

*Biogeosciences Discussions* is the access reviewed discussion forum of *Biogeosciences*

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

# Selective preservation of organic matter in marine environments – processes and impact on the fossil record

**K. A. F. Zonneveld<sup>1</sup>, G. J. M. Versteegh<sup>1</sup>, S. Kasten<sup>2</sup>, T. I. Eglinton<sup>3</sup>, K.-C. Emeis<sup>4</sup>,  
C. Huguet<sup>5</sup>, B. P. Koch<sup>2,12</sup>, G. J. de Lange<sup>7</sup>, J. W. de Leeuw<sup>6,7,8</sup>,  
J. J. Middelburg<sup>7,9</sup>, G. Mollenhauer<sup>2</sup>, F. G. Prahl<sup>10</sup>, J. Rethemeyer<sup>2</sup>, and  
S. G. Wakeham<sup>11</sup>**

<sup>1</sup>Fachbereich 5-Geowissenschaften, Postfach 330440, 27412 Bremen, Germany

<sup>2</sup>Alfred-Wegener-Institut für Polar- and Meeresforschung, Am Handelshafen 12,  
27570 Bremerhaven, Germany

<sup>3</sup>Woods Hole Oceanographic Institution, Fye 111, MS#4, Woods Hole, Ma. 02543, USA

<sup>4</sup>Zentrum für Meeres- und Klimaforschung, Universität Hamburg, Handesstraße 55,  
20146 Hamburg, Germany

<sup>5</sup>University of Washington, School of Oceanography, P.O. Box 355351,  
Seattle, WA 98195, USA

<sup>6</sup>Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790AB,  
Den Burg, The Netherlands

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

|◀

▶|

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

<sup>7</sup> Geochemistry, Faculty of Geosciences, Utrecht University P.O. Box 80.021,  
3508 TA Utrecht, The Netherlands

<sup>8</sup> Institute of Environmental Biology, Faculty of Science, Utrecht University, The Netherlands

<sup>9</sup> Netherlands Institute of Ecology, Centre for Estuarine and Marine Ecology, P.O. Box 140,  
4400 AC Yerseke, The Netherlands

<sup>10</sup> College of Oceanic and Atmospheric Sciences, COAS Administration Building 104, Oregon  
State University, Corvallis, OR 97331-5503, USA

<sup>11</sup> Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, GA 31411, USA

<sup>12</sup> University of Applied Sciences, An der Karlstadt 8, 27568 Bremerhaven, Germany

Received: 3 June 2009 – Accepted: 10 June 2009 – Published: 1 July 2009

Correspondence to: G. J. M. Versteegh (versteegh@uni-bremen.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

## Abstract

The present paper is the result of a workshop sponsored by the Research Centre Ocean Margins, the International Graduate College EUROPROX and the Alfred Wegener Institute for Polar Research. The workshop brought together specialists on organic matter degradation and on proxy-based environmental reconstruction. The paper deals with the main theme of the workshop, understanding the impact of selective degradation/preservation of organic matter (OM) in marine sediments on the interpretation of the fossil record. Special attention is paid to (A) the influence of the molecular composition of OM in relation to the biological and physical depositional environment, including new methods for determining complex organic biomolecules, (B) the impact of selective OM preservation on the interpretation of proxies for marine palaeoceanographic and palaeoclimatic reconstruction, and (C) past marine productivity and selective preservation in sediments.

## 1 Introduction

Sedimentary organic matter (OM) is the major reservoir of organic carbon in the global carbon cycle. In the marine environment it is composed of material derived from the various plankton species that comprise the ecology of primary producers and consumers in overlying surface waters. It is also composed of allochthonous materials introduced erosionally from the land by fluvial and eolian transport processes, products from chemical transformation and condensation as well as re-synthesis products derived from heterotrophic microbial activity which drives OM decomposition during the sedimentary process. Only a fraction of the organic material that is produced within the upper water column, reaches the sea floor where it is degraded further by aerobic and anaerobic degradation and it has been estimated that roughly only about 1% of the originally produced OM might be transferred to the deep biosphere (e.g. Suess, 1980; Hedges and Keil, 1995; Middelburg and Meysman, 2007). During the last few

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



decades it has become clear that preservation is highly selective and that the amount and composition of OM preserved in marine sediments varies greatly among regions and depositional environments.

Marine sedimentary OM forms the basis of many proxies used for reconstructing climate and environment. Since these proxies often provide the basic evidence for these reconstructions, it is essential to have detailed information about the character and influence of selective preservation on them.

The chemical, physical and biological effects on OM degradation as well as the effect of selective degradation on proxy reliability are high-ranked topics within a large number of scientific research disciplines. However, until now “synergic” discussion has been scarce. This is well illustrated by the fact that information about these subjects is scattered throughout the literature in journals of the individual disciplines. Combining this information was the subject of a workshop of the Center for Marine Environmental Sciences (MARUM), the International Graduate College EUROPROX, both based at the University of Bremen, Germany and the Alfred Wegener Institute for Polar Research in Bremerhaven, Germany, from 27 to 30 September 2007. During this workshop specialists from the fields of organic and inorganic geochemistry, biogeochemistry, microbiology, paleoceanography and micropaleontology integrated their expertise on selective degradation/preservation of OM in marine sediments. Within this paper we present an overview of (A) the present state of knowledge of the effect of the molecular composition of OM and the biological and physical depositional environment on OM preservation (B) the potential impact of selective OM preservation on the interpretation of several OM based proxies and methods that are presently used in marine paleoceanographic and palaeoclimatic research with main focus on organic-geochemical and chemical proxies and (C) identification and quantification of past marine production and selective preservation of OM in fossil sediments.

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 1.1 Factors that influence OM preservation

Several factors, sometimes controversial, have long been discussed as the primary controls on OM burial and preservation in sediments. First of all, the amount of OM produced in and supplied to the upper ocean waters determines the rain rate and the composition of OM to the seafloor. This OM input is either generated by primary production in the photic zone or through transport of terrestrial OM into the marine realm. Whereas degradation of the first source of OM occurs entirely within the marine environment, terrestrial OM can already be altered quite significantly before entering the marine environment. OM from both sources may contain compounds that are intrinsically labile or refractory purely on the basis of their molecular structures (e.g. elemental composition, presence of functional groups) and the physical form in which they exist in nature (Sollins et al., 1996; Hedges and Oades, 1997). These aspects will be discussed in Sect. 3.1. The importance of the refractory humic fraction in marine organic matter is discussed in Sect. 3.2 and special attention is paid to Fourier-transform ion cyclotron resonance mass spectrometry as a new method to shed light on the constitution of unresolved complex mixtures. For terrestrial OM, degradation processes in soils and during transport into the marine environment largely influence its molecular structure and determine its degradation potential when entering the marine environment. These processes are addressed in Sect. 3.3.

A second factor that strongly affects OM preservation is oxygen availability which determines the respiratory types of benthic organisms, with anaerobic consortia of micro-organisms being slightly less efficient than aerobic micro-organisms and micro-and macrofauna. Redox oscillations may enhance degradation by promoting symbiosis of aerobes and anaerobes (Canfield, 1994; Aller, 2001; Aller and Blair, 2006). Apart from the effect on the microbial community, oxygen availability, notably in the twilight zone and benthic boundary layer (and thus in surface sediments) largely determines the occurrence and community structure of metazoans. An overview on how this aspect might influence OM degradation and preservation is given in Sect. 3.4.

**BGD**

6, 6371–6440, 2009

### OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Physical factors of the depositional environment such as sediment texture and temperature might have a direct influence on the exposure time to oxygen or other degrading agents such as enzymes. Newly formed polymers during the degradation or aging process can isolate the OM from the degrading agent and as such protect the OM from (further) degradation. Furthermore, the mineral surfaces of the sediments or the macromolecular organic matrices can protect OM from degradation (Hedges and Keil, 1999; van Dongen, 2003; Versteegh et al., 2004; Arnarson and Keil, 2005; de Leeuw et al., 2006; Gupta et al., 2007). More information about these aspects is given in Sect. 3.5.

## 1.2 Influence of selective OM preservation on marine palaeoceanographic proxies

Within the scope of the current concern of global (climatic) change there is an urgent need for accurate estimation of past marine conditions. The role of the oceans in the global carbon cycle is ever more apparent and the international community is seeking answers to questions on the range of variation in marine production, ocean circulation, and carbon sequestration and how these are linked to the atmospheric  $p\text{CO}_2$  variation through Earth's history. Furthermore, the direct link between the upper ocean and the atmosphere means that detailed reconstruction of past conditions in the upper ocean is essential to understand the causes and effects of past climate change. However, proper constraints on the processes that control carbon fluxes between the ocean and the atmosphere and upper ocean circulation are still lacking. This is partly due to constraints and limitations of the proxy methods currently used. Within the last decades it became apparent that diagenetic processes related to OM degradation can strongly influence the initial signals of many proxies impeding the interpretation of the signals. As a result an increasing research effort is made world-wide to quantify this influence. These aspects form the central theme of Sects. 4 and 5 of this manuscript. Within Sect. 4 the effect of selective OM degradation of several lipid-based proxies is being evaluated. The first proxy discussed in Sect. 4.1 is radiocarbon to determine

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the age of sedimentary carbon younger than ~50 ka. The establishment of an accurate detailed stratigraphic framework is an essential aspect of paleoceanographic and paleoclimatic research. Within the last several years the analytical techniques to determine radiocarbon ages of sediments and the transfer to calendar age have improved enormously. However, these detailed measurements document that individual sedimentary OM components can have radiocarbon ages that differ considerably, sometimes as much as several thousands of years. There are strong indications that selective OM degradation of these components forms a major cause for these discrepancies.

We continue the discussion with the consequences of selective preservation of lipids (Sect. 4.2) and especially the impact of selective degradation on two lipid-based proxies (Sects. 4.3 and 4.4) that are used to determine past sea surface temperatures (SSTs); i.e. the long-chain ketone based unsaturation index ( $U_{37}^{K'}$ ) and the  $TEX_{86}$  index, the latter one based on isoprenoidal glycerol dialkyl glycerol tetraethers (GDGTs). Knowledge of SSTs is important for climate models as well as for elucidating the mechanisms of past climate change. Temperature reconstructions beyond the instrumental period strongly rely on well-dated high-resolution proxy-records reconstructed using paleothermometers. Specifically, to reconstruct SST from marine sediment records, a large range of tools and analytical techniques have been developed. Nevertheless, the establishment of detailed upper ocean temperature reconstructions is still not trivial and the improvement of many traditionally used proxies as well as the establishment of new proxies, currently forms the theme of many research programs.

The same holds for the quantitative estimation of the past marine carbon flux through the water column and the amount of carbon burial. Proxies that are presently used to estimate past upper ocean carbon production as well as the preservation and mineralization rates in bottom sediments are discussed in Sect. 5. We start this chapter with an evaluation of barium as a tracer to reconstruct productivity and compare this proxy to the traditionally used proxy for productivity: the amount of total organic carbon in bottom sediments. We continue our discussion in Sect. 5.2 with the use of selective

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



preservation of well recognisable marine OM particles to separate the initial productivity signal from the post depositional aerobic degradational overprint. Although we focus on the use of palynomorphs for which much information is available on their production in the upper water column, this method has the potential to be used with other OM components as well.

## 2 Selected factors affecting OM preservation

### 2.1 OM composition

The predominant fraction of sediment and soil OM is operationally defined as kerogen, high-molecular-weight OM not soluble in organic solvents or water. This kerogen by definition is preserved OM, i.e. the very small fraction of OM (0.5–1%) that continuously escapes from the biochemical cycle into the geosphere.

To determine the origin and structure of kerogen on the molecular level is not an easy task since it is high-molecular in weight and insoluble. However, significant progress has been made over the last decades through use of combined spectroscopic (e.g.  $^{13}\text{C}$  solid state NMR, FT-IR), pyrolytic and specific chemical degradation methods and techniques (de Leeuw et al., 2006 and references cited herein; de Leeuw, 2007). It has become clear that under favourable depositional conditions several types of aliphatic (cutan, cutin, suberan, suberin) and aromatic (lignin, sporopollenin) cell-wall biopolymers biosynthesized to protect organisms, spores, pollen and cysts are selectively preserved relative to polysaccharides, proteins and other biopolymers.

Apart from this selective preservation of biopolymers, novel types of geopolymers can be generated upon early diagenesis depending on the depositional environment. In anoxic marine settings, functionalized lipids or even sugars can react with  $\text{H}_2\text{S}$  or polysulfides resulting in the formation of polymeric substances cross-linked via (poly)sulfur bridges. Upon further diagenesis, these compounds can release the original lipid moieties by C-S cleavage and/or become stabilized geochemically e.g. by

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(benz)thiophene formation (e.g. Sinninghe Damsté and de Leeuw, 1990).

In a similar fashion functional lipids can also polymerize under oxic conditions by oxygen cross linking (e.g. Harvey et al., 1983; Versteegh et al., 2004). The latter phenomenon can be compared to the drying process of linseed oil, a process long known to occur during the drying of oil paint and varnish (Blom, 1936). It should be realized, however, that upon very long oxygen exposure times, as illustrated by the very low levels of OM in oxic deep-sea sediments and oxidized turbidites, essentially all sedimentary OM including the presumed resistant biopolymers and the geopolymers described above, will be mineralized.

## 2.2 Resolving unresolved complex mixtures: molecular characteristics of natural OM determined by FT-ICR-MS

The existence of persistent marine OM such as kerogen has important implications for biogeochemical cycles: (i) it serves as a buffer in the global organic carbon cycle, (ii) it can support the preservation of other organic molecules or trace elements which are applied as proxies in the fossil record and (iii) global environmental changes can alter the preservation of organic matter and can potentially result in major changes in global organic carbon fluxes. For all of these reasons there is a strong need to elucidate sources, preservation and degradation mechanisms of this material using molecular techniques.

The highly complex composition is one of the major obstacles for a comprehensive molecular analysis of kerogen and other comparable organic carbon pools such as particulate or dissolved organic matter in the ocean water column. Until recently no analytical method could provide the resolution to cover this complexity, and molecular information was solely derived from specific extraction and degradation methods which only covered small sub-fractions of the total material. For this reason, the majority of the reworked organic matter in marine sediments and water is still molecularly uncharacterized (Hedges et al., 2000). Whereas in the surface ocean most of the fresh organic matter is relatively well characterised (typically carbohydrates, proteins and lipids), after

**BGD**

6, 6371–6440, 2009

### OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



early diagenesis these “fresh” biomolecules usually contribute less than 10% to the total organic carbon. The remaining 90% persists on longer time scales (e.g. the turnover time of marine dissolved OM in the deep water column is ~5000 years; Williams and Druffel, 1987; Bauer et al., 1992), and its extreme complexity aggravates molecular analyses and hampers our understanding of the biogeochemical cycles by preventing detailed characterization of e.g. the exact sources, bioavailability, and binding to minerals or trace metals.

The recent development of ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-IR-MS; e.g. Marshall et al., 1998) has widened the “analytical window” available for unravelling the composition of “uncharacterizable” complex OM. The technique resolves thousands of individual molecules and so far provided molecular formulas (including N and S compounds) for complex mixtures such as oils (Schaub et al., 2005), terrestrial humic substances (Kujawinski et al., 2002; Stenson et al., 2003; Koch et al., 2007), aerosols (Reemtsma et al., 2006), marine OM (Koch et al., 2005; Hertkorn et al., 2006; Sleighter and Hatcher, 2008) and porewaters of marine sediments (Schmidt et al., 2009). FT-ICR-MS revealed molecular differences between sources and reveals selective molecular preservation induced by processes such as microbial and photo-degradation (Kujawinski et al., 2004; Dittmar et al., 2009). Preceding polarity-based chromatography facilitates separation of dissolved OM into well defined and less complex fractions of different polarity and provides information on selective preservation and the diagenetic state of OM (Koch et al., 2008).

However, the extent of molecular structural information derived by FT-ICR-MS is still limited due to the complexity of ions which are measured simultaneously in the ICR cell. In few cases the sole molecular formula can provide structural information. Large, hydrogen deficient molecules which were identified in natural organic matter in soils (Hockaday et al., 2006) and in the ocean are derived from thermogenic sources such as fossil fuel and biomass burning (black carbon; Kim et al., 2004) and substantially contribute to active marine OM fluxes (Dittmar and Koch, 2006; Koch and Dittmar, 2006). McKenna et al. (2009) recently identified vanadyl porphyrins in raw crude oil

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



using FT-ICR-MS. Recently the isolation of single ions in the ICR cell and subsequent fragmentation allowed new insights into the molecular structure of single compounds (Witt et al., 2009)

All molecular FT-ICR-MS data published so far for natural OM samples from various regions and habitats reveal a striking similarity (e.g. ~30% overlap for marine vs. mangrove dissolved OM, Koch et al., 2005). It appears that, the set of formulas detected in natural OM consisting of carbon, hydrogen and oxygen often covers almost all chemically feasible molecular formulas in the studied size ranges (Hertkorn, 2008). The similarity between the samples is in part derived by the selective ionization process. However, looking at the results of various ionization techniques it can be reasonably hypothesized that the structure of humic substances is fundamentally determined by the predominant (selective) degradation mechanisms and that the sources of OM are less crucial than expected. Based on the enormous diversity of molecular formulas observed for humic substances it also can be hypothesized that the preservation of this material is driven by its sheer complexity, preventing energy efficient microbial degradation.

### 2.3 Controls and preservation of soil derived OM indicated by carbon isotopes

Huge amounts of terrestrial organic carbon (OC) are exported from the continent to the ocean (Schlesinger and Melack, 1981) mainly as particulate and dissolved OC discharged by rivers, thereby directly linking the terrestrial and marine carbon cycles. Much of the discharged OM appears to be highly degraded and to derive from soils (Hedges et al., 1994). However, OM deposited in delta and margin sediments as main depositional areas is predominantly marine-derived indicating that most (>50%) of the soil OC is mineralized during its transport to the ocean (Hedges and Oades, 1997). The fate of terrigenous OM in rivers and in the ocean as well as the nature and fraction of the terrestrial organic carbon preserved in marine sediments is poorly constrained.

