carbon storage occurs in different reservoirs that turn over and exchange with each other (Fig. 1.2; Hedges, 1992; Reeburgh, 1995). The atmosphere, shallow sea and biota are small, rapidly exchanging reservoirs and are coupled by slower transfers to the larger reservoirs such as the deep-sea and sedimentary rocks (Sundquist, 1985; Walker, 1993). Over geological time, about $1.5 \times 10^{22}$ g of OC has accumulated in sedimentary rocks, and this has played key role in modulating atmospheric oxygen concentrations (Hedges, 1992; Emerson and Hedges,

1988). However, continental reservoirs are near steady state and hence burial in marine sediments is the ultimate fate of the OC that escapes remineralisation.

Only when exported to the oceans, significant amounts of terrestrial OM can be preserved for longer time. Most of the particulate fraction of this exported terrestrial OM is deposited close to the shore. The dissolved fraction of exported terrestrial OC enters the large seawater-dissolved OC pool and is apparently oxidised (Reeburgh, 1995).

The global burial flux of total OC within modern marine sediments is estimated at $0.1-0.2x10^{15}$ year$^{-1}$ (Berner, 1989; Hedges, 1992; Hedges and Keil, 1995). Marine plankton photosynthesises ~ $50x10^{15}$ year$^{-1}$ of OC (Siegenthaler and Sarmiento, 1993). About 80% of the total ocean primary production occurs in the open ocean, which accounts for about 90% of the ocean area. However, more than 80% of the preserved OC is deposited in the shelf and continental margin sediments (e.g. Emerson and Hedges, 1988; Hedges, 1992; Reeburgh, 1995). Much of the ocean primary production is recycled in the upper 100 m of the ocean and these recycling process are more efficient in the open ocean than in the coastal waters. Only ~1% of the primary production reaches depths of 4000 m. Further reworking and oxidation of deposited OC by diagenetic reactions occurs in the sediments (e.g. Emerson and Hedges, 1988; Hedges, 1992).

OC burial in marine sediments, in a similar way as in terrestrial sedimentary rocks, balances $O_2$ concentrations in the atmosphere. Any mechanism proposed to control OC preservation includes a feedback buffering atmospheric $O_2$ over geological time (Hartnett et al., 1998). The ultimate burial rate is remarkably small, accounting for roughly 0.1% of global primary production. This means that at least 99.5% of the marine primary production and 50% of terrestrial OM introduced to the ocean must be completely remineralised (oxidised to $CO_2$, $H_2O$ and nutrients; Hedges et al., 1997).
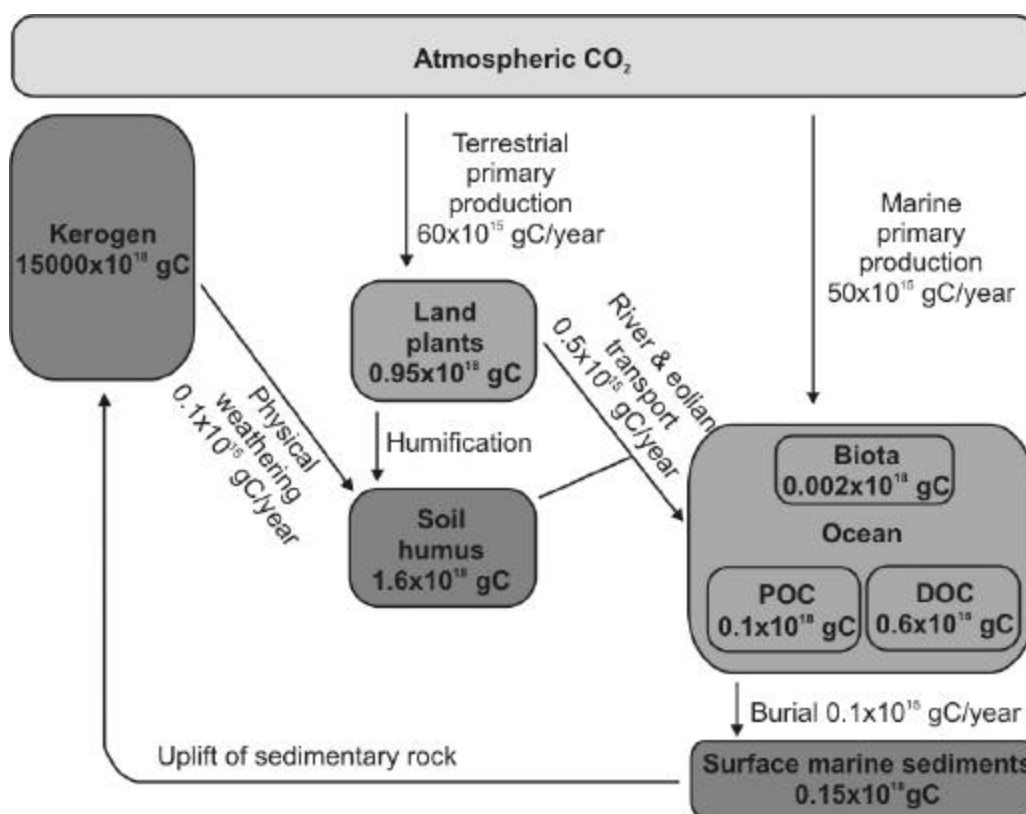
*Figure 1.2. The global OC cycle. Bolded numbers represent size of reservoirs while other numbers represent yearly fluxes (modified after Hedges, 1992).*

### 1.2.2. Preservation of organic matter

Remineralisation is by far the most common fate of recently biosynthesised carbon and thus is the dominant sink term in the global OC balance. Remineralisation of OC is a very efficient process on a global basis: only ~0.1% ($0.1 \times 10^{15}$ year$^{-1}$) of global primary production (terrestrial: $60 \times 10^{15}$ year$^{-1}$; marine $50 \times 10^{15}$ year$^{-1}$) escapes oxidation and is ultimately buried in the marine, primarily fine-grained coastal, sediments (Table 1.1; Berner, 1982; Hedges, 1992; Emerson and Hedges, 1988). Selective degradation of different types of organic materials has been demonstrated in a variety of aquatic environments: in the water column (Wakeham et al., 1984; Suess, 1980), at the water-sediment interface (Prahl et al., 1980; Emerson and Dymond, 1984) and within oxic and anoxic (surface) sediment deposits (Emerson et al., 1985; Hamilton and Hedges, 1988). Most of the OM reaching the seafloor is oxidised within the

sediments, rather than at the sediment-water interface (Reimers and Suess, 1983; Bender and Heggie, 1984). Slower degradation can continue for thousands of years within a bioturbated, oxygen-rich open-ocean sediments (Emerson et al., 1987).

*Table 1.1. OC burial rates ($x10^{12}$ gC year$^{-1}$) in different marine sediments (after Berner, 1989)*

| Sediment type | Burial rate |
|---|---|
| Terrestrial deltaic/shelf sediments | 104 |
| Biogenous sediments (high-productivity areas) | 10 |
| Shallow-water carbonates | 6 |
| Pelagic sediments (low-productivity areas) | 5 |
| Anoxic basins | 1 |

Early diagenesis, although extensive, is typically selective in its initial and intermediate stages (Emerson and Hedges, 1988; Hedges, 1992; Hedges and Prahl, 1993; Reeburgh, 1995). Aerobic oxidisers can oxidise a wide range of substrates to $CO_2$, and are responsible for remineralisation of over 90% of the OM in the sediments. Anaerobic oxidisers have more specific substrate requirements, and can oxidise a restricted number of molecules, often incompletely (Bender and Heggie, 1984; Henrichs and Reeburgh, 1987; Reeburgh, 1995). OM oxidation uses available electron acceptors according to the sequence:

$$O_2 > NO_3^- > Mn(IV) > Fe(III) > SO_4^{2-} > CO_2.$$
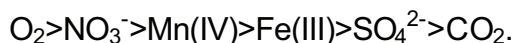
It proceeds through a series of reactions beginning with oxygen reduction, followed by denitrification, metal oxide reduction, sulphate reduction, and finally methanogenesis (Bender et al., 1977; Froelich et al., 1979; Jahnke et al., 1982; Tromp et al., 1995).

The degradation and remineralisation of OM and many redox processes among inorganic species is dependent on bacterial catalysis, which may accelerate such processes up to $10^{20}$-fold relative to the non-biological reaction rate. The particulate detritus consumed by metazoans, and the small organic

molecules taken up by microorganisms in the oxic zone, may be remineralised completely to $CO_2$ through aerobic respiration within the individual organisms. The oxic zone is, however, generally only mm-to-cm thick so that much of the OM remineralisation takes place within the anoxic sediment (Jørgensen, 2006).

The oxidation of OM by microbial sulphate reduction is ubiquitous and the most important geochemical process in anoxic marine sediments (Jørgensen, 1983; Henrichs and Reeburgh, 1987). As shown by Emerson and Hedges (1988) the marine OM is more easily degradable by microbial attack. Therefore, sulphate reduction may lead to an enrichment of terrestrial OM in marine sediments (Lückge et al., 1999).

Originally, the degradation rate of OM was assumed to be first-order with respect to the concentration of labile OM ($G$) and was expressed as

$$dG/dt = -kG$$

where $t$ is time and $k$ is the first-order decay constant (Berner, 1980). Integrated between boundary conditions $t=0$, $G=G_0$ and $t? 8$, $G? 0$, this equation can be presented as

$$G_t = G_0[\exp(-kt)]$$

However, it was recognised that the total OM ($G_t$) in natural environments is comprised of many components ($G_l$) with typically different first-order reactivity ($k_l$) (Jørgensen, 1979; Berner, 1981), which has led Berner (1981) to the development of so-called "multi-$G$" model:

$$G_t = ? G_{0l}[\exp(-kt)]$$

Such a formulation means that decomposition of the total OM pool exhibits higher-order kinetics (Emerson and Hedges, 1988).

In addition to a first order dependence on labile OM, OM oxidation rate also depends on the oxygen exposure time (OET; Fig. 1.3), sedimentation rates and $O_2$ concentrations. In general, sediments with longer OETs have lower OC

contents, as well as lower OC burial efficiencies (Hartnett et al., 1998). Degradation of OM depends weakly on $O_2$ concentrations in pore waters (Berner, 1980; Rabouille and Gaillard, 1991; Cai and Sayles, 1996). Jahnke et al. (1982) and Emerson (1985) showed low OC burial efficiencies in the presence of high bottom-water $O_2$ concentration, and Hartnett et al. (1998) described the highest burial efficiencies in regions with undetectable bottom-water $O_2$. Sedimentation rate also exerts a strong influence on burial efficiency, with increased sedimentation rates enhancing preservation of deposited OM (Tromp et al., 1995; Betts and Holland, 1991; Henrichs and Reeburgh, 1987; Canfield, 1989).
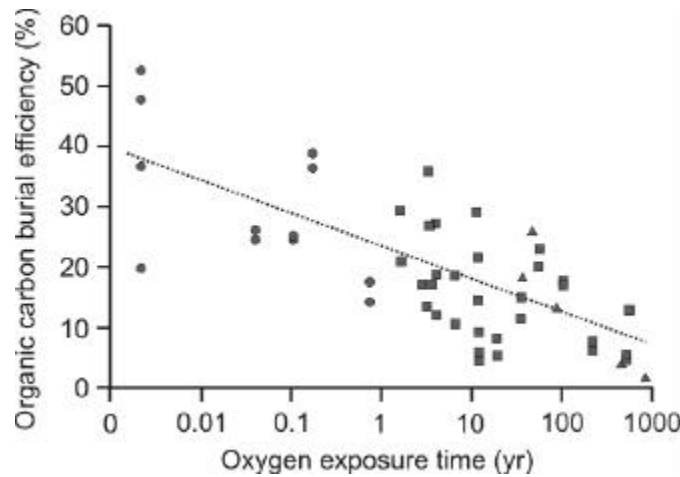


*Figure 1.3. OC burial efficiency as a function of oxygen exposure time. Circles, squares and triangles represent data from Mexican, Washington and Californian margins respectively (after Hartnett et al., 1998).*

Yet other factors that may influence OM decomposition are the age of the OM and bioturbation (Hulthe et al., 1998). Hulthe et al. (1998) have observed that fresh material is degraded at almost equal rate independent of the presence or absence of $O_2$, whereas old material is decomposed significantly faster with $O_2$ than without $O_2$. Furthermore these authors concluded that bioturbation, by exposing old buried material to $O_2$, may enhance OC oxidation in marine sediments and that the oxic-anoxic-oxic redox transitions (deposition

under oxic conditions, burial under anoxia and re-exposure to $O_2$) promotes degradation.

Temperature and pressure may affect the rate of degradation on kinetic grounds. Degradation usually involves enzymatic hydrolysis and reduced temperatures can inhibit enzyme activity because of slower kinetics or decreased bacterial affinity for substrates at lower temperatures. Hydrolysis may also operate slower at increased pressure during OM sink through the water column (Zonneveld et al., in prep.).

## 1.3. Dinoflagellates
### 1.3.1. Biology of the dinoflagellates

Dinoflagellates are unicellular, eukaryotic algae living in the upper water column in both marine and freshwater environments (Evitt, 1985; Fensome et al., 1996). The motile dinoflagellate cells range in size mostly from ~20 to 200 µm and are able to migrate vertically through the water column (Taylor and Pollingher, 1987). They exhibit a variety of feeding strategies out of which the most common are autotrophy, heterotrophy and mixotrophy (a combination of previous two; Schnepf and Elbrächter, 1992). Autotrophic dinoflagellates photosynthesise nutrients taken up directly from the water column (Schnepf and Elbrächter, 1992), whereas heterotrophs feed mostly on diatoms, other dinoflagellates, prasinophytes, ciliates or organic debris (Jacobson and Anderson, 1986).

The life cycle of the dinoflagellates can either have sexual or asexual (cell division) reproduction. However, it is thought that most of the dinoflagellates reproduce sexually (Pfiester and Anderson, 1987). During the sexual reproduction dinoflagellate produce gametes, pairs of which fuse to produce a hypnozygote (Fig. 1.4). The hypnozygote is often protected by a so-called resting cyst (Dale, 1976, 1983), most of which are of an organic composition, although there are also small numbers of calcareous or siliceous cysts known (Kokinos et al., 1998).
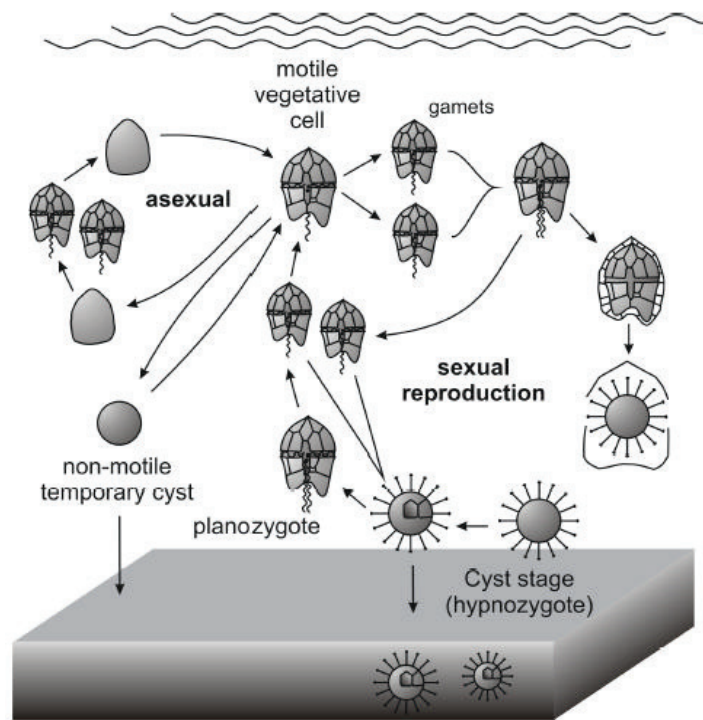
*Figure 1.4. Simplified life cycle of cyst-producing dinoflagellates (from Bockelmann, 2007; after Dale, 1983)*

Cysts formation mostly occurs during or shortly after periods with very high motile cell concentrations and is accompanied by a high nutrient concentration in the water (Ishikawa and Taniguchi, 1996; Montresor et al., 1998). However, encystment could be influenced also by temperature, day length, irradiance and an endogenous rhythm (Anderson and Keafer, 1987). Cysts may survive various adverse environmental conditions such as anoxia, low temperatures and light/nutrient limitation and remain viable for many years under conditions unfavourable for excystment (Dale, 1983). After the dormancy period excystment occurs, during which the protoplast hatches through an opening in the cyst wall (so called archeopyle). Following the excystment, the hatchling joins the motile community and the empty cyst may undergo burial and become fossilised within marine deposits (Dale, 1983).

There are around 2000 living dinoflagellate species, but only about 16% of them are known to form fossilisable dinocysts (Head, 1996). The dinocyst fossil record begins in the Mesozoic, with a major species radiation in the Triassic and

Jurassic (Fig. 1.5; MacRae et al., 1996). Their long geological history has established dinocysts as useful stratigraphic markers used commonly in the petroleum exploration industry. Dinocysts biostratigraphy (e.g. Woollam and Riding, 1983; Dimter and Smelror, 1990; Louwye et al., 2004) is widely used to determine the age of sediments on the basis of marker dinocyst species. They are also very important for palaeoenvironmental reconstructions, since dinocysts distribution and assemblages are related to sea-surface temperature, sea-surface salinity, sea-ice cover and nutrient concentration.
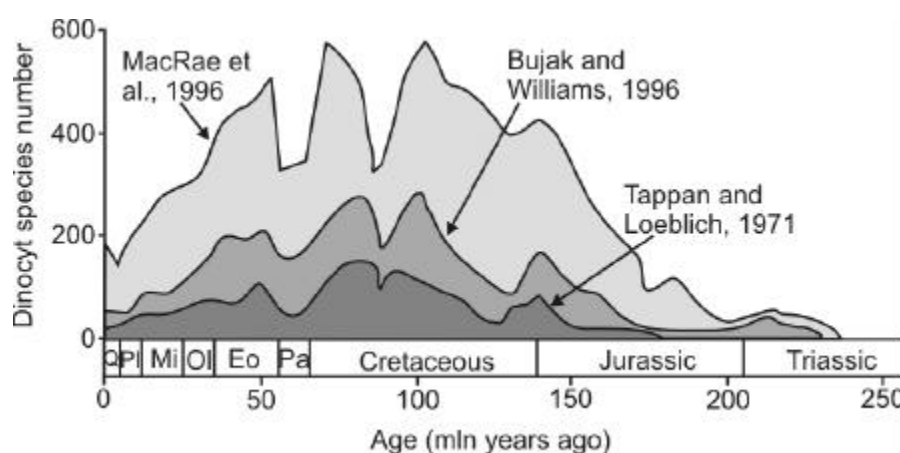


*Figure 1.5. Dinocyst diversity throughout the time (after MacRae et al., 1996).*

**1.3.2. Dinocyst application**

As a constituent of the phytoplankton, dinoflagellates together with diatoms and coccolithophorids, are responsible for the major part of the marine primary production (Parsons et al., 1984). Their cysts often dominate fossil assemblages of primary producer origin within marine sediments (Devillers and de Vernal, 2000). Dinocysts are found in deep and shallow marine environments of all climatic zones (Marret and Zonneveld, 2003), and are recognized as useful indicators of palaeoenvironmental conditions. Dinocyst-based palaeoenvironmental reconstructions include, for instance, estimation of temperatures, salinity and sea-ice cover and past bottom-water $O_2$ concentrations (Rochon et al., 1998; Brinkhuis et al., 1998; Mudie et al., 2002; de Vernal et al., 2005; Bockelmann, 2007). Dinocyst are more important in high

latitudes, where other indicators such as foraminifera, radiolaria or diatoms may dissolve in carbonate/silicate undersaturated waters (e.g. Shemesh et al., 1989). Even sea-surface temperatures of the Southern Ocean can be reconstructed using a dinocyst-based modern analogue technique (Esper and Zonneveld, 2007), proving the potential of dinocysts for quantitative reconstruction of paleoenvironmental conditions in polar regions.

However, as with all proxy indices, the use of dinocysts as environmental proxy has limitations related to dinoflagellate biology/ecology or marine processes. Firstly, the motile dinoflagellates represent a snapshot of actual environmental conditions, while the fossil dinocyst record represents a longer time-averaged period. Secondly, dinocyst assemblages may have been stimulated by factors other than physical water characteristics. Thirdly, an important factor that requires caution in the interpretation of dinocyst associations is transport. Since dinocysts behave like silt particles in the water column (Anderson et al., 1985) they are very prone to lateral transport, which may considerably alter the autochthonous dinocyst association. Another very important process that may alter the primary dinocyst assemblages is (early) diagenesis.

### 1.3.3. Dinocyst degradation

Species-selective degradation of dinocysts as a result of oxidation/acetolysis during the laboratory samples preparations was first described in the 1970s and is now well documented (e.g. Dale 1976; Reid, 1977; Harland, 1983; Schrank, 1988; Marret, 1993; De Schepper et al., 2004; Mudie and McCarthy, 2006). Originally it was believed that in natural environments, where the oxidants have a much lower concentrations, all dinocyst species are equally resistant to aerobic decomposition. In the late 1990s it was established that early diagenesis could be species-selective in natural settings (Zonneveld et al., 1997, 2001). Investigation of the Madeira Abyssal Plain f-turbidite and Mediterranean S1 sapropel revealed that the concentration of several heterotrophic species (e.g. *Protoperidinium* and *Echinidnium species*) was lower in the oxidised part of the sediments in comparison to the unoxidised part,

whereas concentrations of autotrophic species (e.g. *Impagidinium* species) did not change (Zonneveld et al., 1997, 2001). This led the authors to establish that some dinocysts were more sensitive and more resistant to aerobic degradation (S-cysts and R-cysts respectively). Further research has shown that S- and R-cysts form the two end members in the ranking of organic component liability to oxic degradation (Versteegh and Zonneveld, 2002).

Species-selective aerobic degradation of dinocysts has now been proven in a wide range of natural environments (e.g. Reichart and Brinkhuis, 2003; Bockelmann, 2007; Zonneveld et al., 2007) but an important question remained unanswered: what is the rate of dinocyst degradation? The rate of species-selective dinocyst decomposition was assessed first by laboratory experiments. Treating dinocysts samples with $H_2O_2$ (15%), Hopkins and McCarthy (2002) observed that after only 30 minutes of such a treatment *Brigantedinium* cysts (Fig. 1.6) totallydisappeared from the initial assemblage, whereas other dinocysts (*Protoperidinium* species) were severely damaged. This rate of aerobic dinocyst decay cannot be utilised in the natural settings since the availability and concentration of oxidative agents is much lower in natural environments than under above described laboratory conditions. Experiments in the natural environment were designed to obtain information about naturally induced species-selective decay rates (**Chapter 3**).

A method to separate productivity from the preservation signal is based on differences in the degradation potential of R-cysts versus S-cysts (Versteegh and Zonnevel, 2002). According to this method the degradation rate can be estimated from the equation: kt=ln(Xi/Xf) where *k* is the degradation constant, *t* is the reaction time, $X_i$ is the initial concentration of S-cysts and $X_f$ is the final concentration of S-cysts. The *Xi* can be calculated from the fixed relationship between the S-cysts and R-cysts: $AR_{S-cysts}=68*AR_{R-cysts}$ (Zonneveld et al., 2007). This approach was first tested over period of 145 ky on a sediment core from the southeast Atlantic (Versteegh and Zonneveld, 2002) and then used to decouple productivity from preservation in Holocene/Pleistocene sediments from offshore Morocco (Bockelmann, 2007).

Zonneveld et al. (2007) reports an important relationship between the degradation of S-cysts and bottom-water $O_2$ concentrations. The ratio of R-cysts to R+S-cysts can be used as a bottom water oxygen index (BWOI) in the newly developed proxy for past bottom-water $O_2$ concentrations, allowing the reconstruction of annual mean bottom-water $O_2$ concentrations for Pleistocene southeast Atlantic Ocean (Bockelmann, 2007).
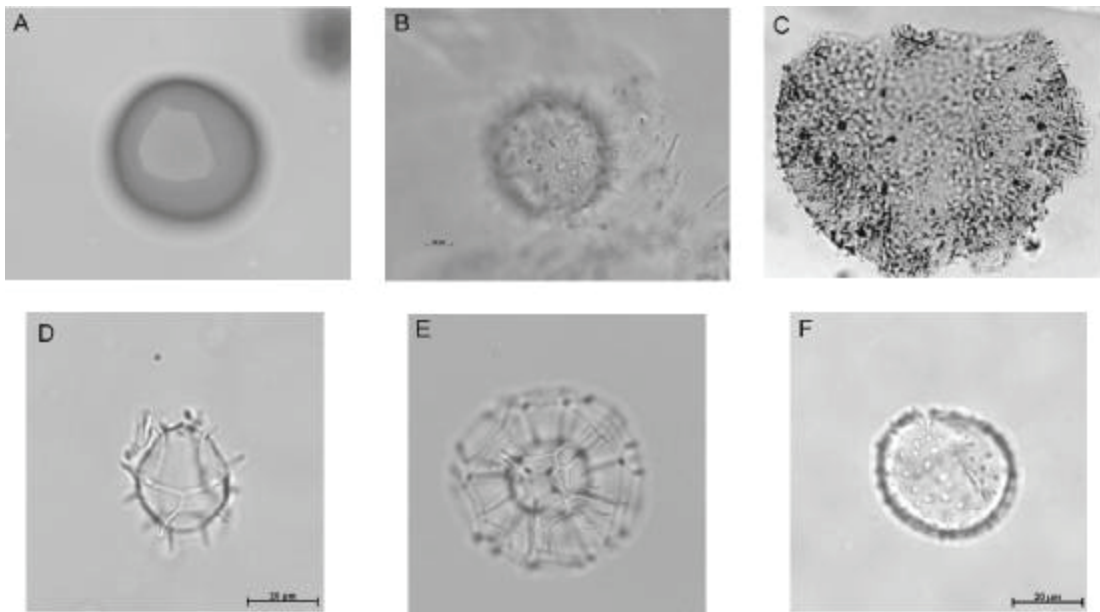


*Figure 1.6. Sensitive (A-C) and resistant (D-F) dinocyst species. A. Brigantedinium spp., B. Echinidinium granulatum, D. Impagidinium aculeatum, E. Nematosphareopsis labyrinthus, F. Operculodinium israelianum (from Marret and Zonneveld, 2003), C. Circulodinium spp. (from Leereveld, 1997).*

## 1.4. Sediment geochemistry

Chemical elements and their contents in marine sediments constitute a useful tool for reconstructing the development of sedimentary environments with respect to past primary productivity, OM preservation, bottom-water redox conditions and terrigenous material input. Therefore, an interdisciplinary multiproxy approach including palynology and inorganic geochemistry was applied.

In natural sedimentary systems, elements like Al, K, Ti and Zr are mostly bound to silicate minerals, and thus document the detrital input from the hinterland. Variations in their element/Al ratios are generally related to the provenance of terrigenous matter (Rinna et al., 2002). In addition, higher Ti/Al or Zr/Al ratios are often indicative for a gravitational sorting mechanism of the particles, e.g. during aeolian transport or by winnowing bottom currents (e.g. Zabel et al., 1999; Schnetger et al., 2000). Al and K variations can be explained, for instance, by an increase in illite as important mineral phase bearing K at the expense of kaolinite (e.g. Hild and Brumsack, 1998). The most common element essentially not affected by biological or diagenetic processes is Al, which forms part of the structural component of most minerals introduced via fluvial and eolian sources. Thus, Al is usually taken as the element of choice for documenting the terrigenous-detrital fraction in continental margin environments (e.g. Brumsack, 2006).

Other elements are mostly related to processes within the water column or sediment. The accumulation rate of solid-phase Ba in marine sediments may serve as a palaeoproductivity tracer (e.g. Schmitz, 1987; Dymond et al., 1992; Paytan et al., 1996). If sedimentary Ba is bound to biogenic barite, high Ba values in the sediments may indicate higher primary productivity in the surface ocean at the time of deposition (e.g. Paytan and Griffith, 2007). However, in organic-rich marine sediments where pore water sulphate is often depleted, biogenic barite is generally poorly preserved and diagenetically remobilized (e.g. McManus et al., 1998). Burial efficiency of barite may also vary with mass accumulation rate (Dymond et al., 1992). In addition, in continental margin regimes, interpreting Ba data may be problematic because a variable portion of sedimentary Ba is bound to detrital minerals (e.g. Eagle Gonneea and Paytan, 2007), and application of a general global lithogenic Ba/Al ratio may introduce errors as well (e.g. McManus et al., 1998; Reitz et al., 2004).

Copper (Cu) is known to be enriched in OM-rich deposits, either as Cu-sulphide, co-precipitated with or incorporated into pyrite, or incorporated in organic matter (e.g. Huerta-Diaz and Morse, 1992; Calvert and Pedersen, 1993; Brumsack, 2006; Tribovillard et al., 2006). High amounts of Cu can be fixed in

high productivity settings owing to bioconcentration by plankton. However, even though Cu as a micronutrient may reach high concentration levels in plankton, it is not necessarily associated with the organic fraction after burial (Brumsack, 2006). Copper may, for instance, undergo dramatic solubility decrease in an $H_2S$-containing water column and be trapped as sulphides (Jacobs et al., 1985). Thus, its use as a paleoproductivity proxy is limited.

Phosphorus (P) is another constituent of marine OM and initially related to productivity. Low sedimentary P content may suggest lower nutrient availability during OM production, whereas high concentration of P are associated with high primary productivity (e.g. Hild and Brumsack, 1998). However, under anoxic conditions an intense P regeneration from the sediments may occur, blurring the primary productivity signal (e.g. Ingall et al., 1993; Ingall and Jahnke, 1997).

It is now well-known that certain elements (e.g. Mn, S, Fe) are useful as indicators of bottom-water or sediment anoxia/euxinia, due to their speciation and subsequent fixation or mobilisation under certain redox conditions (e.g. Morford and Emerson, 1999; Tribovillard et al., 2006 and references therein). Low Mn contents as compared to average shale (e.g. Turekian and Wedepohl, 1961) may be indicative of dysoxic bottom water conditions. Under reducing conditions at the sediment/water interface, soluble $Mn^{2+}$ diffuses from the sediment into $O_2$-depleted bottom waters; in contrast, high Mn concentrations hint at oxic water conditions (e.g. Bruland, 1983; Hild and Brumsack, 1998; Cruse and Lyons, 2004; Turgeon and Brumsack, 2006). However, Mn sometimes may be enriched in anoxic sediments due to Mn-fixation in the carbonate phase (e.g. Huckriede and Meischner, 1996; Brumsack, 2006).

Enrichment of other redox-sensitive and sulphide-residing elements, such as Fe and S, indicates periodic depletion of $O_2$ and potential availability of $H_2S$ in the water column (e.g. Canfield, 1989a,b). Iron is fixed in organic-rich sediments due to its reduction under anoxic conditions and subsequent fixation as pyrite in euxinic conditions (e.g. Berner, 1984). However, silicate-bound Fe is delivered from the hinterland, adding a non-reactive component to the sedimentary Fe pool which is controlled by detrital input (e.g. Cruse and Lyons,

2004; Brumsack, 2006). Also S is enriched in organic-rich sediments due to pyrite formation, and high contents of S are frequently related to anoxic sedimentary environments (e.g. Berner, 1964). A close correlation between S and Fe is generally documenting that S in the sediments is mainly fixed as pyrite (e.g. Berner, 1970, 1984). The high degree of pyritisation of Fe and the excess S indicate $H_2S$-containing pore waters, or even bottom waters, during deposition and diagenesis of the sediments (e.g. Lyons and Severmann, 2006).

