

**Terrigenous organic matter in sediments of the eastern equatorial Atlantic  
- distribution, reactivity, and relation to Late Quaternary climate -**

Dissertation

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## General Outline

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This PhD thesis comprises four sections that have been published (Chapters 2 - 4) or are submitted to be published (Chapter 5) in international peer-reviewed scientific journals. Following the introductory **Chapter 1**, bulk organic records (elemental analysis, stable organic carbon isotopes, Rock-Eval pyrolysis) and first results from biomarker investigations (lignin phenols) from the Congo deep-sea fan (ODP-Site 1075) are presented in **Chapter 2** (Holtvoeth et al., 2001). The authors investigate the temporal frequency of high-amplitude variations in OM sedimentation and preservation and discuss the cyclic occurrence of a stable OM fraction. This fraction led to the definition and application of a new proxy for bulk OM reactivity, i.e. the low-mature/high-mature ratio (lm/hm). It is concluded that terrigenous organic matter was underestimated in earlier studies that used bimodal mixing equations for the interpretation of the isotopic signature of bulk OM (bulk  $\delta^{13}\text{C}_{\text{org}}$ ) to estimate marine and terrigenous amounts. These results emphasize the need for additional information on principle mechanisms of terrigenous OM export to deep-sea settings.

**Chapter 3** (Wagner et al., 2003) therefore elaborates the general importance of terrigenous OM in the modern eastern equatorial Atlantic. Differences in quantity and quality as well as regional distribution patterns of different types of kerogen are established from multidisciplinary investigations of surface samples from a range of marine settings that include organic petrology, palynology, isotopic ratios of bulk OM, Rock-Eval pyrolysis, and terrigenous biomarkers (lignin phenols). A new approach of data evaluation relates temporal variations in the quality of terrigenous OM at the Congo deep-sea fan to an idealized cycle of insolation and the development of continental climate.

Additional biomarker data from the Congo fan lead to new insights that are discussed in **Chapter 4** (Holtvoeth et al., 2003). Relations of parameters sensitive towards bulk OM degradation, OM reactivity and the lignin phenol yields illustrate the complex interplay of primary composition and selective diagenesis. The consideration of nitrogen-rich soil OM (SOM) as a major organic compound provides a new and important aspect for the understanding of organic sedimentation on the Congo deep-sea fan. A key conclusion of this study is that SOM enriched in  $^{13}\text{C}$  and nitrogen may bias terrigenous proportions that have been estimated from established proxies, namely  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios and the isotopic composition (bulk  $\delta^{13}\text{C}_{\text{org}}$ ). A refined model on temporal variations of bulk OM composition off the Congo is presented that links variations in bulk OM composition to central African climate variability.

**Chapter 5** (Holtvoeth et al., submitted) comprises new results from organic geochemical and organic petrological investigations (maceral analysis) of Late Quaternary sections from the Niger deep-sea fan. These are compared to the results from the Congo fan and further support the concept of SOM being a dominant organic fraction in tropical West-African continental margin deposits. Cyclic changes of bulk geochemical signatures are related to the climate-controlled dynamics of soil and vegetation habitats in the catchment areas of both river systems.

**Chapter 6** finally summarizes the new insights on terrigenous OM supply to the eastern equatorial Atlantic developed in the course of this PhD thesis, assembles problems and open questions for future research, and reports latest news from other (biomarker) investigations on the Niger and Congo fans that provide good chances to validate and further develop the key conclusions drawn from this study.

## Abstract

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Production of vegetable biomass in marine and terrigenous ecosystems uses vast amounts of atmospheric CO<sub>2</sub> and therefore is an essential element of the global carbon cycle. Biomass of both, marine and terrigenous origin is buried in marine sediments. Fixed CO<sub>2</sub> thus is taken out of the active carbon cycle for geological time spans. As terrigenous and marine proportions of bulk organic matter (OM) in marine sediments finally mirror the effectiveness of CO<sub>2</sub> fixation by the oceanic and continental biospheres they are of great importance for global carbon budgets and climate modelling. However, there is increasing evidence that terrigenous OM in marine sediments is severely underestimated by conventional interpretation of standard proxies to assess terrigenous and marine OM amounts, for example C<sub>org</sub>/N<sub>tot</sub> ratios and bulk organic carbon isotopes (d<sup>13</sup>C<sub>org</sub>). This study focuses on factors controlling temporal variations in quantity and quality of terrigenous OM export from tropical Africa to the continental margin by two major rivers, the Congo and the Niger. High-resolution multi-proxy investigations were performed on late Quaternary sections of ODP Site 1075 (Congo deep-sea fan, 1200 - 9 ka) and core GeoB 4901 (Niger deep-sea fan, 245 - 0 ka) to characterize the bulk sedimentary OM and to reappraise the role of terrigenous OM. The analytical concept combines elemental analysis (C, N, S), stable organic carbon isotopes (bulk d<sup>13</sup>C<sub>org</sub>), organic petrology (maceral analysis), Rock-Eval pyrolysis, and terrigenous biomarkers (lignin phenols). Degradation rates of bulk OM calculated from C/S ratios and the reactivity of the residual OM as determined by Rock-Eval pyrolysis allow to draw conclusion on the composition of bulk OM and its susceptibility towards microbial degradation prior to burial. Additional information on marine and terrigenous contributions is obtained from palynology, clay mineralogy (Ti/Al ratios), and the determination of biogenic opal.