A number of paleoenvironmental studies are based on the abundance and isotopic composition of terrigenous compounds deposited in marine sediments, particularly on

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



higher plant lipids (e.g. Schefuss et al., 2005; Smittenberg et al., 2006). These studies rely on the resistance of the biomarker compounds to degradation during their way from the land to the ocean and within the sediment. Several investigations of organic compounds in soils and sediments, however, indicate compositional changes of OM during transport as well as in soils and marine sediments due to selective stabilization and degradation of organic compounds (e.g. Huang et al., 1999; Goñi et al., 2005; Mollenhauer and Eglinton, 2007). This results in considerable changes in the abundance and isotopic composition of organic biomarkers in marine sediments and in consequence may provide a misleading picture of terrestrial paleoenvironmental conditions. However, information on sources and transport processes affecting terrestrial OM composition are often based on studies of OM suspended and deposited in rivers as well as in margin sediments and thus consider only part of the transport trajectory (e.g. Opsahl and Brenner, 1997; Bianchi et al., 2007).

Like surface sediments, soils are open systems where carbon is continuously added, lost and microbially recycled (Gleixner et al., 2002). Hence soil OM consists of a vast number of organic compounds at various stages of decomposition and may contain carbon contributions from soil microorganisms, vegetation fires and fossil fuels (Czimczik and Masiello, 2007).  $^{14}\text{C}$  analyses of various soil fractions and organic compounds which yielded ages ranging from years to several thousands of years revealed different stability/turnover rates of these operationally defined carbon pools and gave information on soil OC protection mechanisms (Trumbore and Zheng, 1996; Rethemeyer et al., 2004).

Among the plant compounds considered to be resistant to microbial and enzymatic breakdown, lignin has long been suspected to be slowly biodegradable in soils due to its aromatic structure and non-hydrolysable intra-molecular bonds (Haider, 1992) and used as tracer for terrestrial OC supply to marine sediments (Opsahl and Brenner, 1997; Goñi et al., 2005). Recent studies using  $^{13}\text{C}$  CPMAS-NMR and pyrolysis techniques however, have shown that in soils lignin is altered relatively quickly (e.g. Gleixner et al., 2002; Kiem and Kögel-Knabner, 2003). Lignin degradation in soil seems to

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

depend on climatic conditions and vegetation cover (Otto and Simpson, 2006) and the phenolic subunits of lignin were found to differ in their degradability/turnover rates that decreased in the order cinnamyl > syringyl > vanillyl (Bahri et al., 2006; Heim and Schmidt, 2007). Compound-specific  $^{13}\text{C}$  analyses of lignin phenols that were naturally  $^{13}\text{C}$  labeled by  $\text{C}_3$ – $\text{C}_4$  crop succession were used to determine mean residence times of these compounds. In grassland and arable soils mean the residence times of lignin-derived phenols were in the decadal range and these phenols degrade faster than bulk soil OM turnover (Dignac et al., 2005; Heim and Schmidt, 2007), questioning the assumed high resistance against degradation of these molecules. A similar result was obtained for long-chain *n*-alkanes from terrestrial plant-waxes extracted from arable soils that showed mean residence times of several years to decades indicating no selective preservation during soil OM transformation (Wiesenberg et al., 2008; Marschner et al., 2008). The microbial recycling of presumably inert OM was furthermore indicated by depleted  $^{14}\text{C}$  concentrations of individual microbe-derived phospholipid fatty acids isolated from a soil containing about 50% carbon mainly from lignite (Rethemeyer et al., 2004).

Several recent studies indicate that physicochemical interactions of OM with the mineral soil matrix play an important role for the preservation of soil organic carbon (Marschner et al., 2008 and ref. therein) as well as of marine sedimentary OM (Hedges and Keil, 1995; Keil et al., 1998). In soils the stability of organo-mineral associations varies, depending on grain- and aggregate-size but seems to be influenced by soil properties, management, and climatic conditions (von Lützow et al., 2007 and references therein). However, protective mechanisms seem to be strongly dependent on soil properties, management, and climatic conditions.

These findings indicate the need to consider changes in OM and biomarker composition in soils when investigating terrigenous carbon fluxes to marine settings. There is relatively little information on the export of OM from soils into rivers and on compositional changes of the organic material. Terrestrial paleoenvironmental studies based on marine sediments could benefit from investigation of biomarker alteration on the entire

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



transport trajectory from source to sink. Therefore, stable and characteristic molecular markers are needed in order to trace carbon from terrestrial plants. Because of the importance of physical OC stabilization processes in both marine and terrestrial environments, studies on selective stabilization and degradation of organic compounds in soils and sediments could be improved by bulk and compound-specific analyses of different physical (grain size, density) OM fractions. Redox conditions and the interplay of mixing by biological and/or physical processes in surface sediments are what seem to fine-tune the outcome.

## 2.4 Effects of animals on OM preservation and burial

Most marine sediments are inhabited by a diverse community of metazoans varying in size from few tens of  $\mu\text{m}$  to few dm. These animals have a number of direct and indirect effects on sediment biogeochemistry and OM processing (Meysman et al., 2006). Direct effects of animals on OM processing include organic consumption, transformation and production by animals, while indirect effects relate to modifying textures, biodeposition, bio-irrigation, bioturbation and grazing on bacteria.

Burrowing organisms influence sediment properties such as porosity, permeability, compaction, glue particles together into aggregates upon egestion and tube building and segregate particles during digestion. These processes alter OM-mineral-water interactions and thus the exposure of OM to hydrolytic enzymes and oxidants. Many benthic animals are suspension feeders that obtain their nutritional demands by filtering large quantities of water. These filter feeders are selective and the non-selected and non-assimilated materials are usually deposited as pseudo-faeces or faeces on the sediment surface. This biodeposition flux of OM can be very high in some systems with consequences for OM composition and preservation because of low oxygen, high sulfide conditions. Bio-irrigation and enhanced solute transfer are direct consequences of animal burrows. To supply oxygen and remove metabolites and toxic substances, benthic fauna actively flush their burrows with overlying water. Burrows therefore form a three-dimensional transport network that penetrates and irrigates the surrounding

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sediment tissue and deliver additional oxygen to deeper layers of sediments. Ventilation of animal tubes is often intermittent with the consequence that sediment OM is subject to redox oscillation which is known to stimulate OM degradation (Aller, 2001). Bioturbation, i.e. particle mixing due to animals, has multiple effects on OM processing: labile OM is transported to deeper layers where they may stimulate degradation of refractory OM (priming) and partially degraded material may be upward transported to other redox zones. In mud, animals move forward via cracking and new surface is consequently steadily being produced (Dorgan et al., 2005). This will likely have major consequences for exposure and sorption (and thus degradation) of OM. Animals grazing on bacteria may affect microbial OM processing either positively by transporting labile organic matter to bacteria living at depth and in this way stimulating their growth or negatively by reducing biomass of active organisms (van Nugteren et al., 2009).

Animals are heterotrophic organisms and thus depend on OM for their energy. They directly consume a significant fraction of sediment OM (Moodley et al., 2005); part of this is assimilated and used for secondary production, another part is respired or defaecated. Secondary production of OM in marine sediments has been well studied by benthic ecologists and microbial ecologists (secondary bacterial production) and numerous biomarkers specific for animals and bacteria are known. However, there is no consensus whether secondary produced OM contributes significantly to the organic material that becomes eventually buried. The overall effect of animals on sediment OM processing can most easily be quantified from the difference between diffusive oxygen uptake measurements and total oxygen uptake rates. While these numbers agree in deep-sea sediments, they diverge going from the deep-sea to coastal sediments (Glud, 2008), indicating that animals contribute significantly to OM processing in coastal sediments (Herman et al., 1999).

## 2.5 Physical factors affecting OM behaviour in marine environments

There are several physical factors that influence burial. Because degradation usually involves enzymatic hydrolysis, temperature and pressure affect rates of (bio)chemical

---

### OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



reactions, purely on kinetic grounds. Reduced temperature may inhibit enzyme activity, in part because the kinetics are slower and/or because bacteria may exhibit decreased affinity for substrates at lower temperatures. Macromolecular-hydrolyzing enzymes may function equally well at higher or lower temperatures, but substrates produced by enzymes (as intermediates) might not be effectively taken up by the microbial community. Hydrolysis rates may be reduced at increased pressure that OM experiences as it sinks towards the sediments; however laboratory incubations designed to measure degradation rates often do not consider potential effects of pressure.

The mixing regime that OM experiences in surface sediments is important. Physical mixing (i.e., high turbulence during storm events) and biological mixing by macroorganisms (bioturbation) can irrigate sediments with oxygen, nutrients, and substrates, cause redox oscillations, or physically transport OM between redox zones, all of which effectively increase oxygen exposure (Fig. 1). Mixing or manipulations of particles by animals can cause particle fragmentation and alter particle surface areas, also enhancing exposure of OM to either hydrolytic enzymes or oxygen (Middelburg and Meysman, 2007).

Finally, there is now considerable discussion about how mineral surfaces or macromolecular organic matrices may protect OM from degradation (Fig. 2). Since all surfaces in aquatic systems are coated with some amount of OM, whether a monolayer equivalent, discrete patches of sorbed OM, or OM within pores or interlayers of minerals, this OM may be physically protected from hydrolytic enzymes, although the exact mechanisms are unclear. Enzymes may be too large to access OM in pores or interlayers, but molecular oxygen or peroxides may be able to reach this OM. However, OM that appears to be “refractory” while associated with mineral surfaces may in fact be degradable once it is removed from the mineral surface. There is now sufficient reason to believe that the availability of mineral surface area places an important quantitative constraint on OM efficiency in sediments throughout the ocean (e.g. Hedges and Keil, 1995). However, it appears to act only as a means of coarse adjustment. Finally, bio- or geo-condensation processes can physically “encapsulate” otherwise “labile” OM into

---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

a protective macromolecular organic matrix.

Given the current state of knowledge, several important issues require further research. How valid are current experimental estimates of OM degradation rates given potential inhibitory effects by reduced temperature and increased pressure? There is a need to perform degradation incubations under in-situ conditions. How does interaction with mineral surfaces actually protect OM from degradation? Do different mineral types (e.g., carbonate, opal, lithogenic material) intrinsically lead to differential preservation? What are effects of particle transport (size and density factors, winnowing and sorting, long-range transport to the deep ocean and drift deposits) on preservation?

## 2.6 Degradation and transformation of organic matter (OM) in sediments

The previous sections each highlight selected aspects of the biological, physical and chemical factors influencing organic matter preservation. Clearly, these factors influence each other and their relative importance varies spatially and temporally. Therefore, this section deals with the interrelationships of the factors influencing OM degradation in space and time (Fig. 3). Fed by photo or chemoautotrophic carbon fixation, particular organic matter (POM) reaches the sea floor passively by sedimentation or actively by filter feeding animals. The material consists of many different qualities from extremely labile (e.g. starch) to highly refractory (e.g. black carbon) which may be simplified into two categories labile (LPOM) and refractory particulate organic matter (RPOM). The RPOM also includes labile organic matter which is intrinsically biodegradable but physically protected from biodegradation e.g. by encapsulation by or sorption to inorganic or organic particles. As degradation of OM particles progresses, compounds sorbed to, or protected by, these particles will become released. Probably, there is an equilibrium between sorption/desorption depending on properties of the matrix, pH, compound specific dissolution constants etc. Analogous to POM, dissolved OM (DOM) includes refractory (RDOM) and labile (LDOM) DOM of many different qualities (For simplicity the refractory part is put together with the RPOM in Fig. 3 as ROM). In the sedimentary biosphere, the labile part is composed of small organic molecules

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



resulting in the sedimentary biosphere resulting mainly from extracellular enzymatic activity and cell lysis.

In the oxic part of the sedimentary biosphere, degradation is relatively fast and exponential, decreasing with increasing refractoriness. The organic matter is removed from the oxic zone by biodegradation, bioturbation into the underlying anoxic zone and upward migration of the anoxic zone as sedimentation proceeds. Degraders are bacteria and archaea, unicellular and multicellular eukaryotes (e.g. ciliates, worms). The bacteria and archaea are grazed by eukaryotes. Archaea and bacteria are also killed by (viral) lysis which produces DOM of which most is consumed again by archaea and bacteria. A small part of the bacterial and archaeal OM is (relatively) resistant and accumulates in the sediment as archaeal and bacterial refractive OM (ABROM).

In the anoxic part of the sedimentary biosphere: eukaryotes only live in the uppermost layer, via bioturbation they may return OM to the oxic zone above. The upper part of the anoxic zone includes a succession of redox-zones and associated microbial consortia, each consuming and producing characteristic types of organic matter. Going downwards through these zones the available redox potential and associated energy gain upon organic matter degradation becomes increasingly less. As a result biotransformation rates slow down (symbolised by an angle in the change in pool size with depth at the oxic/anoxic interface in Fig. 3) and some biochemical transformations can't be performed anymore which effectively transfers organic matter requiring these transformations to be digested from the labile to the refractory OM pool (symbolised by the step-change in ROM / LPOM pool sizes at oxic/anoxic interface in Fig. 3). This reduction in biodegradative potential also results in accumulation of small organic (LDOM) and inorganic molecules (e.g. CH<sub>4</sub>, Acetate, H<sub>2</sub>S). These may migrate and be consumed higher up in the sediments in a zone with more favourable redox conditions or escape to the water column. Depending on pressure and temperature, produced CH<sub>4</sub> may be removed from the LDOM as gas hydrate (or released from it). The accumulating small compounds (e.g. acetate) may also change the pH of the sediment, concomitantly changing sorptive and stereo-specific properties of the organic matter and

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



surrounding sediment releasing or removing compounds for biodegradation/chemical transformation. Free sulphur species released by the biochemical processes induce polymerisation of the organic matter by sulphurisation transferring LPOM (and LDOM) to the ROM pool. The downwards decreasing redox potential also reduces the efficiency of the oxidative polymerisation pathway.

In this zone as well as the oxic zone above, the proportion of refractory organic matter (ROM+ABROM+RDOM) increases over time since (1) biodegradation rates decrease with decreasing OM quality, (2) oxidative polymerisation, and in the anoxic zone also sulphurisation, transfer labile organic matter towards the refractory pool and (3) part of the archaeal and bacterial organic matter produced in the sediment (ABROM) can't be degraded.

With increasing depth, temperature and pressure (P/T) increase. Apart from speeding up the chemical polymerisation processes this may also cause desorption of biodegradable material feeding the deep biosphere. Although above a given temperature life becomes impossible, chemical transformation continues. As a result of these processes the LOM and LDOM pools should decrease. However, migration of DOM from the zone below may (as in figure), but doesn't need to counterbalance this process.

Above a critical combination of P/T conditions, fragmentation of the OM exceeds polymerisation. The cracking of the organic matter leads to DOM and CO<sub>2</sub> which sooner or later become bioavailable by migration into the (deep) biosphere. Possible ways are e.g. by direct upwards migration through the sediment, migration with the sediment following the sedimentary cycle(s) of rock formation and erosion and/or by ingestion into the mantle and subsequent volcanic or plutonic activity.

It must be kept in mind that the processes described above are not only selective at molecular level but also at the level of atoms, shifting isotopic compositions. Furthermore, it is important to realise that the physical, chemical and biological properties of the sediment not only determine organic matter preservation and degradation but that this is also true in the opposite direction e.g. through modifying the mineral

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



composition by dissolving carbonate. Understanding both the selectivity and sediment modifying capability of the organic degradation/transformation is important since these processes imply modification of organic and inorganic-matter based sediment-derived proxies which has consequences for the way we reconstruct Earth history.

### 3 The interpretation of several lipid-based marine proxies

#### 3.1 Selective degradation as deduced from radiocarbon measurements

Rapid organic carbon degradation in the uppermost centimetres of marine sediments has long been observed, and concentrations of individual compounds decrease at compound-specific rates (Sun and Wakeham, 1994; Wakeham and Canuel, 2006) within a certain setting. However, down-core concentration profiles of many organic compounds reach a more or less stable background value below the uppermost few centimetres of the sediment. A simple model to explain this observation requires that the sum of a given organic compound is composed of (at least) two components with different reactivities, and the relative contribution of the more reactive component decreases with increasing degree of degradation. At present, it is not well understood where the less reactive component originates, how old it is and why it is protected from degradation.

For components that originate from different sources with distinct stable isotopic signatures and different transport- and intermediate residence times before deposition on the sea-floor, the preferential preservation of one component over the other should result in down-core profiles as illustrated in Figure 4. Carbon isotopic ( $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ ) data show that for short-chain *n*-alkanoic acids (e.g.,  $\text{C}_{16:0}$ ), occurring ubiquitously both in marine and terrestrial environments, the terrigenous component is better preserved in marine sediment. Moreover, this terrigenous component is often pre-aged at the time it is buried (Mollenhauer and Eglinton, 2007).

When only organic biomarkers from marine sources are considered, preferential

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



preservation of one less reactive component, if supplied via lateral advection of pre-aged material, can be detected if compound-specific radiocarbon concentrations are more depleted than expected, e.g., if radiocarbon concentrations in phytoplankton-derived biomarkers like alkenones are lower than in co-occurring near-surface dwelling planktic foraminifera. This is particularly evident when comparing depositional environments with identical input but contrasting levels of oxygenation like flank and depositor sediments from Santa Monica Basin (Mollenhauer and Eglinton, 2007).

Differences in preservation potential of plankton-derived biomarkers found in the same sediments would be expected to result in characteristic radiocarbon concentrations along gradients of increasing degree of degradation (Fig. 5). This could be observed along down-core profiles or along transport trajectories. Radiocarbon concentrations of two plankton-derived organic biomarkers, alkenones and the archaeal membrane lipid crenarchaeol, in core-top sediments along a transect across the Namibian shelf agree with this concept (Fig. 6) (Mollenhauer et al., 2007). These data suggest that crenarchaeol is less likely to be preserved during transport in oxygen-replete waters. The reasons for the enhanced preservation of alkenones during lateral transport remain unclear. The role of biomineral association should be investigated in this context.

Taken into account the observations described above, biomarkers preserved in marine sediment must be considered a distributed property, i.e., a sample consists of a mixture of material from a multitude of sources and with variable radiocarbon signatures. The radiocarbon concentration measured in one sample can consequently be expressed according to a mixing equation as described in Pearson and Eglinton (2000):

$$\Delta^{14}\text{C}_{ij} = \sum_k X_{ij} W_{ik} \Delta^{14}\text{C}_{ijk} / \sum_k X_{ij} W_{ik} \quad (1)$$

where  $W_k$  = fraction of carbon derived from source  $k$ ;  $X_i$  = fraction of total carbon in source  $W$  that belongs to biomarker  $i$ ;  $j$  = sample.

In order to interpret biomarker data, the terms  $W$ ,  $X$ , and the respective  $\Delta^{14}\text{C}$  of the individual components should be known as well as the number of sources contributing.