This short introduction to sediment geochemistry is, in this case, limited only to the background information on the chemical elements that are discussed and interpreted in **Chapter 5**. More thorough discussion of sediment geochemistry is beyond the scope of the presented work.
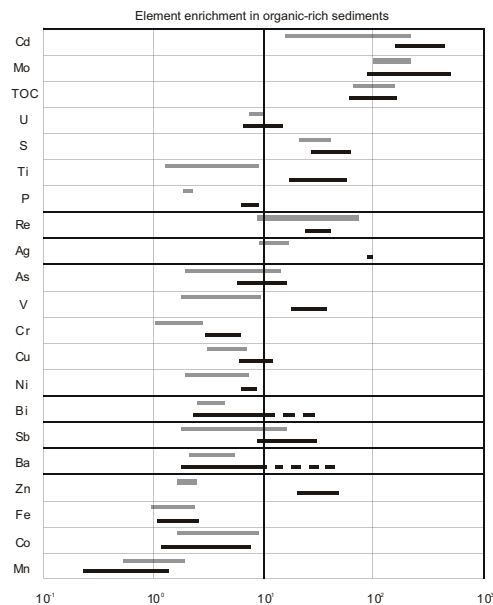


*Figure 1.7. Enrichment of selected elements in organic-rich sediments (after Brumsack, 2006). Black bars represent Cenomanian/Turonian black shales while grey bars represent sapropels.*

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**CHAPTER 2**

**Preservation and organic chemistry of late Cenozoic organic-walled dinoflagellate cysts; a review**

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**Abstract**

Within the last decade considerable information has become available on the effects of early diagenesis on the taphonomy of organic-walled dinoflagellate cysts. Here, we review the information currently available on this topic. After discussing organic matter degradation in general, an overview on the effects of different laboratory treatments on the dinoflagellate cyst association is given. Hereafter, the rates and amount of species-selective degradation in modern and fossil natural environments are discussed. It appears that the availability of oxygen in the sediments is the most important diagenetic variable. Some of the modern dinoflagellate cyst species survive thousands of years in well-oxygenated sediments and are as such amongst the most refractory types of organic matter. Most (but not all) of these refractory species are phototrophic gonyaulacoids. However, the refractory cysts form only a part of the modern gonyaulacoid or phototrophic cyst producing taxa. The modern species most vulnerable to degradation are often produced by

heterotrophic peridinioids. Again, these vulnerable species form only a part of the heterotrophic species and species with a peridinioid plate configuration.

To get insight in the intrinsic properties of the cysts bringing about the selective preservation, we continue with reviewing the understanding of algal cell walls and dinoflagellate cyst walls at the molecular level.

The review documents that cysts of Mesozoic age have different preservation characteristics than Late Cainozoic to Modern species. We propose that over a long periods, taphonomic processes on a molecular level substantially change the cyst wall macromolecular structure and herewith cyst degradability.

Having described the impact of selective preservation on the dinoflagellate cyst assemblages, we continue summarising the methods presently available for the recognition of and correction for this diagenetic overprint. Subsequently, we take advantage of the selective preservation by using it for reconstructing past export-production. Since the rates of dinoflagellate cyst degradation are strongly related to the bottom water oxygen concentration, this opens the way for a new proxy to reconstruct deep ocean oxygen concentrations. The importance of the rate of deep ocean ventilation within the marine global carbon cycle and its relationship with climate change, make this use of selective dinoflagellate cyst preservation an important though unexpected application.

Keywords: dinoflagellate cyst, selective preservation, proxy, macromolecular chemistry, diagenesis, ocean ventilation.

## 2.1. Introduction

Organic-walled dinoflagellate cysts are widespread in modern marine sediments and are known to have a long geological history (MacRea et al., 1996). Their high diversity and fast evolution make them very useful for stratigraphic purposes, especially in sediments where calcareous and/or siliceous microfossils are scarce or absent (Huber et al., 2004). The cyst morphology of virtually all dinoflagellates is species-specific. Upon sedimentation the cysts reflect the distribution of their respective motile stages

in the upper water column at low taxonomic level. Therefore, cyst associations in sediments enable detailed reconstructions of the upper water column. During the last decades methods to establish such reconstructions improved considerably, allowing quantitative estimates of environmental parameters (e.g. Mudie, 1992; Peyron and de Vernal, 2001; de Vernal et al., 2005). Because of their widespread distribution in modern sediments and their prominent abundance in fossil sediments from the Jurassic onward dinoflagellate cysts have been considered to be extremely resistant against degradation (e.g. Dale, 1996). However, recent studies have shown that this does not hold for all modern dinoflagellate cyst species (e.g. Marret, 1993; Hopkins and McCarthy, 2002; Mudie and McCarthy, 2006). It appears that species of some genera are indeed extremely resistant against aerobic degradation whereas others are very vulnerable (Zonneveld et al., 1997; Versteegh and Zonneveld, 2002).

In this paper we give a review and update on the present knowledge about aerobic degradation of organic walled dinoflagellate cysts and its chemical background on the basis of laboratory and field experiments, as well as observations from surface sediments and sediment cores. Furthermore, we discuss how the above-mentioned information can be applied in palaeoceanographical, environmental and climatological research.

## 2.2. Aerobic organic matter degradation

Of the organic matter produced in the photic zone, roughly 90% is degraded in the water column. Of the 10% of the organic matter flux that reaches the seafloor only about one tenth escapes oxidation and is buried in marine sediments. The other 90% is partly degraded via either aerobic or anaerobic pathways. Until now, there is no evidence that dinoflagellate cysts are degraded anaerobically. We therefore constrain this chapter to aerobic OM degradation in the sediments.

The processes leading to preservation of organic material have been the subject of debates and have been extensively reviewed (e.g. Emerson and Hedges, 2003; Eglinton and Repeta, 2003; Burdige, 2007). Within a aerobic

environment organic matter can be degraded chemically or by bacteria (e.g. Jørgensen, 2000; Sun et al., 2002).

Studies on natural diffusion-limited organic matter oxidation, often referred to as "burn-down" events as well as laboratory experiments, reveal that early aerobic diagenesis is highly selective. The rate of degradation of individual organic matter components is usually described as a first-order process (Hedges and Prahl, 1993 and references therein; Cowie et al., 1995; de Lange, 1998; Prahl et al., 2003). In such a first order process, the concentration of labile organic matter component (G) after a given time is dependent on its component specific decay constant (Hedges and Prahl, 1993). Organic components with a high degradation constant (expressed as "k"=degradation constant) will degrade faster than components with low k-values (Fig. 2.1a). Since in first order reaction kinetics, the reaction rate depends on the concentration of the reactant, this rate reduces logarithmically with time. The processes involved in the removal of the component from the sediment are diverse. The removal of a component from the sediments depends on the interplay between biodegradation, chemical and physical processes. For instance, complex biomolecules can vary in their ease of disassembly at the monomer, polymer or supramolecular scale of organisation. Rest products of the degradation reaction can form organic-organic associations composed of detrital molecules, that degrade with more difficultly than the original components (humification). Furthermore, degradation products might be sorbed to mineral surfaces or labile biomolecules might become encapsulated within more recalcitrant ones (Tegelaar et al., 1989; Keil et al., 1994a; Derenne and Largeau, 2001; Mayer, 2004). Degradation might be slowed down as result of biotic exclusion; organisms or their digestive agents are excluded or inhibited from access to organic matter or accumulation of (toxic) metabolites hampers the growth of the degrading organism.

The degradation of organic matter as a whole is however more complex since OM is composed of many components with different degradation constants. The most labile fraction of OM is consumed first whereas more refractory components degrade more slowly. Several degradation models are

based on the assumption of a continuum of k-values of the different components (Middelburg, 1989; Middelburg et al., 1997; Moodley et al., 2005).

Other factors might also influence the degradation of OM such as bioturbation rates, sedimentation rate and water depth (Middelburg, 1989; Hartnett et al., 1998; Hedges et al., 1999). These factors are considered to influence the oxygen exposure time (OET). Laboratory experiments on the effect of bioturbation on the degradation of freshly produced OM in an aerobic water column with and without bioturbating organisms show that increased bioturbation in a oxygenated water column might result in increased preservation of OM (Sun et al., 2002). The reason is that freshly produced OM, that still contains many components that are easily degradable, is quickly transported to deeper sediment layers that are anoxic. Although simultaneously older organic matter from the deeper anoxic zone becomes exposed to oxygen rich waters again, this does not compensate for the effect of the burying of the labile component. However, so far this could not clearly be shown in natural settings. Furthermore, natural environments with sites characterised by oxygenated bottom/pore water where benthic life is absent are extremely rare and non-bioturbated sediments are generally only found in anoxic environments. Consequently, total OM degradation in natural environments is higher at bioturbated sites compared to non-bioturbated sites.
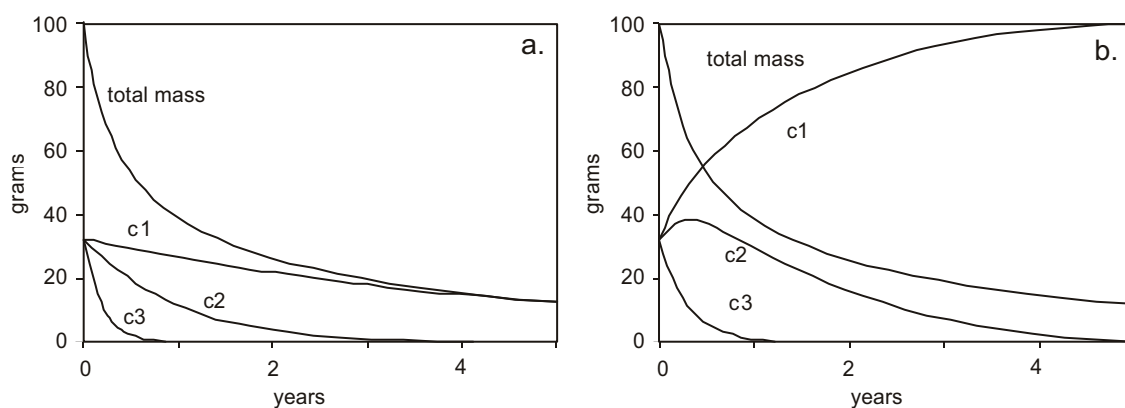


*Figure 2.1. Changes in initial mass versus time of organic matter material composed of three components (C1, C2, C3) that have first order decay constants k of 0.2, 1.0 and 5.0 respectively. A. weight percent, B. relative changes (%). Redrawn after Hedges and Prahl (1993).*

The effect of oxygen concentration on OM concentrations might be more complex. Oxygen may affect the growth or maintenance efficiency of organisms that mineralise OM. Recent studies suggest that oxygen concentration does not have a linear relationship to bacterial biomass-production (Middelburg, 1989; Dauwe et al., 1999; Dauwe et al., 2001; Lee et al., 2004; Moodley et al., 2005).

Considering a mixture of components, such as TOC or a dinoflagellate cyst association, and the logarithmic nature of the degradation process, the most labile components or species will disappear first so that the more refractory components or species will dominate the composition/association with time (Fig. 2.1b). In rich OM samples, the disappearance of the most reactive components/species, results in a noticeable increase in the weight percentage of the most refractory components/species. When other organic components as dinoflagellate cysts are more reactive to aerobic degradation, exposure to oxygen-rich conditions of a sediment sample with a dinoflagellate cyst association that contains species with different k-values, would result in an increase of weight percentage (cyst per gram sediment) of species with low k whereas the calculated accumulation rates remain constant. This because the other components would disappear from the sediment increasing the amount of weight percent of the refractive dinoflagellate cysts. Accumulation rates are calculated independent from sediment weight and would therefore not change. For species with high k-values, the relative abundances, amounts of cyst per gram dry sediment and the calculated accumulation rates would decrease over time.

## 2.3. Selective degradation of cysts during sample preparation

The knowledge that some Late Cainozoic and modern dinoflagellate cyst species can be selectively removed from the assemblages upon chemical treatment has been well documented. Especially "round brown" cysts (*Brigantedinium* spp.) produced by heterotrophic dinoflagellates such as *Protoperidinium* appeared to be absent or rare in sediments that had been prepared by methods including so called "harsh chemical treatments", such as rinsing with hot hydrochloric acid (e.g. Dale, 1976). Reid (1977) observed that

these cysts became bleached and disintegrated when oxidising agents were used. Acetolysis (a 70°C treatment with $CH_3COOH$, $(CH_3CO)_2O$ and $H_2SO_4$) appeared to be an effective way to selectively remove protoperidinioid cysts from a sample (Marret, 1993; Mudie and McCarthy, 2006). Recently Hopkins and McCarthy (2002) showed that only 30 minutes treatment with $H_2O_2$ (15%) is enough to destroy the majority of *Brigantedinium* spp. as well as "other protoperidinoid" cysts, with the complete destruction of these cysts after one hour treatment. *Spiniferites* spp. and *Operculodinium centrocarpum*, appeared to be less sensitive to these treatments whereas *Bitectatodinium tepikiense* and "other gonyaulacoid" cysts do not show a clear response.

Recently we tested the effect of neutralisation with KOH after cold HCL (10%) and HF (40%) treatment (see Marret and Zonneveld, 2003). Subsamples of the homogenised upper cm of sediment from the giant box core GeoB 6412 (southern mid-Atlantic Ridge; 44°15,25'S – 17°38,84'W) were treated with and without neutralisation of KOH (Fig. 2.2). The experiment shows that careful neutralisation with KOH does not alter the association when the solution does not become alkaline. Additional exposure of the material to 10% KOH for one hour results in the loss of pollen and spores only whereas exposure of the material to 10% or 40% KOH for 24 hours, results in a major loss of protoperidinioid cysts. The concentrations of gonyaulacoid cysts were not altered (Fig. 2.2; Bork et al., internal report). Heuser and Stock (1984) discussed the possible effects of the use of acetolysis and OH treatment on pollen from marine sediments and suggest only "brief" neutralisation of HCL and HF with heated 1% KOH.
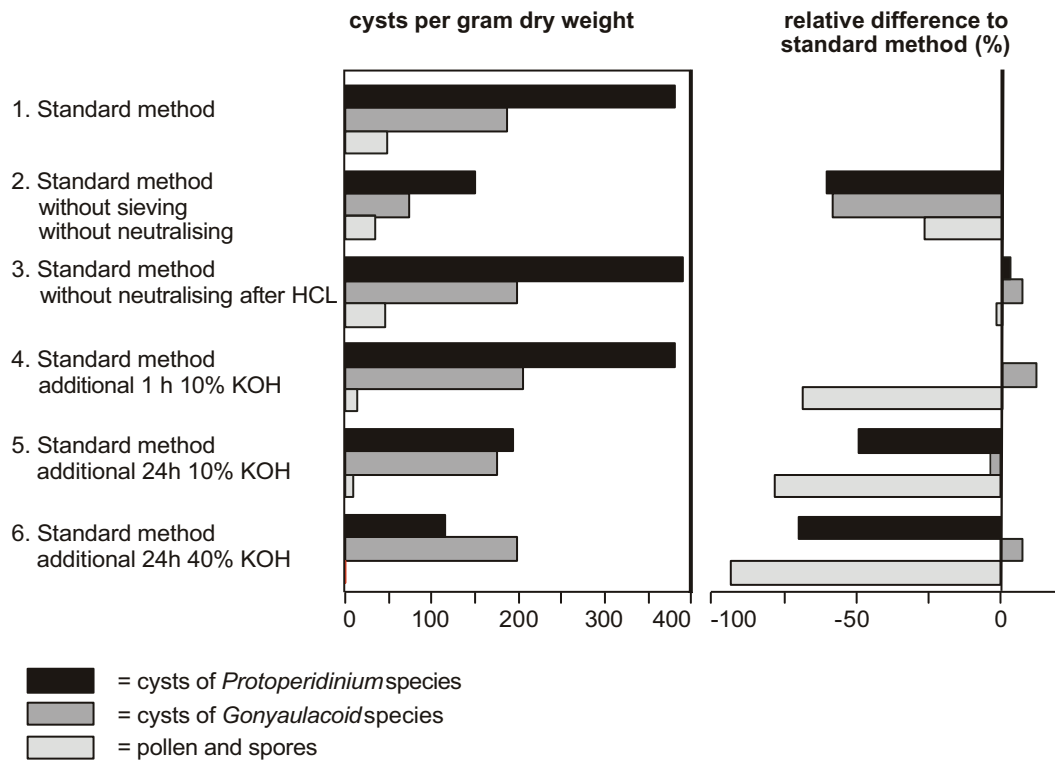
*Figure 2.2. Concentrations of cysts and pollen/spores after several preparation methods. Standard method: 1 cm³ of dry material is weighed, treated with 10% HCl for one hour and neutralised with 10% KOH without the solution becoming alkaline. After this the solution is decanted through a 10 µm precision sieve (Storck-Veco). The sample is successively treated with 40% HF for two days, neutralised with 40% KOH without the solution becoming alkaline and decanted through a 10 ?m precision sieve. A known volume of the sample has been mounted on a slide embedded in glycerine gelatine. In treatment two, the standard treatment is adapted such that no neutralisation has been preformed and for decantation no sieve is used. Treatment 3 is the standard method without a neutralisation step after HCl treatment. Additional to the standard preparation the material has been treated for one hour with 10% KOH (treatment 4), one hour 40% KOH (treatment 5) and 24 hours 40% KOH (treatment 6) respectively. Protoperidinium cysts include cysts of Brigantedinium spp., Echinidinium spp., Lejeunecysta spp., Selenopemphix spp.; gonyaulacoid cysts include Impagidinium species, Operculodinium centrocarpum, Operculodinium israelianum and Nematosphaeropsis labyrinthus.*

Oxidation for 15 seconds with fuming nitric acid and washing with KOH before mounting severely damaged the cysts of the Pliocene cyst species *Barssidinium pliocenicum* (De Schepper et al., 2004)*.* The brief exposure to fuming nitric acid resulted in specimens becoming pale with separation of the cell walls. This confirmed earlier suspicions by Head (1993) and Lentin et al. (1994) that pale or cavate specimens of *Barssidinium* may result from laboratory procedures or partial oxidation rather than represent different species.

The above examples document a large sensitivity of protoperidinioid cysts to oxidative treatments. Some modern gonyaulacoid cysts, however, appear to be sensitive to long HF (40%) exposure (Turon, 1984). Exposure of a North Atlantic sediment sample to cold HF (40%) for 32 days, resulted in a loss of about 20% of *O. centrocarpum*, 40% – 89% of *Spiniferites mirabilis*, 75% - 88% of *Nematosphaeropsis labyrinthus*, 80% - 83% of protoperidinioid cysts, 99% of *B. tepikiense* and 87% - 100% of *Impagidinium sphaericum*.

Dodsworth (1995) shows that aerobic degradation of cysts in cretaceous sediments is different to that of Cenozoic associations. Here, gonyaulacoid cysts of mid-Cretaceous sediments appeared to be more sensitive to oxidative treatments than peridinioid cysts. This indicates that the processes that affect modern assemblages as described in the present paper cannot be directly transferred to fossil assemblages. This also suggests that there is an urgent need to investigate the effects of different laboratory treatments and possible diagenetic effects on older assemblages.

## 2.4. Selective preservation of cysts in natural environments

The first firm indications that modern cyst assemblages might be altered by aerobic degradation in natural environments were published a decade ago as a pilot study on sediments of the Madeira Abyssal Plain (Zonneveld et al., 1997) in a reaction on a paper by Keil et al. (1994b). Sediments of this Plain are characterized by the occurrence of turbidites that consist of a organic-rich ungraded mud that, at times of deposition, had a homogenous chemical and organic composition (Colley et al., 1984; Buckley and Cranston, 1988; de Lange

et al., 1994; Keil et al., 1994a; Cowie et al., 1995). After deposition, oxygen started to penetrate the turbidite from above resulting in partial decomposition of organic matter in the top 50 cm of the studied f-turbidite. This process stopped at the moment a next turbidite covered the site, resulting in a so called "fossil oxidation front". By comparing the cyst concentrations in sediments of the unoxidised part of the turbidite with those in the oxidized part, Zonneveld et al. (1997) observed that cysts of *Protoperidinium* species were selectively degraded whereas cyst concentrations of several gonyaulacoids did not show any change over the front (Fig. 2.3). These results were confirmed by a study of diffusion-limited aerobic decay of organic matter, often referred to as "burn-down" in sediments of the last Eastern Mediterranean Sapropel S1, where similar association and concentration changes were observed when comparing sediments above and below the still active oxidation Front (Fig. 2.4; Zonneveld et al., 2001). Based on these studies Zonneveld et al. (2001) established a table where cyst species were grouped according to their vulnerability (Appendix 2.1). In comparing the different degradation rates of cyst groups with other organic components in the sediments, Versteegh and Zonneveld (2002) showed that the species classified as "extremely resistant" were more refractory than all other organic components measured. The "sensitive" species however were among the most reactive components (Appendix 2.2).
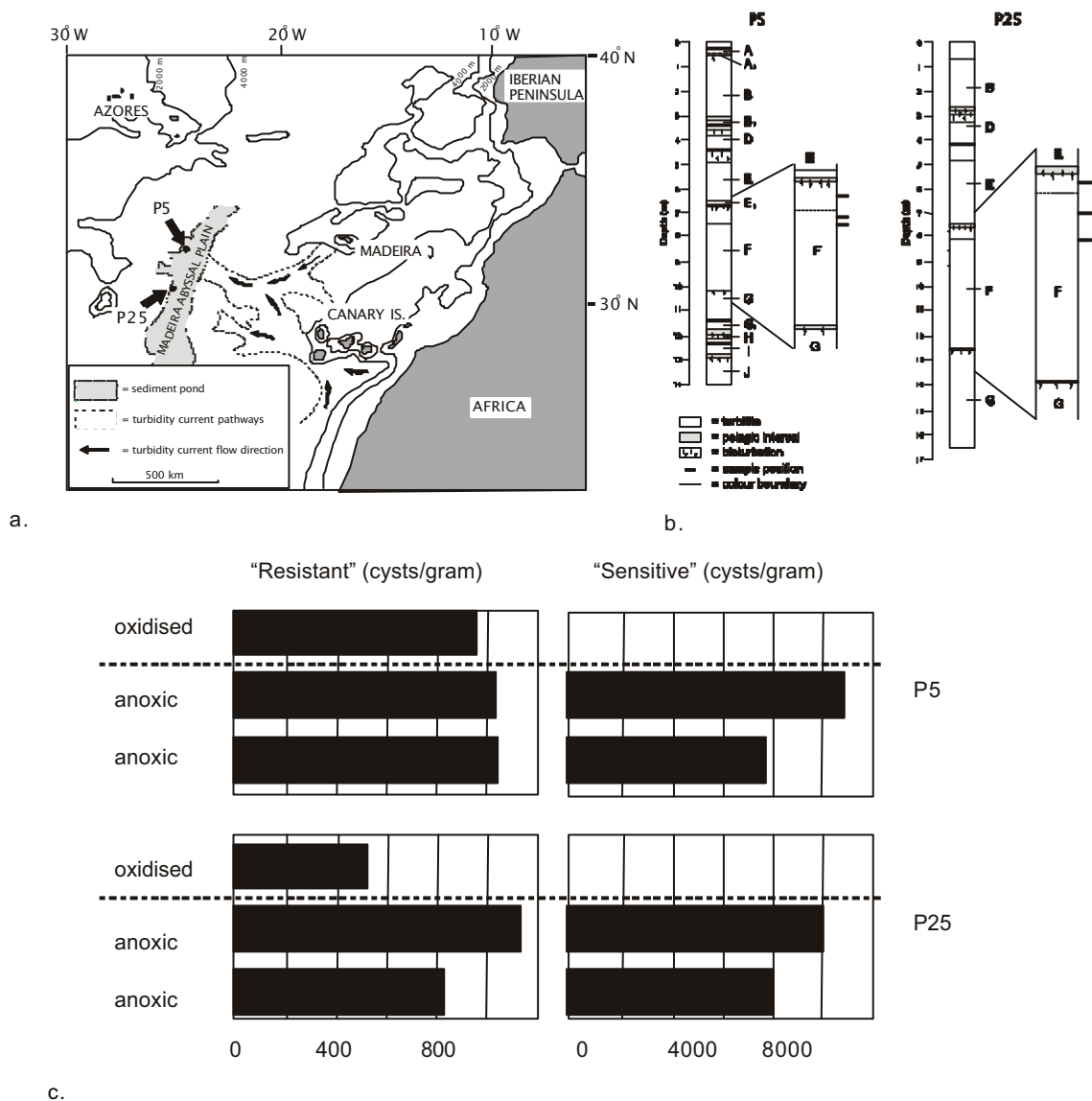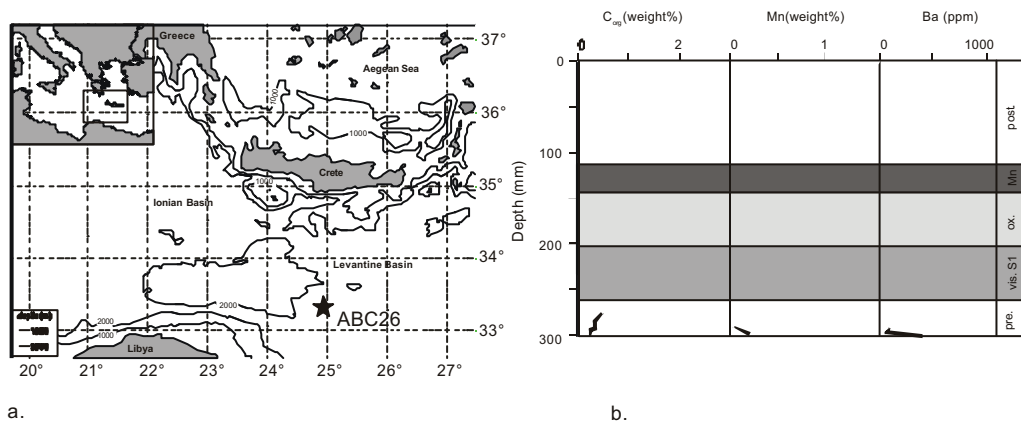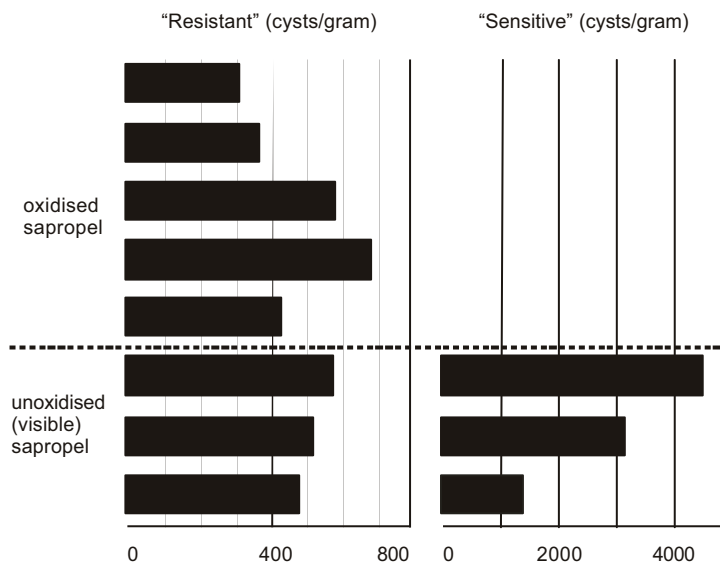
Figure 2.3. Cyst concentration in oxidised and unoxidised sediments of the initially homogenous Madeira Abyssal Plain f-turbidite. A. Sample locations, b. lithological column, c. cyst concentrations. Sensitive cysts: Brigantedinium spp., Echinidinium spp., Lejeunecysta oliva, Selenopemphix nephroides, Selenopemphix quanta, Stelladinium stellatum, Trinovantedinium applanatum. Resistant cysts: Impagidinium aculeatum, Impagidinium paradoxum, Impagidinium patulum, Impagidinium plicatum, Impagidinium sphaericum, Impagidinium velorum, Nematosphaeropsis labyrinthus, Operculodinium israelianum, Polysphaeridium zoharyi.

*Figure 2.4. Cyst concentrations in sediments of the Levantine Basin Core ABC26. a. Core location, b. Concentration versus depth data for $C_{org}$, Mn and Ba in Core ABC26. Pre.= presapropelic layer, vis. S1 = visible sapropel, ox. = oxidised sapropel, Mn = Manganese marker bed, post = post-sapropelic layer. c. cyst concentrations: sensitive cysts: Brigantedinium spp., Echinidinium spp., Cyst of Protoperidinium americanum, Lejeunecysta oliva, Selenopemphix nephroides, Selenopemphix quanta, Protoperidinium stellatum, Resistant cysts: Impagidinium aculeatum, Impagidinium paradoxum, Impagidinium patulum, Impagidinium plicatum, Impagidinium sphaericum, Impagidinium velorum, Nematosphaeropsis labyrinthus, Operculodinium israelianum, Pentapharsodinium dalei, Polysphaeridium zoharyi.*

### 2.4.1 Sediment traps

When the cyst content of sediment trap material is studied from sites where bottom waters are oxygenated, generally a discrepancy can be found between the associations found in the traps compared to those in the underlying sediments. In comparison to the surface sediment samples, trap material is generally enriched in (round brown) *Protoperidinium* cysts (Fig. 2.5). The first to notice this "paradox" was Barrie Dale in his pioneering study of trap material that had been collected during one year in the Pacific, equatorial Atlantic and North Atlantic regions (Dale, 1986; Dale, 1992). In the trap sediments of mooring sites in the western equatorial Atlantic Ocean and in the Panama Bight, the organic walled dinoflagellate cyst association was completely formed by round brown cysts of *Protoperidinium* species (*Brigantedinium* spp.), with the exception of a single finding of *I. sphaericum.* Also in the trap material collected in the northern North Atlantic Ocean, the cyst association is dominated by brown *Protoperidinium* cysts and cysts of the genus *Islandinium* (probably also formed by dinoflagellates with a peridinioid plate configuration). Although Dale discusses the possibility of the differences in accumulation time between trap samples and surface sediments (one year and up to several 100 to 1000 years), and the possibility of lateral transport altering the cyst association, he did not consider selective preservation as a possible explanation for his observations.
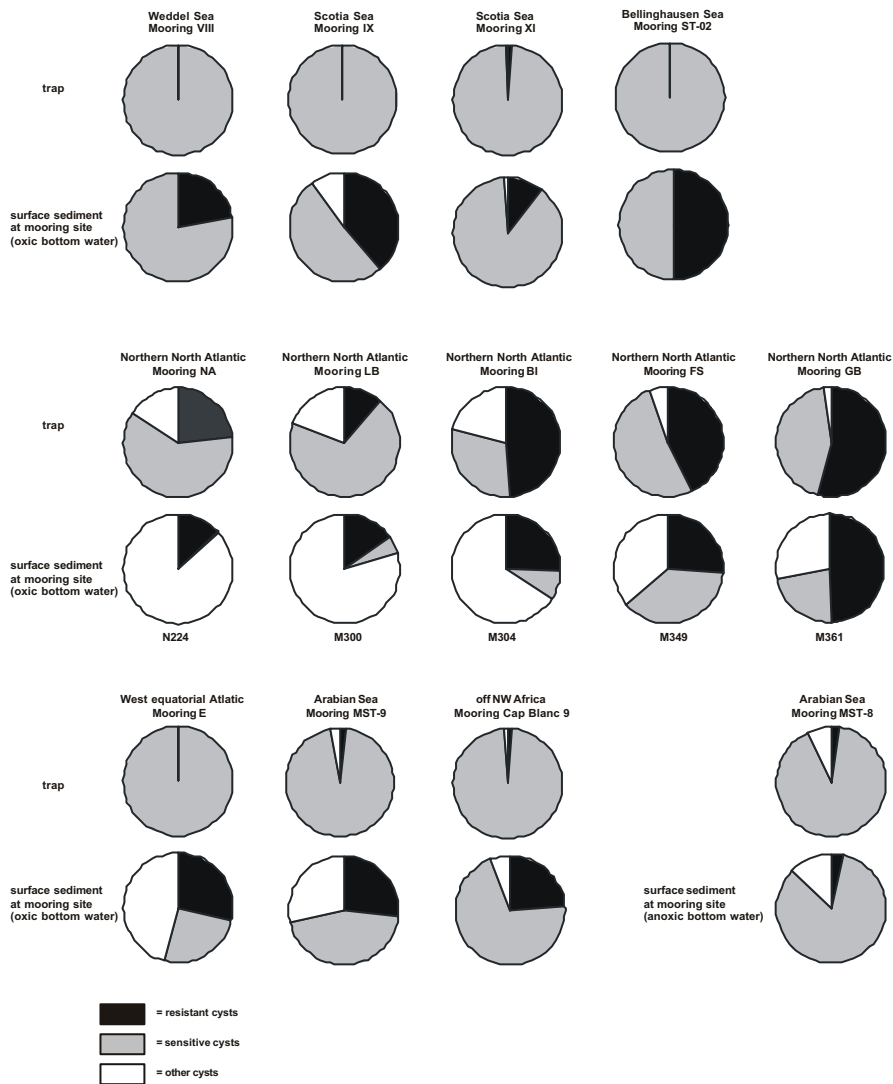
*Figure 2.5. Relative abundances of three groups of cyst species of sediment trap sediments and underlying surface sediments. "Sensitive group" includes all cysts of the genera Brigantedinium, Echinidinium, Islandinium, Lejeunecysta, Protoperidinium, Selenopemphix, Trinovantedinium. "Resistant groups" include all cysts of the genera Impagidinium and Nematosphaeropsis and Operculodinium israelianum, Pentapharsodinium dalei, Polysphaeridium zoharyi. The group of "other cysts" includes cysts of all genera and species. Sediment trap data are derived from: Dale (1992), Dale and Dale (1992), Harland and Pudsey (1999), Susek and Zonneveld (2005) and Zonneveld and Brummer (2000). Sediment sample data have been achieved from the above mentioned publication as well as from Marret and Zonneveld (2003).*

### 2.4.2. Surface sediments

To date, studies on the modern geographic distribution of dinoflagellate cyst species often concentrate on the relationship between cyst distribution and environmental gradients in the upper water column whereas the possible effects of post depositional aerobic degradation on the association are not taken into account (e.g. Pospelova et al., 2004; 2005; Radi et al., 2007). However, there are strong indications that post-depositional degradation in modern sediments can severely alter the dinoflagellate cyst association. For instance, in the western Arabian Sea high bioproduction in the upper water column and moderate rates of thermocline ventilation result in a strong permanent oxygen minimum zone (OMZ) at water depths between about 400m and 1200m. By comparison of the association in surface sediment samples of sites within and outside the oxygen minimum zone in an area where fluxes of the productive sea surface layer can be considered to have been basically identical, Reichart and Brinkhuis (2003) show that OMZ samples are relatively enriched in cysts of *Protoperidinium* compared to sediments that are deposited in oxygen rich water masses. Most gonyaulacoid species show similar concentrations in all sediments of the region. They attribute this to post-depositional species-selective aerobic degradation. Similar results were documented for the region by Versteegh and Zonneveld (2002).