At both river fans, supply of terrigenous lithogenic and organic matter is closely connected to the dynamics of the African hydrological cycle (humidity/aridity, chemical weathering intensity, fluvial run-off, vegetation) which is primarily determined by cyclic fluctuations of insolation. The gradual adjustment process of the continental ecosystem is documented by a phase shift of about 4 kyrs between the precession-controlled insolation cycle (frequency of <sup>a</sup>21 kyrs) and changes in bulk OM quality and quantity, kaolinite supply (reflecting chemical weathering intensity), and pollen assemblages. Significant differences in OM quality and the dynamics of OM sedimentation and preservation, however, distinguish the two river systems.

At the Congo fan, bulk OM contents (TOC) of ODP Site 1075 range from 0.8 to 4.2 % (average: 2.1 %). Low C<sub>org</sub>/N<sub>tot</sub> ratios around 8 (±2) preliminary indicate minor contribution of nitrogen-poor plant material (C<sub>org</sub>/N<sub>org</sub> > 20, marine OM <sup>a</sup>7). Bulk d<sup>13</sup>C<sub>org</sub> ratios averaging around -21 ‰ (± 2 ‰) suggest that only about one third of the bulk sedimentary OM is of terrestrial origin if conventional end-member values are applied for terrigenous (-27 ‰, C<sub>3</sub> plants) and marine (-18 ‰) OM. Results from Rock-Eval pyrolysis indicate kerogen type III - II (mainly terrigenous to mainly marine) and reveal the existence of a conspicuous, thermally stable/high-mature organic component. Although high-mature this component generates astonishing high amounts of hydrocarbons at high pyrolysis temperatures (T<sub>max</sub> >> 450°C). The ratios of hydrocarbons released from low-mature/labile and high-mature/stable OM (lm/hm ratio) during pyrolysis represents a new proxy for bulk OM reactivity/stability that

documents high-amplitude fluctuations in bulk OM composition and/or preservation over the past 1.2 Ma. The integrated view of lm/hm ratios, degradation rates, and lignin phenol concentrations reveals that two different lignin sources (i.e. terrigenous OM fractions) are relatively enriched when labile marine OM is selectively degraded: (1) “fresh” particulate terrigenous OM of relatively high reactivity during arid climates and (2) the stable OM fraction during humid climates.

TOC contents of the Niger fan sediments are lower relative to the Congo fan sediments, 1.4 % on average. Maceral analysis reveals that almost two thirds of the visible organic particles (62 % on average) are of terrigenous origin. Rock-Eval pyrolysis indicates kerogen type III - IV, i.e. dominantly terrigenous to residual types of kerogen. Compared to the Congo fan sediments  $C_{org}/N_{tot}$  ratios and bulk  $\delta^{13}C_{org}$  signatures show higher average values (10.5 and -18.4 ‰, respectively) and much broader ranges. Remarkably, both proxies reveal parallel trends in the late Quaternary profiles. Enhanced values occur during arid climates (e.g. Marine Isotopic Stages 5.2 and 5.4) indicating significant influence of nitrogen-poor particulate OM from  $^{13}C$ -enriched  $C_4$  vegetation. Opposite trends are observed during humid stages 5.3 and 5.5. Notably, a stable OM compound is absent in the Niger fan sediments.

The latter observation provokes a comparison of the OM stocks of the Congo and Niger catchments to identify the potential source of the stable, high-mature OM fraction. Burned material (charcoal, black carbon) as the main source of hydrocarbons from high-mature OM can be excluded as vegetation fires occur in both settings. However, comparison of the soil inventories displays a striking difference: deeply weathered ferallitic soils (Oxisols) are the dominating soil type in the Congo basin but almost absent in the Niger catchment. Oxisols typically contain strongly degraded OM that is effectively bound to clay mineral surfaces (mainly kaolinite) by iron and aluminium oxyhydroxides. The stable terrigenous OM fraction characterizing the Congo fan sediments therefore is suggested to represent kaolinite-bound soil organic matter (SOM) from the Oxisol domains. During humification processes in soils (transformation of plant litter to humic substances) SOM is progressively enriched in nitrogen and  $^{13}C$ . Considering these SOM characteristics and regarding the temporal pattern of  $C_{org}/N_{tot}$  and  $\delta^{13}C_{org}$  in the Niger fan records it is proposed that both proxies are primarily determined by the contribution of SOM from different types of eroded soils which are enriched in nitrogen and depleted in  $^{12}C$  to varying degrees (depending on the level of humification). The very low  $C_{org}/N_{tot}$  ratios of the Congo fan sediments are attributed to the preferential preservation of SOM from Oxisols that reveals highest levels of humification. During arid periods, enhanced proportions of marine OM from elevated, upwelling-induced primary production compensates the diminished contribution of nitrogen-rich SOM from the Congo catchment. Due to the lack of a comparably effective upwelling-related nutrient source off the Niger River, marine OM fluxes are low and probably have been relatively low throughout the Late Quaternary. Effective mineralization of labile OM during sedimentation and early diagenesis therefore resulted in almost entirely residual, terrigenous OM signatures in the Niger fan sediments.