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Independent methods to estimate lateral input would be desirable. To date, the contribution of allochthonous material can only be estimated assuming end-members, and the number of contributing sources allowing for unambiguous solutions is typically limited by the number of independent compound-specific isotope data (typically  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ , cf. Pearson and Eglinton, 2000). A second major piece of information lacking to date is the source from where laterally advected components derive. When studying terrigenous biomarkers in marine sediments, the soils and dust of the hinterland should be investigated. For marine biomarkers, areas of sediment re-suspension or erosion must be identified upstream from the site of deposition.

### 3.2 Selective lipid degradation

In recent years, biomarker ratios have been proposed as indices to gauge changes in sedimentary redox conditions through time. Sinninghe Damsté et al. (2003) coined the ratio of lycopane (a biomarker of presumed marine photoautotrophic origin) to  $n\text{-C}_{31}$  alkane (a biomarker of vascular plantwax origin) as such an index. The integrity of this proxy was tested in modern sediments spanning the oxygen minimum zone (OMZ) in the Peru Upwelling region. Values appeared higher in sediments deposited within the OMZ than in those deposited under less reducing, perhaps aerobic conditions at both shallower and deeper depths. Given that the relative flux of both biomarkers to the seabed was constant throughout the region, the response of the index was consistent with what is now known about the relative diagenetic stability of phytoplankton versus terrestrial-derived biomarkers (Prahl et al., 2003). Although the assumption of a constant, proportional flux into the seabed was argued as justifiable in the case of the modern Peru Upwelling Zone, this assumption is difficult if not impossible to assess objectively in the paleoenvironment. Consequently, stratigraphic variations in the ratio of lycopane:  $n\text{-C}_{31}$  alkane may provide a gauge of changes in sedimentary redox conditions, however such an inference could not be made unequivocally. It could also depict a change in the relative source strength under otherwise very comparable redox conditions at the seabed. How could these two prospects be differentiated objectively?

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Cacho et al. (2000) coined the ratio a long-chain *n*-alcohol ( $C_{26}$ -ol) to *n*-alkane ( $C_{29}$ ) as another biomarker index of sedimentary redox conditions. In this case, both compounds are derived from a terrestrial source. The assumption is that both derive from a *common* terrestrial source where the ratio is fixed at some constant value and the  $C_{26}$ -ol has greater sensitivity to decomposition than the *n*- $C_{29}$  alkane when this source material is deposited under aerobic conditions. Hence, values of the ratio become increasingly elevated as environmental conditions become more aerobic and vice versa.

Study of an aerobic burndown turbidite on the Madeira Abyssal Plain has yielded an observation corroborating the inferred diagenetic sensitivity of this index (Fig. 7). However, as with the lycopane: *n*- $C_{31}$  index, it poses a significant challenge to objectively determine whether or not quantitative variations observed in this terrestrial plantwax index (e.g. Martrat et al., 2007) are just driven by redox conditions at the seabed.

In summary, lipid biomarkers now provide the paleoceanographic community with invaluable eyepieces for evaluation of environmental and climatic change. Nonetheless, these eyepieces would all benefit from continued effort to improve their focus. Diagenetic factors do indeed act to obfuscate the signals we aim to glean from stratigraphic records for specific biomarkers downcore in sediments. Concerted research efforts in the future should help us to identify and clarify the exact nature of these complications and to devise objective methods to extract accurate information about paleoenvironmental and climatic conditions.

### 3.3 The $U_{37}^{K'}$ paleothermometer and the impact of degradation

Downcore stratigraphic records for  $C_{37}$  alkenone concentration have been employed as an gauge for paleoproductivity change (Prahl and Muehlhausen, 1989; Villanueva et al., 1998; Schulte et al., 1999). Although conceptually quite reasonable, sediment trap – sediment comparisons for the NE Pacific Ocean (Prahl et al., 1993) and the Arabian Sea (Prahl et al., 2000; Wakeham et al., 2002) showed that diagenetic processes at the seabed can completely invert the perspective on productivity of alkenone-producers and their contribution to total phytoplankton-derived OM. Thus, results from

this stratigraphic application must always be interpreted cautiously (e.g. Hedges and Pahl, 1993)

In the case study just cited for the NE Pacific Ocean, redox conditions in bottom sediments along the offshore transect varied widely, grading from iron-reducing to manganese-reducing to aerobic. Quite possibly such distortion of biological oceanographic perspective does not occur when dealing with downcore stratigraphic records for a sedimentary environment characterized by more subtle variations in redox conditions. In this circumstance which may be more relevant to a specific marine sedimentary location, the direction of change is perhaps reliably indicated but the magnitude of change would remain arguable.

Figure 8 shows results from analysis of alkenones in surface sediments from three very different oceanographic environments (coastal region off SE Alaska – Pahl-unpublished data, continental margin off Chile-Peru – (Pahl et al., 2006), Oman margin and open Arabian Sea – unpublished data). Data from each environment appear to plot along lines characterized by distinct slopes. Although diagenesis may to some extent be a factor shaping these observations, it seems most likely that these lines convey information about the average phytoplankton ecology of surface waters in each region (Pahl et al., 2009). Alkenone-producing coccolithophorids (De Vargas et al., 2007) are major contributors in surface waters of the Chile-Peru margin relative to the case for coastal waters of SE Alaska where biogenic silica-rich sediments indicate diatom contribution dominates. More detailed research is clearly warranted to determine: 1) how other lipid biomarkers of phytoplankton origin besides the alkenones are impacted under variable redox conditions and subsequently, 2) the reliability of using biomarker ratios to ascertain the impact of climate change on phytoplankton community structure in surface waters (Pahl, 1992).

Since the first report that alkenone unsaturation patterns provide a viable tool for the reconstruction of past sea-surface temperatures (SST) (Brassell et al., 1986), the application has been employed widely and overall, with tremendous success (Herbert, 2003). Nonetheless, we have also learned in this ~20 yr period that  $U_{37}^{K'}$  values are

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



not strictly set by the growth temperature of the alkenone-producers. Non-thermal physiological factors such as a nutrient stress and light availability can significantly impact unsaturation patterns and potentially their paleoceanographic interpretation (e.g. Versteegh et al., 2001; Laws et al., 2001; Prahl et al., 2006). Although the bias caused by these non-thermal physiological effects appears to be in a systematic direction, it is not yet clear how to recognize unambiguously when such bias has occurred and, if so, how to quantitatively account for it.

Early studies both in a natural field setting (Prahl et al., 1989) and in the laboratory with bacterial cultures (Teece et al., 1998) showed  $U_{37}^{K'}$  values, once set by the alkenone-producer, are relative insensitive to alteration despite major aerobic decomposition of the overall biomarker signature. Nonetheless, significant shifts to more positive values, albeit often small, were apparent in results from the early field work (e.g. Hoefs et al., 2002) and more recently from an experimental field study (Kim et al., 2009). Laboratory work with mixed bacterial populations (Rontani et al., 2008) and field observations (Rontani and Wakeham, 2008) have shown that some consortia of aerobes can degrade alkenones selectively, leading to positive shifts in  $U_{37}^{K'}$  equivalent to a  $\sim 2$  to  $3^\circ\text{C}$  increase in growth temperature. Interestingly, in experiments where such  $U_{37}^{K'}$  shifts have been observed, oxidation products indicating selective decomposition of the alkenone double bonds were detected. Such products were not detectable in experiments where alkenones were degraded by aerobic microbial consortia without impact on  $U_{37}^{K'}$ .

Alkenones have now proven very clearly to be a promising tool for SST reconstruction. But, in some circumstances, SST reconstructions based on  $U_{37}^{K'}$  analysis do not pair well with those made using, for example, other statistical (foraminiferal transfer functions) or biogeochemical (Mg:Ca in foraminiferal carbonate) proxies. In such a circumstance, which proxy provides the accurate assessment? To unravel this, the contributions of selective preservation and differences in ecologies of the proxy carrying organisms need to be assessed. We now recognize that selective, aerobic de-

---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



composition of alkenones, which can lead to a positive shift in  $U_{37}^{K'}$  of some significant magnitude, yields telltale metabolic products. Examination of sediment samples yielding “questionable”  $U_{37}^{K'}$  results for the presence of these metabolic products provides an objective (but yet largely unexplored) way to determine if aerobic diagenesis could provide at least some explanation for disagreement in SST assessments.

As briefly described above, we also now know that redox conditions play a role in quantitatively setting the burial efficiency for biomarkers. Although burial efficiency more than likely displays the same general pattern for all biomarkers, declining as sedimentary conditions shift from anaerobic to aerobic, much remains to be learned about the specific quantitative relationship between burial efficiency and redox conditions for different biomarkers. Currently, we know that all biomarkers do not behave the same diagenetically (Wakeham et al., 1997; Prahl et al., 2000). However, more detailed understanding of the specific quantitative relationship for individual biomarkers will clearly be necessary if we want to confidently reconstruct, through examination of downcore stratigraphic records for biomarker ratios, oceanographic details such as the sensitivity of phytoplankton community structure to climate change (Hedges and Prahl, 1993).

### 3.4 The impact of degradation on glycerol dialkyl glycerol tetraethers and the $TEX_{86}$ paleothermometer

The preservation of organic carbon (OC) is strongly dependant on, amongst others, the oxygen exposure time i.e. more OC is degraded generally with longer oxygen exposure time. Bulk OC, long-chain alkenones and glycerol dialkyl glycerol tetraethers (GDGTs) were analysed in oxidized and un-oxidized layers of a selection of organic-rich turbidites deposited at the Madeira Abyssal Plain MAP (Huguet et al., 2007, 2008). These distal, fine-grained, turbidites contain OM that first accumulated on the shelf and subsequently was redeposited in the abyssal plain. Once redeposited the upper part of such relatively homogenous sedimentary units were exposed to oxygenated bottom water leading to oxidation fronts progressing downward until deposition of the next tur-

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



bidite unit took place. As a consequence of this downward oxidation, concentrations of OC, GDGTs and alkenones were reduced by one or two orders of magnitude in the oxidized upper parts of the turbidites compared to the un-oxidized lower parts, indicating substantial degradation (Fig. 9; Huguet et al., 2008 and references therein). Results from the MAP F-turbidite clearly show that there is a sharp decrease of both GDGTs and C<sub>37</sub> alkenones in the oxidized part of the turbidites and are thus severely degraded upon long-term exposure to oxygen (Fig. 9). This is in agreement with previous studies that showed that GDGTs (Schouten et al., 2004) and alkenones are degraded under (sub)oxic conditions (Prahl et al., 2003).

While the abundances of the isoprenoid GDGTs used substantially decrease in the F-turbidite from ca. 4 μg g<sup>-1</sup> sediment in the anoxic part to 0.1 μg g<sup>-1</sup> sediment at the upper oxic part (Fig. 9) in agreement with previously reported results for crenarchaeol (Huguet et al., 2008), this decrease is relatively smaller for the branched GDGTs. As a consequence, the BIT index shows an increase from the anoxic to the oxic part. I.e. from 0.03 in the anoxic to 0.45 in the oxic part of the F-turbidite (Fig. 9; Huguet et al., 2008). There may be several reasons for the enhanced preservation of branched GDGTs. Different biomarkers can have different preservation potentials depending on their chemical structure (de Leeuw and Largeau, 1993; Hoefs et al., 2002; Sinninghe Damsté et al., 2002), and thus branched GDGTs could be chemically more resistant against degradation than isoprenoid GDGTs. However, it is difficult to envisage why polar lipids with branched carbon skeletons should be degraded slower than isoprenoid carbon skeletons as degradation is likely to start at the functionalized glycerol moiety. Finally, in general it has been observed that branched alkyl chains are more easily degradable than isoprenoid chains (Hanford and Peeples, 2002). The results can be better explained by the different origins of the branched GDGTs and isoprenoid GDGTs, i.e. soil derived matter versus marine derived matter. The preferential preservation of terrestrial versus marine organic organic compounds, and of OC in general, has been observed before (e.g. Burdige, 2005). However, up to now it was not possible to assess if this preferential preservation was due to the chemical struc-

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ture of the terrestrial OM, or because the mineral matrix protects it from degradation. These results suggest that the (mineral) matrix to which soil OM is attached enhanced their preservation (Huguet et al., 2008).

Besides having a general impact on OC preservation, oxic degradation may also affect the *relative* distribution of biomarker lipids. Studies of sediments deposited in the MAP (Hoefs et al., 2002) and in the Arabian Sea (Sinninghe Damsté et al., 2002) showed that post depositional oxic degradation not only decreased the concentration of lipid biomarkers by several orders of magnitude, but also that the extent of the degradation was different for different compounds and thus may cause a severe bias in the biomarker distribution. An important effect of this bias is the impact it may have on organic paleoceanographic proxies such as  $U_{37}^{K'}$ ,  $TEX_{86}$  and the branched and isoprenoid tetraether (BIT) index (the latter a proxy for soil organic carbon in sediments – Hopmans et al., 2004). A previous study at the Arabian sea comparing oxidized and un-oxidized samples showed no significant differences in  $TEX_{86}$  (Schouten et al., 2004) and similar results were obtained from an experimental field study, setting out a sediment sample from the Namibian shelf on moorings in oxic and anoxic waters for one year (Kim et al., 2009). However, the exposure times to oxygen in these latter studies were relatively short compared to those in the MAP.

In the case of the F-turbidite both the  $TEX_{86}$  and  $U_{37}^{K'}$  show a positive shift in the oxic layer of the turbidite (Huguet et al., 2009). These results suggest a preferential degradation of the  $C_{37:3}$  alkenones which is in agreement with previous observations (Hoefs et al., 1998; Gong and Hollander, 1999; Kim et al., 2009) and indicates a small but significant effect of diagenesis on the  $U_{37}^{K'}$  temperature proxy. The observed shift in  $TEX_{86}$  also suggests that oxic degradation affects this SST proxy.

The cause of the observed  $TEX_{86}$  shifts may be in the preferential preservation of soil derived GDGTs. Weijers et al. (2006) showed that besides branched GDGTs, isoprenoid GDGTs also occur in soils in varying and relatively small amounts and that this can affect marine  $TEX_{86}$  values if there is a large input of soil OM. In the anoxic part the contribution of terrestrial GDGTs is relatively minor as evidenced by the low BIT val-

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ues ( $<0.1$ ) and thus the  $TEX_{86}$  values are almost exclusively determined by isoprenoid GDGTs from marine sources. In the oxic part of the turbidites, however, the marine derived GDGTs are degraded to a larger extent than soil derived GDGTs because of matrix protection (Huguet et al., 2008) and thus the  $TEX_{86}$  value may be substantially influenced by isoprenoid GDGTs derived from the continent. Thus, the effect of oxic degradation on the  $TEX_{86}$  will depend on the composition of isoprenoidal GDGTs derived from the continent in the original turbidite sediment compared to that in the marine environment and our results suggest that this may vary substantially. Therefore, care should be taken when interpreting  $TEX_{86}$  in sediments which have been exposed for a long time to oxygen. This bias may be assessed by cross correlating BIT indices with  $TEX_{86}$  where a high degree of correlation between the two proxies likely signifies a substantial bias.

#### 4 Past productivity and (selective) OM degradation

As discussed above, elucidating the processes related to (selective) OM degradation is essential for an accurate interpretation of proxy records and characterizing the dynamics of the sedimentary carbon pool also contributes to understanding the biogeochemical cycle of carbon. A proper reconstruction of degradation intrinsically also leads to assessment of past export productivity, another important aspect of the carbon cycle that is critical to carbon preservation. Therefore, this chapter deals with quantification of past productivity in relation to selective degradation.

##### 4.1 Barium as a paleoproductivity proxy/tracer

A close link between the marine geochemistry of barium and biological activity in the ocean has been documented for a variety of water column, sediment trap and sediment studies (Goldberg and Arrhenius, 1958; Chow and Goldberg, 1960; Dehairs et al., 1980; Collier and Edmond, 1984; Bishop, 1988; Dymond et al., 1992). The sedi-

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



mentary Ba content, or more precisely the accumulation rate of so-called biogenic Ba has been proposed as a proxy for modern and past productivity (Bishop, 1988; Dehairs et al., 1991; Dymond et al., 1992). Discrete micron-sized barite ( $\text{BaSO}_4$ ) crystals are the major carriers of non-detrital particulate barium in the water column (Dehairs et al., 1980; Bishop, 1988) and have been implicated as the particulate Ba phase directly related to marine carbon export flux (Dehairs et al., 1980; Dymond et al., 1992). Different terms are used in the literature to define this productivity-related fraction of Ba: “biogenic barium” ( $\text{Ba}_{\text{bio}}$ ), “excess Ba” ( $\text{Ba}_{\text{excess}}$ ) and “marine barite”. Although the Ba proxy has been widely applied and algorithms have been developed to reconstruct paleoproductivity from this inorganic geochemical tracer (e.g. Dymond et al., 1992; Gingele and Dahmke, 1994; Van Os et al., 1994; Francois et al., 1995; Schneider et al., 1997; Nürnberg et al., 1997; Pfeifer et al., 2001; Moreno et al., 2002; Hillenbrand et al., 2003; Weldeab et al., 2003a, b; Reitz et al., 2004) fundamental questions remain concerning the exact mechanism/s of barite formation in the water column and its quantitative relationship to primary production and preservation.

Any possible mechanism for barite formation in the water column has to cope with the undersaturation of seawater with respect to barite (Monnin et al., 1999) and therefore requires either abiotic precipitation within supersaturated microenvironments or direct biologic mediation. Barite generation within bariumsulfate-saturated sub-oxic microenvironments of decaying biogenic debris is generally accepted to be the most likely barite-forming pathway (Bishop, 1988). Supersaturation with respect to barite within settling particles and aggregates may either be the result of sulfate regeneration from oxidation of sulphite or of organic-based sulfur compounds or from dissolution of celestite ( $\text{SrSO}_4$ ) produced by Acantharia and siliceous Radiolaria which leads to a release of both sulfate and barium (Bernstein et al., 1992). In addition, active intracellular formation of barite is observed in benthic xenophyophores (Tendal, 1972; Gooday and Nott, 1982). However, due to the fragile nature of these large bottom-dwelling protozoans and the arising difficulties in sampling and identifying them, their role in the marine barite budget is still not understood.