In surface sediments of the Benguela upwelling area, oxygen concentrations in bottom waters can also be clearly linked to variability in cyst association composition (Bockelmann et al., 2007). The SW African shelf is characterised by an oxygen minimum zone due to upwelling-related high productivity along the shelf-break and reduced ventilation of shelf bottom waters. Sediments on the shelf break, slope and the pelagic ocean floor are in contact with well-oxygenated water. Comparison of the cyst association of surface sediment samples collected along bottom-water oxygen gradients, with a pool of environmental variables (sea-surface temperature, sea-surface salinity, chlorophyll-*a* concentration, upper ocean phosphate and nitrate concentrations, stratification and bottom water oxygen concentrations) shows

that oxygen is among the most important factors explaining the variability in relative cyst abundances. Comparable to the Arabian Sea, sediments of the oxygen minimum zone are enriched in cysts of *Protoperidinium* species (notably *Brigantedinium* spp. and species of the genera *Echinidinium, Lejeunecysta, Polykrikos* and *Selenopemphix*) whereas sites with well-oxygenated bottom waters are enriched in gonyaulacoid species of the genera *Impagidinium*, *Nematosphaeropsis* as well as *Spiniferites mirabilis, Spiniferites ramosus* and *Pyxidinopsis reticulata*.

Recently, a comprehensive study of 62 well-dated upper sediment samples from the Arabian Sea, north-western African Margin (North Atlantic), western equatorial Atlantic Ocean/Caribbean, south-western African margin (South Atlantic) and Southern Ocean (Atlantic sector), revealed that accumulation rates of the cysts group previously classified as "extremely sensitive" (cysts of *Echinidinium, Brigantedinium* and other *Protoperidinium* species) have an logarithmic degrease with increasing bottom water oxygen concentrations (Fig. 2.6; Zonneveld et al., 2007).
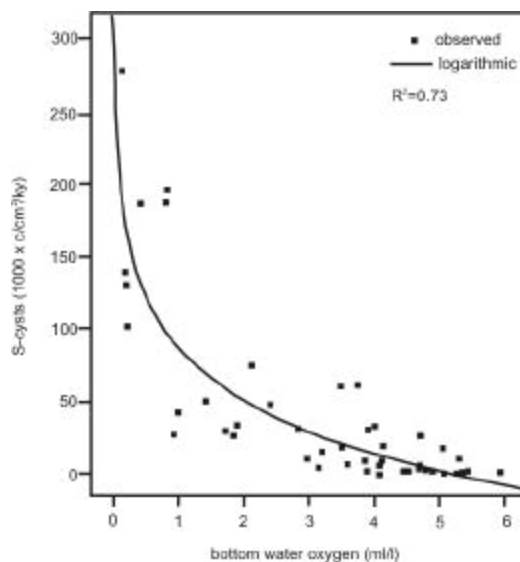


*Figure 2.6. Relationship between accumulation rates of S-cysts (cysts per cm$^2$ per kilo-year (c/cm$^2$/ky) with the sensitive cyst group as defined in Figure 5) and bottom water O$_2$ based on 62 surface sediment samples of modern age. Redrawn from Zonneveld et al. (2007).*

### 2.4.3. Preservation experiments in natural environments

To obtain more quantitative information about the degradation rate of individual cyst species, independent from other factors as differences in production rates and transport effects, a recent experiment has been carried out where sediments of different locations have been exposed for 15 months to oxygen rich and oxygen depleted ocean waters in a natural environment (**Chapter 3**). Exposure sites are located in the Urania and Bannock Basins where anoxic brine bottom waters are overlain by oxygenated intermediate and surface waters. Sub-samples of previously homogenised material from three areas (two previously unoxidised sediments and an oxidised site) have been stored in sample dialysis bags, which membranes that allowing the penetration of oxygen but prevent bacterial exchange. The dialyses bags with the sub-samples were placed in open containers that were connected to sediment traps moored at two sites (35°13'N, 21°30'E and 34°18'N, 20°01'E) within the anoxic brine waters and oxygenated intermediate waters approximately 500 m above the brines. By comparing the cyst composition and concentration of the original material with those of the exposed material, information has been obtained about the possible species selective degradation as result of exposure to oxygenated and anoxic water masses.

After 15 months of deployment the sub-samples exposed to brine waters did not show any concentration or association differences. However, the cyst concentration and association composition of the subsamples from anoxic source sites exposed to the oxygen rich intermediate waters changed remarkably (Fig. 2.7) with a decrease of 30% to 50% cyst/gram dry weight of *Brigantedinium* spp. and *Echinidinium granulatum.* As expected *I. aculeatum, I. plicatum, N. labyrinthus*, *O. israelianum* and cysts of *P. dalei*, which have all been classified as being resistant to degradation in earlier studies, show an increase in weight percentage. Hence they are more resistant to aerobic degradation than most other organic matter components. Cyst associations and concentrations of subsamples from the oxic site did not seem to be affected by the different treatments although cyst concentrations in these samples were so

low that no firm conclusions could be made. This study shows that degradation of cysts can be a very fast process.
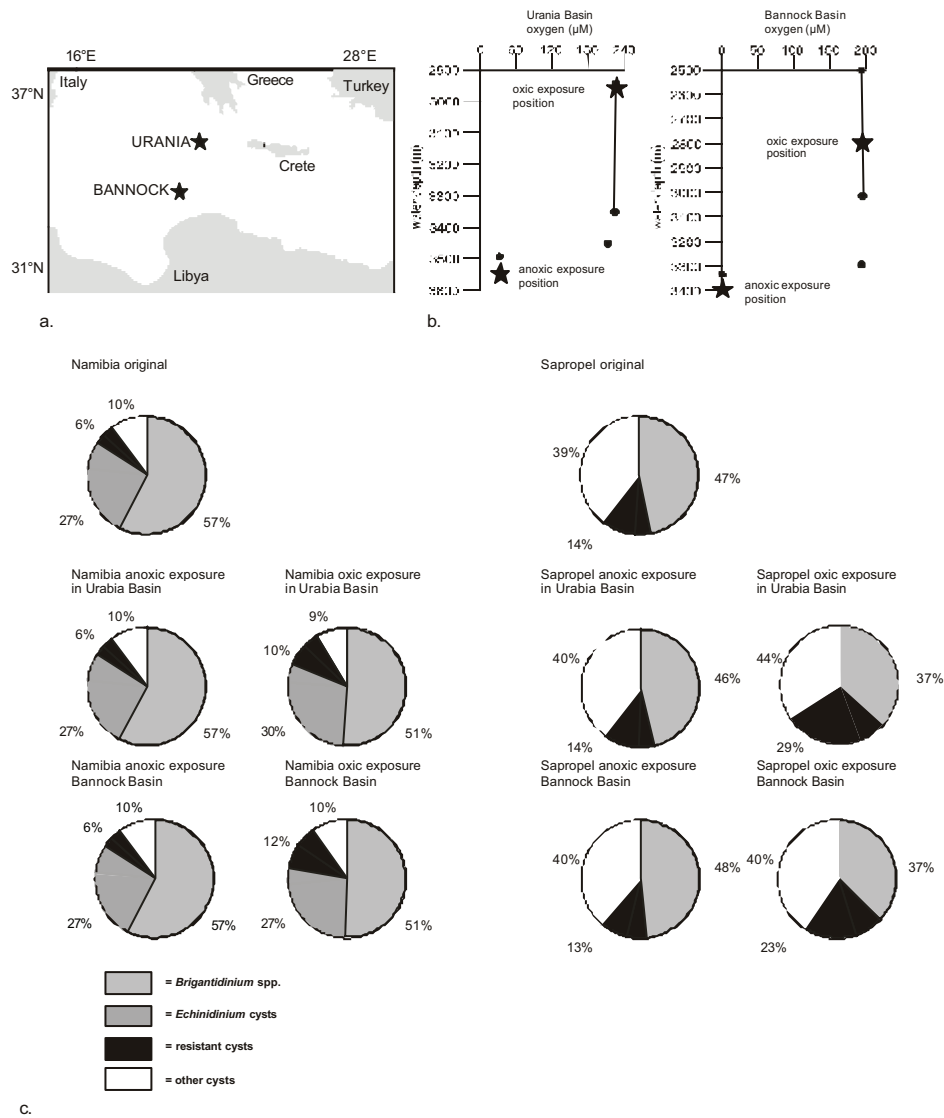


*Figure 2.7. A. Map of the Eastern Mediterranean Sea depicting locations of the Bannock Basin and Urania Basin mooring sites. B. Oxygen concentrations in waters at the mooring sites and exposure position. Oxygen concentration after de Lange et al., (1990). C. Relative abundances of cysts groups of samples from anoxic sediments of the Namibia upwelling area (Namibia) and the S1 sapropel (sapropel) previous to exposure and after 15 months of exposure to well-oxygenated waters and anoxic brine waters.*

### 2.4.4. Late Quaternary time series

To date, only few studies document alteration of Late Quaternary fossil dinoflagellate cyst signals due to postdepositional processes. The first indication that post-depositional species-selective decay has altered the dinoflagellate cyst association comes from a Namibian shelf core (core GeoB 1710). This core is derived from a location where surface waters are not directly influence by year round upwelling but where filaments of upwelled waters can pass frequently (Versteegh and Zonneveld, 2002). Within this study the dinoflagellate cyst information is compared to the planktic and benthic foraminiferal assemblages, stable carbon and oxygen isotope records of planktic and benthic foraminifera, diatom associations, pollen and spore composition, total organic carbon concentrations, $U^K_{37}$ - derived sea surface temperatures and other lipid biomarker concentrations of loliolide + isololiolide, $C_{37}$ alkenones the $n$-$C_{31}$ alkane. It could be documented that severe diagenetic overprinting of the dinoflagellate signal occurred in sediments deposited during oxygen isotope stages 5, 3 and 1. Within these intervals, cysts of *Protoperidinium* species are underrepresented whereas the species previously classified as "resistant" (Appendix 2.1) were not affected.

Reichart and Brinkhuis (2003) document strong modification of dinoflagellate cyst associations by selective degradation in the Western Arabian Sea. They compare the Late Quaternary dinoflagellate cyst records from two cores from the western Arabian Sea with bottom water oxygen conditions reconstructed from the composition of redox sensitive trace metals and benthic faunal characteristics of the studied sediments. They document that *Protoperidinium* cysts (including species of *Brigantedinium*, *Echinidinium, Lejeunecysta, Selenopemphix* and *Trinovantedinium*) were degraded in intervals where bottom waters are assumed to have been oxic. By comparing the *Protoperidinium* cyst concentrations (cyst/g) and relative abundance records from two other cores with the productivity indicators, $C_{org}$, the relative abundance of the planktic foraminifera *Globigerina bulloides* (as upwelling proxy) and the Ba/Al ratio, they show that although severe selective degradation has altered the original signal, past changes in export productivity in this region

are still reflected in the *Protoperidinium* cyst concentration (cysts/gram). In contrast, the relative abundances appeared to be strongly overprinted by diagenesis.

Recently Bockelmann et al. (2007) compared the dinoflagellate cyst record of sediments deposited during the last 20 kilo-years from a core in the NW African upwelling area with chemical data of the same samples. Variability in the ratios Fe/Al, Mn/Al and U/Al have been used to obtain information of the past redox conditions at the core site. Information of these ratios indicates that the bottom waters at the core site were well ventilated at about 13 ka BP and after 9.5 ka BP. Post-depositional oxidation could be documented for the intervals between 14 – 13 ka and between 1.5 – 9.5 ka BP. Bottom water oxygen conditions at the site have been reconstructed to be low between 21 – 14 ka BP and 12.5 – 11.5 ka BP. The authors observe that accumulation rates of the group of "resistant dinoflagellates" (Appendix 2.1) reflect variations in the Ba/Al ratio for intervals. Within this region the Ba/Al ratio can be used as a proxy for palaeoproductivity (Kasten et al., 2001). Accumulation rates of the group of "sensitive species" as well as the weight percent of total organic matter reflect this curve only in those intervals where low-oxygen conditions were reconstructed based on the chemical data.

## 2.5. Organic geochemistry of dinoflagellate cysts
### 2.5.1 Acid resistant cell walls from extant micro-algae

To date, there is only limited information available about the chemical structure of dinoflagellate cyst walls. The records that are available suggest different chemical structures for different cyst species. Before we can discuss these differences in more detail some background information is required about the chemical wall structure of other extant algae that are acid resistant.

The walls of some micro algae are acid resistant. Mostly, these resistant walls consist of a highly aliphatic cell-wall macromolecule composed of unbranched but cross-linked carbon atoms, termed algaenan (Fig. 2.8). This can be concluded despite confusion generated by the different methodologies used for isolating the walls of extant algae. This confusion is largely related to

artificial polymerisation of the cell contents induced by some isolation methods, resulting in high amounts of isoprenoids, sugar- and sugar-protein derivates amongst the isolated cell walls (Brunner and Honegger, 1985; Gelin et al., 1997; Allard et al., 1998). Careful re-examination, with more recent technology avoiding the co-analysis of condensed cytoplasm (e.g. by breaking the cell walls prior to chemical treatment), demonstrate either the absence of a resistant wall for species previously claimed to have one, or the presence of algaenan (Brunner and Honegger, 1985; Blokker et al., 1998; Allard et al., 1998).

It is assumed that only two biochemical pathways lead to the production of resistant algal walls (and resistant plant macromolecules in general): I) the acetate-malate pathway (leading *via* lipid-synthesis to algaenans and the cutin and cutan of higher plant cuticles), and II) the phenylpropanoid pathway (leading to e.g. sporopollenin). However, only a very limited portion of the living and fossil algae has been studied for the presence and composition of acid- and base-resistant cell walls. Most of the studied species belong to the Chlorophyta and most of these are from fresh water environments. The marine realm, with the richest and longest fossil record, has hardly been exploited. New pathways leading to fossilisable biomacromolecules may therefore still await discovery.
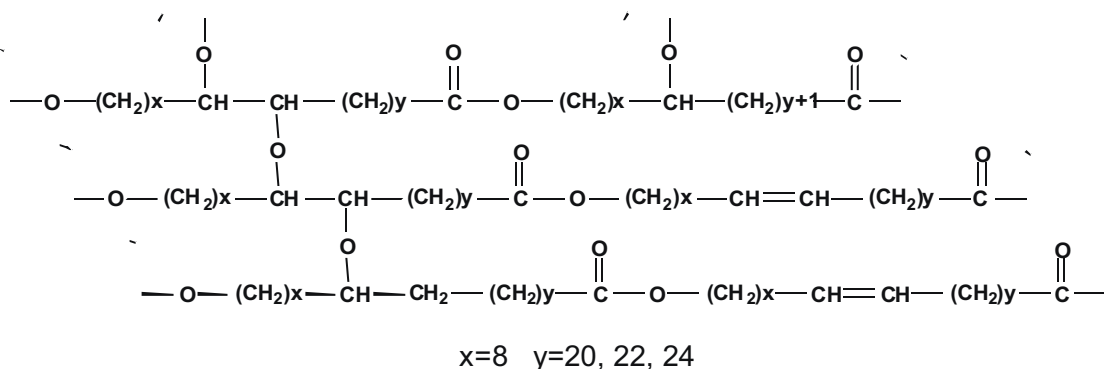


$$x=8 \quad y=20, 22, 24$$

*Figure 2.8. General algaenan structure for green algae, after Blokker et al. (1998)*

### 2.5.2. Algaenans of extant micro-algae

Algaenans (Tegelaar et al., 1989) represent a series of acid and base-resistant aliphatic biomacromolecules. It is important to note that other

compounds may be associated with the algaenan e.g. isoprenoids in the case of *Botryococcus braunii* race L (Bertheas et al., 1999) or sugars in the case of *Coelastrum sphaericum* (Rodríguez and Cerezo, 1996) but they are removed upon hydrolysis. The aliphatic nature suggests that algaenans are biosynthesised via the acetate/malate pathway that leads to fatty acids. Algaenans appear widespread in Chlorophyta and occur in some Eustigmatophyta and has been reported for the motile stage of the dinoflagellate *Gymnodinium catenatum* (Gelin et al., 1999). The walls of some Prasinophyta and the pellicles of several Dinophyta have been reported to be "resistant" (e.g. Morrill and Loeblich III, 1981; Aken and Pienaar, 1985) but information on the wall chemistry is too sparse to infer that they consist of algaenan. For few, more closely analysed, algae a general algaenan structure can be proposed. The algaenan building blocks consist of linear $C_{22}$ to $C_{40}$ even- or odd-numbered carbon chains with functional groups (e.g double bonds, aldehydes, or carboxylic acids) at the terminal positions and one or two mid-chain positions (e.g. ? [9] and ? [18]). In the algaenan the functional groups cross-link the monomers with ether, ester and/or acetal bonds (e.g. Blokker et al., 1998, 1999, 2006; Simpson et al., 2003) whereby in *B. braunii* sometimes linear isoprenoids become incorporated (Metzger et al., 2007). In extant algae, algaenans have almost exclusively been detected for fresh water species. The highly aliphatic (plastic like) algaenan may enable them to spread from one place to another (by wind, birds etc.) and to resist periods of dryness. Most marine species would not necessarily need this. Algaenans are among the most frequently studied resistant algal macromolecules and they have been put forward as sources of fossil fuel such as lacustrine petroleum (e.g. Blokker et al., 2006)

### 2.5.3. Wall polymers of extant dinoflagellates

Dinoflagellates are capable of producing several types of cell coverings. In thecate dinoflagellates, the plates develop in the amphiesmal vesicles. These plates have been reported to contain D-glucose polymers. In microfibrils of the thecal plates of *Scrippsiella hexapraecingula* and *Cryptothecodinium cohnii*

these D-glucose units are joined by ß-(1? 4) linkages, forming cellulose (Sekida et al., 1999; Kwok and Wong, 2003). The glucans making up 95 wt % of the theca of *Peridinium westii* are more complex, containing also ß-(1? 3) linkages (Nevo and Sharon, 1969). This more complex glucan seems to be more difficult to biodegrade (Nevo and Sharon, 1969). The dinoflagellate pellicle and cyst are formed beneath the amphiesmal vesicles. The pellicle wall of *S. hexapraecingula* is three layered whereas that of *Pyrocystis lunula* is two-layered and cellulose microfibrils have only been detected in the innermost layer of the pellicle walls (Swift and Remsen, 1970; Sekida et al., 2004). The composition of the middle and outermost layers is unknown. The pellicles of *Pyrocystis fusiformis* and *P. pseudonocticula* also contain cellulose (Swift and Remsen, 1970). Although algaenan has been reported from the motile stage of the dinoflagellate *Gymnodinium catenatum*, (Gelin et al., 1999) it is not clear from which morphological structure this algaenan has been derived. Apart from thecae and pellicles, dinoflagellates seem to be able to produce a much more resistant kind of cell covering for their resting cysts. This kind of wall biopolymer has been called dinosporin (Fensome et al., 1993). There is only very limited information on recent dinoflagellate cyst walls. The walls of *L. polyedrum* are reported to be relatively condensed and predominantly aromatic, compositionally distinct from 'sporopollenin', unrelated to the walls of green algae (algaenan) and that the isoprenoid tocopherol as an important monomer (Kokinos et al., 1998). Upon re-analysis using the methodology of Blokker et al. (1998) these conclusions are partly confirmed (Versteegh et al. subm.). Indeed, the cysts are not composed of algaenan or sporopollenin-like but there is also no evidence for aromatic groups or tocopherol as an important monomer. Instead, there is a considerable resemblance with cellulose suggesting that the cysts consist of cross-linked carbohydrates. The discrepancy may be attributed to the phosphoric acid treatment (3 weeks) during the cyst wall isolation procedure by Kokinos et al. (1998) which has been shown to produce artefacts (Allard et al., 1998; Allard and Templier, 2000). NMR analysis of *Scrippsiella* sp. cysts suggests yet another, very complex cyst wall macromolecule with a substantial aliphatic component (Hemsley et al., 1994). Preliminary analysis of

the transparent cyst-walls from a culture of the peridinioid *Scrippsiella ramonii* reveals aromatic and aliphatic moieties but no isoprenoid moieties (de Leeuw et al., 2006). In this case the presence of a series of distally unsaturated and a, ? - dicarboxylic acids and a series of methoxy-benzenes upon thermochemolysis suggests a network of linear carbon chains and aromatic rings or carbohydrates making up the biomacromolecule.

The chemical and geological stability of the cysts informs us on a different aspect of dinoflagellate cyst walls. In marine palynology, acetolysis and base treatment are avoided as much as possible upon processing of dinoflagellate assemblages from sediments. The reason is that such treatments destroy many protoperidinioid cysts, notably the brown-walled taxa (e.g. Dale, 1976; Turon, 1984; Schrank, 1988; Marret, 1993; Hopkins and McCarthy, 2002 and pers. obs.). However, base hydrolysis in methanol fails to degrade these protoperidinioid cysts (per obs). This may suggest that the protoperidinioid wall consists of highly polar building blocks. Most gonyaulacoid cysts (including *Lingulodinium*) resist acetolysis and base treatment in methanol or water suggesting that the building blocks of the gonyaulacoid macromolecule are more firmly connected than those in protoperidinioid macromolecules. Interestingly, in the sediments, the resistance of cysts to oxidation parallels their resistance to chemical treatment in the laboratory (Zonneveld et al., 1997, 2001; Versteegh and Zonneveld, 2002).

On the basis of the above, may be concluded that information on the chemistry of dinoflagellate cyst walls is very limited. The fragmentary information present suggests that the walls are unlike the algaenan walls of other algae and do not include an isoprenoid building block. A major problem in achieving more information is that many organic-cyst forming dinoflagellates are notoriously difficult to culture and that inducing cyst formation in culture in sufficient quantities is technically challenging.

## 2.5.4. Fossil dinoflagellates

Whereas the presence of cell contents hampers the isolation and analysis of cell walls of living algae, this problem is absent for analysis of fossil

palynomorphs. However, three other difficulties complicate the evaluation of fossil algal walls. First, isolating pure, monotypic assemblages is difficult. Second, recent counterparts may be absent, as is the case for the Acritarcha. Third, original biomacromolecules may be transformed into a "geomacromolecules", even to such extent that the original biomacromolecular fingerprint is totally lost, whereas the morphological preservation of the palynomorph remains excellent.

Despite these difficulties, several attempts have been made to obtain pure dinoflagellate cyst fractions from sediments, starting in the early 70s (Combaz, 1971). In a few cases, high purity was obtained. Pyrolysis of a monotypical assemblage with 96% of the Gonyaulacoid *Chiropteridium* displays a predominantly aliphatic macromolecule with a clear aromatic signature but without isoprenoids. The pyrolysate resembles that of *S. ramonii* but the aliphatic fragments continue to much longer chain lengths ($C_{30}$ compared to $C_{18}$ for *S. ramonii*). Furthermore, the fatty acids are absent. Analyses on other fossil dinoflagellates also demonstrate signatures varying from almost entirely aliphatic to almost entirely aromatic (de Leeuw et al., 2006). We have to consider these signatures in the light of *post mortem* chemical transformation of the biomacromolecules. This process of transformation is best illustrated on chitin, which is a relatively labile biomacromolecule. Chitin could hitherto not be evidenced, in arthropod fossils older than 25 Ma, even if these fossils were morphologically excellently preserved (Stankiewicz et al., 1997b; Flannery et al., 2001). Linear carbon chains appear to invade and/or replace originally non-aliphatic biomacromolecules such as chitin (Baas et al., 1995; Briggs et al., 1995; Stankiewicz et al., 1997a; Stankiewicz et al., 1998; Stankiewicz et al., 2000) and sporopollenin (van Bergen et al., 1993; Yule et al., 2000; Boom, 2004; de Leeuw et al., 2006) The invading lipids are likely to be derived directly from the source organism (Gupta et al., 2007). This process may occur already during early diagenesis e.g. under influence of reactive sulphur species (sulphurisation), oxygen or other oxidants (oxidative polymerisation) or light. Oxidative polymerisation is held responsible for the formation of the Paleocene dinocasts from Pakistan (Versteegh et al., 2004). These spongy microfossils are

considered to result from exceptionally complete polymerisation of the cell contents of thecate dinoflagellates, which morphologically resulted in the preservation of cingulum and sulcal structures.

Thus the suggestion may be questioned that the very close morphological *and* chemical correspondence between fossil algae and their living counterparts, e.g. for *Tetrahedron minimum* (Goth et al., 1988) also implies that algaenans can survive relatively unchanged in sediments for millions of years.

Another process modifying organic matter is early sulphurisation. Dysoxic to suboxic bottom waters are usually rich in, hydrogen sulphides and molecular sulphur. These sulphur species readily attack functionalised groups, such as double bonds in organic matter (Vairavamurthy and Mopper, 1987; LaLonde et al., 1987; Sinninghe Damsté et al., 1989; Schouten et al., 1994a; Schouten et al., 1994b; de Graaf et al., 1995) and may cause its condensation (Sinninghe Damsté et al., 1989; Schouten et al., 1994a; Gelin et al., 1998; van Dongen, 2003). This process has been suggested to have modified the macromolecular structure of *Thalassiphora pelagica* from the Oligocene Rhine Graben (Versteegh et al., 2007). After carefully picking and cleaning the cysts they appear to be rich in alkylated benzothiophenes upon pyrolysis. These compounds could result from sulphurisation of the original cyst wall biomacromolecule. Alternatively, the poly unsaturated fatty-acid-rich dinoflagellates provide a direct source of aliphatic lipids that could become sulphur bound to the cyst walls during early diagenesis, analogous to the incorporation *Nannochloropsis*-derived long-chain lipids to its fossilisable wall (Gelin et al., 1998). The sulphurisation may also have stabilised the cyst walls by reducing sites on the molecule suitable for microbial attack, and further cross-linking the macromolecule (Moers et al., 1988). We have to consider that in general the chemical transformation from a biomacromolecule to a geomacromolecule doesn't necessarily mimic biosynthesis and as such is likely to reduce the accessibility of the macromolecules for enzymatic breakdown. This is important for studies on the degradability of cysts in ancient sediments (Dodsworth, 1995) since the differences in degradability as assessed for recent cyst taxa may not be valid anymore.

Considering this *post-mortem* polymerisation and sulphurisation of organic matter, the biomacromolecular nature of palynomorphs in rocks older than 30 Ma still remains to be demonstrated.

**2.5.5. Some final remarks on cyst wall chemistry**

It is clear that the analysis of recent and fossil resistant biomacromolecules requires extreme care especially with respect to the purification procedures and maturation. For the extant material, avoiding artificial condensation and oxidative polymerisation of cytoplasm and ester-bound moieties requires constant attention. Notably, condensation reactions may cause addition of aliphatic moieties e.g. by oxidative polymerisation. For the fossil material, contamination by organic particles other than the target taxon is hard to eliminate and can contribute to either an aliphatic or aromatic signal. Furthermore, *post-mortem* migration of aliphatic moieties into, and their condensation onto the macromolecule may occur, sulphurisation may play an important facilitating these processes.

**2.6. Application**

**2.6.1. Correcting for species selective diagenesis to a better-constrained reconstruction of upper water conditions.**

Fossil dinoflagellate cyst assemblages are often used to reconstruct the properties of the upper water column. Different laboratory treatments and organic-geochemical studies suggest that the molecular composition of several extinct species differs from modern species. These differences may arise from evolution in cyst-wall biochemistry. In this case we still can assess the resistance to degradation for these extinct species by means of laboratory or field experiments. However, if the differences in wall composition arise from *post-mortem* modification of the cyst wall chemistry, assessment of the resistance of fossil cysts by means of laboratory or field experiments is of limited value. Resistance to degradation may have been different prior to the fossilisation process. Therefore, the present-day results cannot be transferred directly to pre-Quaternary records.

Nevertheless, the overview given in this paper clearly indicates that the possibility of post depositional diagenetic altering of the primary signal must be taken into account by interpreting Late Quaternary dinoflagellate assemblages. It has become clear that species that strongly resist aerobic degradation are generally phototrophic/mixotrophic gonyaulacoids whereas the majority of the vulnerable species are peridinioid. This implicates that ratios like the P/G (peridinioid/gonyaulacoid) or A/H (autotrophic/heterotrophic), often used to reconstruct variations in past export production have to be used with extreme care. This is very important when bottom water oxygen concentrations varied during the time interval studied. Only in case of extremely good preservation, hence when aerobic degradation has been minimal, the complete dinoflagellate cyst assemblage can be used and the above mentioned ratios reflect export production rates, e.g. when bottom waters have been anoxic throughout the studied time interval or when high sedimentation rates reduced the oxygen exposure time to a minimum (see e.g. Reichart and Brinkhuis, 2003).

At sites where minimal aerobic degradation takes place, such as for instance oxygen minimum zones, accumulation rates of both gonyaulacoid and peridinoid cysts increase in relation to increasing nutrient concentrations in upper waters. "Sensitive cyst" concentrations increase in higher amounts than "resistant cysts" resulting in an increasing P/G ratio (Zonneveld et al., 2007). However, the few detailed studies that are based on well-dated sites suggest that the increase in accumulation rates of both groups is a linear relationship whereas aerobic degradation has a logarithmic effect emphasising "risk" of fossil assemblages being "overprinted" by selective degradation. This does not automatically result in the fact that the initial signal is completely overprinted by selective preservation processes. For example, Mudie (1992) observed that a latitudinal shift in G/P ratio in modern sediments reflects a shift in G/P ratio in plankton data. The fact that selective preservation might have altered the initial signal has to be considered and attempts have to be carried out to estimate the possible rate of "overprint".