It is a fundamental result of this study that SOM is a major bulk OM component in the Congo and Niger deep-sea fan sediments. Due to low  $C_{org}/N_{tot}$  ratios that may even reach values of marine OM and due to depletion of  $^{12}C$ , SOM leads to an underestimation of terrigenous OM proportions in marine sediments. Additionally, the supply of “heavy” terrigenous OM

originating from C<sub>4</sub> plants significantly shifts bulk  $\delta^{13}\text{C}_{\text{org}}$  signatures towards marine values especially at the Niger fan where C<sub>4</sub> grasses are an important element of the vegetation cover throughout the late Quaternary. The contribution of SOM and C<sub>4</sub> plant remains therefore rules out the conventional application of two end-member models for C<sub>org</sub>/N<sub>tot</sub> and bulk  $\delta^{13}\text{C}_{\text{org}}$  to assess marine and terrigenous OM amounts. As long as true terrigenous and marine OM proportions however are unknown TOC cannot be used as paleoproductivity proxy in comparable sedimentary settings with massive continental influence.

## Zusammenfassung

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Die Produktion pflanzlicher Biomasse im marinen wie terrestrischen Ökosystem entzieht der Erdatmosphäre Kohlendioxid und ist damit ein essentielles Element des globalen Kohlenstoffkreislaufs. In ozeanischen Sedimenten wird Biomasse sowohl marinen als auch terrigenen Ursprungs dauerhaft begraben und auf diese Weise das darin fixierte CO<sub>2</sub> dem aktiven Kohlenstoffkreislauf über geologische Zeiträume entzogen. Die terrigenen und marinen Anteile am gesamten organischen Material (OM) mariner Sedimente spiegeln letztendlich die Bedeutung der beiden Biosphären Land und Ozean für die CO<sub>2</sub>-Fixierung wider und sind somit für globale Kohlenstoffbilanzen und Klimamodellierungen von enormer Wichtigkeit. Es mehren sich allerdings die Hinweise, dass bei der konventionellen Anwendung gängiger Proxies zur Abschätzung mariner und terrigener Anteile am gesamtorganischen Material, etwa dem C<sub>org</sub>/N<sub>tot</sub>-Verhältnis oder der Isotopenzusammensetzung des organischen Kohlenstoffs ( $\delta^{13}\text{C}_{\text{org}}$ ), die terrigene Fraktion vielfach stark unterschätzt wurde. Am Beispiel von Tiefseefächersedimenten zweier bedeutender afrikanischer Flüsse, dem Kongo und dem Niger, rekonstruiert deshalb die vorliegende Studie zeitliche Schwankungen in Qualität und Quantität von in die Tiefsee verfrachtetem terrigenem OM und untersucht die zugrunde liegenden Steuermechanismen. Zur Erfassung der relativen Änderungen mariner und terrigener Anteile am gesamtorganischen Material wurden an spätquartären Abschnitten der ODP-Bohrung 1075 (Kongofächer, 1200 - 9 ka) sowie des GeoB-Kerns 4901 (Nigerfächer, 245 - 0 ka) zeitlich hochauflösende „Multiproxy“-Untersuchungen durchgeführt. Diese umfassen Elementaranalyse (C, N, S), Bestimmung der Verhältnisse stabiler organischer Kohlenstoffisotope ( $\delta^{13}\text{C}_{\text{org}}$ ), organische Petrologie (Mazeralanalyse), Rock-Eval-Pyrolyse und terrigene Biomarker (Ligninphenole). Die aus dem C/S-Verhältnis abgeleitete Abbaurate des ursprünglich sedimentierten OM sowie die Reaktivität des residualen OM erlauben Rückschlüsse auf die jeweilige biologische Abbaubarkeit und damit auch auf die Ausgangszusammensetzung des OM vor der weiteren Versenkung und Zersetzung. Ergänzende Informationen zum Eintrag terrigener und mariner Substanzen liefern die Palynologie (Pollenanalyse) und die Tonmineralogie (Ti/Al-Verhältnisse) sowie die Bestimmung der Gehalte an biogenem Opal.

In beiden Fächersystemen ist der Eintrag von lithogenem und organischem Material eng an den hydrologischen Zyklus auf dem afrikanischen Kontinent geknüpft. Humidität und Aridität, Abflussmenge, chemische Verwitterungsintensität und Vegetationsbedeckung wiederum werden durch zyklische Änderungen der Sonneneinstrahlung (Insolation) bestimmt. Dabei dokumentieren sich die allmählichen Anpassungsprozesse des Ökosystems in einer etwa viertausend Jahre umfassenden Phasenverschiebung der Kaolinit- und OM-Konzentrationsänderungen sowie der Änderungen der Pollenvergesellschaftungen in den Fächersedimenten gegenüber dem Insolationssignal (präzessionale Frequenz von durchschnittl. 21 ka). Markante Unterschiede zwischen den beiden Flusssystemen treten jedoch in der Qualität des gesamtorganischen Materials sowie in der Dynamik von OM-Sedimentation und -Erhaltung und zutage.