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



If barite formation in the water column occurs proportionally to OM decomposition in aggregate microenvironments, its link to biological productivity is rather direct. If, however, barite precipitation is primarily coupled to a specific organism, the relationship between biological productivity and barium accumulation in sediments is more complex and quantitative estimates of paleoproductivity from sedimentary Ba contents are questionable. An experimental investigation on barite formation in seawater by Ganeshram et al. (2003) showed that living plankton represents a relatively large pool of labile Ba, which is rapidly released during plankton decomposition and acts as the main source of Ba for barite formation in supersaturated microenvironments. The authors further concluded that the availability of microenvironments seems to be the limiting factor in barite precipitation. Although the “microenvironment mechanism” was conclusively shown to be the dominant barite forming pathway in the experiments performed by Ganeshram et al. (2003), several other studies emphasize that Ba input into the sediment in relation with particular organisms – like acantharians – can also be of relevance in specific ocean areas and/or under particular oceanographic/hydrographic conditions (Bernstein et al., 1992; Bertram and Cowen, 1994).

Despite the uncertainties that still exist with respect to the processes and mechanisms forming biogenic barite, sedimentary barium has proven to be a valuable indicator to trace the initial influx of OM, in certain environments as indicated below. Clear examples illustrating the value of barium as such an indicator have been given for the Eastern Mediterranean (Fig. 10; e.g. van Santvoort et al., 1996; Thomson et al., 1999; de Lange et al., 2008). Here the upper part of an organic-rich unit has been oxidised postdepositionally removing the greater part of the OM fraction but not affecting the biogenic barium content. For these case studies it appears that although most of the OM has been removed by a postdepositional downward progressing oxidation front, the initial signal is nicely reflected by the barite content that seems to have remained unaltered since accumulation. This has in part permitted the reconstruction not only of the most recent sapropel but also of some of the entirely degraded older units (e.g. Thomson et al., 1995, 1999; van Santvoort et al., 1996, 1997). It must be noted here that

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



for the extremely organic-rich (6–30% organic carbon) sapropel units, mobilization of barite has occurred in line with the demonstrated bottom water anoxia during such periods (e.g. Passier et al., 1999). In the latter case, organic carbon preservation is usually enhanced so organic carbon itself is a good indicator of initial organic fluxes. It seems therefore that barite can serve as a useful proxy for moderate initial organic carbon fluxes, in particular since such moderate organic carbon contents often leads to its partly or even total degradation. Similar downward oxidation processes have occurred in the Madeira Abyssal Plain organic-rich units that are of trubiditic origin.

It turns out that such oxidation fronts were also active along major glacial/interglacial transitions. A study in the oligotrophic and low sedimentation regimes of the Equatorial Atlantic Ocean revealed distinct peaks of excess Ba at glacial terminations unrelated to any other productivity proxy (Kasten et al., 2001). Similar Ba spikes at climate transitions not supported by other productivity tracers have also been reported from other locations in the Atlantic and Pacific but have remained unexplained so far (Matthewson et al., 1995; Schwarz et al., 1996). Kasten et al. (2001) could demonstrate that these Ba maxima indeed represent productivity pulses and that the discrepancy between barium and TOC in the transitional sediment intervals (Fig. 10) was caused by complete post-depositional degradation of non-refractory TOC due to the action of downward-progressing oxidation fronts during deglacial nonsteady-state conditions. This hypothesis was further corroborated by a study of Moreno et al. (2002) in the North Canary Basin off Cape Ghir where large productivity events were detected at Terminations I, II and III by a multi-productivity-proxy approach. In their core GeoB 4216 which was characterized by mean sedimentation rates of 4.9 cm/kyr coinciding peaks of Ba and TOC were found. In contrast, at site GeoB 5559 located further offshore and subject to significantly lower sedimentation rates of about 2.4 cm/kyr similar Ba spikes at Terminations were not supported by TOC enrichments.

A supplementary high-resolution analysis performed along the last and the penultimate glacial/interglacial transition in core GeoB 4216 (Fig. 11) from the North Canary Basin serves as a further valuable example supporting the suitability of Ba as a pro-

---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

ductivity tracer in this area (Kasten et al., 2003). The perfect match between Ba (Ba/Ti ratios) and TOC in the lower, unoxidized part of the Ba-enriched sediment intervals (Fig. 11) suggests that the input of  $Ba_{bio}$  or  $Ba_{excess}$  must have occurred proportional to the input flux of TOC and that the TOC/ $Ba_{bio}$  ratio of the particulate material reaching the seafloor must have been more or less constant over time. This close correlation between Ba and TOC as well as the distribution of Ba displaying a broad peak further implies that the Ba profiles indeed trace periods of elevated productivity and do not originate from authigenic barite formation due to sulfide oxidation during the action of the oxidation fronts.

The different degrees of post-depositional TOC oxidation along the glacial/interglacial transitions as shown in the two examples above are controlled by the overall rate of sedimentation as well as the magnitude of change in environmental and depositional conditions that occurred during these full climatic transitions. Using a modelling approach, Jung et al. (1997) demonstrated that sedimentation rate is the dominant factor which controls whether a sapropel is oxidized completely or only partly (also cf. Higgs et al., 1994; van Santvoort et al., 1997). Jung et al. (1997) showed that preservation of elevated concentrations of non-refractory organic carbon is generally improbable when the sedimentation rate is lower than 1–2 cm/kyr. This value corresponds well to the value of about 2 to 2.5 cm/kyr on average for the Ceará Rise site where no correlation between Ba and TOC at glacial/interglacial transitions has been found (Fig. 11). At station GeoB 4216 which is characterized by slightly higher sedimentation rates only the upper part of the TOC-enriched interval has been affected by post-depositional oxidation (Fig. 11).

The use of biogenic or excess barium as a productivity tracer is definitely restricted in (1) continental margin settings subject to high input of either eolian or riverine terrigenous matter or strong lateral material transport (e.g. Reitz et al., 2004 and references therein), and in (2) ocean areas characterized by high-productivity conditions in surface waters (Gingele et al., 1999 and references therein). In particular, the latter sites underlying euphotic surface waters, provide a nice example of how OM breakdown modifies

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



other proxies. These sites mostly have high rates of sedimentary methane production and a shallow (only a few meters below the sediment surface) location of the so-called sulfate/methane transition (SMT) where the anaerobic oxidation of methane with sulfate occurs. Along this geochemical reaction zone the strongest diagenetic redistribution of barite takes place with barite crystals being dissolved when buried into the sulfate-depleted sediments below the SMT and reprecipitation of authigenic/diagenetic barite slightly above the SMT in so-called barite fronts (e.g. Torres et al., 1996; Gingele et al., 1999).

However, as has been shown above, in spite of these limitations, sedimentary Ba can serve as a valuable productivity proxy in overall low productivity and low sedimentation ocean areas where it seems to have considerable advantage over other productivity tracers. Compared to biogenic sediment components like TOC, opal, carbonate or specific molecular organic compounds/biomarkers which are subject to strong and variable degrees of decomposition and/or dissolution both on their way through the water column and after deposition on the seafloor barite has the advantage that as much as about 30% of the primary flux from the photic zone are assumed to be preserved within the sediment (Dymond et al., 1992). Thus, the barium proxy might be a robust supplement for productivity reconstructions from organic or biogenic sediment compounds in that it comes into play in more remote, low sedimentation and well oxygenated depositional environments where organic compounds most severely suffer from diagenetic overprint. Furthermore, the barium proxy may provide an effective way to identify and semi-quantify impact on OM degradation in such settings.

#### 4.2 Influences of diagenesis on $\delta^{15}\text{N}$ composition of bulk sediment as viewed through amino acid preservation

The amino acid composition of sediment samples shows systematic compositional changes upon progressive degradation. This covariance has been used to derive a quantitative degradation index which allows quantifying the quality of OM based solely on its chemical composition (Vandewiele et al., 2009; Dauwe et al., 1999). At the

**BGD**

6, 6371–6440, 2009

### OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



same time, amino acids are the main carriers of nitrogen in OM. Stable isotope ratios of nitrogen are a trusted proxy in reconstructions of nutrient regimes and global productivity patterns from sediments. They have been used to elucidate changes in nitrogen cycling (denitrification,  $N_2$ -fixation) and nutrient utilisation in the global ocean (Ganeshram et al., 2002; Deutsch et al., 2004; Altabet, 2007) and individual ocean basins (Farrell et al., 1995; Haug et al., 1998; Ganeshram et al., 2000) over a large range of geological scales (Haug et al., 1998; Struck et al., 2000; Jenkyns et al., 2001; Altabet et al., 2002). To what extent protein/amino acid degradation affects the nitrogen stable isotope composition ( $\delta^{15}N$ ) of sediments is a matter of ongoing debate.

Mineralization processes apparently enrich the stable isotope mixture of particular N in particles sinking from the euphotic zone with  $^{15}N$  on transit from the sea surface through oxic water columns (Altabet and Francois, 1994; Lehmann et al., 2002; Gaye-Haake et al., 2005). Offsets in  $\delta^{15}N$  by 3–5‰ between particles in the water column and surface sediments have been observed in open ocean sediments (Francois et al., 1992; Francois et al., 1997; Altabet et al., 1999). To complicate matters,  $^{15}N$  depletion in particular organic nitrogen (PON) occurs during diagenesis under oxygen-deficient conditions (Wada et al., 1980; Libes and Deuser, 1988; Lehmann et al., 2002). This is thought to either reflect an increase in bacterial biomass that assimilated isotopically depleted dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), or ammonia, or to reflect inefficient protein degradation due to lack of molecular oxygen at the sediment-water interface. After deposition, preservation of proteins may be aided by rapid sedimentation that efficiently seals relatively pristine OM away from oxygenated bottom waters; similarly, an influence of rapid transfer through the water column by mineral ballasting is indicated by lower  $\delta^{15}N$  ratios in sediments with input of eolian dust (Holmes et al., 2003)

To evaluate possible influences of diagenesis on sediment  $\delta^{15}N$  Möbius et al. (2009) determined amino acid composition and the ratio of stable nitrogen isotopes  $^{15}N/^{14}N$  in sediment cores from the Arabian Sea that bracket large differences in sedimentation rates and oxygenation of the sea floor. All records show a positive correlation of  $\delta^{15}N$

and the reactivity of amino acids and indicate that better preserved OM is enriched in  $^{15}\text{N}$  in the Arabian Sea, consistent with observations by Gaye-Haake et al. (2005). The data thus confirm that changes in the isotopic source signal of nitrate, commonly attributed to variations in the intensity of denitrification in the regional mid-water oxygen minimum zone (OMZ), covary with enhanced OM preservation. Different accumulation rates of the cores apparently have minor effect on either amino acid reactivity or  $\delta^{15}\text{N}$ . The basin-wide comparison of  $\delta^{15}\text{N}$  records shows similar and coeval patterns through time over the last 130 kyr, but different average values of  $\delta^{15}\text{N}$  at each core location.  $\delta^{15}\text{N}$  mean values are positively correlated with water depth and point to more intense degradation in thicker oxic water columns over each site (Gaye-Haake et al., 2005). Hence, relative  $\delta^{15}\text{N}$  patterns in core records do reflect the isotopic composition of source nitrate; however, absolute values are altered during early degradation. Thus  $\delta^{15}\text{N}$  records in the Arabian Sea and elsewhere apparently are reliable proxies for the regional nitrogen cycle on geological time scales, but the records are affected by different diagenetic offsets, making reconstructions of gradients in nitrate availability and nitrate utilisation even in one basin difficult.

### 4.3 The use of selective preservation of organic-walled dinoflagellate cysts to separate the palaeoproductivity from the preservation signals

To date, most proxies used to estimate past marine primary production are based on the chemical and molecular composition as well as on the total amount of OM preserved within marine sediments. However, as discussed in the previous chapters, one of the most important factors determining the rate in which these processes alter the initial signal is the availability of oxygen in bottom/pore waters as well as the oxygen concentration. Detailed estimation of bottom/pore water oxygen concentrations forms a key question in determining the rate of selective OM degradation. Recently, a method to reconstruct bottom water oxygen concentrations has been proposed. This method exploits that organic matter components from the same source may vastly differ in their degradation rates in oxic environments (Versteegh and Zonneveld, 2002; Zonneveld et

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



al., 2007). Organic walled dinoflagellate cysts fulfil these conditions and they appear to be extremely suitable to apply the method. Culturing experiments indicate that these cysts are being produced in the upper part of the water column and that cyst production increases when nutrient, trace element or food availability is enhanced (e.g. Pfiester and Anderson, 1987; Ishikawa and Taniguchi, 1996; Montresor et al., 1998; Kremp and Heiskanen, 1999; Godhe et al., 2001). Studies on material of sediment traps located at different depths at one mooring site indicate that cysts produced in the upper water masses are rapidly transported to deeper water layers, probably in the form of faecal pellets and plankton aggregates and until now species selective degradation in the water column has not been observed (Zonneveld et al., 2009a; Susek et al., 2005). After deposition, the cysts remain at a stable position within the sediments and are only relocated by bioturbation and/or sediment resuspension. Species selective lateral transport within the nepheloid layer or in the water column has not been observed so far (e.g. Marret and Zonneveld, 2003).

By studying the post-depositional aerobic OM degradation at natural oxidation fronts in Late Quaternary sediments of the Madeira Abyssal Plain f-turbidite (140 ka BP), the mid-Holocene Eastern Mediterranean Sapropel S1 and the modern Arabian Sea Oxygen Minimum Zone and surrounding sediments, Versteegh and Zonneveld (2002) discovered that among several OM components, some organic-walled dinoflagellate cyst species are extremely resistant to aerobic degradation. This extreme resistance is supported by degradation experiments in natural environments where no short-term degradation can be observed (Kodranz-Nsiah et al., 2008). Recently it has been shown that accumulation rates of this group of cysts in modern sediments are linearly related to upper ocean chlorophyll-*a* concentrations as measured by satellite imaging (Fig. 12) (Zonneveld et al., 2007). In fossil sediments, accumulation rates of the group of resistant cyst species can strongly be correlated to other productivity proxies such as the Ba/Al ratio (Bockelmann, 2007). By grouping resistant cysts with different ecologies the effects on the cyst production of other environmental factors such as sea surface temperature, salinity and individual nutrient or trace element concentrations can be fil-

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tered out. So far the only exception is formed in areas of strong turbulence in the upper water column such as active upwelling cells. Probably since strong turbulence hampers growth of all dinoflagellates (Ross and Sharples, 2007). Consequently, with the exception of areas influenced by active upwelling, accumulation rates of dinoflagellates resistant to aerobic degradation form a high quality quantitative proxy for quantitative net primary productivity.

In contrast to resistant cysts, laboratory experiments and degradation experiments in natural environments have shown that an other group of organic-walled dinoflagellate cysts is extremely vulnerable to degradation in aerobic environments compared to other OM components (e.g. Marret, 1993; Zonneveld et al., 1997; Versteegh and Zonneveld, 2002; Hopkins and McCarthy, 2002; Mudie and McCarthy, 2006). There is a strong indication that differential degradation results from different molecular structures of the cysts (Zonneveld et al., 2008). Numerous studies on the geographic distribution of dinoflagellate cysts indicate that a mixture of members of both groups of species can be found in all marine sediments (e.g. Marret and Zonneveld, 2003). Sediment trap studies and studies in regions where OM in surface sediments is not altered by aerobic degradation suggest that the production rates of both groups are linearly related (Zonneveld et al., 2009b; Zonneveld et al., 2007). The degradation of the sensitive cysts is, however, logarithmic so that the primary production signal of the sensitive species is often diagenetically overprinted. By assuming a linear relationship between the cyst production of both groups and a logarithmic degradation of vulnerable cysts in aerobic environments, a degradation index can be established. The value of this degradation index calculated from cyst accumulation rates in modern surface sediments shows a strong correlation with bottom water oxygen concentrations (Fig. 13) and might as such form a useful tool to reconstruct past bottom water oxygen concentration and deep ocean ventilation.

The relationship between the cyst degradation index and oxygen concentration in bottom waters is highly non-linear (Fig. 13). Degradation is virtually absent under anoxia. High degradation rates are observed at very low oxygen concentrations to

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



decrease to a more or less constant rate until oxygen concentrations reach 4 ml/l. At higher oxygen concentrations degradation rates increase to  $\infty$ . This non-linear pattern has been explained by suggesting that cysts are being degraded by organisms with oxygen concentration being the limiting factor inhibiting the growth rate of degrading organisms at low oxygen concentrations (Jorge and Livingston, 1999; Guerra-Garcia and García-Gómez, 2005). At intermediate oxygen concentrations the population size of the degrader increases with a constant rate whereas at a certain threshold oxygen concentration the population of the degrader reaches a point where all sensitive cysts are being consumed and the degradation index values increase to infinity.

With the exception of a few species only, the molecular structure of organic dinoflagellate cysts is poorly known (Hemsley et al., 1994; Kokinos et al., 1998; Versteegh and Blokker, 2004; Versteegh et al., 2007). Nevertheless, being part of the organic matter the general processes influencing cyst preservation such as modification of the original cyst wall biomolecule by sulphurisation or oxidative polymerisation into its geomolecular equivalents apply (Versteegh et al., 2007). Furthermore, although degradation rates of individual cyst species are not exactly known, the large differences between the taxa are typically observed between different types of OM. The degradation and transformation of dinoflagellate cysts may function as a model for the degradation of kerogen in general but with the big advantage that (in contrast to most other kerogen) the cysts can be related reliably to their source organism, and thus the original biomolecule, at low taxonomical level. This allows e.g. for elucidating the transformation of kerogen under tightly constrained biological and thus biochemical conditions on geological time scales. Although the use of differential degradation of dinoflagellate cysts seems useful to reconstruct past export production and diagenetic overprint, the method is not restricted to dinoflagellate cysts but is applicable to a wide array of organic components with a common source.

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 5 Conclusion and future perspectives

It appears that most of the factors influencing OM preservation have been identified (Fig. 3). This does not mean that they are fully understood. For many factors the mechanisms by which they operate are partly or even fragmentarily understood such as the role of oxygen on preservation or the roles of polymerisation reactions in enhancing OM preservation. Some factors, e.g. the influence of pressure or mineralogical composition of the sediments have not even taken carefully into consideration. This incomplete understanding of OM breakdown hampers proper assessment of the present carbon cycle and to an even larger extent that operating in the past.

The incomplete understanding of the behaviour of sedimentary OM also hampers the interpretation of OM based proxies (such as the  $U_{37}^K$ ,  $TEX_{86}$  and BIT indices) and other proxies which are modified by processes resulting from OM breakdown (such as biogenic barium). The translation of a given proxy to its environment of formation (transfer function) should thus be expanded by a “deformation function” taking into account the transport and diagenesis-related molecular and atomic fractionations that took place during the period between proxy formation and analysis. To get grip on this deformation, proxies for OM degradation have been devised, despite yet fragmentary knowledge of the factors influencing OM production and preservation. In several depositional environments, these proxies, used either individually or in combination seem to work fine. Quantitative assessment of OM degradation opens a way to accurately reconstruct past productivity. By taking palynomorph concentrations and selective changes in assemblage composition as models for production and preservation of OM correction for selective degradation may be achieved leading to reconstruction of past productivity and bottom water oxygenation.