The easiest way to account for selective degradation of dinoflagellate cysts (to obtain unbiased environmental reconstructions) is to take into account only

those cyst species that resist degradation. However, this method has its limitations since it removes the environmental information that can be extracted from the "sensitive" cyst association. In areas where gonyaulacoid cysts are practically absent, such as the regions north and south of the Arctic Fronts, other correction methods have to be developed.

A relatively simple method to correct for early diagenetic overprint in these frontal regions has been suggested by Esper and Zonneveld (2007). By using a modern analogue technique (MAT) to reconstruct the paleoceanography of the Late Quaternary Southern Ocean (Atlantic Sector), a strong discrepancy was found for some intervals between the dinoflagellate-based summer SST reconstructions and such reconstructions based on diatoms, radiolarians and stable isotopes derived from foraminifera. The dinoflagellate-based SSTs appeared to be extremely high in these intervals. By using the selective degradation index (kt-index), those intervals that might have been overprinted by selective degradation could be determined. By excluding these samples from the MAT analysis, the dinoflagellate-based SST reconstruction corresponds well with the other temperature proxies.

The selective degradation index can be calculated by assuming that the initial rate of production of species classified as resistant and those classified as sensitive is related. Recent studies on well-dated surface sediments show that accumulation rates (AR) of the group of resistant cysts increases with increasing chlorophyll-a concentrations in surface waters (Fig. 2.9; Zonneveld et al., 2007). For shelf sediments where oxygen concentrations are low, the same can be observed for the group of sensitive cysts (Holzwarth et al., 2007). Empirical studies based on material from the surface samples of the OMZ's of the Arabian Sea and the Namibian shelf (SW Atlantic Ocean) as well as Western Arabian Sea sediment traps indicate that this relationship is constant in different regions and settings according to the relationship: AR S-cysts = 68 x AR R-cyst. Based on this relationship, initial concentrations of S-cysts can be calculated by multiplying the AR of R-cysts by 68. The "kt-index" can be calculated according to the first order degradation function: $kt=\ln (X_i/X_f)$ with

$X_f$=final cyst concentration (cysts/cm$^2$/ky) and $X_i$=initial cyst concentration (cysts/cm$^2$/ky).
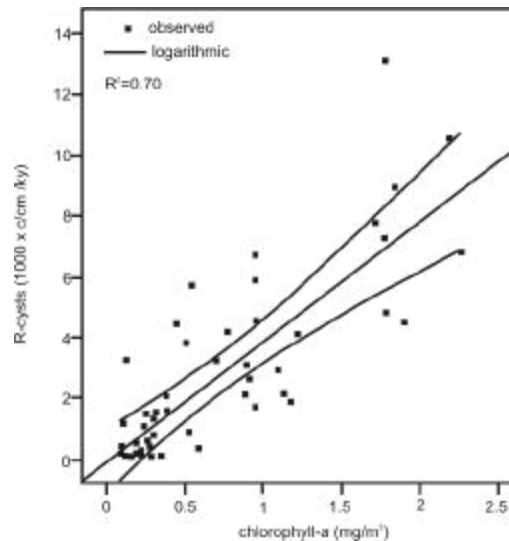


*Figure 2.9. Relationship between accumulation rates of R-cysts and mean annual upper water chlorophyll-a concentrations. Estimated linear relationship with 99.9% confidence limits of mean. Redrawn from Zonneveld et al. (2007).*

## 2.6.2. The use of species selective degradation to recognise differential preservation-states in the past

There are only few examples where selective preservation of organic-walled dinoflagellate cysts has been used in pre-Quaternary palaeoceanographic studies. One study focuses on the Late Pliocene to Early Pleistocene sediments of northwest North Pacific Ocean ODP Site 1179. Here, intervals occur that are characterised by high calcium carbonate contents although the site is more than 1km below the modern calcium compensation depth (McCarthy et al., 2004). Within these intervals high concentrations of *Brigantedinium* cysts are present whereas the intervals without calcium carbonate contain mainly Gonyaulacoid cysts. Considering the different preservation potentials of the dinoflagellate cyst groups and by comparing the foraminifera, pollen, spore, dinoflagellate cyst and dust contents, McCarthy at al. (2004) concluded that this interesting phenomenon results from rapid burial of the calcareous and organic microfossils probably caused by an increased flux of land-derived nutrients, enhancing the sea-surface productivity. The authors suggest that the

associated increase in trace metals triggered algal blooms of e.g. gonyaulacoid dinoflagellates and grazers like the planktic foraminifera and peridinioid dinoflagellates. The enhanced bioproduction in upper waters combined with an increased eolian dust input might have accelerated the sinking of particles resulting in extremely good preservation of microfossils.

## 2.6.3. Dinoflagellate cysts as bottom water oxygen concentration indicators

By grouping cysts with different ecologies, those environmental factors that influence the cyst production, transport and preservation of all species in the group in a similar way, have a strong relationship with the total cyst accumulation of that group. On the contrary, a damped effect occurs for factors that influence only part of the species within the group, or influence individual species of the group in different ways. Recently it has been shown that the degradation rate, "kt" of the group of dinoflagellate cysts classified as "extremely sensitive" shows an S-shape curve in relationship to bottom-water oxygen concentration according to the equation $O_2=5.17/1+e^{-1.23(kt-2.058)}$; $r^2=0.85$ (Fig. 2.10; Zonneveld et al., 2007). This suggests degradation of dinoflagellate cysts by aerobic bacteria with the bottom water oxygen concentration being a limiting factor for bacterial growth (Jorge and Livingston, 1999; Guerra-Garcia and García-Gómez, 2005). Upon anoxia, degradation is absent. When oxygen concentrations increase, the amount of degrading bacteria can increase resulting in higher degradation rates. At a certain point, all S-cysts are being consumed and the kt value will increase to 8. Therefore, the above mentioned relationship can form the basis for establishing quantitative estimates of past deep-ocean oxygen concentrations. Such estimates have been quite problematic when calculated from other proxies such as those based on sediment structure, the (bio-) chemical content of sediments and the chemical and isotopic composition of microfossils or on numerical models (e.g. Francois et al., 1997; Toggweiler, 1999; Ninnemann and Charles, 2002; Matear and Hirst, 2003; McManus et al., 2004; Ivanochko and Pedersen, 2004).
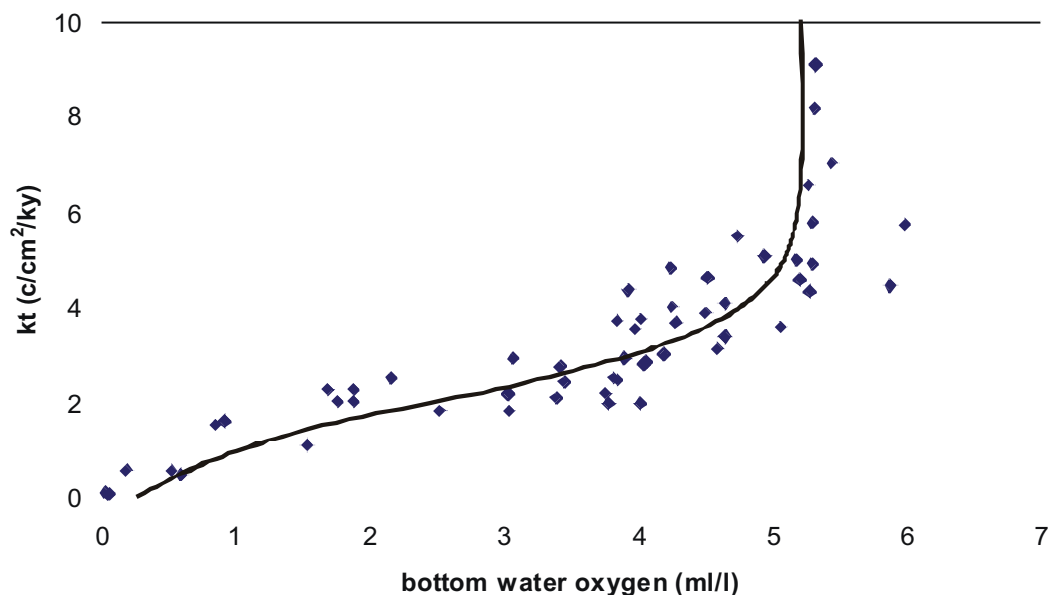
*Figure 2.10. Relationship between the degradation expressed of S-cysts by kt and bottom water $O_2$. Redrawn from Zonneveld et al. (2007).*

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**CHAPTER 3**

**A natural exposure experiment on short-term species-selective aerobic degradation of dinoflagellate**

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**Abstract**

Although studies have shown that organic-walled dinoflagellate cysts can undergo species-selective aerobic degradation, the alteration rate of this process is not known. Here we provide data on the decay rates of individual cyst species from a degradation experiment in which sediment samples from (a) anoxic Namibian shelf and (b) anoxic part of the eastern Mediterranean S1 sapropel have been exposed to oxic and anoxic conditions in natural environments. The two types of sediment were stored in bags composed of a dialyse membrane that allows oxygen penetration but prevents bacterial exchange. Sediment bags were placed in open containers connected to sediment traps and moored for 15 months in anoxic brines and oxic intermediate waters of the Urania and Bannock Basins areas. Within the short experimental time (15 months), exposure to oxygenated waters resulted in a 30% to 50% reduction in concentration of cysts attributable to *Brigantedinium* spp. and *Echinidinium granulatum.* Other species or species groups such as *Spiniferites* spp., *Lingulodinium machaerophorum* and *Echinidinium* spp. appear

to be less sensitive. A slight increase in cyst concentration is observed for *Nematosphaeropsis labyrinthus*, *Echinidinium aculeatum*, *Operculodinium israelianum*, and *Impagidinium aculeatum*, indicating that these cyst species are more resistant to early aerobic diagenesis. Exposure to anoxic conditions has not lead to detectable differences between initial and exposed composition and concentration.

Our study is the first to document that species-selective degradation of dinocysts in oxygenated natural environments is a rapid process that changes considerably dinocyst concentrations and assemblages.

Keywords: dinoflagellate cysts, organic matter, oxygen, taphonomy

## 3.1. Introduction

Fossil organic-walled dinoflagellate cyst (dinocyst) assemblages are increasingly used in palaeoclimatic research and the methods to establish such reconstructions have improved considerably during the last decades (e.g. Peyron and de Vernal, 2001; de Vernal et al., 2005). However, for an accurate interpretation of the fossil signal it is essential to know the processes that might have influenced the fossilisation process. Although species-selective degradation of dinocysts as a result of oxidation during laboratory samples preparation is well known since the mid 1970's (e.g. Dale 1976; Reid, 1977; Harland, 1983; Schrank, 1988; Marret, 1993; Louwye et al., 2004; Mudie and McCarthy, 2006) it was generally belived that (early) diagenesis would not alter significantly dinocyst associations in natural environments since the concentrations of oxidants in nature are much lower. However, a decade ago it was discovered that in natural environments, early diagenesis could also be species-selective (Zonneveld et al., 1997, 2001). Although some modern dinocyst species appeared to be more resistant to aerobic degradation than the other organic components measured so far, some species appeared to be among the most labile organic components (Versteegh and Zonneveld, 2002). Several studies have confirmed these observations and documented species selective aerobic degradation under wide range of natural environments (e.g.

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Reichart and Brinkhuis, 2003; McCarthy et al., 2004; Bockelmann et al., 2007; Zonneveld et al., 2007). Laboratory experiments indicated that the oxidation of certain dinocyst species might be a rapid process. Hopkins and McCarthy (2002) showed that only 30 minutes treatment with $H_2O_2$ (15%) is enough to destroy the majority of *Brigantidinium* cysts as well as other cysts formed by *Protoperidinium* species. De Schepper et al. (2004) documented oxidation for 15 seconds with fuming nitric acid followed by a washing with KOH to damage severely Pliocene cyst species *Barssidinium pliocenicum*. However, the concentrations of the oxidative agents used in laboratory experiments are much higher than in the natural environment and until now there is no information on the speed of aerobic degradation of dinocyst species in nature.

We have exposed sediment collected from two different anoxic locations to different oxygen concentrations in a natural environment for 15 months. The Bannock and Urania Basin of the Eastern Mediterranean area (Fig. 3.1) with their oxygenated intermediate and surface waters and underlying anoxic brines served as an ideal natural laboratory. By comparing the dinocyst content of the exposed material with that of the original sediment, information can be obtained about the degradation rates of individual species.

### 3.2. Materials and methods

To test the effect of oxygen on dinocyst preservation, two types of sediment have been collected from:

(a) Namibian mud-belt. The Namibian mud-belt region is located close to one of the most active upwelling cells of the world. High primary production in the surface waters and reduced ventilation of the shelf bottom waters result in an oxygen minimum zone with anoxic bottom/pore water conditions that existed throughout the Holocene (e.g. Chapman and Shannon, 1985; Mollenhauer et al., 2004; Holzwarth et al., 2007). We homogenised the upper 30 cm of sediment of Holocene age collected with a multicorer at sites 200 (22°51' S – 14°28' E, depth 28.9 m), 201 (22°46' S – 14°28' E, depth 36.5 m) and 202 (22°38' S – 14°18' E, depth 72.2 m) during the *R.V. Meteor*

cruise M57-3 (Zabel et al., 2005). Minimal alteration by early diagenetic processes was assumed.

(b) bulk eastern Mediterranean S1 sapropel sediment. Eastern Mediterranean sapropels are assumed to be deposited during increased productivity in surface waters and/or enhanced preservation due to oxygen depletion in the bottom waters and hence their $C_{org}$ content is >2 wt% (e.g. de Lange et al., 1989; Calvert et al., 1992; van Santvoort et al., 1996). Major mineral phases in the S1 sapropels are calcite, clay minerals, and quartz with clay minerals assemblage consisting of smectites, illite, chlorite and kaolinite (Martínez-Ruiz et al., 2003). The S1 sapropel is of early Holocene age (Thomson et al., 1999). We homogenised sediments from the reduced parts of the S1 sapropel of several cores in the eastern Mediterranean and assumed that minimal aerobic degradation had taken place.

Each sediment type was divided into five sub-samples. 20 ml of each sub-sample was transferred to sample dialysis bags, which have a membrane that allows oxygen penetration but prevents bacterial exchange. Four sub-samples were placed in open containers that were connected to sediment traps; the fifth sub-sample was dried and stored until further analysis. Sediment traps were moored for 15 months (June 2003 - September 2004) at two sites: the Urania (UB; 35°13'N, 21°30'E) and Bannock (BB; 34°18'N, 20°01'E) Basin areas, in anoxic brines and overlying oxic intermediate waters, approximately 500 m above the brines (Fig. 3.1). A sharp interface between oxic seawater and anoxic brine waters lies at 3276 m and 3493 m depth in the Bannock and Urania Basin respectively (de Lange et al., 1990a; Medriff Consortium, 1995). Oxygen concentration in the oxygenated part of the water column is approximately 200 µM in the Bannock and Urania Basin areas (Hydes et al., 1988; Bregant et al., 1990; de Lange et al., 1990a). Brine waters are characterised not only by a total absence of oxygen but also by the relatively enhanced salinity, sulphide and methane concentrations (de Lange et al., 1990b; Boldrin and Rabitti, 1990; Luther et al., 1990; Karisiddaiah 2000). Howell and Thunell (1992) showed that more organic carbon is preserved in the surface sediments of the anoxic areas of Bannock Basin than in the zone adjacent to the brines. They determined

organic carbon preservation factors of 2.5% and 0.2% for the anoxic and oxygenated areas respectively.
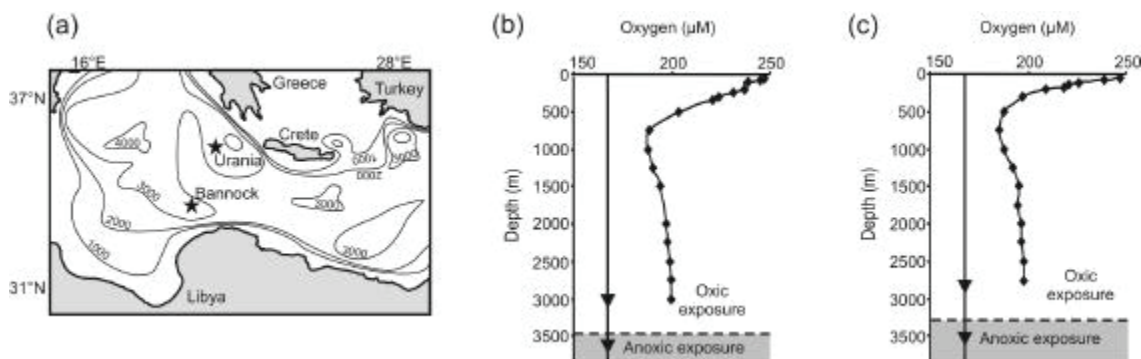


*Figure 3.1. (a) Location of the Urania and Bannock basins areas in Eastern Mediterranean, (b) oxygen concentrations in areas of Urania Basin and (b) Bannock Basin with indicated position of sediment traps. Oxygen concentration data were collected during R/V Pelagia cruise PASSAP 2000. Dashed lines represent oxic seawater-anoxic brine interface depth (after de Lange et al., 1990a; Medriff Consortium, 1995).*

Retrieved sub-samples and the original material were randomly numbered by one of the authors (K. Z.) before laboratory treatment. After recoding, the material was dried, weighted, treated with cold HCl 10% and HF 38% and sieved through a 20 µm precision sieve (Stork Veco, mesh 508). The sample residues were centrifuged (8 min, 3500 rpm) and concentrated to 1.0 ml. Fifty µL of homogenised sample was embedded into glycerine jelly and insulated from the air by paraffin wax. All slides were analysed for dinocysts by one of us (M. K-N.). If possible up to 200 specimens were counted. The errors and accuracy of this method are given in de Vernal et al. (1987). To avoid "biased results" the counting was accomplished blind.

Dinocysts concentrations were calculated by dividing the cysts counted by the dry weight analysed. Confidence intervals were calculated according to the method of Howarth (1998). The significance of observed composition changes in relation to the initial association has been calculated using chi-square ($?^2$)

tests. The counts, confidence intervals and results of ?²-test are presented in Appendices 3.1-3.3.

The oxygen measurements were made by routine triplicate Winkler titration during the PASSAP 2000 cruise with *RV Pelagia*.

## 3.3. Results

There were no major changes in dinocyst concentrations compared to the original material for both the Namibian and sapropel sub-samples when exposed to anoxic conditions. The ?²-tests show that the differences between anoxic and original associations are not significant at the 99.5% confidence intervals with 6 and 5 degree of freedom (d. f.).

The Namibian and sapropelic sub-samples exposed to oxic conditions showed significant decreases in the total concentration of dinocysts at the 99.5% confidence interval (6 and 5 d.f.). Subtle differences occurred between the different samples as summarized below.

### 3.3.1. Namibian sub-samples oxic exposure

The Namibian sub-samples exposed to oxygenated waters are characterised by a decrease in concentration of *Brigantedinium* spp. from 96000 cysts per 1 gram of dry sediment (from hereon referred to as c/g) to 63000 c/g and 74000 c/g in UB and BB basin area respectively, whereas concentrations of *Echinidinium granulatum* change from 13000 c/g to 6500 c/g and 7000 c/g in the UB and the BB respectively. *Echinidinium* cysts that could not be identified on a species-level were grouped into *Echinidinium* spp. Their concentrations decrease from 18000 c/g to 17000 c/g in UB and to 16000 c/g in the BB. The concentration of *Operculodinium israelianum* and *Echinidinium aculeatum* increase from 5000 c/g to 8600 c/g and 14500 c/g to 17000 c/g, respectively in the BB but remain relatively unchanged in the UB. Concentrations of *Nematosphaeropsis labyrinthus* increase from 5000 c/g to 7000 c/g and 9000 c/g in the UB and the BB respectively (Fig. 3.2).
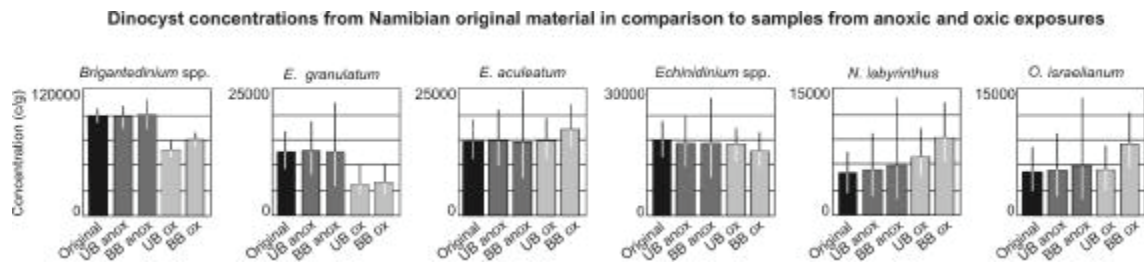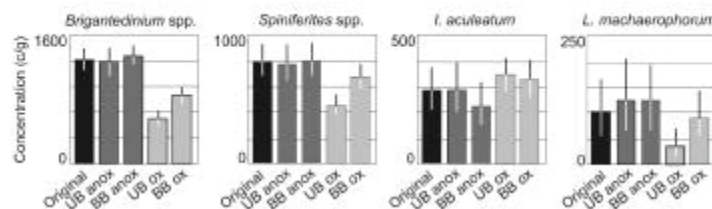
Figure 3.2. Absolute abundances with indicated 95% confidence intervals for selected dinocyst species in: Namibian original sample, Namibian samples from anoxic exposure at the UB and BB, Namibian samples from oxic exposure at the UB and BB.
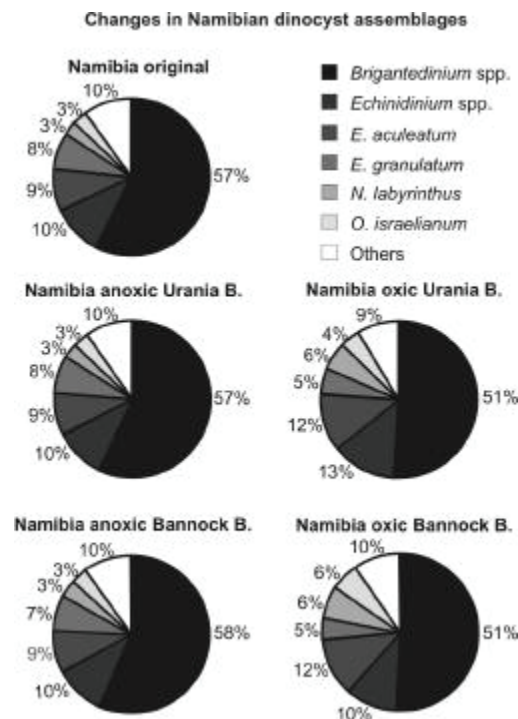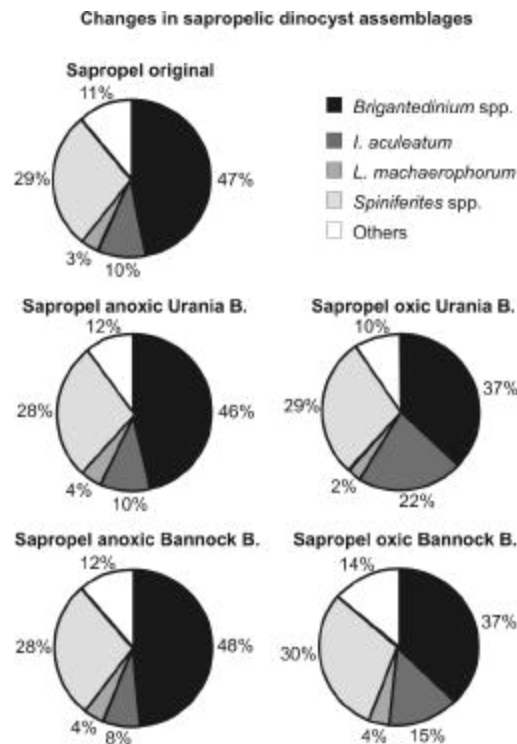


Figure 3.3. Relative abundances of dinocyst species in Namibian samples under oxic and anoxic conditions at the UB and BB.

The changes in the concentration also result in shifts of the relative abundances of species. Percentages of *Brigantedinium* spp. and *E. granulatum* decrease by about 12% and 35% from 57% to 51% (*Brigantidinium*) and 8% to 5% (*E. granulatum*). Relative abundances of *Echinidinium* spp. increase from 10% to 13 % in the UB but do not change in the area of BB. Percentages of *O.*

*israelianum* increase by only 1/3rd in the UB but double from 3% to 6% in the BB. Proportions of *N. labyrinthus* double from 3% to 6% whereas proportions of *E. aculeatum* increase by 1/3rd from 9% to 12% in the UB and the BB (Fig. 3.3).

### 3.3.2. Sapropel S1 sub-samples oxic exposure

Sapropelic sub-samples exposed to oxygen-rich conditions are characterised by a decrease in concentrations of *Brigantedinium* spp. from 1300 c/g to 600 c/g and 800 c/g in the UB and the BB respectively. Concentrations of *Spiniferites* spp. are reduced from 800 c/g to 450 c/g and 700 c/g in UB and the BB respectively. Concentrations of *Lingulodinium machaerophorum* decrease from 100 c/g to 40 c/g and 90 c/g in the UB and the BB respectively. Concentrations of *Impagidinium aculeatum* increase from 280 c/g to 350 c/g and 330 c/g in UB and the BB respectively (Fig. 3.4). A remarkable change in assemblage can be observed. Relative abundances of *Brigantedinium* spp. decrease by about 1/4th from 47% to 37%, whereas relative abundances of *I. aculeatum* almost double to make up about 1/5th of the total association (Fig. 3.5).



*Figure 3.4. Absolute abundances with indicated 95% confidence intervals for selected dinocyst species in: sapropelic original sample, sapropelic samples from anoxic exposure at the UB and BB, sapropelic samples from oxic exposure at the UB and BB.*

*Figure. 3.5. Relative abundances of dinocyst species in sapropelic samples under oxic and anoxic conditions at the UB and BB.*

## 3.4. Discussion

The decrease in concentration of *Brigantedinium* spp., *E. granulatum* and to lesser extent *Echinidinium* spp., *L. machaerophorum* and *Spiniferites* spp. during exposure to oxygenated sea-waters and their consequent grouping as sensitive and moderately sensitive to oxic degradation respectively, meet our expectations based on dinocyst taphonomy (Zonneveld et al., 1997, 2001; Hopkins and McCarthy, 2002) and comparisons with earlier studies (e.g. Zonneveld and Brummer, 2000; Reichart and Brinkhuis, 2003, Bockelmann, 2007). Slight increases of *N. labyrinthus*, *O. israelianum*, *I. aculeatum* and *E. aculeatum* concentrations and their classification as resistant species are also largely predictable (Zonneveld et al., 1997, 2001) although increase of *E. aculeatum* concentrations was not documented in previous studies. An increase in resistant dinocysts per gram dry weight sediment results probably from rapid decomposition of other more reactive components (Fig. 3.8; Hedges and Prahl, 1993). Versteegh and Zonneveld (2002) show that the resistant species are

composed of one of the most resistant organic components in nature. Although investigation of other organic constituents falls outside the scope of our research, we assume that our samples contained many more reactive components other than dinocysts, since the study material originated from sites with limited early diagenesis and hence an unaltered original OM composition.
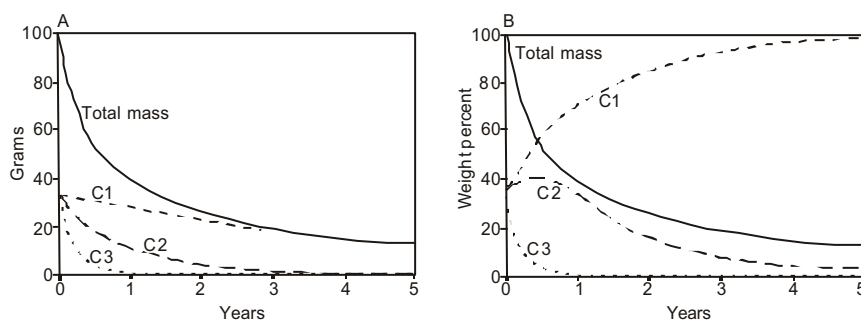


*Figure 3.6. Components degradation vs. time: a) initial mass and b) weight percentages of specific components; C1, C2, and C3 represent resistant, moderately degradable and sensitive components (after Hedges and Prahl, 1993).*

Similar results concerning preservation of specific dinocyst taxa were previously reported for the Madeira Abyssal Plain, Eastern Mediterranean S1 sapropel, modern and Late Quaternary eastern Arabian Sea, Atlantic sector of the Southern Ocean and modern Namibian shelf, where distinct sediment intervals had experienced paleo-oxidation (Zonneveld et al., 1997, 2001; Zonneveld and Brummer, 2000; Reichart and Brinkhuis, 2003; Bockelmann et al., 2007; Esper and Zonneveld, 2007). The dinocyst assemblage of the unoxidised part of the Madeira Abyssal Plain turbidite was reported to be dominated by *Protoperidinium* cysts (e.g. *Brigantedinium* spp.), whereas the oxidised part from the same turbidite was dominated by *I. aculeatum*, *N. labyrinthus* and *Spiniferites* species (Zonneveld et al., 1997). The discrepancies between dinocyst associations obtained from sediment traps in the Arabian Sea and underlying surface sediments suggests that *Echinidinium* species and *Protoperidinium* cysts are degraded in oxygen-rich waters (Zonneveld and

Brummer, 2000). Comparable results were obtained for Mediterranean S1 sapropel which upper part was affected by aerobic degradation. Concentrations of *Protoperidinium* cysts and *Echinidinium* species dropped dramatically at the transition from unoxidised to oxidised sapropel intervals but no decrease was observed for *N. labyrinthus and Impagidinium* species (Zonneveld et al., 2001). These studies suggested that all *Echinidinium* species are extremely sensitive to aerobic degradation (Zonneveld et al., 1997, 2001), however, low cyst counts in these studies resulted in the grouping of all *Echinidinium* species into one group thus preventing the documentation of individual species. Here we show that *E. granulatum* is more sensitive than *Echinidinium* spp., whereas *E. aculeatum* is more resistant. Our results suggest that within one morphogenus several species behave differently with respect to aerobic degradation. At present the cyst-theca relationships of *Echinidinium* species are not known, therefore it is unclear if the individual morpho-species within this genus are biologically related. More studies about the cyst-theca relationships of dinoflagellates, genetical studies and organic-geochemical studies of species level are required to explain the possible causes of species selective preservation.

Reichart and Brinkhuis (2003) reported accumulation rates of *Protoperidinium* species from a central Arabian Sea sediment core to be 10 times higher when the site was inside Oxygen Minimum Zone in comparison to an interval deposited under oxic conditions. Plotted abundances of *Protoperidinium* species against bottom water oxygen concentrations showed a rapid decrease in relative *Protoperidinium* abundances when oxygen concentrations were above 2.5 ml/L (Fig. 7 in Reichart and Brinkhuis, 2003). At lower oxygen levels the abundances remain relatively constant. McCarthy et al. (2004) interpreted low palynomorph concentrations (especially protoperidiniacean dinocysts) in sediments from North Pacific as a result of, among others, oxidising activity of bottom currents. These samples were dominated by gonyaulacean cysts, mostly *Impagidinium* and *Spiniferites*. The authors hypothesised that good preservation of the protoperidiniacean

dinocysts in other samples was caused by relatively faster OM sedimentation and burial.