Die organischen Kohlenstoffgehalte liegen im Kongofächer zwischen 0,8 und 4,2 % (durchschnittl. 2,1 %). Niedrige C<sub>org</sub>/N<sub>tot</sub>-Verhältnisse von 5,8 bis 10,1 (im Mittel 8,3) deuten

zunächst auf einen untergeordneten Beitrag stickstoffarmen Pflanzenmaterials hin ( $C_{org}/N_{org} > 20$ , marines OM  $\approx 7$ ). Die Isotopenverhältnisse des gesamtorganischen Materials liegen zwischen  $-19\text{‰}$  und  $-23,5\text{‰}$  (Mittelwert:  $-21,1\text{‰}$ ). Ihre konventionelle Interpretation mit zwei Endgliedern für terrigenes  $C_3$ -Pflanzenmaterial ( $-27\text{‰}$ ) und marines OM ( $-18\text{‰}$ ) suggeriert, dass durchschnittlich nur ein Drittel des sedimentären OM aus terrestrischen Quellen stammt. Die Charakterisierung des OM durch die Rock-Eval-Pyrolyse ergibt die Kerogentypen III bis II (überwiegend terrigen bis überwiegend marin). Bemerkenswert ist die Entdeckung einer thermisch relativ stabilen, hochmaturen organischen Komponente, die trotz ihres vermeintlich hohen Reifegrades bei hohen Pyrolysetemperaturen ( $T_{max} \gg 450^\circ\text{C}$ ) erstaunlich große Mengen an Kohlenwasserstoffen (KW's) freisetzt. Das erstmalig bestimmte Verhältnis von KW's aus labilem, immaturem OM und „stabilem“, hochmaturem OM (lm/hm = low-mature versus high-mature) zeigt ausgeprägte Schwankungen über die letzten 1,2 Mio. Jahre und spiegelt zyklische Wechsel in der Zusammensetzung bzw. der Erhaltung des gesamtorganischen Materials wider. Die wechselseitigen Beziehungen von lm/hm-Verhältnis, Abbauraten und Ligninphenolkonzentrationen zeigen, dass beim selektiven Abbau des sehr labilen marinen organischen Materials zwei ligninhaltige (d.h. terrestrische) OM-Fractionen relativ angereichert werden: (1) „frisches“ partikuläres terrigenes OM verhältnismäßig hoher Reaktivität (Pflanzenreste) während trockener Klimabedingungen und (2) relativ stabiles OM während humider Klimaphasen.

Die OM-Konzentrationen in den Sedimenten des Nigerfächers sind mit durchschnittlich  $1,4\%$  niedriger als diejenigen der Kongofächersedimente. Die Mazeralanalyse ergibt, dass im Mittel  $62\%$  der sichtbaren organischen Partikel terrestrischen Ursprungs sind. Die Rock-Eval-Pyrolyse belegt entsprechend die Kerogentypen III und IV, d.h. überwiegend terrigenes und residuales Kerogen. Verglichen mit den Sedimenten des Kongofächers sind die  $C_{org}/N_{tot}$ -Verhältnisse und die  $\delta^{13}C_{org}$ -Werte im Durchschnitt höher ( $10,5$  bzw.  $-18,4\text{‰}$ ) und weisen zudem eine größere Spannbreite auf ( $6,6$  bis  $12,9$  bzw.  $-16,8$  bis  $-20,7\text{‰}$ ). Bemerkenswerterweise zeigen beide Proxies über das gesamte spätquartäre Profil parallele Tendenzen. Erhöhte Werte treten während arider Klimaverhältnisse auf, z.B. in den marinen Isotopenstadien 5.2 und 5.4, und zeigen damit einen erhöhten Einfluss von stickstoffarmem partikulärem OM aus  $^{13}C$ -angereicherter  $C_4$ -Pflanzenvegetation auf die organisch-geochemischen Signaturen an. Der entgegengesetzte Trend ist beispielsweise während der humiden Isotopenstadien 5.3 und 5.5 zu beobachten. Auffällig ist, dass eine hochmature, stabile OM-Komponente in den Sedimenten des Nigerfächers fehlt.

Diese Feststellung gibt Anlass zu einer vergleichenden Betrachtung der OM-Ressourcen innerhalb der Einzugsgebiete von Kongo und Niger, um die mögliche Quelle der stabilen bzw. hochmaturen OM-Komponente zu identifizieren. Verbranntes oder verkohltes Material kann insofern ausgeschlossen werden, da Vegetationsbrände in beiden Einzugsgebieten auftreten. Ein Vergleich des Inventars diverser Bodentypen offenbart allerdings einen höchst auffälligen Unterschied: tiefgründig verwitterte ferallitische Böden (Oxisole) dominieren im Kongobecken, fehlen aber nahezu vollständig im Bereich des Nigereinzugsgebietes. Oxisole beinhalten jedoch mikrobiell stark degradiertes OM, das über Eisen- und Aluminium-Oxyhydroxide effektiv an Tonmineraloberflächen, vor allem von Kaolinit, gebunden ist. Die für die Sedimente des Kongofächers typische hochmature/stabile OM-Komponente ist daher höchstwahrscheinlich das an Kaolinite gebundene organische Material erodierter Oxisole. Die