*Acknowledgements.* We thank Stefan Schouten for usefull comments on an earlier version of the manuscript. We acknowledge generous financial support by the Center for Marine Environmental Sciences (MARUM), the International Graduate College EUROPROX and the Alfred Wegener Institute of Polar Research enabling the realisation of the “Workshop on Selective

**BGD**

6, 6371–6440, 2009

### OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Preservation of Organic Matter: Processes and Impact on the Fossil Record” which formed the basis of this paper. GJMV acknowledges support by the German Science Foundation (DFG grant VE486/2).

## References

- 5 Aller, R. C.: Transport and reactions in the bioirrigated zone, in: The Benthic Boundary Layer, edited by: Boudreau, B. P. and Jørgensen, B. B., Oxford University Press, Oxford, 269–301, 2001.
- Aller, R. C. and Blair, N. E.: Carbon remineralization in the Amazon-Guianas tropical mobile mudbelt: A sedimentary incinerator, *Continent. Shelf. Res.*, 26(17–18), 2241–2259, 2006.
- 10 Altabet, M. A.: Constraints on oceanic N balance/imbalance from sedimentary  $^{15}\text{N}$  records, *Biogeosciences*, 4, 75–86, 2007, <http://www.biogeosciences.net/4/75/2007/>.
- Altabet, M. A. and Francois, R.: The use of nitrogen isotopic ratio for reconstruction of past changes in surface ocean nutrient utilization, in: *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean’s Role in Global Change*, edited by: Zahn, R., Pedersen, T. F., Kaminiski, M. A., and Labeyrie, L., Springer, Berlin, 281–306, 1994.
- 15 Altabet, M. A., Higginson, M. J., and Murrey, D. W.: The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric  $\text{CO}_2$ , *Nature*, 415, 159–162, 2002.
- Arnarson, T. S. and Keil, R. G.: Influence of organic-mineral aggregates on microbial degradation of the dinoflagellate *Scrippsiella trochoidea*, *Geochim. Cosmochim. Acta*, 69(8), 2111–2117, 2005.
- 20 Bahri, H., Dignac, M. F., Rumpel, C., Rasse, D. P., Chenu, C., and Mariotti, A.: Lignin turnover kinetics in an agricultural soil is monomer specific, *Soil Biol. Biochem.*, 38(7), 1977–1988, 2006.
- 25 Bauer, J. E., Williams, P. M., and Druffel, E. R. M.:  $^{14}\text{C}$  activity of dissolved organic carbon fractions in the north-central Pacific and Sargossa Sea, *Nature*, 357, 667–670, 1992.
- Bernstein, R. E., Byrne, R. H., Betzer, P. R., and Greco, A. M.: Morphologies and transformations of celestite in seawater: The role of acantharians in strontium and barium geochemistry, *Geochim. Cosmochim. Acta*, 56(8), 3273–3279, 1992.

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Bertram, M. A. and Cowen, J. P.: The form, composition and origin of marine barite, *Eos*, 75, p. 382, 1994.
- Bianchi, T. S., Wysocki, L. A., Stewart, M., Filley, T. R., and McKee, B. A.: Temporal variability in terrestrially-derived sources of particulate organic carbon in the lower Mississippi River and its upper tributaries, *Geochim. Cosmochim. Acta*, 71(18), 4425–3744, 2007.
- Bishop, J. K. B.: The barite-opal-organic carbon association in oceanic particulate matter, *Nature*, 332, 341–343, 1988.
- Blom, A. V.: Quelques remarques sur le mécanisme de séchage des peintures à l'huile, *Peintures, Pigments, Vernis*, 13, 156–162, 1936.
- Bockelmann, F.-D.: Selective preservation of organic-walled dinoflagellate cysts in Quaternary marine sediments: An oxygen effect and its application to paleoceanography, Ph.D., Bremen University, 1–130, 2007.
- Brassell, S. C., Eglinton, G., Marlowe, I. T., Pflaumann, U., and Sarnthein, M.: Molecular stratigraphy: a new tool for climatic assessment, *Nature*, 320, 129–133, 1986.
- Burdige, D. J.: Burial of terrestrial organic matter in marine sediments: A re-assessment, *Glob. Biogeochem. Cycl.*, 19(4), GB4011, doi:10.1029/2004GB002368, 2005.
- Cacho, I., Grimalt, J. O., Sierro, F. J., Shackleton, N. J. and Canals, M.: Evidence for enhanced Mediterranean thermohaline circulation during rapid climatic coolings, *Earth Planet. Sci. Lett.*, 183(3–4), 417–429, 2000.
- Canfield, D. E.: Factors influencing organic carbon preservation in marine sediments, *Chem. Geol.*, 114, 315–329, 1994.
- Chow, T. J. and Goldberg, E. D.: On the marine geochemistry of barium, *Geochim. Cosmochim. Acta*, 20(3–4), 192–198, 1960.
- Collier, R. and Edmond, J.: The trace element geochemistry of marine biogenic particulate matter, *Progr. Oceanogr.*, 13(2), 113–199, 1984.
- Czimczik, C. I. and Masiello, C. A.: Controls on black carbon storage in soils, *Glob. Biogeochem. Cycl.*, 21, GB3005, doi:10.1029/2006GB002798, 2007.
- Dauwe, B., Middelburg, J. J., Herman, P. M. J., and Heip, C. H. R.: Linking diagenetic alteration of amino acids and bulk organic matter reactivity, *Limnol. Oceanogr.*, 44(7), 1809–1814, 1999.
- de Lange, G. J., Thomson, J., Reitz, A., Slomp, C. P., Principato, M. S., Erba, E., and Corselli, C.: Synchronous basin-wide formation and redox-controlled preservation of a Mediterranean sapropel, *Nature Geosci.*, 1, 606–610, 2008.

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- de Leeuw, J. W.: On the origin of sedimentary aliphatic macromolecules: A comment on recent publications by Gupta et al., *Org. Geochem.*, 38(9), 1585–1587, 2007.
- de Leeuw, J. W. and Largeau, C.: A review of macromolecular compounds that comprise living organisms and their role in kerogen, coal and petroleum formation, in: *Organic Geochemistry. Principles and Applications*, edited by: Engel, M. H. and Macko, S. A., Plenum Press, New York, 23–72, 1993.
- de Leeuw, J. W., Versteegh, G. J. M., and van Bergen, P. F.: Biomacromolecules of plants and algae and their fossil analogues, *Plant Ecol.*, 189, 209–233, doi:10.1007/s11258-005-9027-x, 2006.
- De Vargas, C., Aubry, M.-P., Probert, I., and Young, J.: Origin and evolution of Coccolithophores: from coastal hunters to oceanic farmers, in: *Evolution of Primary Producers in the Sea*, edited by: Falkowski, P. G. and Knoll, A., Academic Press, London, 251–285, 2007.
- Dehairs, F., Chesselet, R., and Jedwab, J.: Discrete suspended particles of barite and the barium cycle in the open ocean, *Earth Planet. Sci. Lett.*, 49(2), 528–550, 1980.
- Dehairs, F., Stroobants, N., and Goeyens, L.: Barite formation in the southern-ocean water column, *Mar. Chem.*, 35(1–4), 399–410, 1991.
- Deutsch, C., Sigman, D. M., Thunell, R. C., Meckler, A. N., and Haug, G. H.: Isotopic constraints on glacial/interglacial changes in the oceanic nitrogen budget, *Glob. Biogeochem. Cycl.*, 18, GB4012, doi:10.1029/2003GB002189, 2004.
- Dignac, M. F., Bahri, H., Rumpel, C., Rasse, D. P., Bardoux, G., Balesdent, J., Girardin, C., Chenu, C., and Mariotti, A.: Carbon-13 natural abundance as a tool to study the dynamics of lignin monomers in soil: an appraisal at the Closeaux experimental field (France), *Geoderma*, 128(1–2), 3–17, 2005.
- Dittmar, T., Koch, B., and Jaffé, R.: Tools for studying biogeochemical connectivity among tropical coastal ecosystems, in: *Techniques to study the exchange of organic matter and nutrients among tropical ecosystems*, edited by: Nagelkerken, I., Springer, Berlin, in press, 2009.
- Dittmar, T. and Koch, B. P.: Thermogenic organic matter dissolved in the abyssal ocean, *Mar. Chem.*, 102(3–4), 208–217, 2006.
- Dorgan, K. M., Jumars, P. A., Johnson, B., Boudreau, B. P., and Landis, E.: Burrowing mechanics: Burrow extension by crack propagation, *Nature*, 433, p. 475, 2005.
- Dymond, J., Suess, E., and Lyle, M.: Barium in deep-sea sediment: a geochemical indicator of

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- paleoproductivity, *Paleoceanogr.*, 7, 163–181, 1992.
- Farrell, J. W., Pedersen, T. F., Calvert, S. E., and Nielsen, B.: Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean, *Nature*, 377, 514–517, 1995.
- 5 Francois, R., Honjo, S., Manganini, S. J., and Ravizza, G. E.: Biogenic barium fluxes to the deep-sea: implications for paleoproductivity reconstruction, *Glob. Biogeochem. Cycl.*, 9(2), 289–301, 1995.
- Ganeshram, R. S., François, R., Commeau, J., and Brown-Leger, S. L.: An experimental investigation of barite formation in seawater, *Geochim. Cosmochim. Acta*, 67(14), 2599–2605, 2003.
- 10 Ganeshram, R. S., Pedersen, T. F., Calvert, S. E., and François, R.: Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorus inventories, *Nature*, 415(6868), 156–159, 2002.
- Ganeshram, R. S., Pedersen, T. F., Calvert, S. E., McNeill, G. W., and Fontugne, M. R.: Glacial-interglacial variability in denitrification in the world's oceans: causes and consequences, *Paleoceanogr.*, 15(4), 361–376, 2000.
- 15 Gaye-Haake, B., Lahajnar, N., Emeis, K.-C., Unger, D., Rixen, T., Suthhof, A., Ramaswamy, V., Schulz, H., Paropkari, A. L., Guptha, M. V. S., and Ittekkot, V.: Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean, *Mar. Chem.*, 96(3-4), 243–255, 2005.
- 20 Gingele, F. and Dahmke, A.: Discrete barite particles and barium as tracers of paleoproductivity in South Atlantic sediments, *Paleoceanogr.*, 9(1), 151–168, 1994.
- Gingele, F. X., Zabel, M., Kasten, S., Bonn, W. J., and Nürnberg, C. C.: Biogenic Barium as proxy for paleoproductivity: methods and limitations of application, in: *Use of Proxies in Oceanography*, edited by: Fischer, G. and Wefer, G., Springer, Berlin, 365–392, 1999.
- 25 Gleixner, G., Poirier, N., Bol, R., and Balesdent, J.: Molecular dynamics of organic matter in a cultivated soil, *Org. Geochem.*, 33(3), 357–366, 2002.
- Glud, R. N.: Oxygen dynamics of marine sediments, *Mar. Biol. Res.*, 4(4), 243–289, 2008.
- Godhe, A., Norén, F., Kulenstierna, M., Ekberg, C., and Karlson, B.: Relationship between planktonic dinoflagellate abundance, cysts recovered in sediment traps and environmental factors in the Gullmar Fjord, Sweden, *J. Plankton Res.*, 23(9), 923–938, 2001.
- 30 Goldberg, E. D. and Arrhenius, G. O. S.: Chemistry of Pacific pelagic sediments, *Geochim. Cosmochim. Acta*, 13(2–3), 199–212, 1958.
- Gong, C. and Hollander, D. J.: Evidence for differential degradation of alkenones under con-

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- trasting bottom water oxygen conditions: Implication for paleotemperature reconstruction, *Geochim. Cosmochim. Acta*, 63, 405–411, 1999.
- Goñi, M. A., Yunker, M. B., Macdonald, R. W., and Eglinton, T. I.: The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort Shelf of the Arctic Ocean, *Mar. Chem.*, 93(1), 53–73, 2005.
- Gooday, A. J. and Nott, J. A.: Intracellular barite crystals in two Xenophyophores, *Aschemonella ramuliformis* and *Galatheaemmina sp.* (protozoa: rhizopoda) with comments on the taxonomy of *A. ramuliformis*., *J. Mar. Biol. Ass. U. K.*, 62(3), 595–605, 1982.
- Guerra-Garcia, J. M. and García-Gómez, J. C.: Oxygen labels versus chemical pollutants: do they have similar influence on macrofaunal assemblages? A case study in a harbour with two opposing entrances, *Environ. Pollut.*, 135, 281–291, 2005.
- Gupta, N. S., Michels, R., Briggs, D. E. G., Collinson, M. E., Evershed, R. P., and Pancost, R. D.: Experimental evidence for the formation of geomacromolecules from plant leaf lipids, *Org. Geochem.*, 38(1), 28–36, 2007.
- Haider, K. K.: Problems related to the humification processes in soils of the temperate climate, in: *Soil Biochemistry*, edited by: Bollag, J.-M., Marcel Dekker, New York, 55–94, 1992.
- Hanford, M. J. and Peeples, T. L.: Archaeal tetraether lipids, *Appl. Biochem. Biotechnol.*, 97(1), 45–62, 2002.
- Harvey, G. R., Boran, D. A., Chesal, L. A., and Tokar, J. M.: The structure of marine fulvic and humic acid, *Mar. Chem.*, 12, 119–132, 1983.
- Haug, G. H., Pedersen, T. F., Sigman, D. M., Calvert, S. E., and Nielsen, B.: Glacial/interglacial variations in production and nitrogen fixation in the Cariaco Basin during the last 580 kyr, *Paleoceanogr.*, 13(5), 427–432, 1998.
- Hedges, J. I., Cowie, G. L., Richey, J. E., Quay, P. D., Brenner, R., Strom, M., and Forsberg, B.: Origin and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids, *Limnol. Oceanogr.*, 39(4), 743–761, 1994.
- Hedges, J. I., Eglinton, G., Hatcher, P. G., Kirchman, D. L., Arnosti, C., Derenne, S., Evershed, R. P., Kögel-Knabner, I., de Leeuw, J. W., Littke, R., Michaelis, W., and Rullkötter, J.: The molecularly-uncharacterized component of nonliving organic matter in natural environments, *Org. Geochem.*, 31, 945–958, 2000.
- Hedges, J. I. and Keil, R. G.: Sedimentary organic matter preservation: an assessment and speculative synthesis, *Mar. Chem.*, 49, 81–115, 1995.
- Hedges, J. I. and Keil, R. G.: Organic geochemical perspectives on estuarine processes: sorp-

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- tion reactions and consequences, *Mar. Chem.*, 65, 55–65, 1999.
- Hedges, J. I. and Oades, J. M.: Comparative organic geochemistries of soils and marine sediments, *Org. Geochem.*, 27, 319–361, 1997.
- Hedges, J. I. and Prahl, F. G.: Early diagenesis: consequences for applications of molecular biomarkers, in: *Organic Geochemistry, Principles and Applications*, edited by: Engel, M. H., Macko, S. A., and Jones, D. S., Plenum Press, New York, 237–253, 1993.
- Heim, A. and Schmidt, M. W. I.: Lignin is preserved in the fine silt fraction of an arable Luvisol, *Org. Geochem.*, 38(12), 2001–2011, 2007.
- Hemsley, A. R., Barrie, P. J., and Chaloner, W. G.: Studies of fossil and modern spore and pollen wall biomacromolecules using  $^{13}\text{C}$  solid state NMR, *NERC Spec. Publ.*, 94(1), 15–19, 1994.
- Herbert, T. D.: Alkenone paleotemperature determinations, in: *The Oceans and marine geochemistry*, edited by: Elderfield, H., Elsevier, Amsterdam, 391–432, 2003.
- Herman, J. P., Middelburg, J. J., van de Koppel, J., and Heip, C. H. R.: Ecology of estuarine macrobenthos, *Adv. Ecol. Res.*, 29, 195–240, 1999.
- Hertkorn, N., Benner, R., Frommberger, M., Schmitt-Kopplin, P., Witt, M., Kaiser, K., Kettrup, A., and Hedges, J. I.: Characterization of a major refractory component of marine dissolved organic matter, *Geochim. Cosmochim. Acta*, 70(12), 2990–3010, 2006.
- Higgs, N. C., Thomson, J., Wilson, T. R. S., and Croudace, I. W.: Modification and complete removal of eastern Mediterranean sapropels by postdepositional oxidation, *Geology*, 22, 423–426, 1994.
- Hillenbrand, K.-D., Grobe, H., Diekmann, B., Kuhn, G., and Fütterer, D. K.: Distribution of clay minerals and proxies for productivity in surface sediments of the Bellingshausen and Amundsen seas (West Antarctica) – Relation to modern environmental conditions, *Mar. Geol.*, 193(3–4), 253–271, 2003.
- Hockaday, W. C., Grannas, A. M., Kim, S., and Hatcher, P. G.: Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil, *Org. Geochem.*, 37(4), 501–510, 2006.
- Hoefs, M. J. L., Rijpstra, W. I. C., and Sinninghe Damsté, J. S.: The influence of oxic degradation on the sedimentary biomarker record I: Evidence from Madeira Abyssal Plain turbidites, *Geochim. Cosmochim. Acta*, 66, 2719–2735, 2002.
- Hoefs, M. J. L., Versteegh, G. J. M., Rijpstra, W. I. C., de Leeuw, J. W., and Sinninghe Damsté,