Laboratory experiments and standard acetolysis procedures have also indicated the relative sensitivity of *Brigantedinium* spp. to oxidation (Marret, 1993; Hopkins and McCarthy, 2002; Mudie and McCarthy, 2006). After an hour of treatment with hydrogen peroxide Brigantedinium spp. were completely dissolved as result of oxidation, whereas *O. centrocarpum* and *Spiniferites* spp. appeared to be more resistant (Hopkins and McCarthy, 2002). In another study absolute counts of *Brigantedinium* spp. decreased roughly 12 times when treated with acetolysis in comparison to the same sample processed with HF only (Mudie and McCarthy, 2006). Loss, disintegration and bleaching of peridiniacean cysts resulting from oxidation during palynological preparations were identified by several researchers (Reid, 1977; Harland, 1983; Schrank, 1988; De Schepper et al., 2004; Louwye et al., 2004).

Furthermore, Persson and Rosenberg (2003) documented that "brown-cysts", mainly *Protoperidinium* and *Dipsopsalis*-like species, were preferentially grazed by deposit feeders in a laboratory experiment in comparison to for example *L. machaerophorum*, *Spiniferites* spp. or *Penthapharsodinium dalei*.

Our study shows more complete recovery of dinocyst assemblage after exposure of material to anoxic brines and is in line with earlier studies that report better dinocyst recovery from sediments deposited under anoxic conditions (Zonneveld et al., 1997, 2001; Reichart and Brinkhuis, 2003).

During our experiment samples were stored in dialysis membrane that can be penetrated by $O_2$ but not by bacteria. Observed changes in dinocyst associations suggest that the degradation of dinocysts might be a purely chemical reaction. However, the original material was not autoclaved previous to exposure, and therefore, may not have been free of living bacteria. Recently, Zonneveld et al. (2007) suggested that the degradation of organic-walled dinocysts was limited by aerobic bacterial growth and showed that oxygen concentration is an important factor affecting dinocyst degradation. Dinocysts are one of the significant constituents of marine organic matter (OM) and, therefore, their species-selective decomposition is based on the same premises

as degradation of the entire OM. OM degradation in marine sediments is thought to be a first order process dependent on OM concentration and the exposure time to oxygen (Middelburg, 1989; Hedges and Prahl, 1993; Canfield, 1994; Hartnett et al., 1998; Sun et al., 2002; Keil et al., 2004). However, Rabouille and Gaillard (1991) and Arthur et al. (1998) included oxygen concentration as another boundary condition for OM degradation. Oxic conditions seem to trigger OM decomposition but the process need not involve molecular oxygen as a causative electron acceptor (Hedges et al., 1999). It is often assumed that large part of OM degradation is bacterially mediated (Colley et al., 1984) with bacteria gaining their energy from the oxidation of organic carbon (Canfield, 1994).

From above comparisons it can be concluded that species-selective degradation of dinocysts is already well documented, however, most of the studies report on the qualitative aspect of the phenomenon. Our experiment is the first to provide quantitative estimates on dinocyst degradation rates in the natural environment. The experiment mimics natural conditions while the dialysis membranes around the samples prevent any influence of transport, primary productivity or grazing on samples composition. Oxygen is the only influencing factor, thus allowing unequivocal interpretation of the observed changes as a result of aerobic degradation. The 15-month exposure to oxic waters severely altered the dinocyst association showing a reduction of sensitive dinocyst concentrations by 24-57%. These results imply that selective degradation is a rapid process and needs to be acknowledged in the interpretation of fossil and (sub) recent dinocyst records. For example, an initial dinocyst-based reconstruction of palaeotemperatures in the Southern Ocean gave extremely high, unrealistic results, however, when corrected for selective dinocyst degradation SSTs appeared comparable to reconstructions based on other proxies (Esper and Zonneveld, 2007).

Our results imply also that degradation is likely to overprint signals from other processes as dinocysts are formed and become part of the export production and transported from the shelf into the deep sea. Shelf sediments are generally dominated by *Brigantedinium* and/or *Echinidinium* species (e.g.

Marret and de Vernal, 1997; Marret and Zonneveld, 2003; Holzwarth et al., 2007). Often shelf sediments are deposited under low oxygen concentrations in bottom or pore waters (e.g. Chapman and Bailey, 1991). If these sediments are then transported from the shelf to the deeper oceanic areas by, for example slumping processes, debris flows, winnowing or dispersal in nepheloid layers (for overview see Inthorn et al., 2006), they may be exposed to well-oxygenated waters and may alter rapidly, with their characteristic "shelf" signal being lost and rapidly "overprinted" by diagenetic processes.

### 3.5. Conclusions

Results of our natural experiment clearly show that the dinocyst assemblage changed significantly during a 15-month exposure to oxic seawater. Concentrations of sensitive dinocyst are reduced by up to 57%, whereas no significant changes were observed after exposure to anoxic conditions.

Most studies on dinocysts degradation in the natural environment are based on comparison between oxidised and unoxidised parts of the same sediment core usually spanning several thousands of years. Our study investigates for the first time the degradation of dinocysts assemblages with a known initial composition under known redox conditions in the natural environment during a short period of time. The experiment excludes the influence of primary productivity, transport processes and grazing on the assemblages and allows testing the effect of oxygen as determining factor. It implies that early diagenesis takes place rapidly under aerobic conditions and thus cannot be neglected on any time scale.

Our results also caution against a simplified use of fossil dinocyst assemblages to represent the production of dinoflagellates in the upper water column.

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# CHAPTER 4

## Organic-walled dinoflagellate cyst decomposition in the Southern Ocean sediments: implications for aerobic organic carbon degradation

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## Abstract

Organic carbon (OC) burial is an important process influencing the atmospheric $CO_2$ concentration and global climate change therefore it is essential to obtain information on the factors determining its preservation. The Southern Ocean is believed to play an important role in sequestering $CO_2$ from the atmosphere via burial of OC. Here we investigate the degradation of organic-walled dinoflagellate cysts (dinocyst) in two short cores from the Southern Ocean to obtain information on the factors influencing OC preservation. On the base of a calculated degradation index kt, we conclude that both cores are affected by species-selective aerobic degradation of dinocysts. Further we calculate a degradation constant *k* using oxygen exposure time derived from the ages of our cores. *k* displays a strong relationship with pore water $O_2$ suggesting that

decomposition of OC is dependent on the bottom and pore water $O_2$ concentrations.

Keywords: organic-walled dinofllagelate cysts, oxygen, organic carbon, degradation

## 4.1. Introduction

Southern Ocean is often believed to play an important role in modulating atmospheric $CO_2$ levels and hence in respect to global climate changes. Different reconstructions show that atmospheric $CO_2$ during last glacial period was reduced by ~80 ppm in comparison to preindustrial modern times (e.g. Siegenthaler and Wenk; Moore et al., 2000). However, the mechanism responsible for lowering $CO_2$ level is not yet well understood. For example one hypothesis assumes that sea-ice expansion caused permanent surface water stratification south of the Antarctic Polar Front and resulted in reduced vertical mixing and thus preventing the ventilation of $CO_2$-rich deep water and $CO_2$ release to the atmosphere (e.g. Francois et al., 1997; Sigman and Boyle, 2000). Another hypothesis links lower $CO_2$ level with carbon sequestration in marine sediments as a result of higher primary productivity caused by enhanced dust delivery to the Southern Ocean during the last glacial stage (e.g. Martin et al., 1990). However, high primary productivity alone does not influence carbon sequestration. It is the export production and more importantly the organic carbon (OC) burial in marine sediments that can remove carbon from the global carbon cycle at a longer time scale. Unfortunately only 0.1% of the produced OC is ultimately preserved whereas the major part is oxidised back to $CO_2$, $H_2O$ and nutrients (Hedges et al., 1997) and, thus introducing carbon back to the sea-water and the atmosphere therefore it is important to estimate both primary productivity and the degradation rates of OC as accurately as possible.

Recently a method to separate productivity from preservation and thus a way to quantify OC degradation was proposed based on the selective degradation of organic-walled dinoflagellate cysts (dinocysts) under oxic conditions (Versteegh and Zonneveld, 2002). According to the authors the

production of dinocyst sensitive to aerobic decay (S-cysts) is related to production of dinocyst resistant to oxic decomposition (R-cysts) and depends on the degradation constant $k$ and the oxygen exposure time (OET). Proposed method was successfully used to decouple preservation from productivity in southeastern Atlantic sediments over the past 145 ky, however, assumption of $k$ being constant makes the given method a rather qualitative approach (Versteegh and Zonneveld, 2002). Further work revealed that dinocyst degradation in the sediments is strongly related to $O_2$ concentrations in the bottom waters (Zonneveld et al., 2007). Dinocysts are significant contributors of OC in marine sediments hence their degradation is based on the same premises as entire OC pool decay. Rabouille and Gaillard (1991) and Arthur et al. (1998) hypothesised that $O_2$ concentrations may influence OC degradation. OC degradation in marine sediments is commonly considered a first order process dependent only on OC concentration and OET (Middelburg, 1989; Hedges and Prahl, 1993; Canfield, 1994; Hartnett et al., 1998; Sun et al., 2002; Keil et al., 2004).

Here we investigate two short cores from the Atlantic sector of the Southern Ocean to further explore if $O_2$ concentration is one of the factors influencing degradation of dinocysts and OC in general. To obtain this information we compare the calculated degradation constant $k$ with the pore water $O_2$ concentrations. Additionally we assess the applicability of the dinocysts as a proxy in areas characterised by variable primary production and $O_2$ profiles.

## 4.2. Regional setting

Atlantic sector of the Southern Ocean is characterised by the eastward flowing Antarctic Circumpolar Current (ACC) that is driven by strong westerly winds (Orsi et al., 1995). The ACC is bound to the north by the Subtropical Front (STF) that is positioned on average at 41°40'S (Lutjeharms and Valentine, 1984). At the STF, the northward flowing Subantarctic Surface Water (SASW) sinks beneath the much warmer and saltier Subtropical Surface Water (STSW) producing large temperature and salinity gradients (Orsi et al., 1995). Within the ACC three frontal systems can be distinguished: the Subantarctic Front (SAF),

the Antarctic Polar Front (APF) and the Southern ACC Front (SACCF; Fig. 4.1). The SAF is positioned at ~45°S and indicated by the rapid northward sinking of the salinity minimum associated with the Antarctic Intermediate Water (AAIW; Lutjeharms, 1985; Whitworth and Nowlin, 1987; Orsi et al., 1995). The Subantarctic Zone (SAZ) is located between the SAF and the APF which is indicated by large temperature gradient at mean position of ~50°S (Lutjeharms and Valentine, 1984). South of the APF, the Antarctic Polar Frontal Zone (APFZ) extends to the SACCF that is indicated by temperature gradient (Lutjeharms, 1985; Orsi et al., 1995). The Antarctic Surface Water (AASW) extends from the APF southwards. Below the AASW, the warm and saline eastward flowing Circumpolar Deep Water (CDW) occupies the deep layers of the ACC. The CDW is divided into the Upper CDW (UCDW) and the Lower CDW (LCDW) with the former characterised by low $O_2$ and high nutrient concentrations and the later one by high salinities. Still deeper the CDW is underlain by the Antarctic Bottom Water (ABW; Orsi et al., 1995).
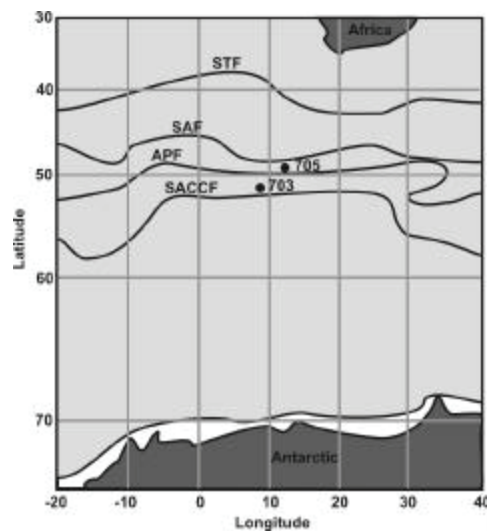


Fig. 4.1. Core sites locations and major oceanographic features of the Atlantic sector of the Southern Ocean: STF – Subtropical Front, SAF – Subantarctic Front, APF – Antarctic Polar Front, SACCF - Southern Antarctic Circumpolar Current Front (after Sauter et al., 2005).

## 4.3. Materials and methods

The multicorer cores PS65/705 and PS65/703 (hereafter referred to as 705 and 703 respectively) were taken during *R/V Polarstern* expedition ANT XXI/4 in 2004 the high-productivity belt along the APF (core 705; 49°00,06' S and 12°15,32' E) and in a region of low surface productivity south of the APF (core 703; 52°35,12' S and 09°00,19' E) respectively (Fig. 4.1; Sauter et al., 2005; Sachs, 2007). Core 705 could be divided into three parts (Sauter et al., 2005). The lower part (28-21 cm) was composed of homogeneous grey to white mud. The middle part (21-13 cm) contained inhomogeneous brown diatomaceous mud. The upper part (13-0 cm) consisted of inhomogeneous, brown, extremely soft, diatomaceous fluffy sediment. Contrary to core 705, sediment of core 703 consisted of homogeneous light brown diatomaceous mud throughout (20-0 cm; Sauter et al., 2005).

For dinocyst analysis, the upper 25 and 10 upper cm of sediment cores 705 and 703 were sampled with 0.5-2.5 cm resolution, respectively. The material was dried overnight at 60°C. Samples were treated with cold 10% HCl and cold 40% HF in order to remove carbonates and silicates, respectively. After every acid treatment, samples were carefully neutralised with KOH. The digested samples were sieved through a 20 µm precision sieve (Stork Veco, mesh 508), treated with ultrasonic vibration and sieved again. The sample residues were centrifuged (8 min, 3500 rpm) and concentrated to 1.0 or 1.5 ml. Part of each residue was embedded into glycerine jelly and insulated from the air by paraffin wax. If possible up to 100 dinocysts were counted. Errors and accuracy of this method are given in de Vernal et al. (1987). The counts were subsequently used to calculate dinocyst concentrations by dividing the amount of cysts counted by the amount of dry weight analysed. Dinocyst fluxes were derived from dinocyst concentrations and sedimentation rates.

In order to obtain information on the dinocyst preservation the *kt* index was calculated for each sample according to the equation given in Versteegh and Zonneveld (2002):

$$kt = \ln(X_i/X_f) \qquad (1)$$

where $k$ is the degradation constant, $t$ is the OET, $X_f$ is the observed dinocyst flux (dinocyst/cm$^2$/y) and $X_i$ is the initial dinocyst flux calculated from the fixed relationship between fluxes of S- and R-cysts (Appendix 4.1; Zonneveld et al., 2007):

$$\text{Flux}_{\text{S-cysts}} = 68 * \text{Flux}_{\text{R-cysts}} \qquad (2)$$

The degradation constant $k$ was calculated using equation (1) assuming that in the oxygenated samples OET is equal to the age of the samples. The $k$ was then compared to *in situ* pore-water $O_2$ concentrations published in Sachs (2007) (Fig. 2b and 4b).

Sample age and sedimentation rates were calculated from $^{210}$Pb data using the Constant Flux Model of Robbins (1978). According to this model the age of given sediment layer can be derived from the equation:

$$t = 1/?*\ln(G_z/G_0) \qquad (3)$$

where $t$ is the age of the bottom of a given sediment layer $z$ in years, $G_z$ is the inventory of $^{210}$Pb$_{\text{excess}}$ below depth $z$, $G_0$ is the total inventory of $^{210}$Pb$_{\text{excess}}$ in sediment and $?$ is the decay rate constant for $^{210}$Pb equal to 0.0311 yr$^{-1}$ (Ferdelman et al., 2006).

Gamma analysis for the determination of $^{210}$Pb (47 kev), $^{40}$K (1460 kev) and the $^{226}$Ra daughter products $^{214}$Pb (295 and 352 kev) and $^{214}$Bi (609 kev) were performed on dried and powdered samples that were sealed at least 21 days prior to measurements to ensure secular equilibrium between $^{226}$Ra and daughter products $^{214}$Pb, $^{214}$Bi.

Total organic carbon (TOC) was determined on freeze-dried and ground material by Leco Carbon Determinator (CS-125). Prior analysis material was treated with HCl in order to remove carbonates.

In our work we used pore-water $O_2$ concentrations published in Sachs (2007). Pore-water $O_2$ profiles were measured *in situ* by means of an autonomous deep-sea microprofiler (Unisense A/S, Denmark) deployed in combination with a free-fall lander system at the location of sediment sampling. The profiler was equipped with up to five Clark type oxygen sensors (Unisense A/S) with a tip diameter of ~25 µm and a stirring sensitivity <2%, pre-calibrated according to Sauter et al., 2001. Sensors were lowered through the sediment

water interface into the sediment with a vertical resolution of 0.5 mm during a measuring period of typically 5-6 hours at the sea floor (Sachs, 2007).

## 4.4. Results

### 4.4.1. Core 703

Core 703 spans period of 142 years from 1862 to 2004 AD and sedimentation rates range between 0.03 and 1.13 cm/yr (Appendix 4.2)

During counting 14 dinocyst taxa were encountered out of which 4 taxa made up 80-98% of the dinocyst assemblages. *Brigantedinium* spp. generally made up 27-57%, *S. antarctica* 17-45%, *I. sphaericum* 1-24% and *I. aculeatum* 0.5-12% of the dinocyst associations. *N. labirynthus* was absent in the upper part of the core and present in the lower part contributing 5 to 13% of the dinocyst assemblage (Fig. 4.2a).

Total dinocyst fluxes increased from 1 to 100 dinocysts per cm$^2$ per year (dc/cm$^2$/yr) from the bottom to the top of the section. Fluxes of *Brigantedinium* spp. and *S. antarctica* rose from 0.5 to 60 and 40 dc/cm$^2$/yr respectively, towards the top of the core. Fluxes of *I. sphaericum* reached up to 1.5 dc/cm$^2$/yr throughout the core (Fig. 4.2b).
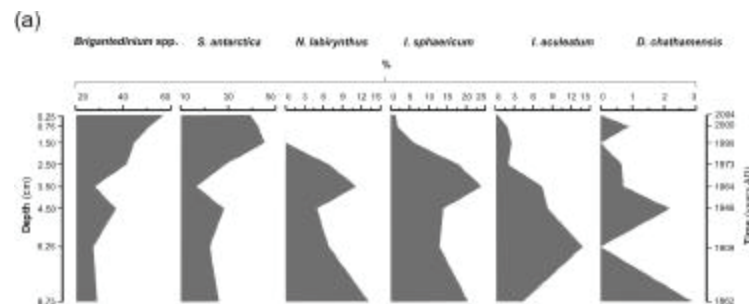


*Fig. 4.2. a) Percentages of selected dinocyst taxa in core 703.*
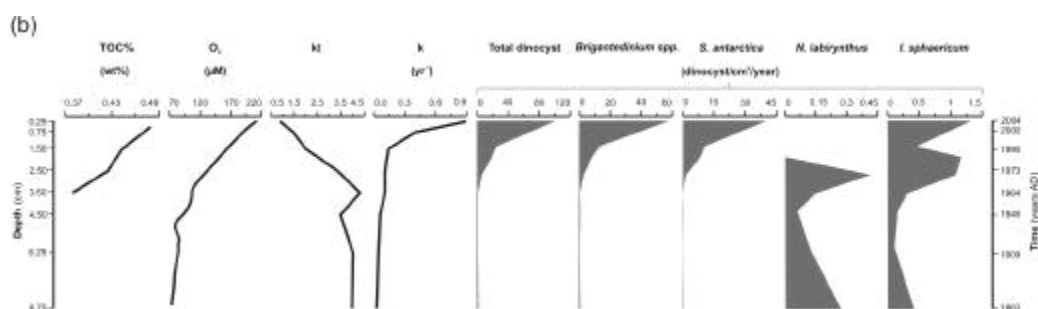
*Fig. 4.2. b) TOC, pore-water O₂ concentrations, kt index, degradation constant k and fluxes of selected dinocyst taxa in core 703.*

TOC was measured only for the upper 4 cm of the core and increased slightly but continuously upsection from 0.38 to 0.48% (Fig. 4.2b).

The values of the *kt* index decreased generally from 4 at the bottom to 1 at the top of the core (Fig. 4.2b). The degradation constant *k* increased upwards from 0.03 up to 0.90 yr$^{-1}$ (Fig. 4.2b). *k* decreases exponentially with decreasing pore-water $O_2$ concentrations according to the equation: $y = 0{,}0051e^{0{,}0239k}$, $R^2 = 0{,}9417$ (Fig. 4.3).

**Core 703**



$y = 0{,}0051e^{0{,}0239x}$

$R^2 = 0{,}9417$
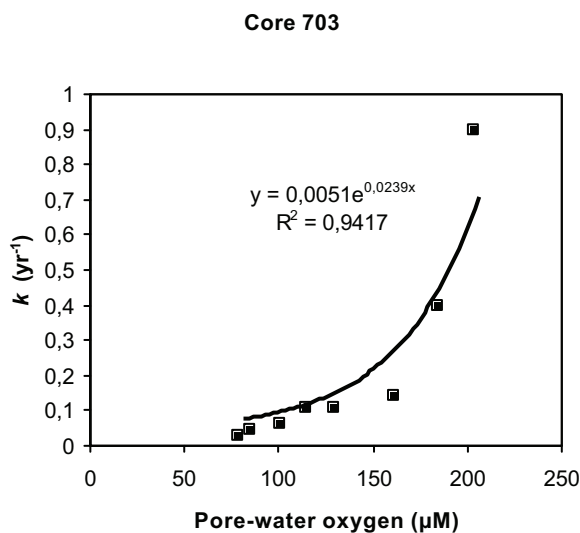
*Fig. 4.3. Relationship between degradation constant k and pore water $O_2$ concentrations in core 703.*

100

**4.4.2. Core 705**

Core 705 spans interval of 169 years from 1985 to 2004 AD. Sedimentation rates are lower (0.06-0.22cm/yr) in the lower part of the core and higher (0.29-1.56 cm/yr) in the upper part of the core (Appendix 4.3).

During counting 15 dinocyst taxa were encountered out of which 4 taxa made up 80-99% of the dinocyst associations. *Brigantedinium* spp. generally made up 40-70%, *S. antarctica* 20-40%, *N. labirynthus* 2-15% and *I. sphaericum* 8-35% of the dinocyst assemblages with only few values ranging below these levels. Other species never reached the 5% abundance level except for *D. chathamense* and *I. aculeatum* whose percentages rose periodically up to 7% each (Fig. 4.4a).

Total dinocyst fluxes in this core ranged from 7 to 360 dc/cm$^2$/yr with generally much higher values in the uppermost samples. Bottom of the core was characterised by low fluxes of *Brigantedinium* spp. (2-30 dc/cm$^2$/yr) that rose up in the 1901-1950 AD interval (up to 70 dc/cm$^2$/yr). Above, they decreased and reached the lowest values (4-10 dc/cm$^2$/yr) in the core during the 1950-1979 AD interval. Towards the top of the core the fluxes increased gradually to reach the highest level (150 and 200 dc/cm$^2$/yr) in 2000 and 2004 AD samples (Fig. 4.4b). Similar trends can be observed for *S. antarctica* with low fluxes at the bottom of the core (1-9 dc/cm$^2$/yr), an increase in the 1901-1950 AD interval (13-40 dc/cm$^2$/yr), a drop in the middle part of the core (2-7 dc/cm$^2$/yr), and a subsequent recovery (up to 80 dc/cm$^2$/yr) towards the top of the core. *N. labirynthus* and *I. sphaericum* displayed lowest fluxes (1-2 and 2-5 d/cm$^2$/y respectively) in the lowermost samples. Their fluxes gradually increased towards the top of the core reaching maximum values (17 and 18, and 38 and 45 dc/cm$^2$/yr respectively) in the samples from 2000 and 2004 AD (Fig. 4.4b).

TOC ranged from 0.35 to 0.55% with generally lower values in the lower part of the core and higher in the middle followed by a decrease until 1992 AD and a subsequent recovery towards the top of the core (Fig. 4.4b).

Values of the *kt* index ranged generally from 3 to 4 throughout the core (Fig. 4.4b). Samples from 1850 and 1967 AD have a *kt*>4 whereas samples

dated at 1835, 1907 and 1937 AD display a *kt*<2. *k* values in the anoxic part of the core ranged from 0.01 to 0.10 yr$^{-1}$ without a significant trend (fig. 4.4b). In the oxygenated part of the core *k* increases upwards from 0.16 up to 30 yr$^{-1}$. *k* is exponentially related to the pore-water $O_2$ concentrations according to the equation: $y=0{,}1449e^{0{,}0336k}$, $R^2=0{,}9726$ (Fig. 4.5).
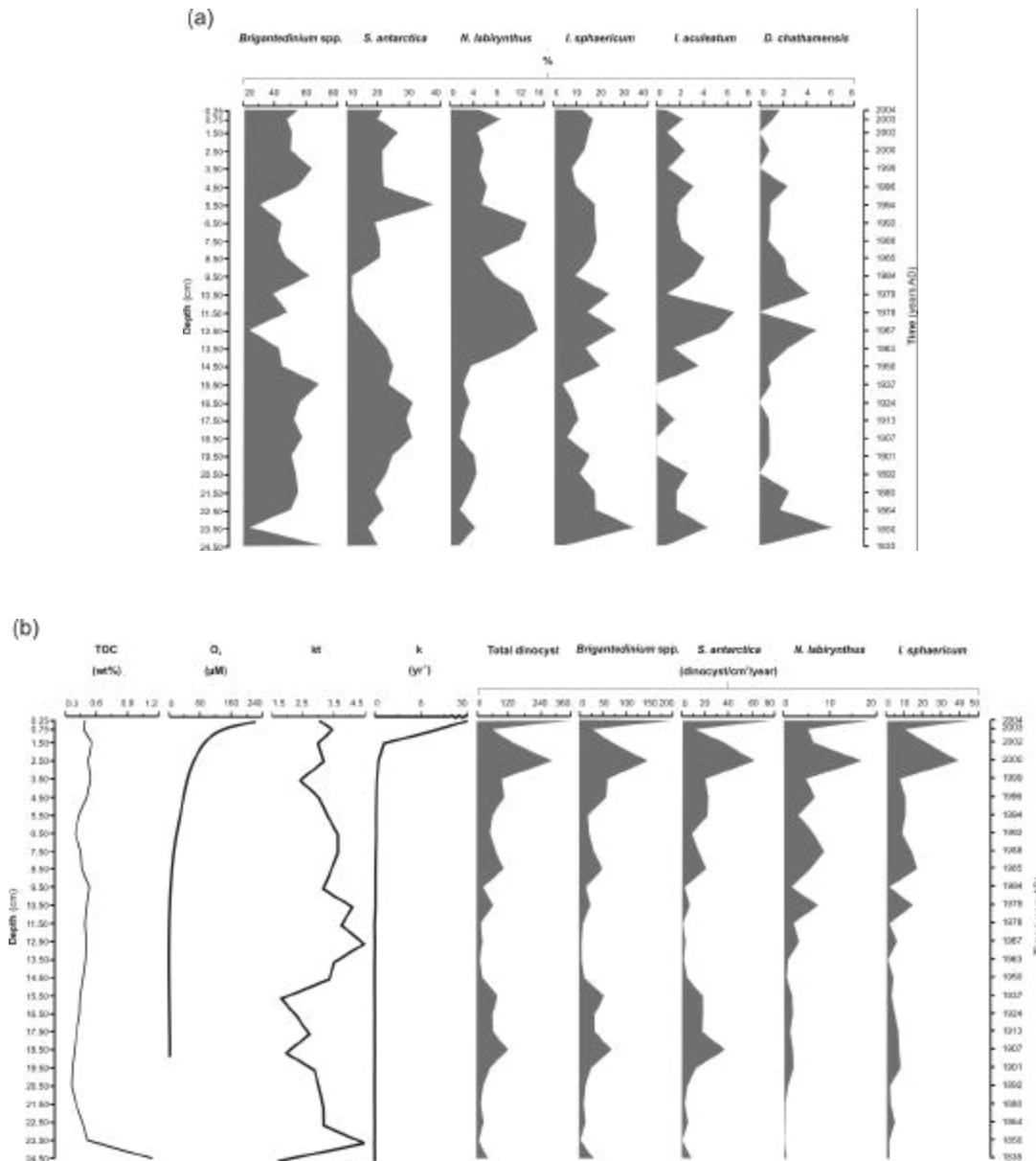


*Fig. 4.4. a) Percentages of selected dinocyst taxa and b) TOC, pore-water $O_2$ concentrations, kt index, degradation constant k and fluxes of selected dinocyst taxa in the core 705.*
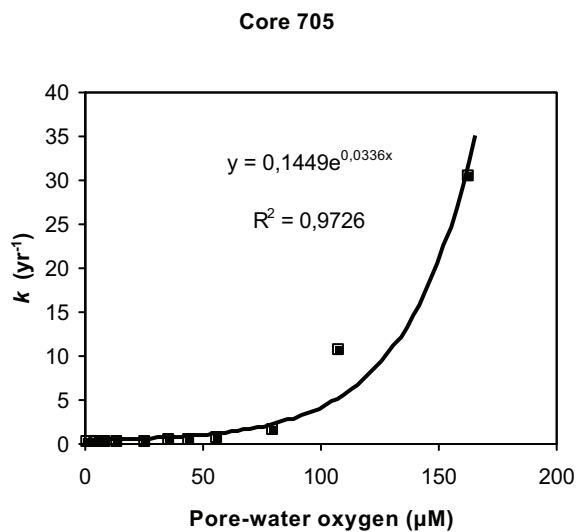
**Core 705**



Fig. 4.5. Relationship between degradation constant k and pore water $O_2$ concentrations in core 705.

## 4.5. Discussion

The dinocyst associations in both cores are dominated by heterotrophic taxa *Brigantedinium* spp. and *S. antarctica* as a second species in abundance except for ~1990 AD in the 703 and the 1996-1992 period in the 705 core where brief dominance of *S. antarctica* is observed. Autotrophic species *I. sphaericum* and *N. labirynthus* are always third and fourth in abundance respectively. Our dinocyst assemblage is, therefore, reminiscent of late Quaternary and recent dinocysts assemblages from the northern part of the Southern Ocean (Esper and Zonneveld, 2002, 2007) and of the southerly subunit of dinocyst association north of 60°S described by Harland et al. (1998) for core-top samples from the Scotia Sea and the Falkland Trough. Sediment trap studies from the Scotia Sea also indicated associations dominated by *Brigantedinium* spp. and *S. antaractica* with presence of autotrophic gonyaulacacean dinocysts (Harland and Pudsey, 1999). The dominance of heterotrophic species in the assemblages is in agreement with cores locations at the APF and south of it since heterotrophic dinoflagellates are known to feed predominantly on diatoms (Jacobson and Anderson, 1986) and upwelling along APF is characterised by very high diatom abundances (Zielinski and Gersonde,

1997). Increased heterotrophic dinoflagellate growth was recently associated with the diatom productivity also in the Arctic region (Richerol et al., 2008).

The analysed 10 cm interval of the 703 core spans 142 years from 1862 to 2004 AD. The $^{210}$Pb measurements suggest that sedimentation rates were relatively lower (0.03-0.05 cm/y) in the lower half of the core in comparison to the upper half (0.05-0.13 cm/y). Total dinocyst fluxes increase towards the top of the core as does TOC, however, individual dinocyst species behave differently. Fluxes and percentages of *Brigantedinium* spp. and *S. antarctica* increase upwards while *I. sphaericum* percentages drop upwards although its fluxes increase. If changes in primary productivity were responsible for changes in dinocyst patterns we would expect more proportional increase of all taxa fluxes and no significant changes in dinocyst percentages, which is not the case. Such dinocyst trends as described here are characteristic for assemblages affected by selective aerobic degradation. *Brigantedinium* spp. and *S. antarctica* are S-cysts and *I. sphaericum* belong to R-cysts thus the decomposition of the former ones could cause an increase in the percentages of the later (e.g. Zonneveld et al., 1997, 2001; Hopkins and McCarthy, 2002; Reichart and Brinkhuis, 2003; Esper and Zonneveld, 2007; Kodrans-Nsiah et al., subm). The continuous decrease of the calculated *kt* index towards the top of the core supports the hypothesis of selective degradation and hints at much better dinocyst preservation in the upper part than in the lower part of the core. We, therefore, conclude that in this case the dinocyst record is the result of species-selective aerobic degradation instead of changes in primary productivity.