im Nigereinzugsgebiet vorherrschenden Bodentypen sind hingegen junge, sandige Entisole, die nur sehr wenig OM enthalten, ferner tonhaltige Alfisole und tonige Ultisole. Im Unterschied zu den Entisolen enthalten die Letztgenannten deutlich mehr OM. Dieses weist zudem einen erheblich höheren Grad der Humifizierung auf, eines biochemischen Prozesses, der zu niedrigeren  $C_{org}/N_{tot}$ -Verhältnissen führt sowie zu einer relativen Anreicherung des schweren Kohlenstoffisotops ( $^{13}C$ ) aufgrund des vorzugsweisen mikrobiellen Abbaus von  $^{12}C$ -dominierten OM-Bestandteilen. Angesichts der engen Beziehung von  $C_{org}/N_{tot}$ -Verhältnissen und  $\delta^{13}C_{org}$ -Werten sowie ihrer klimagekoppelten Muster in den spätquartären Sedimenten des Nigerfächers kann der Schluss gezogen werden, dass beide Proxies vor allem den wechselnden Eintrag unterschiedlichen Bodenmaterials widerspiegeln, welches je nach Humifizierungsgrad mehr oder weniger stark stickstoff- und  $^{13}C$ -angereichert ist. Die sehr niedrigen  $C_{org}/N_{tot}$ -Verhältnisse der Sedimente des Kongofächers geben dann die vorzugsweise Erhaltung des hochgradig degradierten bzw. humifizierten bodenorganischen Materials aus Oxisolen wider. Während arider Klimaphasen kompensiert die proportional bessere Erhaltung marinen organischen Materials aus der durch verstärkten Auftrieb massiv angefachten Primärproduktion den verminderten fluviatilen Eintrag von stickstoffreichem bodenorganischen Material. Optimale Bedingungen für die Erhaltung von labilem marinem OM treten auf dem Kongofächer während der Übergänge von ariden zu humiden bzw. humiden zu ariden Klimaphasen auf, wenn windgesteuerter Auftrieb und fluviatiler Sediment- und Nährstoffeintrag sich die Waage halten. Da eine vergleichbare auftriebsgebundene Nährstoffzufuhr im ozeanischen Bereich vor dem Nigerdelta nicht stattfindet, ist der Eintrag von marinem OM in die Sedimente des Nigerfächers möglicherweise während des gesamten Quartärs vergleichsweise gering gewesen. Die effektive Mineralisierung des labilen organischen Materials während der Sedimentation und frühen Diagenese führt schließlich zu den terrigenen Signaturen der Nigerfächersedimente.

Es ist ein bedeutendes Ergebnis dieser Studie, dass bodenorganisches Material eine wesentliche Komponente des gesamtorganischen Materials in den Sedimenten der Kongo- und Niger-Tiefseefächer bildet. Aufgrund seiner niedrigen  $C_{org}/N_{tot}$ -Verhältnisse, welche sogar die Werte des marinen OM erreichen können, sowie der Abreicherung von  $^{12}C$ , führt das bodenorganische Material zu einer teilweise drastischen Unterschätzung der terrigenen Anteile am gesamtorganischen Material mariner Sedimente. Darüber hinaus verschiebt der Eintrag von isotopisch schwerem  $C_4$ -Pflanzenmaterial (trop. Gräser) die  $\delta^{13}C_{org}$ -Signaturen hin zu marinen Isotopenverhältnissen. Dies ist insbesondere auf dem Nigerfächer der Fall, da  $C_4$ -Gräser während des gesamten Spätquartärs und bis heute ein wesentliches Element der Vegetation im Nigereinzugsgebiet darstellen. Der Eintrag von bodenorganischem Material und  $C_4$ -Pflanzenrückständen schließt daher die konventionelle Anwendung von  $C_{org}/N_{tot}$  und  $\delta^{13}C_{org}$  zur Abschätzung mariner und terrigener Anteile über ein bimodales Mischungsmodell kategorisch aus. Solange das tatsächliche Verhältnis von terrigenem zu marinem OM jedoch nicht bekannt ist, kann der Gehalt an gesamtorganischem Material (TOC) als Paläoproduktivitätsproxy zumindest in vergleichbar stark kontinental beeinflussten sedimentären Systemen nicht angewendet werden.

## Abbreviations

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a	= year
Ad/Al	= acid/aldehyde ratio
AR	= accumulation rate
BC	= black carbon
BSTFA	= N,O-bis(trimethylsilyl)trifluoroacetamide
C	= cinnamyl phenols ( <i>p</i> -coumaric acid, ferulic acid)
C <sub>org</sub>	= organic carbon
DOC	= dissolved organic carbon
FID	= flame ionisation detector
GC	= gas chromatography
HC	= hydrocarbon(s)
HI	= hydrogen index
ITCZ	= Intertropical Convergence Zone
ka, kyrs	= kiloyears (1000 years)
Λ	= lambda (sum of lignin phenols)
lm/hm	= low-mature/high-mature ratio
LSR	= linear sedimentation rate
Ma	= million years
mcd	= metres composite depth
MS	= mass spectrometry
N <sub>org</sub>	= organic nitrogen
N <sub>tot</sub>	= total nitrogen
OC	= organic carbon
OI	= oxygen index
OM	= organic matter
PDB	= Pee Dee Belemnite
POC	= particulate organic carbon
POM	= particulate organic matter
S	= syringyl phenols (syringaldehyde, syringic acid, acetosyringone)
S <sub>tot</sub>	= total sulfur
SOM	= soil organic matter
SR	= sedimentation rate
T <sub>max</sub>	= temperature of maximum hydrocarbon generation
TCD	= thermal conductivity detector
TOC	= total organic carbon
V	= vanillyl phenols (vanillin, vanillic acid, acetovanillone)
VPDB	= Vienna-Pee Dee Belemnite