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- J. S.: Postdepositional oxic degradation of alkenones: implications for the measurement of palaeo sea surface temperatures, *Paleoceanogr.*, 13(1), 42–49, 1998.
- Holmes, E., Lavik, G., Fischer, G., and Wefer, G.: Nitrogen isotopes in sinking particles and surface sediments, in: *The South Atlantic in the Late Quaternary*, edited by: Wefer, G., Mulitza, S., and Rathmeyer, V.), Springer, Berlin, 143–165, 2003.
- Hopkins, J. A. and McCarthy, F. M. G.: Post-depositional palynomorph degradation in Quaternary shelf sediments: a laboratory experiment studying the effects of progressive oxidation, *Palynol.*, 26, 167–184, 2002.
- Hopmans, E. C., Weijers, J. W. H., Schefuss, E., Herfort, L., Sinninghe Damsté, J. S., and Schouten, S.: A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids, *Earth Planet. Sci. Lett.*, 224(1–2), 107–116, 2004.
- Huang, Y., Li, B., Bryant, C., Bol, R., and Eglinton, T. I.: Radiocarbon dating of aliphatic hydrocarbons: A new approach for dating passive-fraction carbon in soil horizons, *Soil Sci. Soc. Am. J.*, 63, 1181–1187, 1999.
- Huguet, C., de Lange, G. J., Gustafsson, O., Middelburg, J. J., Sinninghe Damsté, J. S., and Schouten, S.: Selective preservation of soil organic matter in oxidized marine sediments (Madeira Abyssal Plain), *Geochim. Cosmochim. Acta*, 72(24), 6061–6068, 2008.
- Huguet, C., de Lange, G. J., Kim, J.-H., Sinninghe Damsté, J. S., and Schouten, S.: Selective preservation of soil-derived glycerol diacyl glycerol tetraether lipids in oxidized marine sediments, in: *Tex86 Paleothermometry: Proxy validation and application in marine sediments*, edited by: Huguet, C., Utrecht university, Utrecht, 87–104, 2007.
- Huguet, C., Kim, J.-H., de Lange, G. J., Sinninghe Damsté, J. S., and Schouten, S.: Effects of long-term oxic degradation on the  $U_{37}^{K'}$ ,  $TEX_{86}$  and BIT organic proxies, *Org. Geochem.*, submitted, 2009.
- Ishikawa, A. and Taniguchi, A.: Contribution of benthic cysts to the population dynamics of *Scrippsiella* spp. (Dinophyceae) in Onagawa Bay, northeast Japan, *Mar. Ecol. Progr. Ser.*, 140, 169–178, 1996.
- Jenkyns, H. C., Gröcke, D. R., and Hesselbo, S. P.: Nitrogen isotope evidence for water mass denitrification during the Early Toarcian (Jurassic) oceanic anoxic event, *Paleoceanogr.*, 16(6), 593–603, 2001.
- Jorge, R. M. F. and Livingston, A. G.: A novel method for characterisation of microbial growth kinetics on volatile organic compounds, *Appl. Microbiol. Biotechnol.*, 52, 174–178, 1999.
- Jung, M., Ilmberger, J., Mangini, A., and Emeis, K.-C.: Why some Mediterranean sapropels

---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- survived burn-down (and others did not), *Mar. Geol.*, 141, 51–60, 1997.
- Kasten, S., Haese, R. R., Zabel, M., Rühlemann, C., and Schulz, H. D.: Barium peaks at glacial terminations in sediments of the equatorial Atlantic Ocean – relicts of deglacial productivity pulses?, *Chem. Geol.*, 175, 635–651, 2001.
- 5 Kasten, S., Zabel, M., Heuer, V., and Hensen, C.: Processes and signals of non-steady state diagenesis in deep-sea sediments, in: *The South Atlantic in the Late Quaternary*, edited by: Wefer, G., Mulitza, S., and Rathmeyer, V., Springer, Berlin, 431–459, 2003.
- Keil, R. G., Tsamakis, E., Giddings, J. C., and Hedges, J. I.: Biochemical distributions (amino acids, neutral sugars, and lignin phenols) among size-classes of modern marine sediments  
10 from Washington coast, *Geochim. Cosmochim. Acta*, 62, 1347–1364, 1998.
- Kiem, R. and Kögel-Knabner, I.: Contribution of lignin and polysaccharides to the refractory carbon pool in C-depleted arable soils, *Soil Biol. Biochem.*, 35(1), 101–118, 2003.
- Kim, J.-H., Hugué, C., Zonneveld, K. A. F., Versteegh, G. J. M., Sinninghe Damsté, J. S., and Schouten, S.: Stability of the TEX<sub>86</sub> and U<sub>37</sub><sup>K</sup> temperature proxies upon a one year field incubation experiment., *Org. Geochem.*, 73, 2888–2898, 2009.
- 15 Kim, S. W., Kaplan, L. A., Benner, R., and Hatcher, P. G.: Hydrogen-deficient molecules in natural riverine water samples—evidence for the existence of black carbon in DOM, *Mar. Chem.*, 92(1–4), 225–234, 2004.
- Knicker, H. and Hatcher, P. G.: Sequestration of organic nitrogen in the sapropel from Mangrove Lake, Bermuda, *Org. Geochem.*, 32(5), 733–744, 2001.
- 20 Koch, B. P. and Dittmar, T.: From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter, *Rapid Commun. Mass. Spectr.*, 20(5), 926–932, 2006.
- Koch, B. P., Ludwiczowski, K. U., Kattner, G., Dittmar, T., and Witt, M.: Advanced characterization of marine dissolved organic matter by combining reversed-phase liquid chromatography and FT-ICR-MS, *Mar. Chem.*, 111, 233–241, 2008.
- 25 Koch, B. P., Witt, M., Engbrodt, R., Dittmar, T., and Kattner, G.: Molecular formulae of marine and terrigenous dissolved organic matter detected by electrospray ionization fourier transform ion cyclotron resonance mass spectrometry, *Geochim. Cosmochim. Acta*, 69(13), 3299–3308, 2005.
- 30 Koch, B. P., Witt, M., Kattner, G., and Dittmar, T.: Fundamentals of molecular formula assignment to ultrahigh resolution mass data of natural organic matter, *Anal. Chem.*, 79, 1758–1763, 2007.
- Kodranz-Nsiah, M., Zonneveld, K. A. F., and de Lange, G. J.: Species-selective aerobic degra-

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



dation of dinoflagellate cysts – results of a natural exposure experiment, *Rev. Palaeobot. Palynol.*, 152, 32–39, 2008.

Kokinos, J. P., Eglinton, T. I., Goñi, M. A., Boon, J. J., Martoglio, P. A., and Anderson, D. M.: Characterisation of a highly resistant biomacromolecular material in the cell wall of a marine dinoflagellate resting cyst, *Org. Geochem.*, 28(5), 265–288, 1998.

Kremp, A. and Heiskanen, A.-S.: Sexuality and cyst formation of the spring-bloom dinoflagellate *Scrippsiella hangoei* in the coastal northern Baltic Sea, *Mar. Biol.*, 134, 771–777, 1999.

Kujawinski, E. B., Del Vecchio, R., Blough, N. V., Klein, G. C., and Marshall, A. G.: Probing molecular-level transformations of dissolved organic matter: insights on photochemical degradation and protozoan modification of DOM from electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry., *Mar. Chem.*, 92(1–4), 23–37, 2004.

Kujawinski, E. B., Freitas, M. A., Zang, X., Hatcher, P. G., Green-Church, K. B., and Jones, R. B.: The application of electrospray ionization mass spectrometry (ESI MS) to the structural characterization of natural organic matter, *Org. Geochem.*, 33(3), 171–180, 2002.

Laws, E. A., Popp, B. N., Bidigare, R. R., Riebesell, U., Burkhardt, S., and Wakeham, S. G.: Controls on the molecular distribution and carbon isotopic composition of alkenones in certain haptophyte algae, *Geochem. Geophys. Geosys.*, 2(1), 2000GC000057, 2001.

Lehmann, M. F., Bernasconi, S. M., Barbieri, A. and McKenzie, J. A.: Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis, *Geochim. Cosmochim. Acta*, 66(20), 3573–3584, 2002.

Libes, S. M. and Deuser, W. G.: The isotope geochemistry of particulate nitrogen in the Peru upwelling area and the Gulf of Maine, *Deep-Sea Res.*, 35(4), 517–533, 1988.

Marret, F.: Les effets de l'acétolyse sur les assemblages des kystes de dinoflagellés, *Palynosci.*, 2, 267–272, 1993.

Marret, F. and Zonneveld, K. A. F.: Atlas of modern organic-walled dinoflagellate cyst distribution, *Rev. Palaeobot. Palynol.*, 125(1), 1–200, 2003.

Marschner, B., Brodowski, S., Dreves, A., Gleixner, G., Gude, A., Grootes, P. M., Hamer, U., Heim, A., Jandl, G., Ji, R., Kaiser, K., Kalbitz, K., Kramer, C., Leinweber, P., Rethemeyer, J., Schaeffer, A., Schmidt, M. W. I., Schwark, L., and Wiesenberg, G. L. B.: How relevant is recalcitrance for the stabilization of organic matter in soils?, *J. Plant. Nutr. Soil Sci.*, 171(1), 91–110, 2008.

Marshall, A. G., Hendrickson, C. L., and Jackson, G. S.: Fourier transform ion cyclotron resonance mass spectrometry: A primer, *Mass Spectr. Rev.*, 17(1), 1–35, 1998.

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Martrat, B., Grimalt, J. O., Shackleton, N. J., de Abreu, L., Hutterli, M. A., and Stocker, T. F.: Four climate cycles of recurring deep and surface water destabilisations on the Iberian Margin, *Science*, 317, 502–507, 2007.
- Matthewson, A. P., Shimmield, G. B., Kroon, D., and Fallick, A. E.: A 300 kyr high-resolution aridity record of the North African continent, *Paleoceanogr.*, 10(3), 667–692, 1995.
- McKenna, A. M., Purcell, J. M., Rodgers, R. P., and Marshall, A. G.: Identification of vanadyl porphyrins in a heavy crude oil and raw asphaltene by atmospheric pressure photoionization fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, *Energy Fuel.*, 23(4), 2122–2128, 2009.
- Meysman, F. J. R., Middelburg, J. J., and Heip, C. H. R.: Bioturbation: A fresh look at Darwin's last idea, *Trends Ecol. Evol.*, 21(12), 688–695, 2006.
- Middelburg, J. J. and Meysman, F. J. R.: Burial at sea, *Science*, 316, 1294–1295, 2007.
- Möbius, J., Gaye, B., Lahajnar, N., Bahlmann, E., and Emeis, K.-C.: Influences on sedimentary  $\delta^{15}\text{N}$  in the Arabian Sea over the last 130 kyr, *Biogeosci.*, in preparation, 2009.
- Mollenhauer, G. and Eglinton, T. I.: Diagenetic and sedimentological controls on the composition of organic matter preserved in California Borderland Basin sediments, *Limnol. Oceanogr.*, 52(2), 558–576, 2007.
- Mollenhauer, G., Inthorn, M., Vogt, T., Zabel, M., Sinninghe Damsté, J. S., and Eglinton, T. I.: Aging of marine organic matter during cross-shelf lateral transport in the Benguela upwelling system revealed by compound-specific radiocarbon dating, *Geochem. Geophys. Geosys.*, 8(9), Q09004, doi:10.1029/2007GC001603, 2007.
- Monnin, C., Jeandel, C., Cattaldo, T., and Dehairs, F.: The marine barite saturation state of the world's oceans, *Mar. Chem.*, 65(3–4), 253–261, 1999.
- Montresor, M., Zingone, A., and Sarno, D.: Dinoflagellate cyst production at a coastal Mediterranean site, *J. Plankton Res.*, 20(12), 2291–2312, 1998.
- Moodley, L., Middelburg, J. J., Soetaert, K., Boschker, H. T. S., Herman, P. M. J., and Heip, C. H. R.: Similar rapid response to phytodetritus deposition in shallow and deep-sea sediments, *J. Mar. Res.*, 63(2), 457–469, 2005.
- Moreno, A., Nave, S., Kuhlmann, H., Canals, M., Targarona, J., Freudenthal, T., and Abrantes, F.: Productivity response in the North Canary Basin to climate changes during the last 250 000 yr: a multi-proxy approach, *Earth Planet. Sci. Lett.*, 196(3–4), 147–159, 2002.
- Mudie, P. J. and McCarthy, F. M. G.: Marine palynology: potentials for onshore-offshore correlation of Pleistocene-Holocene records, *Trans. Royal Soc. S. Afr.*, 61(2), 139–157, 2006.

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Nürnberg, C. C., Bohrmann, G., Schlüter, M., and Frank, M.: Barium accumulation in the Atlantic sector of the Southern Ocean: Results from 190 000-year records, *Paleoceanogr.*, 12(4), 594–603, 1997.

Opsahl, S. and Brenner, R.: Distribution and cycling of terrigenous dissolved organic matter in the ocean, *Nature*, 386, 480–482, 1997.

Otto, A. and Simpson, M. J.: Evaluation of CuO oxidation parameters for determining the source and stage of lignin degradation in soil, *Biogeochem.*, 80, 121–142, 2006.

Passier, H. F., Bosch, H.-J., Nijenhuis, I. A., Lourens, L. J., Böttcher, M. E., Leenders, A., Sinninghe Damsté, J. S., de Lange, G. J., and de Leeuw, J. W.: Sulphidic Mediterranean surface waters during Pliocene sapropel formation, *Nature*, 397, 146–149, 1999.

Pearson, A. and Eglinton, T. I.: The origin of *n*-alkanes in Santa Monica Basin surface sediment: a model based on compound-specific  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  data, *Org. Geochem.*, 31(11), 1103–1116, 2000.

Pfeifer, K., Kasten, S., Hensen, C., and Schulz, H. D.: Reconstruction of primary productivity from the Barium contents in surface sediments of the South Atlantic Ocean, *Mar. Geol.*, 177(1/2), 13–24, 2001.

Pfiester, L. A. and Anderson, D. M.: Dinoflagellate life-cycles and their environmental control, in: *The biology of dinoflagellates*, edited by: Taylor, F. J. R., Blackwell Scientific Publishers, Oxford, 611–648, 1987.

Prahl, F. G.: Prospective use of molecular paleontology to test for iron limitation on marine primary productivity, *Mar. Chem.*, 39(1–3), 167–185, 1992.

Prahl, F. G., Collier, R. B., Dymond, J., Lyle, M., and Sparrow, M. A.: A biomarker perspective on prymnesiophyte productivity in the northeast Pacific Ocean, *Deep-Sea Res. I*, 40(10), 2061–2076, 1993.

Prahl, F. G., Cowie, G. L., de Lange, G. J., and Sparrow, M. A.: Selective organic matter preservation in “burn-down” turbidites on the Madeira Abyssal Plain, *Paleoceanogr.*, 18(2), 1052, doi:2002PA000853, 2003.

Prahl, F. G., de Lange, G. J., Lyle, M., and Sparrow, M. A.: Post-depositional stability of long-chain alkenones under contrasting redox conditions, *Nature*, 341, 434–437, 1989.

Prahl, F. G., Dymond J. and Sparrow M. A.: Annual biomarker record for export production in the central Arabian Sea, *Deep-Sea Res. II*, 47(7-8), 1581-1604, 2000.

Prahl F. G., Mix A. C. and Sparrow M. A.: Alkenone paleothermometry: Biological lessons from marine sediment records off western South America, *Geochim. Cosmochim. Acta*, 70(1),

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



101-117, 2006.

Prahl, F. G. and Muehlhausen, L. A.: Lipid biomarkers as geochemical tools for paleoceanographic study, in: *Productivity of the Ocean: Present and Past*, edited by: Berger, W. H., Smetacek, V. S., and Wefer, G., Wiley, Chichester, 271–289, 1989.

5 Prahl, F. G., Rontani, J.-F., Zabeti, N., Walinski, S. E., and Sparrow, M. A.: Summer-biased sea-surface temperature record for alkenones in SE Alaskan surface sediments., *Geochim. Cosmochim. Acta*, in review, 2009.

10 Reemtsma, T., These, A., Venkatachari, P., Xia, X. Y., Hopke, P. K., Springer, A., and Lindscheid, M.: Identification of fulvic acids and sulfated and nitrated analogues in atmospheric aerosol by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, *Anal. Chem.*, 78(24), 8299–8304, 2006.

Reitz, A., Pfeifer, K., de Lange, G. J., and Klump, J.: Biogenic barium and the detrital Ba/Al ratio: a comparison of their direct and indirect determination, *Mar. Geol.*, 204(3–4), 289–300, 2004.

15 Rethemeyer, J., Kramer, C., Gleixner, G., Wiesenberg, G. L. B., Schwark, L., Andersen, N., Nadeau, M. J., and Grootes, P. M.: Complexity of soil organic matter: AMS <sup>14</sup>C analysis of soil lipid fractions and individual compounds, *Radiocarb.*, 46(1), 465–473, 2004.

20 Rontani, J.-F., Harji, R., Guasco, F., Prahl, F. G., Volkman, J. K., Bhosle, N. B., and Bonin, P.: Degradation of alkenones by aerobic heterotrophic bacteria: Selective or not?, *Org. Geochem.*, 39, 34–51, 2008.

Rontani, J.-F. and Wakeham, S. G.: Alteration of alkenone unsaturation ratio with depth in the Black Sea: Potential roles of stereomutation and aerobic biodegradation, *Org. Geochem.*, 39(9), 1259–1268, 2008.

25 Ross, O. N. and Sharples, J.: Swimming for survival: a role of phytoplankton motility in a stratified turbulent environment, *J. Mar. Systems*, 70(3–4), 248–262, 2008.

Schaub, T. M., Rodgers, R. P., Marshall, A. G., Qian, K., Green, L. A., and Olmstead, W. N.: Speciation of aromatic compounds in petroleum refinery streams by continuous flow field desorption ionization FT-ICR mass spectrometry, *Energy Fuel.*, 19(4), 1566–1573, 2005.

30 Schefuss, E., Schouten, S., and Schneider, R. R.: Climatic controls on central African hydrology during the past 20,000 years, *Nature*, 437, 1003–1006, 2005.

Schlesinger, W. H. and Melack, J. M.: Transport of organic carbon in the worlds rivers, *Tellus*, 33(2), 172–178, 1981.

Schmidt, F., Elvert, M., Koch, B. P., Witt, M., and Hinrichs, K.-U.: Molecular characterization of

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



dissolved organic matter in pore water of continental shelf sediments, *Geochim. Cosmochim. Acta*, 73(11), 3337–3358, 2009.

Schneider, R. R., Price, B., Müller, P. J., Kroon, D., and Alexander, I.: Monsoon related variations in Zaire (Congo) sediment load and influence of fluvial silicate supply on marine productivity in the east equatorial Atlantic during the last 200 000 years, *Paleoceanogr.*, 12(3), 463–481, 1997.

Schouten, S., Hopmans, E. C., and Sinninghe Damsté, J. S.: The effect of maturity and depositional redox conditions on archaeal tetraether lipid palaeothermometry, *Org. Geochem.*, 35, 567–571, 2004.

Schulte, S., Rostek, F., Bard, E., Rullkötter, J., and Marchal, O.: Variations of oxygen-minimum and primary productivity recorded in sediments of the Arabian Sea, *Earth Planet. Sci. Lett.*, 173(3), 205–221, 1999.