OC degradation, and hence also dinocyst degradation, manifests a first-order dependence on the reactivity of OC and OET (Middelburg, 1989; Canfield, 1994; Hartnett et al., 1998; Sun et al., 2002; Keil et al., 2004). *In situ* pore-water $O_2$ concentrations measurements at the site 703 indicate oxic conditions throughout the core (Sachs, 2007). Under the assumption of a steady state situation the age of our samples would mirror the OET with the bottom sample being exposed to $O_2$ for 142 years and the top samples for only a few years thus it is not surprising that dinocyst preservation should be worse in the lower

part than in the upper part of the core. The calculated degradation constant $k$ increases with decreasing OET, which supports the fact that degradation depends on the reactivity of OC. The most reactive OC is degraded fast whereas the degradation of less reactive components proceeds slowly over a longer time. In our case the most sensitive dinocysts are decomposed within the upper 3 cm of the core (corresponding to ~30 years of OET), however degradation of the less sensitive dinocysts proceeds over the longer time period at slower rates which is indicated by a lower $k$ value. $k$ also correlates positively with measured pore-water $O_2$ concentrations implying that the degradation is dependent not only on the presence-absence of the pore-water $O_2$ but as well on the $O_2$ concentration. As $O_2$ diffuses from the bottom water into the sediment it is ultimately consumed by OC degradation. A certain amount of $O_2$ can oxidise only a limited amount of OC. In our case an average of 0.03 mol $O_2$ per $m^2$/yr can oxidise up to 0.25 gC per $m^2$/yr (calculated according to Fick's First Law and OC: $O_2$ ratio 106:138; Froelich et al., 1979; Schulz, 2005). Accordingly, higher $O_2$ concentrations would cause the degradation of a larger amount of OC in the same period of time. Less reactive OC and lower $O_2$ levels would cause a decreasing $k$ with an increasing OET.

However, although $O_2$ is available throughout the whole length of the core, degradation seems not to change significantly over the lower 7 cm which would imply that although degradation is dependent on the $O_2$ concentration, in this case the final limiting factor might be availability of the reactive components as the amount of S-cysts in the lower part of the core nears to zero.

In core 705 the degradation index $kt$ is relatively constant through time, samples with assumed OET of few years experienced the same degree of degradation as samples exposed for 25 years. That would suggest that degradation in this case depends solely on the other factors than OET. Throughout the entire core, and especially in the upper half, there were high abundances of S-cysts preserved in the sediment. Hence, the availability of labile OC does not seem to be the limiting factor for the degradation. However, in this case $O_2$ is consumed much faster resulting in oxygen-depleted conditions in the lower part of the sediments thus pointing to the limiting role of the $O_2$. The

calculated constant $k$ for the oxic part of the core correlates well with pore-water $O_2$ concentrations. This would, again, suggest a dependence of OC degradation on $O_2$ concentrations. Recently Zonneveld et al. (2007) have found a significant relationship between dinocyst degradation and bottom-water $O_2$ concentrations. This supports our observations since pore-water $O_2$ concentrations are dependent, among other factors, on the concentration of $O_2$ in the bottom waters that diffuses downwards into sediments. Furthermore, Bockelmann et al. (subm) concluded that dinocysts degradation is dependent on the bottom-water $O_2$ concentrations until critical $O_2$ level of ~3 ml/L, above this level degradation seems to be controlled by the flux of S-cysts.

The early diagenetic processes discussed above explain well the dinocyst pattern of core 703 but do not for the core 705. Due to faster $O_2$ depletion in the sediments of core 705, a considerable amount of S-cysts could have been escaped degradation. As pointed out earlier, the relatively uniform $kt$ index throughout this core suggest that dinocyst associations in all samples were affected by selective preservation at the same level and hence their pattern, but not their absolute numbers, can be interpreted in terms of palaeoenvironmental changes. The exception may be the few samples with much higher or lower $kt$ values than the average 3-4, which will be discussed later in the text.

The analysed 25 cm of core 705 span 170 years from 1835 to 2004 AD. However, the lower half of the studied section was deposited during 145 years whereas the upper half during a relatively short period of 25 years. Not surprisingly, the upper part of the section comprises the distinct fluffy sediment layer described by Sauter et al. (2005) and hypothesised to be relatively rapidly deposited during prolonged periods ofenhanced sedimentation in comparison to the rest of the core, (Sachs, 2007). Indeed, sedimentation rates inferred from $^{210}$Pb are generally much lower for the lower half (0.06-0.22 cm/y) then for the upper half of the core (0.29-1.56 cm/y). Such a subdivision of the core is also reflected in the dinocyst flux pattern with generally low rates in the lower part of the core and increasing rates in the upper part.

The bottom of the core (1835-1901 AD) consists of the proper homogenous sediment (Sauter et al., 2005) and is characterised by very low fluxes of all

dinocyst species. It is followed by an interval (1901-1950 AD) of higher fluxes of *Brigantedinium* spp. and *S. antarctica* and low and stable fluxes of *N. labirynthus* and *I. sphaericum.* As heterotrophs, species grouped within *Brigantedinium* spp. and *S. antarctica* depend on the prey availability, and therefore they are very abundant in high-productivity areas such as, for example, upwelling regions (Harland et al., 1998). Additionally *S. antarctica* is generally associated with cold water masses and proximity of seasonal sea-ice cover (Marret and de Vernal, 1997; Harland et al., 1999). Increased fluxes of these two taxa could indicate a northern shift of the APF (Howe et al., 2002) and, concomitantly, a high-productivity upwelling area. A displacement of these features would result not only in relatively higher prey availability, and therefore better conditions for heterotrophic species growth but also in relatively lower sea-surface temperatures and proximity of the maximum sea-ice limit - the conditions favourable for *S. antarctica*. Upper (1950-1979 AD), at the termination of the sediment proper/fluffy sediment interface fluxes and percentages of *Brigantedinium* spp. and *S. antarctica* deacrease again and reach their lowest level in the core. This coincides with a sharp peak in percentages of *N. labirynthus* accompanied by high percentages of *I. sphaericum* although peaks of similar magnitude were not observed for fluxes. In polar domains *N. labirynthus* and *I. sphaericum* are interpreted as representative of relatively warmer water masses and permanently ice-free conditions (Howe et al., 2002; McMinn et al., 2001). This, in contrast to the previous interval, may suggest a southern shift of the APF and the introduction of relatively higher sea-surface temperatures. This is further supported by increased percentages of another two species *D. chathamense* and *I. aculeatum* that are thought to be associated with relatively warmer waters (McMinn et al., 2001; Marret and de Vernal, 1997). However, higher fluxes of heterotrophic taxa in the 1901-1950 AD interval as well as lower fluxes in the 1950-1979 AD interval may be related not only to changes in palaeoenvironment but also to selective preservation/degradation of dinocysts under aerobic conditions as suggested by $kt<2$ and $kt>4$ respectively in comparison to the other samples ($3<kt<4$). If samples with these dffering $kt$

values are excluded from the analysis the whole interval 1901-1979 seems to have much more stable dinocyst fluxes and indicate stable palaeoceanographic conditions.

Upwards (1979-2004 AD) the fluxes of *Brigantedinium* spp. and *S. antarctica* increases again to reach approximately the same values as in the 1901-1950 AD interval with exception of samples from 2000 and 2004 AD where fluxes reached even higher values. This would indicate the return to a more northern location of the APF and the associated high-productivity belt. The prominent feature of this section is a short-term peak of *S. antarctica* percentages coinciding with a sharp drop in percentages of *Brigantedinium* spp. at 1992-1996 AD. The shift to *S. antarctica*-dominated assemblages is generally indicative of colder conditions since this species is associated with cold water masses and the proximity of seasonal sea-ice cover (Marret and de Vernal, 1997; Harland et al., 1999). In our case this suggest the coldest sea-surface conditions within the studied period. Our hypothesis is further corroborated by sea-ice concentration data collected by NOAA ([www.cdc.noaa.gov](www.cdc.noaa.gov)). The sea-ice concentration averaged over the period 1992-1996 AD shows a northern shift (by 1°) of the maximum sea-ice limit in comparison to adjacent periods.

## 4.6. Conclusions

Both cores are characterised by low dinocyst fluxes that, at least partially, may be the result of selective degradation of heterotrophic species. Our results indicate that early diagenesis may significantly influence the primary fossil signal and, as in case of core 703, prevent the recognition of palaeoenvironmental changes. The relationship between calculated $k$ values and pore-water $O_2$ concentrations suggests that the degradation of OC is dependent on the bottom- and pore-water $O_2$ concentration as well as on the labile OC fraction and OET. The $O_2$ concentration seems to be more important limiting factor for diagenetic processes at lower $O_2$ concentrations whereas at higher $O_2$ levels the availability of reactive OC is crucial. Recognition of the selective degradation may lead to differentiation between primary and

overprineted signals and hence enable the accurate interpretation of fossil records as demonstrated for core 705.

## Acknowledgements

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**CHAPTER 5**

**Are the Kimmeridge Clay deposits affected by "burn-down" events? A palynological and geochemical approach**

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**Abstract**

Two independent analytical approaches, palynological and inorganic geochemical, were applied to identify potential oxygenation "burn-down" events in the upper Kimmeridge Clay Formation (KCF) deposited in the Jurassic Wessex Basin. The KCF interval spanning 121.82-122.72 m depth was sampled from the Swanworth Quarry 1 borehole (Dorset, UK) at 2.5-5.0 cm resolution. Samples were analysed for total organic carbon (TOC), palynofacies components, organic-walled dinoflagellate cysts (dinocysts), and concentrations of elements that are known to be productivity- and/or nutrient-related (e.g. Cu, P), detrital (e.g. Al, Ti, Zr) and redox-sensitive/sulfide-forming (e.g. Fe, Mn, S).

Overall, TOC contents exceed 2 wt%, with a maximum of 8.8 wt% at 122.37 cm depth and elevated values in the central part of the investigated interval. This interval of relatively higher TOC values correlates well with the maximum

recovery of marine palynomorph absolute abundances and low Al values, suggesting that TOC is primarily of marine organic matter.

Sharp changes in Fe/Al, Mn/Al and S at 122.37 m depth mark a shift from anoxic/euxinic conditions in the lower part of the studied interval to more oxic conditions in its upper part. Such a shift could explain the relatively high TOC and marine palynomorphs abundances in the lower part of the studied interval as a result of better preservation, and the subsequent decrease as an effect of a "burn-down", i.e. organic matter oxidation.

Although the shift in redox-sensitive elements is very sharp and the major changes in TOC and marine palynomorphs occur at the same level, the changes in TOC and marine palynomorphs are gradual and less pronounced. As the amount of marine palynomorphs and TOC content diminishes from the middle part of the studied section upwards, species-specific changes in dinocyst assemblages can be observed.  In particular, abundances of *Circulodinium* spp., *Cyclonephelium* spp., *Sirmiodinium grossi*, *Senoniasphaera jurassica* and *Systematophora* spp. decrease rapidly in comparison to other species, such as *Glossodinium dimorphum* and *Cribroperidinium* sp. 1.

We suggest that enhanced organic matter preservation due to anoxic/euxinic conditions was the reason for high TOC and marine palynomorphs values in the central part of the studied interval.  Oxygenation of bottom and pore waters within the sediment was most probably the cause for decreasing TOC values and reduced recovery of marine palynomorphs towards the top of the studied interval.


Keywords: Kimmeridge Clay, preservation, productivity, oxidation, palynology, trace metals


## 5.1. Introduction

The specific early diagenetic features of "burn-down" events are a widespread phenomenon in (sub-) recent marine deposits. They have been identified, for instance, in Mediterranean sapropels (Thomson et al., 1995; Van Santvoort et al., 1996; Jung et al., 1997; Crusius & Thomson, 2003), in

turbidites of the Cape Verde (Wilson et al., 1985; Thomson et al., 1993; Robinson, 2000) and Madeira Abyssal Plains (Cowie et al., 1995; De Lange, 1998; Crusius & Thomson, 2003) as well as at glacial/interglacial transitions in the deposits from equatorial Atlantic ocean (Kasten et al., 2001). A "burn-down" event is the aerobic oxidation of organic matter in the sediment, and is indicated, among others, by degradation of TOC, dissolution of calcium carbonate, oxidation of reduced S (e.g. Prahl et al., 2003) and ferrous Fe (e.g. Kasten et al., 2001), and decreased abundance of palynomorphs (e.g. Versteegh and Zonneveld, 2002; Traverse, 2007). Such oxidation fronts are clear signs of rapid redox changes in sedimentary systems and also in the water column from anoxic to (sub-)oxic conditions. Therefore if present in Quaternary deep-sea deposits, these events might also be identifiable in older marine sediments deposited during similar transitional periods that experienced changes in bottom water and sediment redox conditions.

As one of the major source rocks for North Sea oil, the Kimmeridge Clay Formation (KCF) has been extensively studied not only for its petroleum potential, but also regarding palaeoclimatic and palaeoenvironmental conditions that led to the formation of Upper Jurassic/Lower Cretaceous oil-prone sediments. In particular, several studies have dealt with the relative importance of high surface water primary productivity *versus* evolution of oxygen-depleted bottom water and sediments for the high organic matter (OM) content of the deposits, applying micropalaeontological and palynological methods as well as organic and inorganic geochemical techniques (e.g. Gallois, 1976; Farrimond et al., 1984; Oschmann, 1988, 1990; Wignall, 1990; Herbin et al., 1991, 1995; Huc et al., 1992; Lallier-Vergès et al., 1993; Jenkyns et al., 1994, 2002; Jones et al., 1994; Tribovillard et al., 1994; Ramanampisoa & Disnar, 1994; Boussafir et al., 1995; Tyson, 1996; Helz et al., 1996; Boussafir & Lallier-Vergès, 1997; Pearson, 2000; Lees et al., 2004; Pearson et al., 2004; Tyson, 2004; Tribovillard et al., 2005).

The KCF was deposited in the Wessex Basin during Late Jurassic times (e.g. Mller, 1990; Gallois, 2000). It has been reconstructed that sedimentation occurred in a quiet and shallow (50-100 m water depth) marine environment

with fluctuating oxygen conditions (e.g. Oschmann, 1988). It has been widely postulated that the Wessex Basin was periodically anoxic alternating with shorter or longer oxygenation events (e.g. Tyson et al., 1979; Oschmann, 1988, 1990; van Kaam-Peters et al., 1997; Waterhouse, 1999). There are several very organic-rich intervals within the KCF (e.g. Blackstone, Blake's Bed 2) intercalated with - or followed by - less organic-rich beds (Morgans-Bell et al., 2001). Many authors have suggested that the organic-rich intervals are the result of enhanced preservation due to anoxic bottom waters (e.g. Tyson et al., 1979; Oschmann, 1988; Wignall and Myers, 1988; Miller, 1990; Matthews et al., 2004; Weedon et al., 2004). They have argued that interface between oxygenated and suboxic/anoxic waters cyclically rose and fell and, when reaching the sediment-water interface, caused diminished preservation of accumulated OM and hence the less organic-rich facies. However, several other studies suggest that increased primary productivity was the reason for high OM accumulation (e.g. Gallois, 1976; Lallier-Verges et al., 1993; Bertrand and Lallier-Verges, 1993;Tribovillard et al., 1994). It is hypothesised that enhanced primary productivity caused increased OM accumulation, leading to production of large quantities of $H_2S$, which, in turn, could result in euxinic conditions and enhanced OM preservation.

To shed more light on this discussion and to investigate if "burn-down" events might have affected KCF we have carried out a multidisciplinary study on sediments from the Upper KCF. Of particular interest for palaeoenvironmental interpretations of such an ancient OM-rich deposits are enrichment/depletion and distribution patterns of redox-sensitive and sulphide-forming trace metals, as they have the potential to trace changes in the water column and sediment geochemistry during the time of deposition (e.g. Calvert & Pedersen, 1993; Morford & Emerson, 1999; Nijenhuis et al., 1999; Lipinski et al., 2003; Algeo et al., 2004; Tribovillard et al., 2005; Brumsack, 2006; review by Tribovillard et al., 2006). Information on redox conditions, OM preservation and primary productivity can also be obtained by detailed palynofacies analysis and studies of organic-walled dinoflagellate cysts (e.g. Tyson, 1993; Zonneveld et al., 1997, 2001; Al-Ameri et al., 1999; Devillers & de Vernal, 2000; Bucefalo

Palliani et al., 2002; Reichart & Brinkhuis, 2003; Ruf, et al., 2005; Ercegovac & Kostic, 2006).

## 5.2. Materials and methods

### 5.2.1. Materials

In order to obtain an insight into short-term palaeoenvironmental changes in the Kimmeridge Clay Formation, we sampled core material from the Swanworth Quarry 1 from Dorset, drilled at the type locality of the KCF (Fig. 5.1; Gallois, 2000), with vertical sample resolution of 2.5 to 5 cm. The sampled interval spans 118.57-123.62 m drilling depth and is of Tithonian age (the *pallasioides* and *rotunda* ammonite zones; Fig. 5.2; e.g. Gallois, 2000; Morgans-Bell et al., 2001).
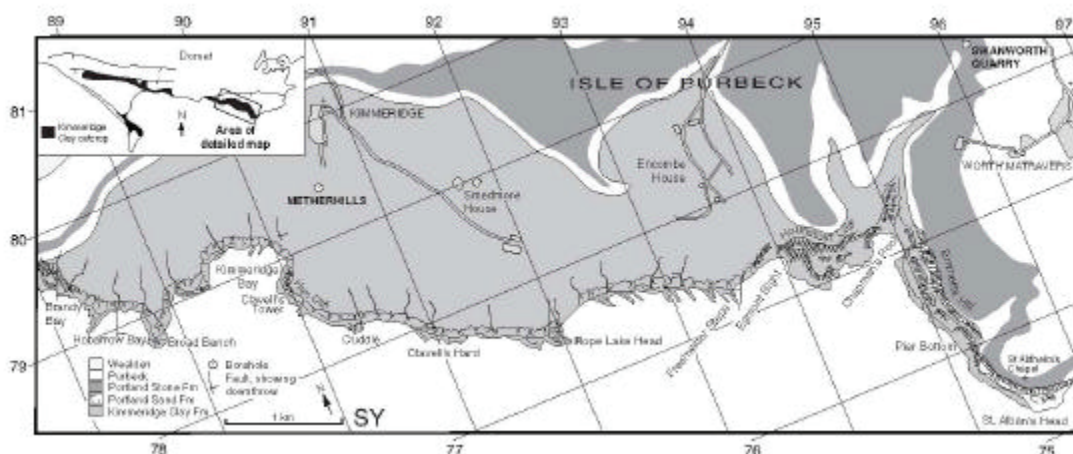


*Fig. 5.1. The Kimmeridge Clay Formation outcrop in Dorset, UK and the location of the Swanworth Quarry 1 borehole (after Morgans-Bell et al., 2001).*

The investigated core was drilled as part of the Natural Environmental Research Council (NERC) Special Topic "Rapid Global Geological Events (RGGE) Kimmeridge Drilling Project". Additional data concerning that project are available on http://kimmeridge.earth.ox.ac.uk/ index.php. The core is stored, and was sampled, at the facilities of the British Geological Survey (BGS) Headquarters in Keyworth, UK. All subsequent sample preparations and analyses were done at the School of Ocean & Earth Science, National

Oceanography Centre, Southampton, UK, and the University of Bremen, Germany.

For this study, a total of 26 samples (121.82-122.72 m depth) from the lowermost *rotunda* ammonite zone were selected. The studied section consists of light to medium grey mudstone in the upper and lower parts and dark grey shelly mudstone in the middle part. As a marker horizon, the dark grey mudstone comprises the lateral equivalent of Blake's Bed 2, a distinct oil shale interval with organic carbon values close to 10 wt%. Furthermore, it is the youngest interval of the KCF with notably elevated organic carbon and calcium carbonate values, therefore marking the end of the period of enhanced OM burial. The sampling resolution was largely limited to 2.5 cm by the flaking and desiccated nature of the core material. For intervals with minor lithological changes, a vertical resolution of 5 cm was regarded as sufficient for the purposes of this project. Each sample was split for palynological and geochemical investigations, respectively.
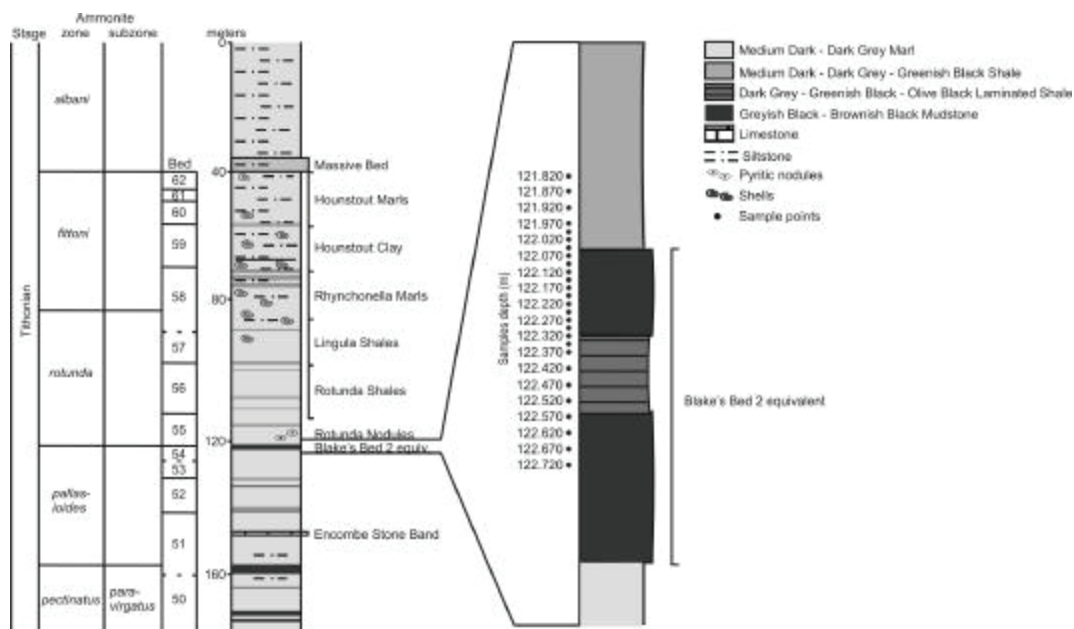


*Fig. 5.2. Summary stratigraphic log of the upper Upper Kimmeridge Clay Formation (after Morgans-Bell et al., 2001) and a detailed log of the studied interval (after Coe et al. published on http://kimmeridge.earth.ox.ac.uk/index.php.), sample positions are indicated.*

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### 5.2.2. Palynological methods

The material for palynological preparation was broken down, and 0.5 g to 5.0 g of each sample were treated with cold 32% HCl and cold 60% HF in order to remove carbonates and silicates, respectively. Samples were spiked with *Lycopodium* spore tablets and boiled in 32% HCl for 1 min to remove neo-formed fluorides. After every acid treatment, samples were carefully neutralised. The digested samples were sieved through a 15 µm nylon mesh, treated with ultrasonic vibration for up to 35 s and sieved again. Part of each residue was mounted on a glass microscope slide using Elvacite 2044 prior to analysing the palynofacies and the dinocyst composition of each sample. At least 300 particles were counted on each slide (excluding *Lycopodium*) under the light microscope. *Lycopodium* spores were counted simultaneously and used to calculate the absolute abundances of palynofacies categories and dinocysts following the method of Stockmarr (1971).

### 5.2.3. Geochemical methods

For geochemical investigations, samples were freeze-dried, and ground and homogenized with an agate pestle and mortar. TOC and inorganic carbon (IC) were measured using a Leco 200 CS carbon sulphur analyser. In a first step, total carbon (TC) was determined. Afterwards, the material was decalcified with 12.5% HCl, washed twice with MilliQ water and dried at 60° C. The carbonate-free sediment was measured again for total carbon to analyse the remaining TOC fraction. The carbonate or IC fraction was calculated with the equation $CaCO_3$ (%) = (TC - TOC) * 8.33. The accuracy of the measurements was determined as ~3 % by analysing a range of marble standards with C contents of 0.5-12 %.

For determining the elemental composition of the sediment, a total acid digestion was performed on the dried and ground samples. The sediment was treated with a mixture of suprapure hydrofluoric, hydrochloric and nitric acid and heated in a microwave oven to about 200° C. The resulting solution of acids and elemental and ionic species was evaporated to remove the acid mixture, the remaining dry powder was re-dissolved in 1% nitric acid for subsequent

analysis. Measurements of major (Al, Ca, Fe, K, Mg, Na, P, S, Ti) and minor (Ba, Cr, Cu, Mn, Ni, Sr, V, Zn, Zr) elements in the solution were done with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin-Elmer), with a relative standard deviation of < 3 % (for Cu and Ni < 10 %).

### 5.2.4. Statistical methods

To determine the relationship between dinocysts and chemical element distribution and environmental parameters, multivariate ordination techniques of the CANOCO software (ter Braak & Smilauer, 1998) were applied. Principal Component Analysis (PCA) is a commonly used method for data with linear distributions. This method determines the strength of relationships between categories and the theoretical environmental gradients by applying linear regressions (Jongman et al., 1987). Two main environmental variables that are assumed to cause the biggest variation in the dataset are plotted as two perpendicular axes (PCA axes) by means of a two-way weighted summation algorithm. The first PCA axis represents the variable that explains the dataset best, and the second PCA axis also explains the dataset best but only when uncorrelated with first PCA axis (Jongman et al., 1987).

### 5.3. Results
### 5.3.1. Geochemistry
### 5.3.1.1. Total organic carbon and inorganic carbon

The lower part of the interval is characterised by TOC values between ~4.0 and 8.0 wt% (Fig. 5.3). Further up-section the TOC pattern demonstrates a relatively continuous and gradual decrease from a peak value of 8.8 to ~3.0 wt% within an interval of about 40 cm (122.37-121.95 m core depth). Inorganic carbon (IC) remains at values of 13.3-27.2 wt% in the lower part of the interval and drops upwards. However, the continuity of IC decrease is interrupted by a sharp peak of more than 32.5 wt% at 122.25 m core depth. Notably, this IC peak correlates with a minor, but still clearly visible drop of TOC. Apart from this anomalous peak, the highest calcite content, of 27.2 wt%, is reached at 122.47 m, a few centimetres below the TOC peak. In the upper part of interval IC

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roughly parallels the TOC pattern decreasing from ~27.2 to 10.4 wt% within the uppermost 40 cm. Mean values for TOC and calcite of 5.4 wt% and 19.9 wt%, respectively, as well as their high variability are in line with the TOC and carbonate data published by Morgans-Bell et al. (2001).
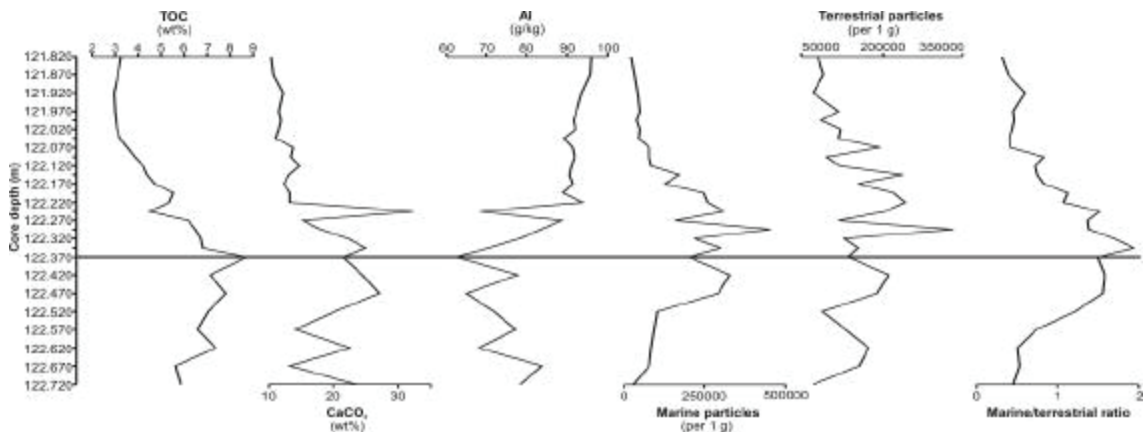


*Fig. 5.3. Plots of total organic carbon (TOC, wt%), calcium carbonate (CaCO₃, wt%) and aluminum (g/kg) contents, alongside absolute abundances of total marine particles (per g sediment), total terrestrial particles (per g sediment) and the marine/terrestrial ratio, plotted against sediment depth (cm).*

### 5.3.1.2. Detrital elements: Al, B, Cr, K, Mg, Ti and Zr

In natural sedimentary systems, this group of elements is mostly bound to silicate minerals, and thus is a proxy for detrital input from the hinterland. In the KCF interval, we find a very close correlation between all of these elements (correlation coefficients with Al are 0.83 for B, 0.96 for Cr, 0.93 for K, 0.82 for Mg, 0.94 for Ti, 0.90 for Zr) in addition to  minor variations in the respective element/Al ratios (Appendix 5.1). Thus, we refer to Al only as a representative for all measured detrital elements. Plotted versus depth (Fig. 5.3), there is an interval with a slight up-section increase of concentrations of these elements and remarkably low variability between 122.27 and 121.82 m. The lower part of the interval is much more variable in all detrital elements, and the concentration pattern negatively correlates with the TOC record. In the lower and middle part of the interval the Al content is only ~30-60 % of its values above 122.27 m.

### 5.3.1.3. Primary productivity- and/or nutrient-related elements: Ba, Cu, P

Being an often-applied paleoproductivity proxy, marine biogenic barium or, more precisely barite ($BaSO_4$) can, under certain conditions, provide insights regarding palaeoenvironmental fluctuations recorded within a sedimentary succession (e.g. Goldberg & Arrhenius, 1958; Dehairs et al., 1980; Bishop, 1988; Dymond et al., 1992; Francois et al., 1995; Kasten et al., 2001). In our KCF interval Ba has lower contents (0.17-0.23 g/kg) but higher variability below 122.245 m depth and higher values above this depth (up to 0.27 g/kg). However, it has been argued that barium is not a good paleoproductivity proxy in the KCF (Tribovillard et al., 1994). Our findings imply that the Wessex Basin depositional environment did not allow the development of a genetic link between marine barite and surface primary production. In Mediterranean sapropels, marine barite is the preferred proxy for reconstructing fluctuations in paleoproductivity. Furthermore, it is applied to estimate the original thickness of sapropels, as the labile marine OM is often oxidized by downward-propagating burn-down fronts. In the Wessex Basin however, its use is hampered for several reasons: first, maximum water depths of a few hundreds of metres (e.g. Tyson et al., 1979; Aigner, 1980; Oschmann, 1988) are too shallow for the synsedimentary barite formation mechanism (e.g. Dymond et al., 1992; Von Breymann et al., 1992; Klump et al., 2000). Second, Ba can be seen to correlate well with detrital elements (e.g. correlation coefficient of Ba with Al, $R^2$ = 0.94), suggesting that it is mainly bound to silicate minerals, and not to barite.

Copper is known to be enriched in OM-rich deposits relative to average shale (see below; e.g. Calvert & Pedersen, 1993), either forming Cu sulphides (e.g. Skei et al., 1996; Brumsack, 2005), co-precipitated with or incorporated into pyrite (e.g. Huerta-Diaz & Morse, 1992), or passively sorbed to organic substance (e.g. Morel & Price, 2003; Tribovillard et al., 2006). In our samples (Fig. 5.4), there is a very close relationship of Cu/Al with TOC ($R^2$ = 0.85) rather than with S ($R^2$ = 0.37), indicating that Cu is bound to OM rather than as sulphides.