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## 1. Introduction

### 1.1 The enigmatic role of terrigenous organic matter in the deep sea

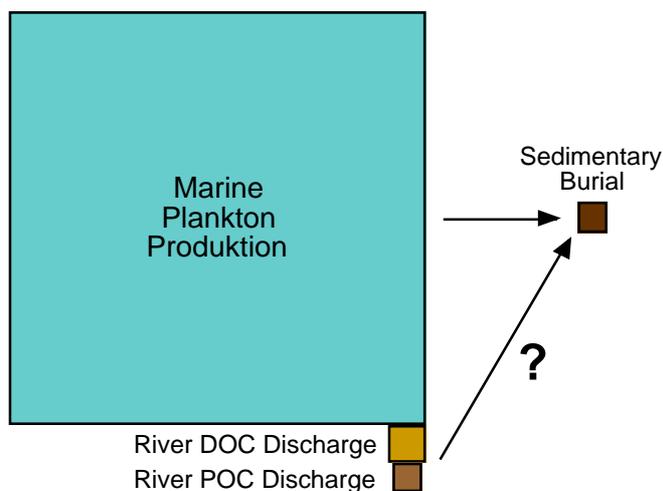
Approximately one-third of all actively cycling (non-fossil) organic carbon is stored in the ocean, two-thirds on land (Hedges et al., 1997) of which two-thirds, again, are deposited in soils (Zech et al., 1997). However, virtually no organic matter (OM) is preserved on eroding continental platforms over geological time scales. Only the export of terrestrial organic matter to aquatic environments, its burial in sedimentary basins that consist over geological time scales, maintains the information carried by terrigenous OM as, e.g., on the type of vegetation and the climatic boundary conditions. Marine sediments therefore comprise unique and precise archives of the climatic development on adjacent continental areas. The role and importance of terrigenous organic matter in deep-sea settings, nevertheless, is still under debate especially regarding its role within the global carbon cycle.

All microbial turnover of organic substances, those biochemical processes that finally determine whether a given aquatic sedimentary setting acts as a sink of organic carbon or CO<sub>2</sub>, respectively, actually depends on the bioavailability or the reactivity of the supplied organic matter. However, a simple two-component system of  $\pm$ labile or reactive autochthonous OM (e.g. from marine primary productivity and bacterial biomass in the sediment) and more stable or less-reactive allochthonous OM (terrigenous OM, likely pre-oxidized during transport or temporary storage in soils or shelf sediments) does not exist in natural systems. Instead, there is a broad variety of allochthonous compounds that considerably differ in their specific reactivity, from “fresh” particulate OM (e.g. plant litter) over humus and soil OM (SOM) exposing various (soil/environment-specific) degrees of humification to black carbon (charcoal). One can easily imagine that these diverse types of OM have significantly different chances to enter the geological record due to selective preservation. This diversity already demonstrates that terrigenous organic matter preservation with regard to its variable initial diagenetic stage and specific sources is more complex than often considered, and little is known about the interrelation between sedimentation of different terrigenous OM mixtures and bulk OM preservation in aquatic settings. It is therefore inevitable to obtain more information that specifies the quality of the terrigenous organic fraction to utilise its information potential, e.g. on paleoclimate and paleovegetation.

Three processes mainly transfer terrigenous OM from land to the ocean: river discharge, eolian dust export (Meyers, 1997), and at high latitudes glaciomarine transport (Stein & McDonald, 2003). Rivers provide the major conduit toward the preservation of terrigenous organic matter in oceanic sediments (Hedges & Keil, 1995). They carry about 1% of the terrestrial productivity to the ocean, in form of dissolved and particulate organic matter (DOM, POM), approximately  $0.4 \cdot 10^{15}$  t/y (Schlesinger and Melack, 1981; Siegenthaler and Sarmiento, 1993). Eolian fluxes have been estimated to be lower than  $0.1 \cdot 10^{15}$  t/y. (Romankevich, 1984). Though major amounts of terrigenous OM are transported to the sea by rivers eolian dust input may provide the dominant or even the only source of terrigenous OM in oceanic areas without any significant river influence, e.g. in areas adjacent to arid landmasses like the eastern tropical Atlantic off western Africa (Wagner and Dupont, 1999; Wagner, 2000). Realistic budgets on glaciomarine supply of terrigenous and fossil-reworked

OM are hardly available up to now (see Stein & McDonald, 2003 for details), however, a number of investigations from the Nordic Seas and the Arctic Ocean emphasize the importance of that mechanism (e.g., Wagner & Hölemann, 1995; Fahl and Stein, 1997; Stein and Schubert, 1996).