Schwarz, B., Mangini, A., and Segl, M.: Geochemistry of a piston core from Ontong Java plateau (western equatorial Pacific): Evidence for sediment redistribution and changes in paleoproductivity, *Geol. Rundschau*, 85(3), 536–545, 1996.

Sinninghe Damsté, J. S. and de Leeuw, J. W.: Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: State of the art and future research, *Org. Geochem.*, 16, 1077–1101, 1990.

Sinninghe Damsté, J. S., Kuypers, M. M. M., Schouten, S., Schulte, S., and Rullkötter, J.: The lycopane/C<sup>31</sup> *n*-alkane ratio as a proxy to assess palaeoacidity during sediment deposition, *Earth Planet. Sci. Lett.*, 209(1–2), 215–226, 2003.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., and Reichart, G. J.: The influence of oxic degradation on the sedimentary biomarker record II. Evidence from Arabian Sea Sediments, *Geochim. Cosmochim. Acta*, 66, 2737–2754, 2002.

Sleighter, R. L. and Hatcher, P. G.: Molecular characterization of dissolved organic matter (DOM) along a river to ocean transect of the lower Chesapeake Bay by ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, *Mar. Chem.*, 110(3–4), 140–152, 2008.

Smittenberg, R. H., Eglinton, T. I., Schouten, S., and Sinninghe Damsté, J. S.: Ongoing buildup of refractory organic carbon in boreal soils during the Holocene, *Science*, 314(5803), 1283–1286, 2006.

Sollins, P., Homann, P. and Caldwell, B. A.: Stabilization and destabilization of soil organic matter: mechanisms and controls, *Geoderma*, 74(1–2), 65–105, 1996.

**BGD**

6, 6371–6440, 2009

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Stenson, A. C., Marshall, A. G., and Cooper, W. T.: Exact masses and chemical formulas of individual Suwannee River fulvic acids from ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectra, *Anal. Chem.*, 75(8), 1275–1284, 2003.
- 5 Struck, U., Emeis, K.-C., Voss, M., Christiansen, C., and Kunzendorf, H.: Records of southern and central Baltic Sea eutrophication in  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of sedimentary organic matter, *Mar. Geol.*, 164(3–4), 157–171, 2000.
- Suess, E.: Particulate organic carbon flux in the oceans – surface productivity and oxygen utilization, *Nature*, 288, 260–263, 1980.
- 10 Sun, M.-Y. and Wakeham, S. G.: Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin, *Geochim. Cosmochim. Acta*, 58, 3395–3406, 1994.
- Susek, E., Zonneveld, K. A. F., Fischer, G., Versteegh, G. J. M., and Willems, H.: Organic-walled dinoflagellate cyst production related to variations in upwelling intensity and lithogenic influx in the Cape Blanc region (off NW Africa), *Phycol. Res.*, 53(2), 97–112, 2005.
- 15 Teece, M. A., Getliff, J. M., Leftley, J. W., Parkes, R. J., and Maxwell, J. R.: Microbial degradation of the marine prymnesiophyte *Emiliana huxleyi* under oxic and anoxic conditions as a model for early diagenesis: long chain alkadienes, alkenones and alkyl alkenoates, *Org. Geochem.*, 29, 863–880, 1998.
- 20 Tendal, O. S.: A monograph of the Xenophyphoria (Rhizopoda, Protozoa), *Galathea Report*, 12, 1–103, 1972.
- Thomson, J., Higgs, N. C., Wilson, T. R. S., Croudace, I. W., de Lange, G. J., and van Santvoort, P. J. M.: Redistribution and geochemical behaviour of redox-sensitive elements around S1, the most recent eastern Mediterranean sapropel, *Geochim. Cosmochim. Acta*, 59(17), 3487–3501, 1995.
- 25 Thomson, J., Mercone, D., de Lange, G. J., and van Santvoort, P. J. M.: Review of recent advances in the interpretation of eastern Mediterranean sapropel S1 from geological evidence, *Mar. Geol.*, 153, 77–89, 1999.
- Torres, M. E., Brumsack, H. J., Bohrmann, G., and Emeis, K. C.: Barite fronts in continental margin sediments: a new look at barium remobilization in the zone of sulfate reduction and formation of heavy barites in diagenetic fronts, *Chem. Geol.*, 127(1–3), 125–139, 1996.
- 30 Trumbore, S. E. and Zheng, S. H.: Comparison of fractionation methods for soil organic matter  $^{14}\text{C}$  analysis, *Radiocarb.*, 38(2), 219–229, 1996.

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- van Dongen, B. E.: Natural sulfurization of carbohydrates in marine sediments: consequences for the chemical and carbon isotopic composition of sedimentary organic matter, *Geol. Ultratrajectina*, 224, 1–149, 2003.
- van Nugteren, P., Herman, P. M. J., Moodley, L., Middelburg, J. J., Vos, M., and Heip, C. H. R.: Spatial distribution of detrital resources determines the outcome of competition between bacteria and a facultative detritivorous worm, *Limnol. Oceanogr.*, 54(5), 1413–1419, 2009.
- Van Os, B. H. H., Lourens, L. J., Hilgen, F. J., de Lange, G. J., and Beaufort, L.: The formation of Pliocene sapropels and carbonate cycles in the Mediterranean – diagenesis, production and productivity, *Paleoceanogr.*, 9(4), 601–617, 1994.
- van Santvoort, P. J. M., de Lange, G. J., Langereis, C. G., Dekkers, M. J., and Paterne, M.: Geochemical and paleomagnetic evidence for the occurrence of "missing" sapropels in eastern Mediterranean sediments, *Paleoceanogr.*, 12(6), 773–786, 1997.
- van Santvoort, P. J. M., de Lange, G. J., Thomson, J., Cussen, H., Wilson, T. R. S., Krom, M. D., and Ströhle, K.: Active post-depositional oxidation of the most recent sapropel (S1) in sediments of the eastern Mediterranean Sea, *Geochim. Cosmochim. Acta*, 60, 4007–4024, 1996.
- Vandewiele, S., Cowie, G., Soetaert, K., and Middelburg, J. J.: Amino acid biogeochemistry and organic matter degradation state across the Pakistan margin oxygen minimum zone, *Deep-Sea Res II*, 56(6–7), 376–392, 2009
- Versteegh, G. J. M. and Blokker, P.: Resistant macromolecules of extant and fossil microalgae, *Phycol. Res.*, 52(4), 325–339, 2004.
- Versteegh, G. J. M., Blokker, P., Marshall, C. R., and Pross, J.: Macromolecular composition of the dinoflagellate cyst *Thalassiphora pelagica* (Oligocene, SW Germany), *Org. Geochem.*, 38, 1643–1656, 2007.
- Versteegh, G. J. M., Blokker, P., Wood, G., Collinson, M. E., Sinninghe Damsté, J. S., and de Leeuw, J. W.: Oxidative polymerization of unsaturated fatty acids as a preservation pathway for microalgal organic matter, *Org. Geochem.*, 35, 1129–1139, 2004.
- Versteegh, G. J. M., Riegman, R., de Leeuw, J. W., and Jansen, J. H. F.:  $U_{37}^K$  values for *Isochrysis galbana* as a function of culture temperature, light intensity and nutrient concentrations, *Org. Geochem.*, 32, 785–794, 2001.
- Versteegh, G. J. M. and Zonneveld, K. A. F.: Use of selective degradation to separate preservation from productivity, *Geology*, 30(7), 615–618, 2002.
- Villanueva, J., Grimalt, J. O., Labeyrie, L. D., Cortijo, E., Vidal, L., and Turon, J.-L.: Precessional

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- forcing of productivity in the North Atlantic Ocean, *Paleoceanogr.*, 13(6), 561–571, 1998.
- von Lütow, M., Kögel-Knabner, I., Ekschmitt, K., Heinz, F., Guggenberger, G., Matzner, E., and Marschner, B.: SOM fractionation methods: Relevance to functional pools and to stabilization mechanisms, *Soil Biol. Biochem.*, 39(9), 2183–2207, 2007.
- 5 Wada, E., Goldberg, E. D., Horibe, Y., and Saruhashi, K.: Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments, in: *Isotope Marine Chemistry*, edited by: Goldberg, E. D., Horibe, Y., and Saruhashi, K., Uchida Rokakuho, Tokyo, 375–398, 1980.
- Wakeham, S. G. and Canuel, E. A.: Degradation and preservation of organic matter in marine sediments, in: *Handbook of Environmental Chemistry*, edited by: Hutzinger, O., Springer, Berlin, 295–321, 2006.
- 10 Wakeham, S. G., Lee, C., Hedges, J. I., Hernes, P. J., and Peterson, M. L.: Molecular indicators of diagenetic status in marine organic matter, *Geochim. Cosmochim. Acta*, 61, 5363–5369, 1997.
- 15 Wakeham, S. G., Peterson, M. L., Hedges, J. I., and Lee, C.: Lipid biomarker fluxes in the Arabian Sea, with a comparison to the equatorial Pacific Ocean, *Deep-Sea Res. II*, 49(12), 2265–2301, 2002.
- Weijers, J. W. H., Schouten, S., Spaargaren, O. C., and Sinninghe Damsté, J. S.: Occurrence and distribution of tetraether membrane in soils: Implications for the use of the BIT index and the TEX<sub>86</sub> SST proxy, *Org. Geochem.*, 37, 1680–1693, 2006.
- 20 Weldeab, S., Emeis, K.-C., Hemleben, C., Schmiedl, G., and Schulz, H.: Spatial productivity during formation of Sapropels S5 and S6 in the Mediterranean Sea: evidence from Ba contents, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 191, 169–190, 2003a.
- Weldeab, S., Siebel, W., Wehausen, R., Emeis, K.-C., Schmiedl, G., and Hemleben, C.: Late Pleistocene sedimentation in the Western Mediterranean Sea: implications for productivity changes and climatic conditions in the catchment areas, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 190, 121–137, 2003b.
- 25 Wiesenberg, G. L. B., Schwartzbauer, J., Schmidt, M. W. I., and Schwark, L.: Plant and soil lipid modification under elevated atmospheric CO<sub>2</sub> conditions: II. Stable carbon isotopic values ( $\delta^{13}\text{C}$ ) and turnover, *Org. Geochem.*, 39(1), 103–117, 2008.
- Williams, P. M. and Druffel, E. R. M.: Radiocarbon in dissolved organic-matter in the Pacific Ocean, *Nature*, 330, 246–248, 1987.
- 30 Witt, M., Fuchser, J., and Koch, B. P.: Fragmentation studies of fulvic acids using collision

**BGD**

6, 6371–6440, 2009

---

**OM preservation –  
processes and  
impact**K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



induced dissociation fourier transform ion cyclotron resonance mass spectrometry, *Anal. Chem.*, 81(7), 2688–2694, 2009.

Zonneveld, C. A. F., Bockelmann, F.-D., and Holzwarth, U.: Selective preservation of organic walled dinoflagellate cysts as a tool to quantify past net primary production and bottom water oxygen concentrations, *Mar. Geol.*, 237(3–4), 109–126, doi:10.1016/j.margo.2006.10.023, 2007.

Zonneveld, C. A. F., Susek, E., and Fischer, G.: Interannual and seasonal variability of the organic-walled dinoflagellate cyst production in the coastal upwelling region off Cape Blanc (Mauritania), *J. Phycol.*, in press, 2009a.

Zonneveld, K. A. F., Chen, L., Möbius, J., and Mahmoud, M. S.: Environmental significance of dinoflagellate cysts from the proximal part of the Po-river discharge plume (off southern Italy, Eastern Mediterranean)., *J. Sea Res.*, doi:10.1016/j.seares.2009.02.003, in press, 2009b.

Zonneveld, K. A. F., Versteegh, G. J. M., and de Lange, G. J.: Preservation of organic walled dinoflagellate cysts in different oxygen regimes: a 10 000 years natural experiment, *Mar. Micropaleontol.*, 29, 393–405, 1997.

Zonneveld, K. A. F., Versteegh, G. J. M., and Kodranz-Nsiah, M.: Preservation of Late Cenozoic organic-walled dinoflagellate cysts; a review, *Mar. Micropaleontol.*, 86, 179–197, 2008.

**BGD**

6, 6371–6440, 2009

---

## OM preservation – processes and impact

K. A. F. Zonneveld et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

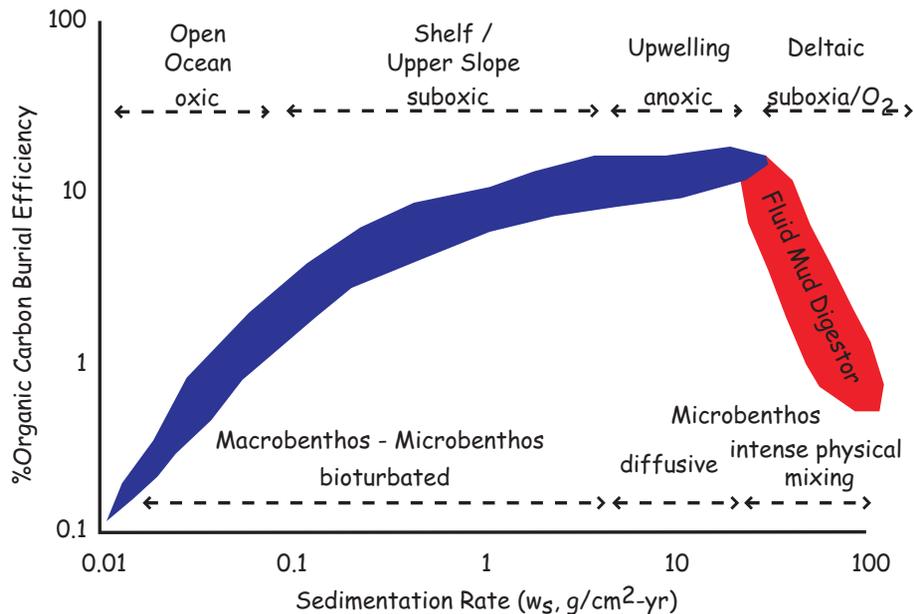
Printer-friendly Version

Interactive Discussion



**OM preservation – processes and impact**

K. A. F. Zonneveld et al.



**Fig. 1.** Cartoon illustrating the complex, multivariate nature of the biological and/or physical processes in surface sediments fine-tuning the organic matter burial efficiency in different marine sedimentary settings.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

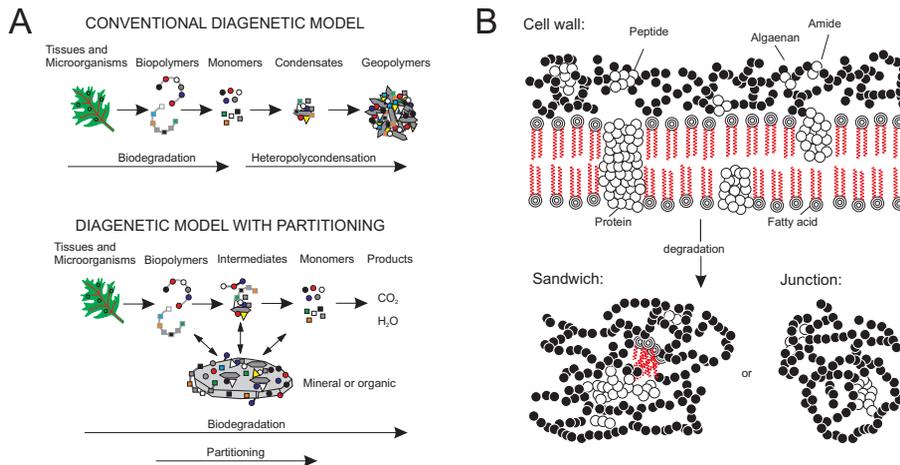
Printer-friendly Version

Interactive Discussion



OM preservation –  
processes and  
impact

K. A. F. Zonneveld et al.



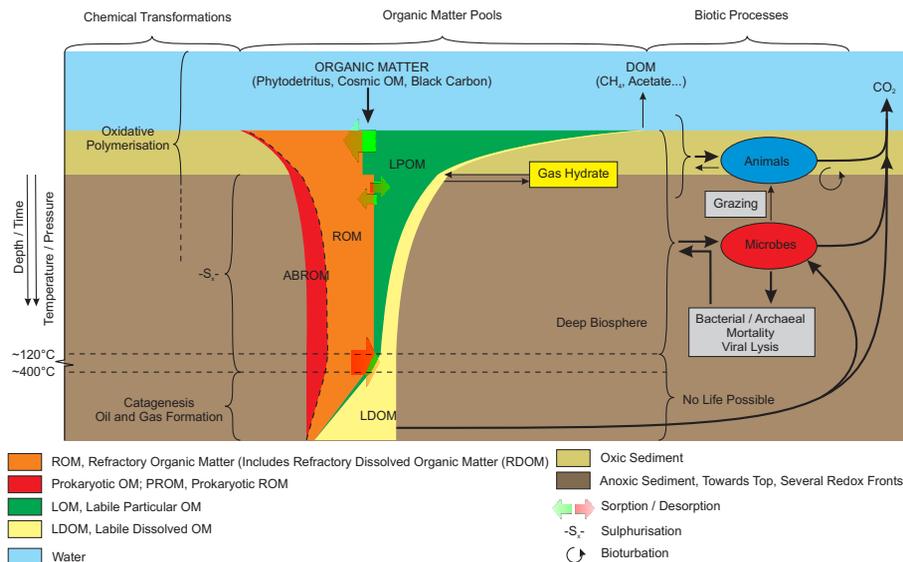
**Fig. 2.** Physical protection of organic matter. **(A)** Conventional biodegradation/ repolymerisation model (top) and alternative biodegradation/sorption model for organic matter diagenesis and preservation (bottom) (modified from Hedges and Keil, 1999). **(B)** Schematic illustrations of (above) the structure of an algaenan-containing cell wall and (below) proteinaceous organic matter “encapsulated” within degraded algal cell wall material (modified from Knicker and Hatcher, 2001).

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



**OM preservation – processes and impact**

K. A. F. Zonneveld et al.



**Fig. 3.** Degradation and transformation of organic matter (OM) in sediments. Left, chemical transformation processes; Centre, organic matter pools; Right, biotic processes. The sizes of the organic matter pools and their size reduction with time/depth underestimate the actual degradation, they are not in scale but indicate processes and relative changes (for further explanation see Sect. 2.6).