Phosphorus is another constituent of marine OM, and thus can be related to productivity and preservation. The distribution of P in these samples does not

correlate well with detrital elements, carbonate, organic carbon or iron. Maximum P contents of ~2.33 g/kg sediment are reached in 122.02 m depth, and lowest values of 0.88 g/kg occur around the TOC and S maxima in 122.47 m. Figure 5.4 shows that the organic carbon/phosphorus (TOC/P) ratio has a pattern very similar to the TOC record, with values of 80-90 around the highest TOC peaks, and decreased ratios of 15-20 and 40-50 further upcore and downcore, respectively.
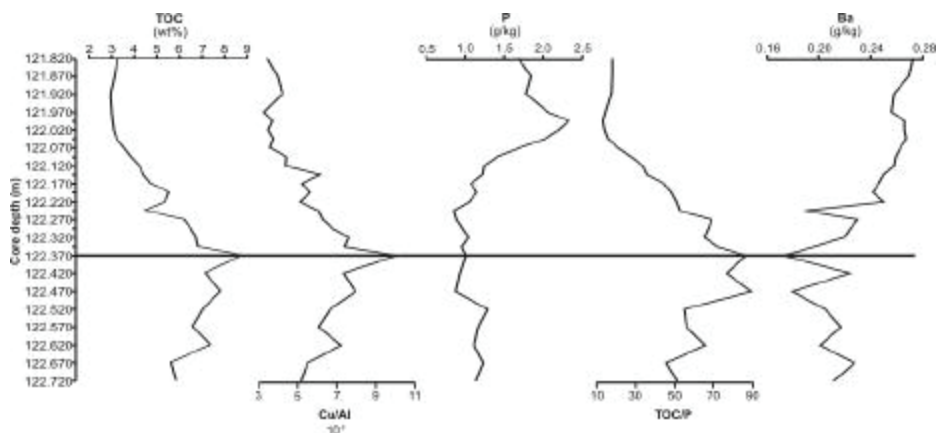


*Fig. 5.4. Plots of TOC content (wt%), Cu/Al ratio (ppm/%), bulk P (g/kg), TOC/P ratio (%/%) and bulk Ba (g/kg) against borehole core depth.*

### 5.3.1.4. Potentially redox-sensitive/sulphide-forming elements: Fe, Mn, S

Mean Mn content for the investigated KCF interval is generally depleted relative to average shale. Mn/Al correlates positively with S and Fe/Al, and negatively with the Fe/S as visible in Figure 5.5. Sulphur is generally high to very high in the studied sediment interval, with concentrations ranging from 1.5 wt% in the upper to 5.5 wt% in the lower part. Iron, although usually not enriched with respect to average shale in this interval, shows a very similar depth distribution to S, with a correlation coefficient of S/Al to Fe/Al of 0.97. The relatively consistent Fe/Al ratio of 0.43 found in the upper part of the interval (with iron contents ranging between ~35 and 45 g/kg), and is used to estimate a maximum background detrital value for Fe in these sediments. This value of 0.43 is distinctly lower than the equivalent value of average shale, which is 0.54.

In contrast, in the lower part of the interval (below 122.37 m), Fe contents vary between ~40 and 60 g/kg, and the Fe/Al ratio is twice as high as in the upper part (up to 0.84).
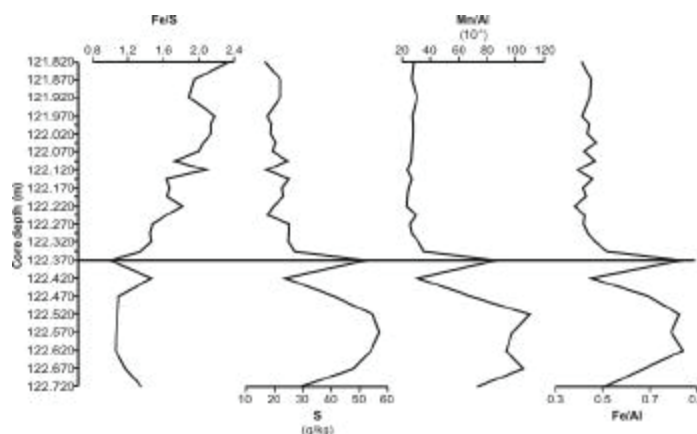


Fig. 5.5. Plots of the Fe/S ratio (%/%), the bulk S content (g/kg), the Mn/Al ratio (ppm/%) and the Fe/Al ratio (%/%) against borehole core depth.

### 5.3.1.5. Elemental enrichment factors

In inorganic geochemical studies of both modern and ancient sediments, the calculation of elemental enrichment factors (EF) is a common method used to compare deposits of different ages to each other and different locations in terms of the palaeoenvironmental conditions prevailing during their formation (e.g. Brumsack, 2006). Here, the application of element/Al ratios is undertaken to exclude dilution by biogenic or authigenic sediment components, and the EFs of trace elements are also calculated relative to average shale (Turekian & Wedepohl, 1961; Wedepohl, 1991). These data are then compared with other anoxic deposits, namely Mediterranean sapropels (e.g. Warning & Brumsack, 2000; Brumsack, 2006) and Cretaceous black shales (Brumsack, 2006; Hetzel et al., 2006). The EFs do not take into account small-scale concentration variations over depth and do not give information about the speciation of the respective elements in the solid phase. However, the mean values of elemental enrichments can give important hints concerning general genetic similarities or differences.

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Enrichment factors are presented in Figure 5.6. Elements enriched towards average shale are Cr, Cu, Ni, P, Sr, V and Zn (EFs of 2.25-1.10). The EFs of typically OM-bound elements like Cu, Ni, P and Sr are all above 1. Elements depleted compared to average shale are Ba, K, Mg, Mn, Ti and Zr (EFs of 0.42-0.93).
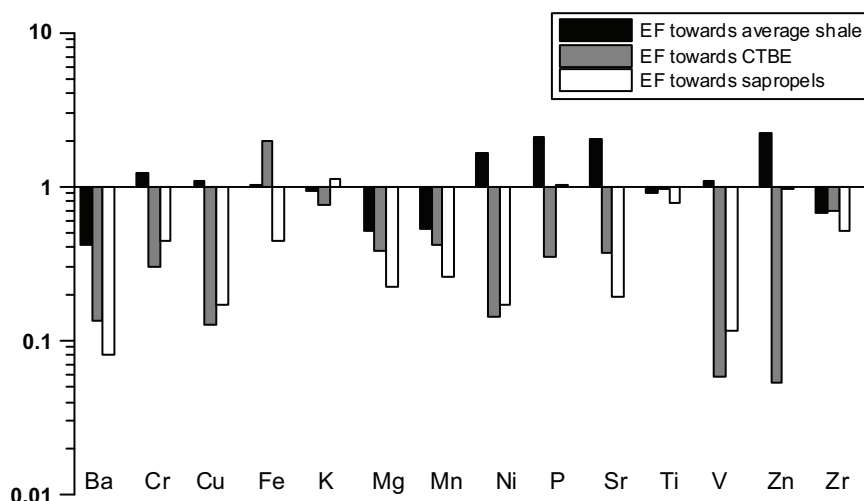


*Fig. 5.6. Calculated elemental enrichment factors (EFs) of KCF samples relative to average shale (Turekian and Wedepohl, 1961; Wedepohl, 1991), relative to mean values of the Cenomanian/Turonian Boundary Event shales (CTBE; Brumsack, 2006), and Late Quaternary sapropels of the eastern Mediterranean (Warning & Brumsack, 2000). Values <1 = depletion, values >1 = enrichment.*

## 5.3.2. Palynofacies

The analysed samples are generally characterised by high amounts of particulate organic matter (POM), reaching a maximum in the middle of the studied KCF interval (122.520-122.145 m). Samples from the lower and central parts of the interval (122.720-122.145 m) are characterised by visually greater amounts of amorphous organic matter (AOM), which decreases towards the top of the interval. The palynofacies assemblages are dominated by marine palynomorphs in the central part of the investigated section and by terrestrial particles in the lower and upper parts.

### 5.3.2.1. Terrestrial particles

Figure 5.3 demonstrates that terrestrial particles display rather stable absolute abundances, with only a minor drop (from 120 000-334 000 to 70 000-90 000 particles/g) in the uppermost samples (121.92-121.82 m). Brown wood which is the most abundant terrestrial particle, displays higher absolute abundances (53 000-188 000 particles/g) in the deeper and middle part of the interval, and decreased relative abundances in the middle part of the section (15-30%) compared to the upper- and lowermost samples (35-50%; Fig. 5.7-5.8). Gymnosperm pollen shows high absolute and relative abundances (40 000-100 000 grains/g and 10-30%, respectively) in the deeper and middle part of the studied section and displays a decreased abundance (from 23 000-112 000 to 5000-11 000 grains/g) only in the uppermost part of the interval (121.92-121.82 m). The gymnosperm assemblage is dominated by *Classopollis* pollen.

Bisacate pollen, spores and black wood (with exception of samples from 121.92-121.82 m) constitute an insignificant portion of the palynofacies assemblages (0-3%, 0-2% and 0-4%, respectively).
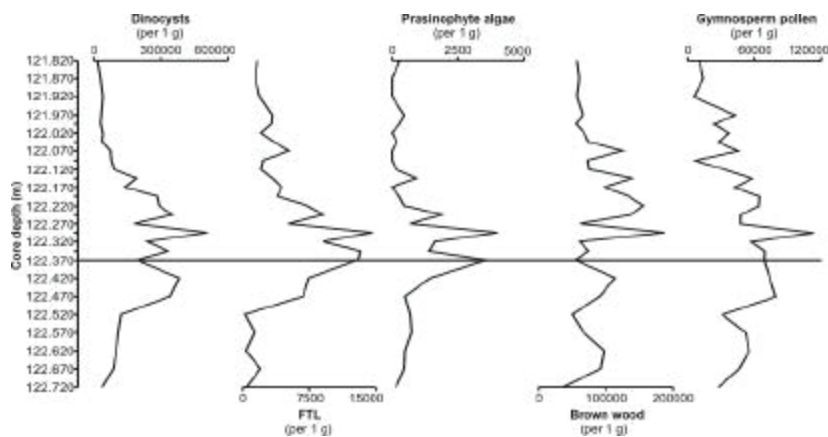


*Fig. 5.7. Absolute abundances (per g sediment) of selected palynofacies categories: total amount of dinocysts, foraminiferal test linings (FTL), prasinophyte algae, brown wood and gymnosperm pollen.*

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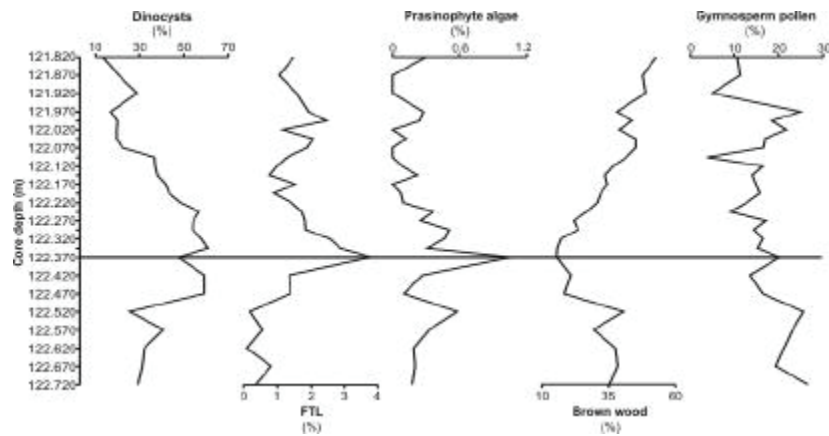
*Fig. 5.8. Relative abundances (%) of selected palynofacies categories: dinocysts, foraminiferal test linings (FTL), prasinophyte algae, brown wood and gymnosperm pollen.*

### 5.3.2.2. Marine palynomorphs

Total marine palynomorphs are characterised by higher absolute and relative abundances (100 000-455 000 particles/g and 42-65% respectively) in the central part of the interval (Fig. 5.3). Dinocysts constitute the majority of the marine palynomorphs. Figures 5.4 and 5.5 show that their highest absolute and relative abundances (170 000-500 000 cysts/g and 40-60%, respectively) occur in the middle of the described section, and that these decrease significantly upwards (to 50 000-100 000 cysts/g and 14-37%; Fig. 5.7-5.8). Proximate dinocysts contribute 10-40%, chorate 3-15% and cavate 1-20% of the palynofacies assemblages. Abundances of these three groups of dinocysts generally follow the trend of total dinocyst concentrations and are higher in the lower and middle part of the studied interval. A total of 36 dinocyst species were encountered, of which *Cribriperidinium* sp. 1, *Sirmiodinium grossi*, *Systematophora* spp. (including *Systematophora areolata*), *Circulodinium* spp., *Glossodinium dimorphum*, *Cyclonephelium* spp. and *Senoniasphaera jurassica* have the highest absolute and relative abundances. *Circulodinium* spp., *Cyclonephelium* spp., *S. jurassica, Systematophora* spp. and *S. grossi* have higher absolute and relative abundances (4000-48 000 cysts/g and 3-14%, 1000-16 000 cysts/g and 2-6%, 10 000-85 000 cysts/g and 6-25%, 9000-39 000

cysts/g and 6-20%, 3000-20 000 cysts/g and 2-6% respectively) in the lower and middle part of the interval (122.720-122.145 m; Fig. 5.9-5.10). *Cribroperidinium* sp. 1 is characterised by highest absolute and relative abundances (20 000-110 000 cysts/g and 8-24% respectively) in the central part of the section. The absolute abundance of *G. dimorphum* is higher (5000-37 000 cysts/g) in the lower and middle part of the studied interval; however, its relative abundance does not follow the same pattern, but oscillates cyclically from low (2-4%) to higher portions (up to 11%) throughout the section.

Prasinophyte algae have higher absolute abundances in the centre of the investigated section (500-4000 algae/g; Fig. 5.7-5.8). Foraminiferal test linings (FTLs), prasinophyte algae, and acritarchs are characterised by overall low abundances throughout the studied section.
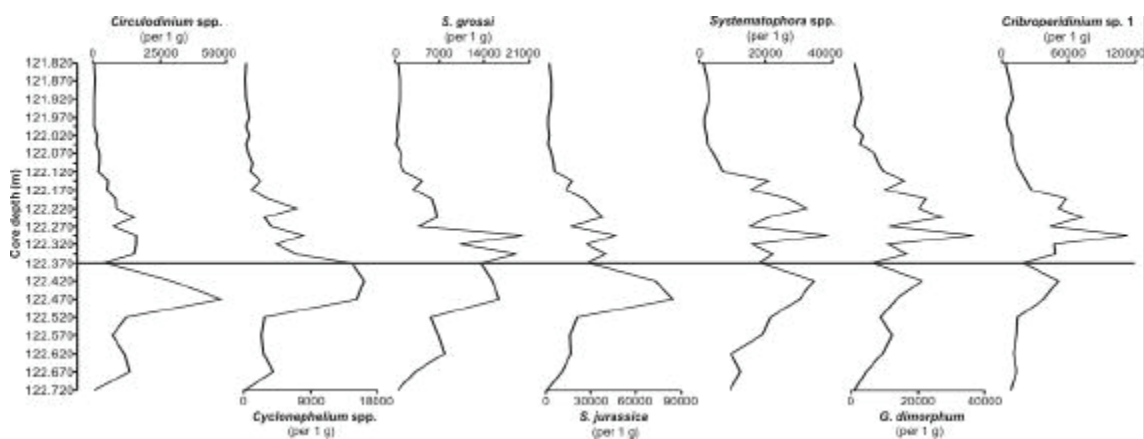


*Fig. 5.9. Absolute abundances (per g sediment) of selected dinocyst taxa: Circulodinium spp., Cyclonephelium spp., Sirmiodinium grossi, Senoniasphaera jurassica, Systematophora spp., Glossodinium dimorphum, Cribroperidinium sp. 1.*

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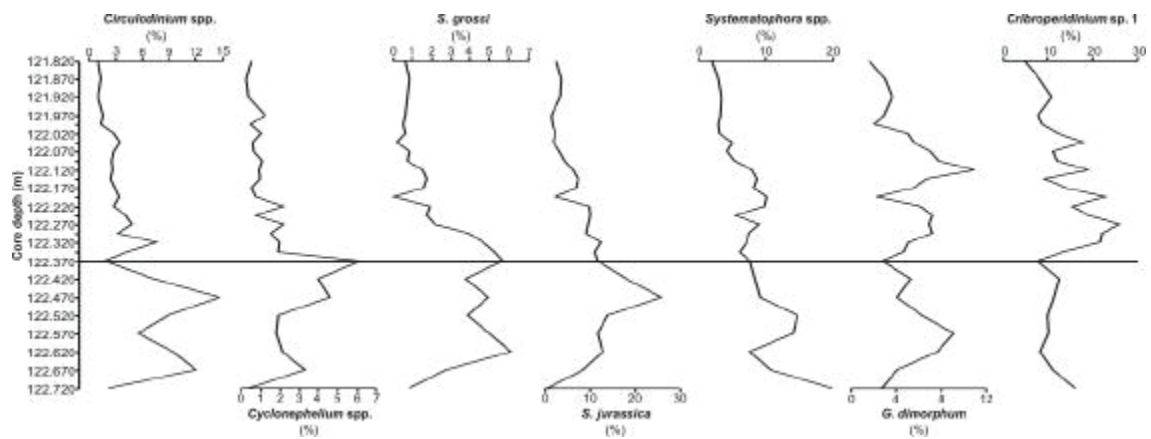
*Fig. 5.10. Relative abundances (%) of selected dinocyst taxa: Circulodinium spp., Cyclonephelium spp., Sirmiodinium grossi, Senoniasphaera jurassica, Systematophora spp., Glossodinium dimorphum, Cribroperidinium sp. 1.*

### 5.3.3. PCA

During PCA analysis, which was applied to dinocyst, palynofacies and chemical element data, five dinocyst species: *Circulodinium* spp., *Cyclonephelium* spp., *S. jurassica*, *S. grossi* and *Systematophora* spp., prasinophyte algae and TOC were grouped together on one side of the first PCA axis (Fig. 5.11) which explains 66% of the dataset variation; Ba and brown wood were placed on the opposite side of the axis. The second axis, of which one end is dominated by redox-sensitive elements (Fe, Mn, S), explains 23% of total variation.
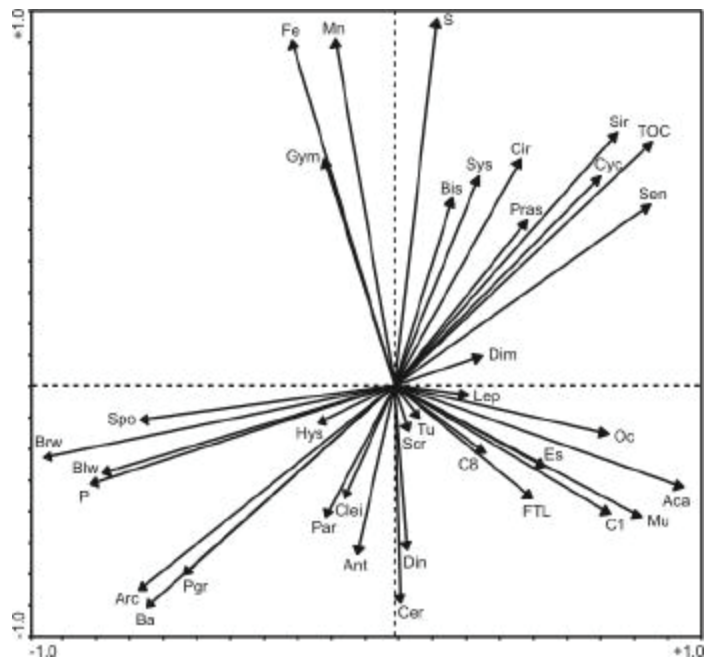
Fig. 5.11. Results of PCA analysis showing the variations in dinocyst, palynofacies and chemical data distribution. Aca – Acanthaulax spp., Ant – Pareodinia antenata, Arc – acritarchs, Ba – barium, Bis – bisacate pollen, Blw – black wood, Brw – brown wood, C1 – Cribroperidinium sp. 1, C8 – Cribroperidinium sp. 8, Cer – Pareodinia ceratophora, Cir – Circulodinium spp., Clei – Cleistosphaeridium spp., Cyc – Cyclonephelium spp., Dim – Glossodinium dimorphum, Din – Dingodinium jurassicum, Es – Escharisphaeridia spp., Fe – iron, FTL – foraminiferal test linings, Gym – gymnosperm pollen, Hys – Hystrichodinium pulchrum, Lep – Leptodinium subtile, Mn – manganese, Mu – Muderongia spp., Oc – Occisucysta balios, P – phosphorus, Par – Pareodinia spp., Pgr – Prolixosphaeridium granulosum, Pras – prasinophyte algae, S – sulphur, Scr – Scriniodinium spp. , Sen – Senoniasphaera jurassica, Sir – Sirmiodinium grossi, Spo – spores, Sys – Systematophora spp., TOC – total organic carbon, Tu – Tubotuberella apatela.

## 5.4. Discussion

Based on the overall palynological and inorganic geochemical record of the KCF interval investigated, we find that it can be separated into a lower and an upper part. The lower part, reaching to about the middle of the interval, is

characterized by elevated abundances of marine palynomorphs, TOC and calcite contents, a low contribution of terrigenous elements and enriched redox-sensitive/sulphide-forming elements. This pattern basically reverses in the upper part, where contents of detrital elements are high, marine palynomorph abundances and TOC and calcite contents are lower, and enrichments of elements indicative of oxygen-depleted conditions are low.

The detrital element and terrestrial palynomorph and phytoclast contents of the sediment indicate a major contribution of terrestrial input to bulk sediment accumulation. With TOC contents exceeding 2 wt% over the whole interval investigated, the sediment is referred to as black shale. The TOC contents are high (up to 8.8%) in the lower and middle part of the studied interval, and moderate (2-3%) in the upper part. The data for the short vertical succession investigated here correlates well with the TOC and carbonate data presented for the Swanworth Quarry 1 borehole by Morgans-Bell et al. (2001; also available on the RGGE website: http://kimmeridge.earth.ox.ac.uk/ graphiclog.php). Based on that TOC record, Weedon et al. (2004) calculated depositional and burial flux of OM in the Kimmeridgian Wessex Basin, resulting in an average export production of 220 g C $m^{-2}a^{-1}$ in a 38 ka cycle. This is even lower than the present-day average export production on continental shelves (~270 g C $m^2a^{-1}$), but was punctuated by some periods of strongly enhanced productivity. Their calculations for the interval investigated here yield a maximum export production of ~300 g C $m^2a^{-1}$, which has to be regarded as intermediate to low compared to modern values. Tyson (2004), in his work on TOC variation in the KCF, provides even lower palaeoproductivity estimates in the uppermost part of the KCF, below 50 g C $m^{-2}a-1$.

In the light of elevated OM values inferred from our EFs and palynofacies data, we suggest an intermediate marine productivity, supported by nutrients derived from proximal sediment source areas.

From the observed good to very good linear correlation of detrital elements (Appendix 5.2), we infer that the source of terrigenous material did not change through the period of deposition (e.g. Tribovillard et al., 1994). This is confirmed by rather stable proportions of the phytoclasts. As expected, the detrital fraction

shows a clear negative correlation towards carbonate, indicating that marine biogenic and terrigenous components were diluting each other. Such a dilution effect can be seen in the middle of the studied interval, where we observe a significant shift from terrestrial-dominated to marine-dominated palynofacies assemblage. This change results mainly from much higher recovery of marine palynomorphs, in particular dinocysts, while the abundance of terrestrial particles remains relatively stable.

The TOC pattern parallels the distribution of marine palynomorphs, and groups together with marine palynomorphs on the same side of PCA axis. In contrast it correlates negatively with the detrital elements and plots on the other end of the PCA axis from terrestrial particles, indicating that the TOC record is primarily bound to marine primary productivity rather than to continental OM input.

Higher TOC content and marine palynomorph abundances in the central part of the studied interval in comparison to the upper part, imply higher primary palaeoproductivity in the surface waters of the Wessex Basin, enhanced preservation of OM under oxygen-depleted bottom water and sediment conditions, or a combination of both.

Changes in Cu values that parallel the TOC profile indicate that Cu is primarily bound to the OM export flux, and is not significantly remobilised diagenetically due to hydrogen sulphide production. This implies that differences in palaeoproductivity may have been triggered by variations in the availability of micronutrients like Cu, and was thus the reason for the shift in marine palynomorphs and TOC content of the sediments. However, if enhanced productivity is indeed responsible, elevated values of other nutrient-related elements such as P would be expected, which is not the case. In addition, abundances of terrestrial particles, such as brown wood, do not vary significantly throughout the interval, suggesting that run-off and hence nutrient delivery from the hinterland was stable.

The pattern of the C/P ratio indicates a preferential removal of P from OM in the centre of the interval. Selective P recycling under anoxic conditions has been reported from various modern and ancient anoxic environments (e.g.

Ingall et al., 1993; Slomp et al., 2002; Benitez-Nelson et al., 2007), indicating the most reducing conditions in the centre of the investigated interval. The P peak in the upper interval could be a combined effect of phosphate re-adsorption onto Fe oxides (e.g. Slomp et al., 1996; Eijsink et al., 1997) and less selective P removal from OM, which both point to less reducing conditions in the upper interval.

A significant shift in redox conditions at ~122.37 m drilling depth, which is also the location of the highest TOC content observed in this interval, is indicated by redox-sensitive element (Fe, Mn, S) patterns. Anoxic sediments are generally depleted in Mn relative to average shale (Calvert and Pedersen, 1993; Brumsack, 2006). In terms of mean Mn content, this is also the case in the KCF interval. However, the fact that Mn correlates well with S and Fe and correlates negatively with the Fe/S ratio is contradictory to this. We suggest that in the case of KCF deposition, Mn was possibly co-precipitated with or incorporated into Fe-sulphides. Indeed, Huerta-Diaz & Morse (1992), in their extensive study on the degree of trace metal pyritization, found that Mn exhibits a good linear correlation to the degree of pyritization (DOP) as soon as a certain threshold concentration of hydrogen sulphide (>1 µmol/l) in pore waters is reached. Similar findings are reported by Lyons & Severmann (2006) from the anoxic basins of the Black Sea, Orca Basin and Effingham Inlet, where Mn is scavenged by Fe oxides and subsequently undergoes a similar transformation to Mn sulphide.

In the sediments investigated, the relationships between Fe, Al and S provide important information about the redox milieu during deposition. The strongly enhanced values of Fe/Al below 122.37 m depth correlate with a low Fe/S ratio, indicating that below this depth, iron is mainly bound to sulphides. Values of the Fe/Al ratio above average shale levels have been reported from areas such as the Black Sea (Wijsman et al., 2001; Anderson & Raiswell, 2004) and are interpreted as a sign for syngenetic pyrite formation, i.e. within the water column. Using this information, the abrupt change to much lower Fe/Al values above 122.37 m documents a dramatic shift in bottom water redox conditions. This change might have been triggered by a rapid oxygenation of

the water column and sediment, thereby oxidizing sedimentary pyrite in the sediment through downward propagation of an oxidation front. The iron and sulphur records are corroborated by the magnetic susceptibility record published on the RGGE website. That record shows low susceptibility values of ~$10*10^{-5}$ SI at the depth interval where TOC, S and Fe/Al are elevated, indicating the dominance of the paramagnetic iron sulphide pyrite. Above this depth, susceptibility rises to more than $20*10^{-5}$ SI, which is paralleled by lower TOC and S contents, and higher Fe/S ratio and DOP, documenting a shift to ferromagnetic Fe (oxyhydr)oxides. Thus, the borehole depth of 122.37 m must represent the maximum oxygen penetration depth, as below this the original anoxic sediment signature is preserved.

High abundances of marine palynomorphs and hence high TOC values in the lower part of the studied interval might therefore be caused by better preservation of OM during and after deposition. Preservation of OM is known to be enhanced under anoxic, and especially euxinic, conditions (e.g. Middelburg, 1989; Canfield, 1994; Hartnett et al., 1998; Sun et al., 2002; Keil et al., 2004). The centre of our KCF interval is characterised by elevated abundances of AOM that co-occurs with relatively increased absolute abundances of prasinophyte algae, indicating that this section of the sediment could have been deposited in a dysoxic/anoxic setting (Tyson, 1995; Al-Ameri et al., 1999; Ercegovac & Kostic, 2006). The dominance of terrestrial particles in the upper part of the studied interval indicates more oxic conditions (Tyson, 1987; Ercegovac and Kostic, 2006). Under such conditions, OM is degraded due to its prolonged exposure time to oxygen (Hartnett et al., 1998). The much more pronounced decrease of marine compared to terrestrial particles could be an effect of greater resistance of the latter to decomposition processes, since the woody phytoclasts contain lignin that decays more slowly than most other organic compounds (Canfield, 1994 and references therein; Baldock et al., 2004).

More oxic conditions in the upper part of the interval are also demonstrated by a drop in the dinocyst abundances, with all dinocyst species decreasing significantly. However *Circulodinium* spp., *Cyclonephelim* spp., *Sirmiodinium*

*grossi*, *Senoniasphaera jurassica* and *Systematophora* spp. experienced a stronger decrease than *Glossodinium dimorphum* and *Cribroperidinium* sp. 1. The abundances of *Circulodinium* spp., *Cyclonephelim* spp., *S. grossi*, *S. jurassica* and *Systematophora* spp. closely parallel the TOC pattern and group together with TOC during PCA analysis, which suggests they are possibly affected by changes in redox conditions. Both a general and a differential degradation of dinocysts suggest that dinocyst assemblages are affected by species-selective preservation/degradation. The process of species-selective dinocyst preservation is known from modern and quaternary sediments and documented by natural and laboratory experiments (Zonneveld et al., 1997, 2001; Hopkins and McCarthy, 2002; **Chapter 3**). For Cretaceous dinocysts, laboratory experiments have also confirmed species-specific degradation potential (Schrank, 1988). However, no similar studies have yet been carried out on Jurassic species. In the data collected for this study there is a major shift in relative dinocyst abundances which occurs at ~122.37 m depth. Changes in absolute abundances of dinocyst species are visible at the same depth, but are much less pronounced.

Mediterranean sapropels and Atlantic turbidites have also been the subject of palynological studies that reported a rapid decrease in concentrations of dinocysts and pollen at the OBFs (Zonneveld et al., 1997, 2001; Versteegh and Zonneveld, 2002). For example, the total dinocyst concentrations of the oxidised part of an Atlantic turbidite yielded only 10% of the dinocyst abundances from the unoxidised turbidite section (Zonneveld, 1997). Although we observe a drop in total concentrations of dinocysts and pollen in the oxidised part of our KCF interval, this decrease is, however, rather gradual, unlike the rapid decrease seen in the case of the turbidites and sapropels.

The fact that the TOC and marine palynomorph records do not show a similar, very rapid change as observed at oxidation fronts in Mediterranean sapropels or turbidites from the Madeira Abyssal Plain - might be due to the relatively large contribution of more refractory terrestrial organic matter to the total organic carbon pool in the KCF. In addition, very high S values argue strongly for production of hydrogen sulphide, and thus euxinic conditions, in the

sediments. Sulphur in anoxic sediments is in general either bound to metal sulphides, mostly pyrite, or to sulphurized organic matter. Organic matter in the KCF is known to be strongly sulphurized through excess in hydrogen sulphide production during microbial sulphate reduction relative to reactive Fe(III) minerals in the sediment (e.g. Boussafir & Lallier-Vergès,1997; Werne et al., 2000; Riboulleau et al., 2003). This mechanism of "natural vulcanisation" (Boussafir & Lallier-Vergès, 1997) increases the preservation potential of organic molecules under anoxic conditions. These two facts might explain why the KCF OM was less reactive and degradable by oxygen penetrating into the sediment. Therefore we believe that any oxygen burndown front would not alter, or ultimately consume, the OM in such a way as described for Mediterranean sapropels, but rather generate a gradual upcore decrease of TOC as observed in our samples.