It is a common assumption that sedimentation and burial of terrigenous OM is restricted to deltas and continental shelf areas and that only a minimum amount of terrigenous OM passes the continental slopes towards the deep sea (Hedges and Parker, 1976; Gearing et al., 1977). However, recent investigations demonstrate that terrigenous OM is often severely underestimated in marine sediments as for example in the Gulf of Mexico (Ruttenberg and Goñi, 1997; Goñi et al., 1998; Onstad et al., 2000) with predominantly riverine terrigenous OM supply (e.g. by the Mississippi) or in the central equatorial Atlantic (Verardo and Ruddiman, 1996; Wagner, 2000) where terrigenous OM from western Sahara and savannah regions is delivered by the trades as part of the dust plume. On the other hand, there are indications for a massive loss of terrigenous OM in oceanic (Hedges et al., 1997) and deltaic settings (Keil et al., 1997) even though terrigenous OM is expected to resist severe microbial degradation (Tissot and Welte, 1984; Emerson and Hedges, 1988). The problem is illustrated by the finding that riverine discharge of POM alone accounts for all the organic carbon now being buried in marine sediments (Bernier, 1989; Hedges & Keil, 1995; Hedges et al., 1997, Fig. 1.1).



**Figure 1.1:** Relations of global autochthonous OM production, terrigenous OM supply and organic carbon burial in marine sediments (from Hedges et al., 1997).

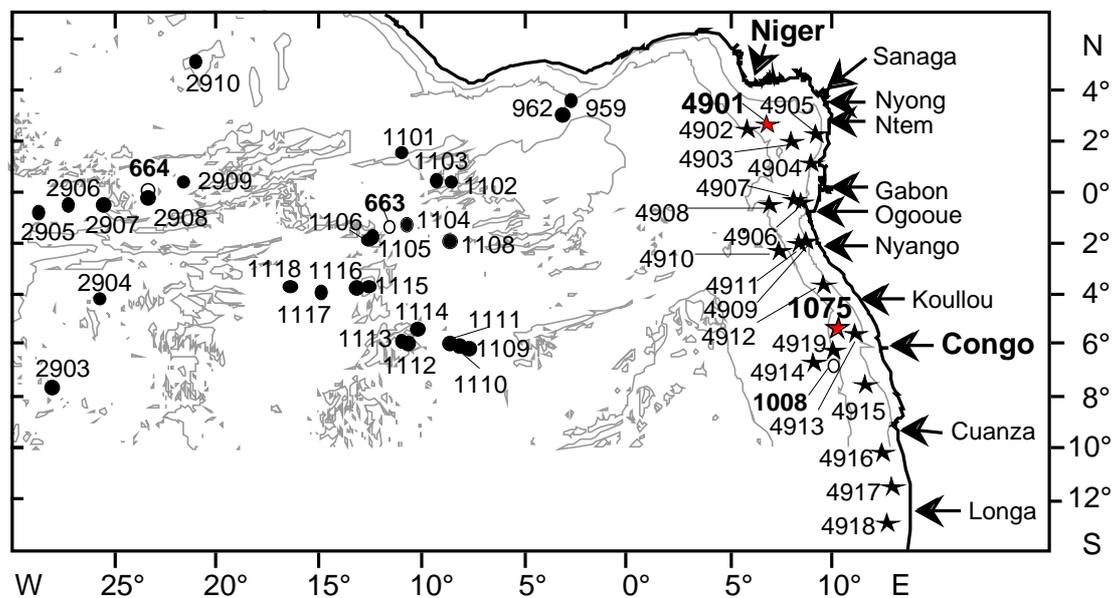
It is therefore confusing that most organic materials in marine sediments apparently are autochthonous as indicated by extensive molecular and isotopic evidence (Hedges & Keil, 1995). Even sedimentary organic matter accumulating in deltas and along open continental margins, together accounting for more than 90% of all marine organic carbon burial, appears to be predominantly derived from marine production (Hedges et al., 1997). These discrepancies provoke Hedges et al. (1997) to ask: “What happens to terrestrial organic matter in the ocean?” Either terrigenous OM delivered to the oceanic system actually is more rapidly and extensively mineralised than previously assumed or the conclusions drawn from molecular and isotopic investigations so far are to some extent misleading - or both.

## 1.2 Scope of this study

This study investigates the transfer of terrigenous organic matter from tropical Africa to the central and eastern equatorial Atlantic to detect the main controlling factors of terrigenous OM sedimentation and preservation in the deep sea. Most suitable settings to study the fate of terrigenous OM in oceanic sediments are deep-sea fans off major river systems as they represent the most direct link between continental discharge and the deep-sea environment. The investigations therefore focus on the fluvial export of terrigenous OM through the Congo and Niger rivers and its variability during the late Quaternary as well as on eolian supply of terrigenous OM to pelagic oceanic regions. Variations in terrigenous OM supply and composition (particulate OM, SOM, charcoal/black carbon) are expected to reflect the development of past continental climate conditions (aridity/humidity cycles) that determine type and distribution of vegetation, fluvial run-off, and weathering and drainage intensity in the various vegetation/soil habitats. Thus, the ultimate motivation is to develop a new conceptual model that links continental climate variability and bulk sedimentary OM composition in eastern equatorial Atlantic deep-sea areas off the Congo and the Niger. Another important aspect coming along with the investigation of bulk OM composition is the relevance of selective degradation or preservation of the various OM components. Determination of both, extent of passed microbial decay and reactivity of the residual (recent) OM, allows conclusions on the primary composition of bulk OM as marine and terrigenous OM compounds differ significantly in their susceptibility towards biochemical degradation.