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

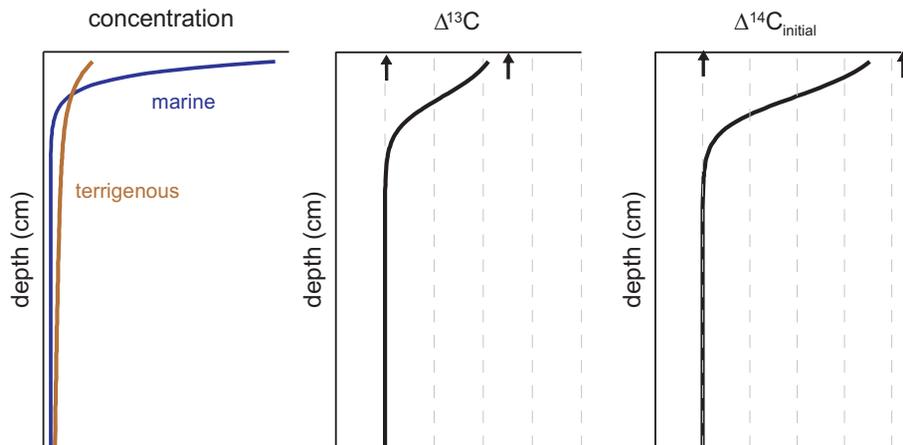
Printer-friendly Version

Interactive Discussion



OM preservation –  
processes and  
impact

K. A. F. Zonneveld et al.



**Fig. 4.** Conceptual diagram illustrating down-core profiles in relative concentration of a compound that can be derived both from marine and terrestrial sources. If the materials from the two sources differ in stable isotopic and radiocarbon signatures, the more rapid decay of the marine component would result in  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  profiles as illustrated. Arrows indicate assumed isotopic composition of the marine and terrigenous components.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

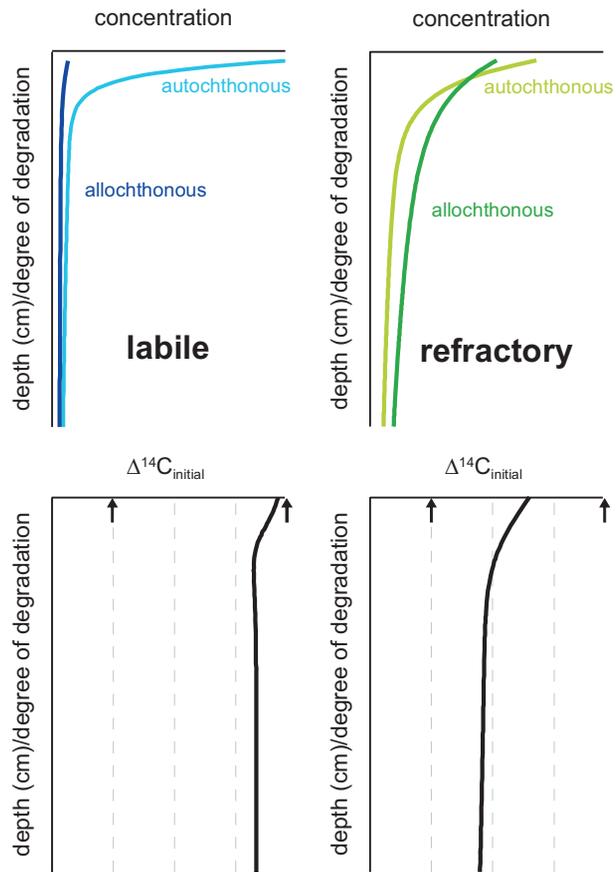
Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Fig. 5.** Conceptual diagram illustrating the effect of preferential degradation of autochthonous, unprotected material on  $\Delta^{14}\text{C}$  profiles of two marine compounds with different decay rates.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

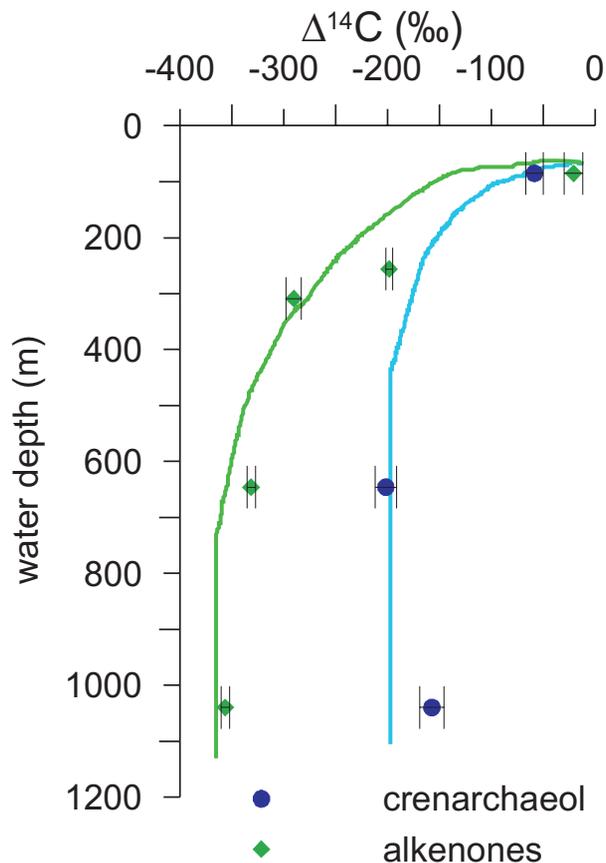
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.

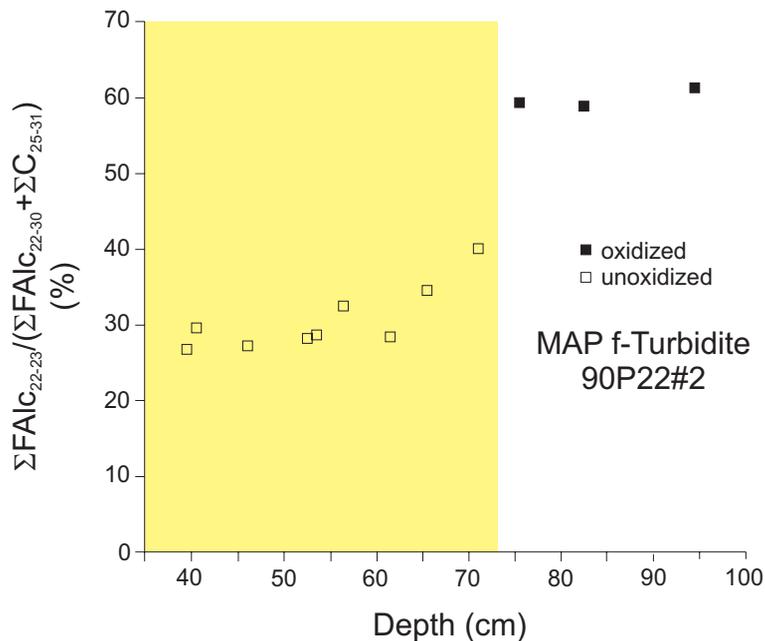


**Fig. 6.** Radiocarbon concentrations of alkenones and crenarchaeol in core-top samples along an offshore transect across the Namibian Shelf and slope (Mollenhauer et al., 2007). Lines are hand-drawn and suggest more rapid degradation of crenarchaeol than alkenones.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

OM preservation – processes and impact

K. A. F. Zonneveld et al.



**Fig. 7.** Study of an aerobic burndown turbidite on the Madeira Abyssal Plain which supports the inferred diagenetic sensitivity of the long-chain n-alkanol ( $C_{26}$ -ol) to n-alkane ( $C_{29}$ ) index (unpublished data).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

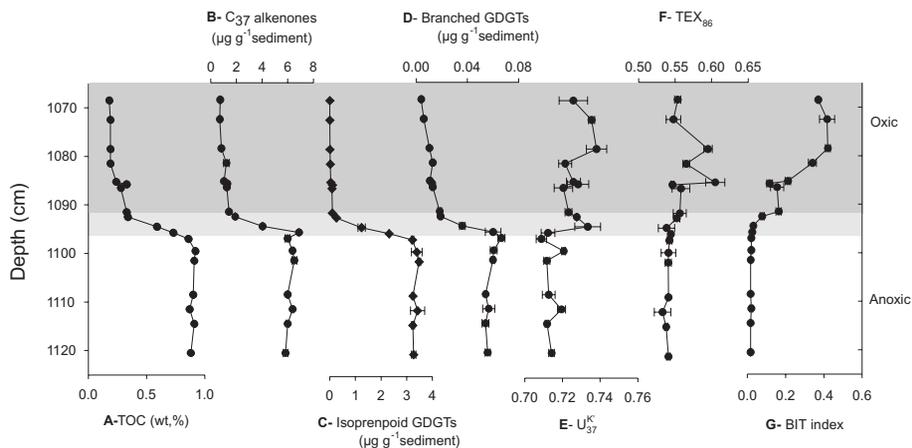
Interactive Discussion





## OM preservation – processes and impact

K. A. F. Zonneveld et al.



**Fig. 9.** Profile of **(A)** TOC (wt. %), **(B)** C<sub>37</sub> alkenones abundance (μg g<sup>-1</sup> sediment), **(C)** summed abundance of isoprenoid (μg g<sup>-1</sup> sediment), **(D)** Branched GDGTs abundance (μg g<sup>-1</sup> sediment), **(E)** U<sub>37</sub><sup>K</sup>, **(F)** TEX<sub>86</sub>, and **(G)** BIT index across the oxidation front in the F-turbidite (Huguet et al., 2008).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

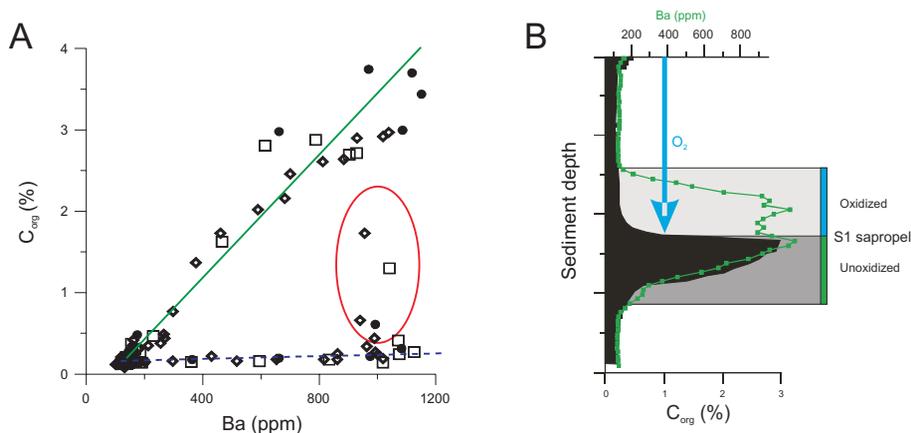
Printer-friendly Version

Interactive Discussion



OM preservation – processes and impact

K. A. F. Zonneveld et al.



**Fig. 10. (A)** Percentage  $C_{org}$  versus total Ba content for sediments in cores UM15 (dots), UM26 (diamonds), and UM35 (open squares) (modified from van Santvoort et al., 1996). The green line indicates the trend for un-oxidized samples, the blue dashed line those for oxidized samples, whereas the red oval indicates partly oxidized samples. **(B)** total Ba and  $C_{org}$  in eastern Mediterranean sediment (modified from de Lange et al., 2008), illustrating the progression of the oxidation front (=removal of  $C_{org}$  while maintaining Ba content).

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

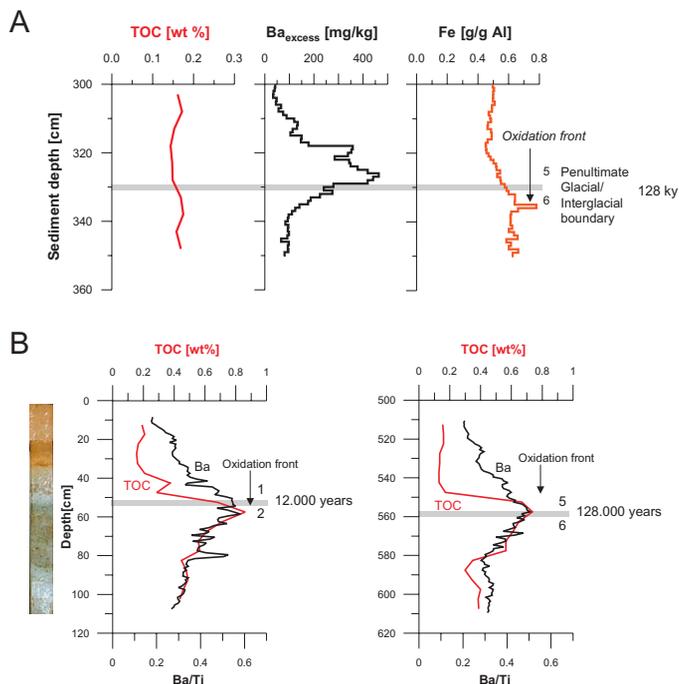
Printer-friendly Version

Interactive Discussion



OM preservation – processes and impact

K. A. F. Zonneveld et al.



**Fig. 11.** (A) Complete post-depositional oxidation of non-refractory TOC across the penultimate glacial/interglacial transition (oxygen isotope stage boundary 6/5) in sediments of site GeoB 1523 on the Céara Rise (modified from Kasten et al., 2001). The initially present TOC has been degraded – leaving solid-phase Ba as a relict. The distribution of Fe with a distinct peak below the glacial/interglacial boundary marks the depth to which the oxidation front progressed down and then remained fixed for a considerable time before moving up again – adapting to the new geochemical conditions. (B) Action of oxidation fronts across full glacial/interglacial boundaries in sediments of the Canary Island region (core GeoB 4216). While the Ba/Ti and TOC profiles perfectly match in the lower part of the Ba peaks, a discrepancy between these two parameters is found in the upper part which points to a partial post-depositional TOC oxidation (modified from Kasten et al., 2003). While TOC is selectively degraded during re-oxidation of the previously sub-oxic sediment Ba is not affected by this aerobic decay of organic matter or oxidation of possible pre-formed sulfides and can thus serve as valuable indicator of the initial productivity pulses at this site.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

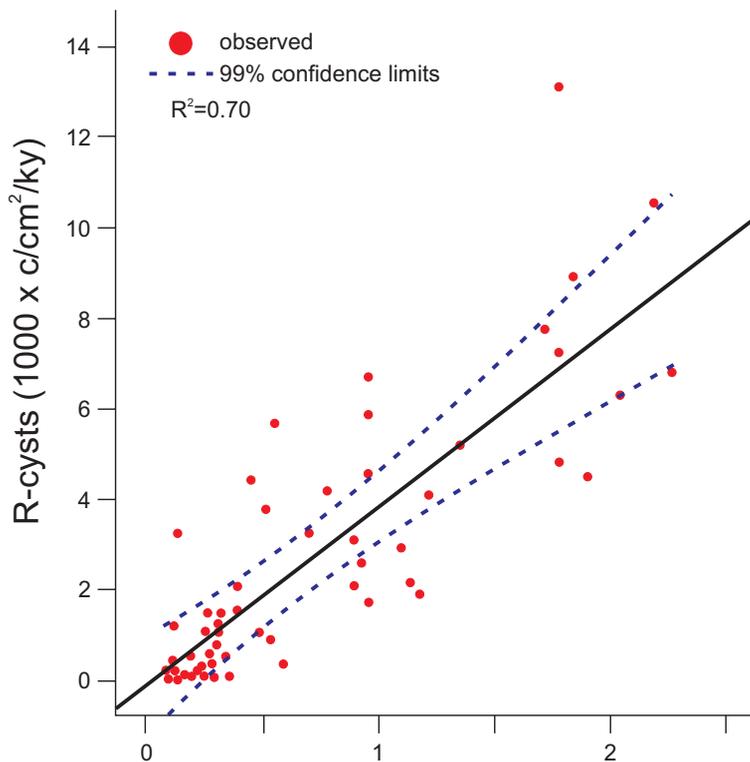
Printer-friendly Version

Interactive Discussion



**OM preservation –  
processes and  
impact**

K. A. F. Zonneveld et al.



**Fig. 12.** Relationship between accumulation rates of resistant cysts (R-cysts) and mean annual upper water chlorophyll-*a* concentrations. Estimated linear relationship with 99.9% confidence limits of mean (modified from Zonneveld et al., 2007).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

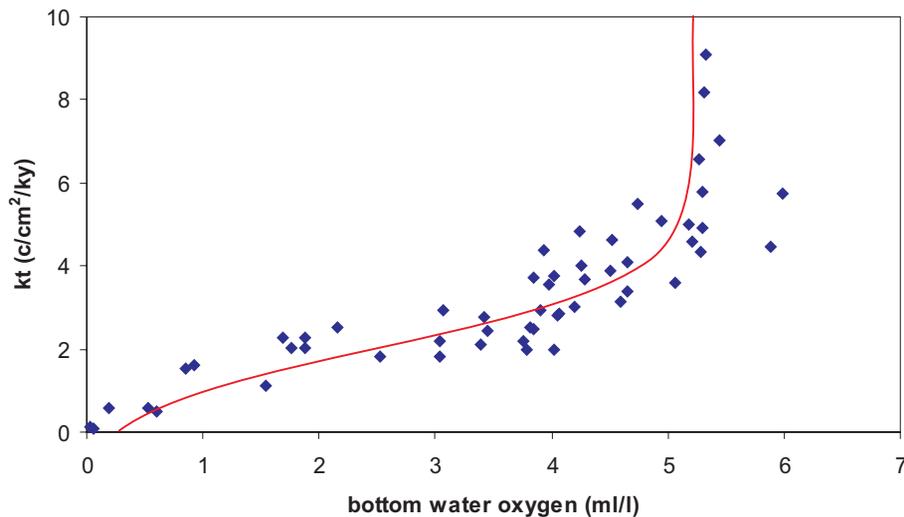
Printer-friendly Version

Interactive Discussion



OM preservation –  
processes and  
impact

K. A. F. Zonneveld et al.



**Fig. 13.** Relationship between the degradation S-cysts expressed as  $kt$  and bottom water oxygen concentration  $[O_2]$ .  $k$ =degradation constant;  $t$ =time (ky), whereby a first-order decay is assumed,  $kt=\ln(X_i/X_f)$  with  $X_f$ =final cyst concentration (cysts  $\text{cm}^{-2} \text{ky}^{-1}$ ) and  $X_i$ =initial cyst concentration (cysts  $\text{cm}^{-2} \text{ky}^{-1}$ ) (modified from Zonneveld et al., 2007).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)