The chemical composition of the KCF interval investigated here is generally similar to average shale composition (Turekian & Wedepohl, 1961), but differs significantly from classic black shales such as the Late Cretaceous Cenomanian-Turonian Boundary Event (CTBE) deposits and Pliocene-Pleistocene Mediterranean sapropels (review by Brumsack, 2006). On the other hand, the depositional setting of the KCF in the shallow Tithonian Wessex Basin differs markedly from the basins where CTBE deposits and sapropels accumulated. Enrichments of Cr, Cu, Ni, P, Sr, V and Zn are in accordance with the common EFs of black shales, but nonetheless, these enrichments in the KCF are considerably lower than in CTBE or sapropel deposits. This indicates that conditions characteristic for black shale formation, such as high primary productivity, oxygen deficiency or even free hydrogen sulphide in bottom waters, were present, but much less pronounced during KCF deposition.

Although triggered by the same general mechanism, i.e. a rapid increase of oxygen in bottom waters after a period of oxygen depletion, the imprints of oxidation fronts and their palaeoenvironmental interpretation may be manifested in different ways in different depositional settings. Major palaeogeographical differences between the Mediterranean and Atlantic sedimentary settings and the Jurassic Wessex Basin are (1) the water depths, which were more than

2000 m for the Mediterranean sapropels (Thomson et al., 1995; Van Santvoort et al., 1996), more than 4000 m for Atlantic cores (Wilson et al., 1985; Thomson et al., 1993; Cowie et al., 1995; De Lange, 1998; König et al., 1999; Robinson, 2000), but only a few 100 m for the Wessex Basin (Gallois & Cox, 1974; Oschmann, 1988; Gallois, 2000); (2) the distance to a potential source of detrital sediments and terrigenous organic matter, which is much shorter for a shelf than for an open ocean setting; (3) the persistence of anoxic/euxinic conditions at the sea floor, which is supposed to have been much more stable during KCF deposition than during the rather punctuated sapropel periods. These differences, in turn, substantially influence the geochemistry of the respective sediments.

## 5.5. Conclusions

The studied KCF interval can be divided into two parts characterised by different proportions of marine and terrestrial POM and different chemical compositions. The lower part is characterised by a high TOC content and greater abundances of marine palynomorphs, all of which decrease in the upper part of the interval. The concentrations of redox-sensitive elements indicate more anoxic and more oxic conditions in the lower and upper part of the interval respectively. Palynofacies analysis also suggests more oxic conditions in the upper part of the section. Rapid changes in sediment chemistry indicating a shift in redox conditions occur at about 122.37 m drilling depth, but the changes in TOC and palynofacies are more gradual. The major reason for these changes is probably post-depositional OM degradation by down-section penetration of oxygen.

## Acknowledgements

## 5.6. References

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## CHAPTER 6

### Conclusions

Although the dinocyst-based method to separate productivity from preservation gives important background information for quantifiying OM degradation, there are still several tangling questions that have to be answered before the method can be used in a broader scope. In the presented work we have addressed three of these questions.

*(1) What is the S-cyst degradation rate?* Although selective degradation of dinocysts is a known process, its rate is still unknown. Laboratory experiments have proven that already half an hour is enough to oxidise a considerable number of S-cysts in the assemblage (Hopkins and McCarthy, 2002). In the natural environments this process is slower but still faster than generally assumed. One-year exposure to oxygenated seawater already leads to significant changes in dinocyst assemblages with the most sensitive dinocysts (i.e. *Brigantedinium* spp. and *Echinidinium granulatum*) decreasing by 24-57% (**Chapter 2 and 3**). This implies that selective degradation is an important factor to be taken into account even when analysing freshly deposited material and that it cannot be neglected on any timescale.

*(2) What is the relationship between S-cysts degradation and $O_2$ concentrations?* Species-selective dinocyst degradation, as well as degradation of entire OM, was initially considered to be a first-order process with respect to labile components concentration and the OET. Zonneveld et al. (2007) showed that the dinocyst degradation in surface sediments depends on $O_2$ concentration in the bottom waters (Zonneveld et al., 2007). The dinocyst assemblages from two sediment cores from the Southern Ocean were affected by species-selective aerobic degradation. The calculated degradation constant *k* of S-cysts correlates strongly with the pore-water $O_2$ concentrations implying that the dinocyst degradation, and hence the OM decomposition, is dependent

not only on the OET and concentration of reactive components but also on the bottom- and pore-water $O_2$ concentrations (**Chapter 4**).

*(3) Are extinct dinocyst prone to species-selective aerobic degradation?* The modelling of the future climate cannot be made without looking at past climatic changes. Understanding the factors that governed the very warm climate of the Mesozoic could considerably improve understanding global warming processes that take place today. It is suspected that one of the major reasons for the Mesozoic greenhouse world was high $CO_2$ concentration in the atmosphere. Atmospheric $CO_2$ concentration is influenced by burial and degradation of OM, hence the quantification of early diagenetic processes in the Mesozoic sedimentary basins could to be very important. One of the methods employed in the quantification of OM burial/decay is selective dinocyst degradation. Currently, information on selective dinocyst degradation in Mesozoic is scarce. It was noted in laboratory processing that certain Cretaceous dinocyst are very sensitive to oxidation (Schrank et al., 1988). No information is available on *in situ* dinocyst degradation in Cretaceous deposits or on the decomposition of Jurassic species. Our work leads to the conclusion that Jurassic dinocysts are prone to selective degradation, although the dinocyst association changes observed across the reconstructed oxidation front are not as rapid as in sapropels or turbidites (**Chapter 5**).

Coupling palynological and geochemical methods for palaeoenvironmental reconstructions, especially reconstructions of redox conditions, appear to be a powerful tool. The application of independent proxies to investigate the same deposits leads to cross-testing of obtained results and better understanding of once ongoing processes since very often the different approaches not only confirm each others' results but provide complimentary information that would be difficult to extract when using one method alone (**Chapter 5**).

Although previous and ongoing research adds significantly to understanding the influence of (early) diagenesis on fossil records and on OM preservation, several important questions are still to be answered.

There is still little information available on what causes the selective preservation. Different research suggests that the cause lies in the chemical composition of the OM components. Chemical studies on dinocyst wall composition show that S-cysts are mainly composed of aliphatic moieties while R-cysts consist of aromatic compounds (e.g. Kokinos et al., 1998). However very recently it was suggested that above results might originate from artefacts (**Chapter 2**) and hence the ground for the selective dinocyst preservation remains still enigmatic. In spite of this, dinocyst-wall chemistry seems to be one of the major topics to focus on in future research.

In the present work, the importance of dinocyst selective degradation for OM decomposition studies is emphasised. This has consequences for research on $CO_2$ sequestration and climate changes as well as for reconstruction of primary productivity and oceanographic conditions. However,these are not the only aspects for which selective dinocyst preservation is an important factor. Dinocysts are broadly used in petroleum industry to assess the age and maturity of petroleum deposits. It is essential to know which marker species might be sensitive to aerobic degradation and hence affect dinocyst-based biostratigraphy of the deposits.

Chemistry of dinocyst walls and degradation of marker species are two important problems that have to be addressed if we want to come closer to understanding selective preservation mechanisms. The results of the presented project provide a deeper insight pressing issues on species-selective dinocyst decay and therefore contribute significantly to the research on the vast topic of OM degradation.

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*Appendix 2.1. Dinoflagellate cyst species grouped with respect to their sensitivity to oxygen availability in pore waters according to Zonneveld et al. (2001).*

| | |
|---|---|
| Extremely sensitive | Cysts of *Protoperidinium* species (a.o. *Brigantedinium* spp.)<br>*Echinidinium* species |
| Moderately sensitive | *Lingulodinium machaerophorum*<br>*Protoceratium reticulatum*<br>*Pyxidinopsis reticulatum*<br>*Spiniferites* species (including *Spiniferites bentorii, Spiniferites mirabilis, Spiniferites pachydermus* and *Spiniferites ramosus*) |
| Resistant | *Nematosphaeropsis labyrinthus*<br>*Impagidinium aculeatum*<br>*Impagidinium paradoxum*<br>*Impagidinium patulum*<br>*Impagidinium plicatum*<br>*Impagidinium sphaericum*<br>*Operculodinium israelianum*<br>*Pentapharsodinium dalei*<br>*Polysphaeridium zoharyi* |

*Appendix 2.2. Degradation factors of organic matter types. Cyst and Pollen in numbers per dry gram sediment. ox., oxidised; unox., unoxidized; Df, degradation factor; k, degradation constant; LCK, long chain ketones; LL, loliolide and isololiolide; n.d., not detectable. Data after Prahl et al. (1997) and Zonneveld et al (1997, 2001). \*$C_{29}$ and $C_{31}$ alkanes; [†]$C_{26}$ and $C_{28}$ alkanes; [§]$C_{20}$ to $C_{30}$ alkanes.*

| | Sample | TOC% | Resistant cysts | Sensitive cysts | Pollen | *n*-alkanes (µg/g) | n-acids (µg/g) | LCK | LL |
|---|---|---|---|---|---|---|---|---|---|
| Mediterranean S1 Sapropel | ox. | 0.44 | 434 | 5.1 | 832 | 1.17* | 0.83[#] | n.d. | n.d. |
| | unox. | 2.65 | 580 | 4516 | 13903 | 3.92* | 5.87[#] | abund | abund |
| | Df | 6.02 | 1.33 | 885.5 | 16.7 | 3.3 | 7.1 | | |
| | k | 4.2 | 0.7 | 15.9 | 6.6 | 2.8 | 4.6 | | |
| Madeira Abyssal Plain f-turbidite | ox. | 0.185 | 756 | 15.6 | 82 | 61.05[§] | 64.75[§] | 109 | |
| | unox. | 0.973 | 1032 | 8710 | 2070 | 96.52^ | 389^ | 919 | |
| | Df | 5.26 | 1.37 | 558 | 25.2 | 1.58 | 6.01 | 8.42 | |

*Appendix 3.1. Count data of organic-walled dinoflagellate cyst*

| Sub-sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Namibia original | 331.5 | 6.0 | 12.0 | 1.5 | 3.5 | 1.0 | 0.0 | 50.5 | 43.5 | 61.5 | 4.0 | 5.5 |
| Namibia ox UB | 200.5 | 1.0 | 7.0 | 0.5 | 1.0 | 0.0 | 0.0 | 47.5 | 21.0 | 53.0 | 5.0 | 0.5 |
| Namibia anox UB | 160.0 | 0.0 | 6.0 | 1.0 | 0.0 | 1.0 | 0.0 | 25.0 | 21.5 | 28.5 | 1.5 | 3.5 |
| Namibia ox BB | 217.5 | 6.0 | 3.0 | 1.0 | 0.0 | 1.0 | 0.0 | 50.5 | 20.0 | 45.0 | 5.0 | 2.0 |
| Namibia anox BB | 75.0 | 0.0 | 2.5 | 0.0 | 0.0 | 0.0 | 0.0 | 11.0 | 9.5 | 13.0 | 1.0 | 2.0 |
| Sapropel original | 186.5 | 0.0 | 0.0 | 1.0 | 0.0 | 0.0 | 4.5 | 0.0 | 0.0 | 8.0 | 6.0 | 0.0 |
| Sapropel ox UB | 133.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.0 | 0.0 | 0.0 | 2.0 | 17.0 | 0.0 |
| Sapropel anox UB | 139.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6.0 | 0.0 | 0.0 | 4.5 | 7.0 | 0.0 |
| Sapropel ox BB | 168.0 | 0.0 | 1.0 | 4.0 | 0.0 | 0.0 | 4.0 | 1.0 | 1.0 | 4.0 | 15.5 | 0.0 |
| Sapropel anox BB | 177.5 | 0.0 | 1.0 | 1.0 | 0.0 | 0.0 | 4.5 | 1.0 | 0.0 | 5.0 | 9.0 | 0.0 |

| Sub-sample | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Namibia original | 17.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 7.0 | 17.5 | 1.0 | 9.5 | 0.0 |
| Namibia ox UB | 22.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.5 | 16.5 | 3.0 | 7.5 | 0.0 |
| Namibia anox UB | 9.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.5 | 9.0 | 2.0 | 5.0 | 0.0 |
| Namibia ox BB | 27.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6.0 | 25.5 | 5.0 | 8.0 | 0.0 |
| Namibia anox BB | 4.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.0 | 4.5 | 1.5 | 2.5 | 0.0 |
| Sapropel original | 3.0 | 40.5 | 1.0 | 5.0 | 0.0 | 2.0 | 14.5 | 3.0 | 4.0 | 2.0 | 114.5 | 2.0 |
| Sapropel ox UB | 1.0 | 80.0 | 0.0 | 4.0 | 1.0 | 1.0 | 9.0 | 2.0 | 4.0 | 1.0 | 105 | 0.0 |
| Sapropel anox UB | 2.0 | 31.0 | 0.0 | 0.0 | 1.0 | 2.0 | 13.5 | 2.5 | 2.5 | 2.0 | 85.5 | 1.0 |
| Sapropel ox BB | 5.0 | 66.5 | 0.0 | 3.5 | 3.0 | 2.0 | 19.0 | 3.0 | 8.0 | 1.0 | 138.0 | 4.0 |
| Sapropel anox BB | 2.0 | 29.0 | 0.0 | 3.0 | 1.0 | 1.0 | 15.5 | 3.0 | 4.0 | 2.0 | 104.5 | 2.0 |

| Sub-sample | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|
| Namibia original | 0.0 | 6.5 | 579.0 | 0.27570 | 1,25 | 168008.71 |
| Namibia ox UB | 0.0 | 4.0 | 395.0 | 0.04250 | 7,50 | 123921.57 |
| Namibia anox UB | 0.0 | 3.0 | 280.5 | 0.00210 | 80,00 | 166964.29 |
| Namibia ox BB | 0.0 | 4.0 | 427.0 | 0.11830 | 2,50 | 144378.70 |
| Namibia anox BB | 0.0 | 1.5 | 130.5 | 0.00096 | 80,00 | 169921.88 |
| Sapropel original | 4.0 | 0.0 | 400.5 | 0.47060 | 30,00 | 2836.80 |
| Sapropel ox UB | 1.0 | 0.0 | 363.5 | 0.77530 | 30,00 | 1562.84 |
| Sapropel anox UB | 2.0 | 0.0 | 302.0 | 0.16650 | 65,00 | 2790.48 |
| Sapropel ox BB | 7.0 | 0.0 | 454.5 | 0.81040 | 25,00 | 2243.34 |
| Sapropel anox BB | 2.0 | 0.0 | 367.0 | 0.25590 | 50,00 | 2868.31 |

UB – Urania Basin area, BB – Bannock Basin area, ox – oxic exposure, anox – anoxic exposure, 1 – *Brigantedinium* spp., 2 – *Protoperidinium americanum*, 3 – *Protoperidinium conicum*, 4 – *Protoperidinium subinerme*, 5 – *Protoperidinium leonis*, 6 – *Protoperidinium pentagonum*, 7 – *Protoperidinium compressum*, 8 – *Echinidinium aculeatum*, 9 – *Echnidinium granulatum*, 10 – *Echinidinium* spp., 11 – cyst of *Pentapharsodinium dalei*, 12 – cyst of *Polykrikos kofoidii*, 13 – *Nematosphaeropsis labyrinthus*, 14 – *Impagidinium aculeatum*, 15 – *Impagidinium paradoxum*, 16 – *Impagidinium sphaericum*, 17 – *Impagidinium plicatum*, 18 – *Impagidinium* spp., 19 – *Lingulodinium machaerophorum*, 20 – *Operculodinium centrocarpum*, 21 – *Operculodinium israelianum*, 22 – *Operculodinium* spp., 23 – *Spiniferites* spp., 24 – *Spiniferites mirabilis*, 25 – *Spiniferites bullouides*, 26 – *Spiniferites ramosus*, 27 – total counts, 28 – total weight of the sub-sample in grams, 29 – part of the sub-sample counted in %, 30 – cysts concentration per 1 gram dry sediment.

*Appendix 3.2. The 95% lower and upper confidence limits for absolute and relative abundances of the selected dinocyst species. UB – Urania Basin area, BB – Bannock Basin area, ox – oxic exposure, anox – anoxic exposure.*

| Sample | Species | Absolute abundances (cysts/1 g) | | | Relative abundances (%) | | |
|---|---|---|---|---|---|---|---|
| | | Concentration | Lower limit | Upper limit | Percentage | Lower limit | Upper limit |
| Namibia original | *Brigantedinium* spp. | 96191.51 | 89551.96 | 103029.46 | 57.25 | 53.30 | 61.32 |
| | *E. aculeatum* | 14653.61 | 11048.04 | 19023.02 | 8.72 | 6.58 | 11.32 |
| | *E. granulatum* | 12622.42 | 9274.60 | 16751.46 | 7.51 | 5.52 | 9.97 |
| | *Echinidinium* spp. | 17845.48 | 13878.88 | 22549.87 | 10.62 | 8.26 | 13.42 |
| | *N. labyrinthus* | 4932.90 | 2898.96 | 7828.28 | 2.94 | 1.73 | 4.66 |
| | *O. israelianum* | 5077.98 | 3010.97 | 8004.44 | 3.02 | 1.79 | 4.76 |
| Namibia ox UB | *Brigantedinium* spp. | 62901.96 | 56950.21 | 69141.54 | 50.76 | 45.96 | 55.79 |
| | *E. aculeatum* | 14901.96 | 11193.35 | 19390.33 | 12.03 | 9.03 | 15.65 |
| | *E. granulatum* | 6588.24 | 4136.23 | 9928.84 | 5.32 | 3.34 | 8.01 |
| | *Echinidinium* spp. | 16627.45 | 12723.92 | 21290.69 | 13.42 | 10.27 | 17.18 |
| | *N. labyrinthus* | 7058.82 | 4514.77 | 10484.26 | 5.70 | 3.64 | 8.46 |
| | *O. israelianum* | 5176.47 | 3026.12 | 8238.77 | 4.18 | 2.44 | 6.65 |
| Namibia anox UB | *Brigantedinium* spp. | 95238.10 | 85837.98 | 105038.20 | 57.04 | 51.41 | 62.91 |
| | *E. aculeatum* | 14880.95 | 9840.21 | 21497.58 | 8.91 | 5.89 | 12.88 |
| | *E. granulatum* | 12797.62 | 8134.60 | 19076.50 | 7.66 | 4.87 | 11.43 |
| | *Echinidinium* spp. | 16964.29 | 11579.17 | 23887.18 | 10.16 | 6.94 | 14.31 |
| | *N. labyrinthus* | 5357.14 | 2484.66 | 10023.30 | 3.21 | 1.49 | 6.00 |
| | *O. israelianum* | 5357.14 | 2484.66 | 10023.30 | 3.21 | 1.49 | 6.00 |
| Namibia ox BB | *Brigantedinium* spp. | 73541.84 | 66865.52 | 80526.87 | 50.94 | 46.31 | 55.77 |
| | *E. aculeatum* | 17075.23 | 12940.58 | 22052.90 | 11.83 | 8.96 | 15.27 |
| | *E. granulatum* | 6762.47 | 4183.85 | 10310.57 | 4.68 | 2.90 | 7.14 |
| | *Echinidinium* spp. | 15215.55 | 11302.79 | 19991.76 | 10.54 | 7.83 | 13.85 |
| | *N. labyrinthus* | 9298.39 | 6244.32 | 13286.51 | 6.44 | 4.32 | 9.20 |
| | *O. israelianum* | 8622.15 | 5686.44 | 12500.86 | 5.97 | 3.94 | 8.66 |
| Namibia anox BB | *Brigantedinium* spp. | 97656.25 | 83845.30 | 111805.76 | 57.47 | 49.34 | 65.80 |
| | *E. aculeatum* | 14322.92 | 7393.17 | 24777.14 | 8.43 | 4.35 | 14.58 |
| | *E. granulatum* | 12369.79 | 5984.35 | 22371.99 | 7.28 | 3.52 | 13.17 |
| | *Echinidinium* spp. | 16927.08 | 9341.66 | 27922.05 | 9.96 | 5.50 | 16.43 |
| | *N. labyrinthus* | 5859.38 | 1800.58 | 13920.71 | 3.45 | 1.06 | 8.19 |
| | *O. israelianum* | 5859.38 | 1800.58 | 13920.71 | 3.45 | 1.06 | 8.19 |
| Sapropel original | *Brigantedinium* spp. | 1321.01 | 1186.23 | 1463.42 | 46.57 | 41.82 | 51.59 |
| | *Spiniferites* spp. | 811.02 | 690.39 | 944.27 | 28.59 | 24.34 | 33.29 |
| | *I. aculeatum* | 286.87 | 209.26 | 382.72 | 10.11 | 7.38 | 13.49 |
| | *L. machaerophorum* | 102.71 | 57.52 | 168.77 | 3.62 | 2.03 | 5.95 |
| | Other resistant | 120.41 | 71.05 | 190.33 | 4.24 | 2.50 | 6.71 |
| Sapropel ox UB | *Brigantedinium* spp. | 573.97 | 499.19 | 655.01 | 36.73 | 31.94 | 41.91 |
| | *Spiniferites* spp. | 451.44 | 381.58 | 528.89 | 28.89 | 24.42 | 33.84 |
| | *I. aculeatum* | 343.95 | 280.62 | 416.10 | 22.01 | 17.96 | 26.62 |
| | *L. machaerophorum* | 38.69 | 17.89 | 72.64 | 2.48 | 1.14 | 4.65 |
| | Other resistant | 116.08 | 77.82 | 166.02 | 7.43 | 4.98 | 41.91 |
| Sapropel anox UB | *Brigantedinium* spp. | 1288.98 | 1137.08 | 1450.89 | 46.19 | 40.75 | 51.99 |
| | *Spiniferites* spp. | 790.02 | 654.65 | 941.90 | 28.31 | 23.46 | 33.75 |
| | *I. aculeatum* | 286.44 | 198.95 | 399.02 | 10.26 | 7.13 | 14.30 |
| | *L. machaerophorum* | 124.74 | 68.38 | 207.96 | 4.47 | 2.45 | 7.45 |
| | Other resistant | 115.50 | 61.53 | 196.55 | 4.14 | 2.20 | 7.04 |
| Sapropel ox BB | *Brigantedinium* spp. | 829.22 | 732.72 | 932.89 | 36.96 | 32.66 | 41.58 |
| | *Spiniferites* spp. | 681.15 | 589.64 | 781.10 | 30.36 | 26.28 | 34.82 |
| | *I. aculeatum* | 328.23 | 259.40 | 408.74 | 14.63 | 11.56 | 18.22 |
| | *L. machaerophorum* | 93.78 | 57.13 | 144.73 | 4.18 | 2.55 | 6.45 |
| | Other resistant | 172.75 | 122.18 | 236.61 | 7.70 | 5.45 | 10.55 |
| Sapropel anox BB | *Brigantedinium* spp. | 1387.26 | 1244.70 | 1537.69 | 48.37 | 43.39 | 53.61 |
| | *Spiniferites* spp. | 816.73 | 689.70 | 957.69 | 28.47 | 24.05 | 33.39 |
| | *I. aculeatum* | 226.65 | 154.47 | 319.86 | 7.90 | 5.39 | 11.15 |
| | *L. machaerophorum* | 121.14 | 69.46 | 195.56 | 4.22 | 2.42 | 6.82 |
| | Other resistant | 148.50 | 90.72 | 228.51 | 5.18 | 3.16 | 7.97 |

*Appendix 3.3. The χ² values obtained for the samples with indicated degrees of freedom (d.f.). UB – Urania Basin area, BB – Bannock Basin area, ox – oxic exposure, anox – anoxic exposure*

| Sample | D. f. | χ² |
|---|---|---|
| Namibia ox UB | 6 | 25,93 |
| Namibia anox UB | 6 | 0,27 |
| Namibia ox BB | 6 | 42,39 |
| Namibia anox BB | 6 | 0,27 |
| Sapropel ox UB | 5 | 78,64 |
| Sapropel anox UB | 5 | 0,67 |
| Sapropel ox BB | 5 | 32,09 |
| Sapropel anox BB | 5 | 3,68 |
| Surface ox UB | 4 | 21,19 |
| Surface anox UB | 4 | 9,54 |
| Surface ox BB | 4 | 4,37 |
| Surface anox BB | 4 | 13,06 |

*Appendix 4.1. List of S- and R-cysts (after Zonneveld et al., 1997, 2001; Esper and Zonneveld, 2007; Bockelmann et al., subm).*

| Sensitive dinocysts (S-cysts) | Resistant dinocysts (R-cysts) |
|---|---|
| *Brigantedinium* spp. | *Impagidinium aculeatum* |
| Selenopemphix antarctica | *Impagidinium patulum* |
| *Echinidinium* spp. | *Impagidinium sphaericum* |
| Cyst of *Protoperidinium* spp. | *Impagidinium plicatum* |
| | *Impagidinium strialatum* |
| | *Impagidinium* spp. |
| | *Namatosphaeropsis labyrinthus* |
| | *Operculodinium centrocarpum* |
| | *Operculodinium israelianum* |
| | *Spiniferites* spp. |

*Appendix 4.2. Age of the samples and sedimentation rates in the core 703*

| Sample depth (cm) | Sample mid-point | Age (AD) | Sedimentation rate (cm/yr) |
|---|---|---|---|
| 0.0-0.5 | 0,25 | 2004 | 0,13 |
| 0.5-1.0 | 0,75 | 2000 | 0,05 |
| 1.0-2.0 | 1,5 | 1990 | 0,06 |
| 2.0-3.0 | 2,5 | 1973 | 0,12 |
| 3.0-4.0 | 3,5 | 1964 | 0,05 |
| 4.0-5.0 | 4,5 | 1946 | 0,03 |
| 5.0-7.5 | 6,25 | 1909 | 0,05 |
| 7.5-10.0 | 8,75 | 1862 | 0,05 |

*Appendix 4.3. Age of the samples and sedimentation rates in the core 705*

| Sample depth (cm) | Sample mid-point | Age (AD) | Sedimentation rate (cm/yr) |
|---|---|---|---|
| 0.0-0.5 | 0,25 | 2004 | 1,56 |
| 0.5-1.0 | 0,75 | 2003 | 0,33 |
| 1.0-2.0 | 1,5 | 2002 | 0,41 |
| 2.0-3.0 | 2,5 | 2000 | 0,94 |
| 3.0-4.0 | 3,5 | 1999 | 0,46 |
| 4.0-5.0 | 4,5 | 1996 | 0,36 |
| 5.0-6.0 | 5,5 | 1994 | 0,50 |
| 6.0-7.0 | 6,5 | 1992 | 0,30 |
| 7.0-8.0 | 7,5 | 1988 | 0,36 |
| 8.0-9.0 | 8,5 | 1985 | 0,88 |
| 9.0-10.0 | 9,5 | 1984 | 0,19 |
| 10.0-11.0 | 10,5 | 1979 | 0,64 |
| 11.0-12.0 | 11,5 | 1978 | 0,10 |
| 12.0-13.0 | 12,5 | 1967 | 0,22 |
| 13.0-14.0 | 13,5 | 1963 | 0,08 |
| 14.0-15.0 | 14,5 | 1950 | 0,08 |
| 15.0-16.0 | 15,5 | 1937 | 0,08 |
| 16.0-17.0 | 16,5 | 1924 | 0,09 |
| 17.0-18.0 | 17,5 | 1913 | 0,17 |
| 18.0-19.0 | 18,5 | 1907 | 0,18 |
| 19.0-20.0 | 19,5 | 1901 | 0,10 |
| 20.0-21.0 | 20,5 | 1892 | 0,08 |
| 21.0-22.0 | 21,5 | 1880 | 0,06 |
| 22.0-23.0 | 22,5 | 1864 | 0,07 |
| 23.0-24.0 | 23,5 | 1850 | 0,07 |
| 24.0-25.0 | 24,5 | 1835 | 0,07 |

*Appendix 5.1. Selected element/Al ratios*

| Depth (m) | Cr/Al*10$^{-4}$ | K/Al | Mg/Al | Ti/Al | Zr/Al*10$^{-4}$ | B/Al*10$^{-4}$ |
|---|---|---|---|---|---|---|
| 121,82 | 12,992786 | 0,29407959 | 0,09514922 | 0,05141335 | 13,4703363 | 35,5462182 |
| 121,87 | 12,7394338 | 0,28966761 | 0,09262263 | 0,05053436 | 13,6847746 | 35,6828095 |
| 121,92 | 12,8911292 | 0,29426925 | 0,09145686 | 0,04948054 | 13,2247835 | 35,5308668 |
| 121,97 | 12,9068162 | 0,29755061 | 0,09332589 | 0,05001089 | 13,7745713 | 36,5615325 |
| 121,995 | 13,0661826 | 0,30095428 | 0,0971426 | 0,05227543 | 14,0300445 | 35,5582949 |
| 122,02 | 12,9308912 | 0,29704683 | 0,09642746 | 0,05187081 | 14,0164655 | 35,4643666 |
| 122,045 | 13,0423317 | 0,29274945 | 0,09845182 | 0,0536259 | 14,2795543 | 35,367274 |
| 122,07 | 12,7138609 | 0,28262949 | 0,09025274 | 0,05031084 | 12,9388593 | 34,2986156 |
| 122,095 | 12,6110575 | 0,27817697 | 0,08868145 | 0,05042873 | 13,4031002 | 33,7406238 |
| 122,12 | 12,4453618 | 0,27488725 | 0,08888878 | 0,0505688 | 12,6622072 | 33,7451461 |
| 122,145 | 12,7997611 | 0,27558518 | 0,08624088 | 0,04940609 | 12,6076543 | 33,3895715 |
| 122,17 | 12,6010302 | 0,27184137 | 0,08339469 | 0,04898083 | 12,4319349 | 33,0609929 |
| 122,195 | 12,7494645 | 0,26937789 | 0,08261247 | 0,0485312 | 11,9622565 | 32,4592969 |
| 122,22 | 12,5637746 | 0,26956393 | 0,0809622 | 0,04745885 | 11,8330419 | 33,3045261 |
| 122,245 | 12,7750757 | 0,26519352 | 0,0839902 | 0,04924244 | 12,2015636 | 33,8690484 |
| 122,27 | 12,4553198 | 0,26735115 | 0,07778511 | 0,04594808 | 11,5408594 | 33,0577311 |
| 122,295 | 12,6473312 | 0,26648768 | 0,0793707 | 0,04626788 | 11,8707284 | 32,4566461 |
| 122,32 | 12,5242373 | 0,26766518 | 0,08238078 | 0,04791441 | 12,3153923 | 32,8386015 |
| 122,345 | 12,6529156 | 0,26834338 | 0,08161396 | 0,04638044 | 11,9584858 | 29,797597 |
| 122,37 | 12,8954948 | 0,27510874 | 0,08077932 | 0,04405837 | 11,7944543 | 12,3419455 |
| 122,42 | 12,1171428 | 0,27054894 | 0,08220259 | 0,04568461 | 11,5413119 | 33,4216104 |
| 122,47 | 12,1572365 | 0,27399806 | 0,08070078 | 0,04143004 | 11,1610038 | 14,1074789 |
| 122,52 | 11,8354685 | 0,28787104 | 0,08709766 | 0,04312297 | 11,5931594 | 21,0186733 |
| 122,57 | 11,5062413 | 0,27786342 | 0,08189427 | 0,04497895 | 11,9130913 | 30,6634922 |
| 122,62 | 12,0261093 | 0,27737844 | 0,08437141 | 0,044841 | 12,1280371 | 20,0017403 |
| 122,67 | 11,469469 | 0,27714921 | 0,08166154 | 0,04425836 | 11,3458354 | 33,3557267 |
| 122,72 | 11,6816781 | 0,27864103 | 0,08504407 | 0,04518178 | 11,5387093 | 34,7176606 |

*Appendix 5.2. Coefficient of regression $R^2$ (Y=B*X+A) for selected elements.*

| Elements | Al | K | Mg | Ti | Zr |
|----------|------|------|------|------|------|
| Al | 1 | 0.93 | 0.82 | 0.94 | 0.90 |
| K | 0.93 | 1 | 0.95 | 0.93 | 0.95 |
| Mg | 0.82 | 0.95 | 1 | 0.91 | 0.94 |
| Ti | 0.94 | 0.93 | 0.91 | 1 | 0.97 |
| Zr | 0.90 | 0.95 | 0.94 | 0.97 | 1 |

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