## 1.3 Study area and environmental settings

### 1.3.1 Sample locations

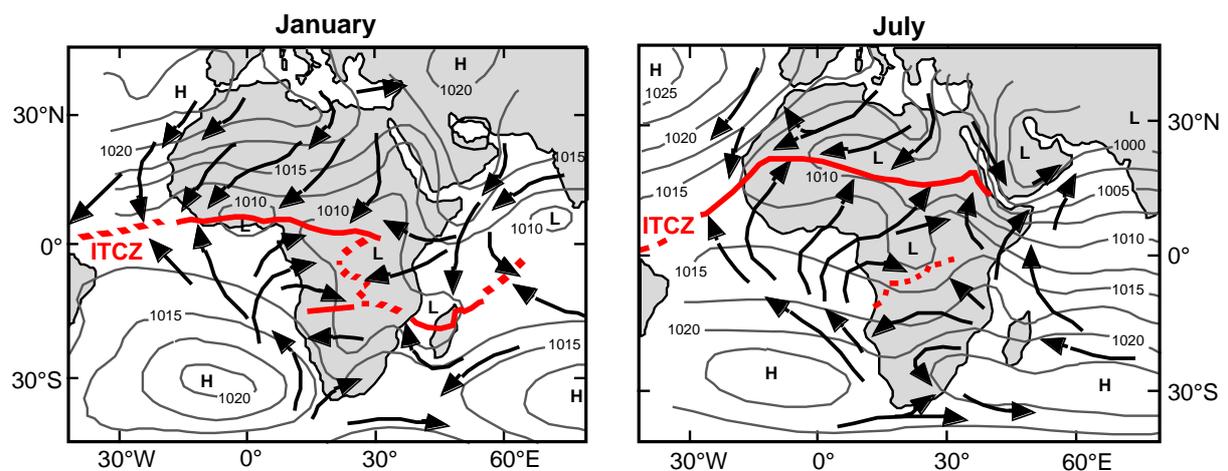


**Figure 1.2:** Core positions, surface sample locations, and African rivers between 6°N and 14°S; filled circles: locations along the open ocean E-W transect, stars: surface sediments from the near-continental N-S transect; ODP-Site 1075 is located at the northern rim of the Congo deep-sea fan at 2996 m water depth, gravity core GeoB 4901 derives from the Niger deep-sea fan from 2184m water depth.

Studied materials derive from late Quaternary sections of ODP-Site 1075 (0 - 1.2 Ma) at the northern Congo deep-sea fan (2996 m water depth; ODP Leg 175, Wefer et al., 1998) and of gravity core GeoB 4901 (0 - 250 ka) taken by from the Niger deep-sea fan (2184 m water depth; *Meteor* Cruise M41/1, Schulz et al., 1998). Surface samples derive from proximal areas along the central and southern African continental margin and from distal regions of the equatorial Atlantic between 5°N and 8°S (*Meteor* Cruises M29/3 and 41/1, Schulz et al., 1995, 1998; Fig. 1.2, previous page).

### 1.3.2 General pattern of modern tropical African climate

Humidity in the central African tropics is generally controlled by the seasonal N-S migration of the Intertropical Convergence Zone (ITCZ) in response to the oscillation of maximum solar irradiation and heating of the landmasses between the tropics. This results in two belts north and south of the equator with strong monsoon precipitation during the summer and dry winters and an equatorial zone with two annual maxima of rainfall. North of the equator, along the coast of Equatorial Western Africa, the rainy season usually begins in February or March. During the boreal summer/austral winter (northern position of the ITCZ at ~20°N) moist air masses flow from the Gulf of Benguela northwards and cause extensive precipitation: the southwest monsoon (Fig. 1.3). South of the equator enhanced trade winds contemporaneously force eolian dust export from the South African arid regions, e.g. Kalahari (savannah) and Namib Desert, as well as strong upwelling of nutrient-rich intermediate waters along the southern and central African continental margins. Opposite, during boreal winter/austral summer, the northeast trades carry dry air masses from the arid Sahel and Sahara regions towards the south. Especially from December through February the northeast trades are often loaded with dust. These dust-laden winds are locally known as *Harmattan*. On geological time scales, the principle mechanism of insolation forced climate changes remains. Orbital parameters modulate the insolation pattern in the tropics, especially the precession of the Earth's axis with periodicities from 19 to 23 kyrs (Berger and Loutre, 1992), thereby amplifying or lowering either trades or monsoon over Africa leading to cyclic alternations of stronger aridity and humidity.



**Figure 1.3:** seasonal pattern of atmospheric circulation over Africa (redrawn from Mpounza and Samba-Kimbata, 1990). During the boreal winter, dry air masses flow from the Sahara towards the southwest (most prominent: Harmattan) that export huge amounts of dust to the equatorial Atlantic. During the boreal summer moist air invades the southern part of West Africa and the equatorial regions from the Gulf of Benguela (monsoon).

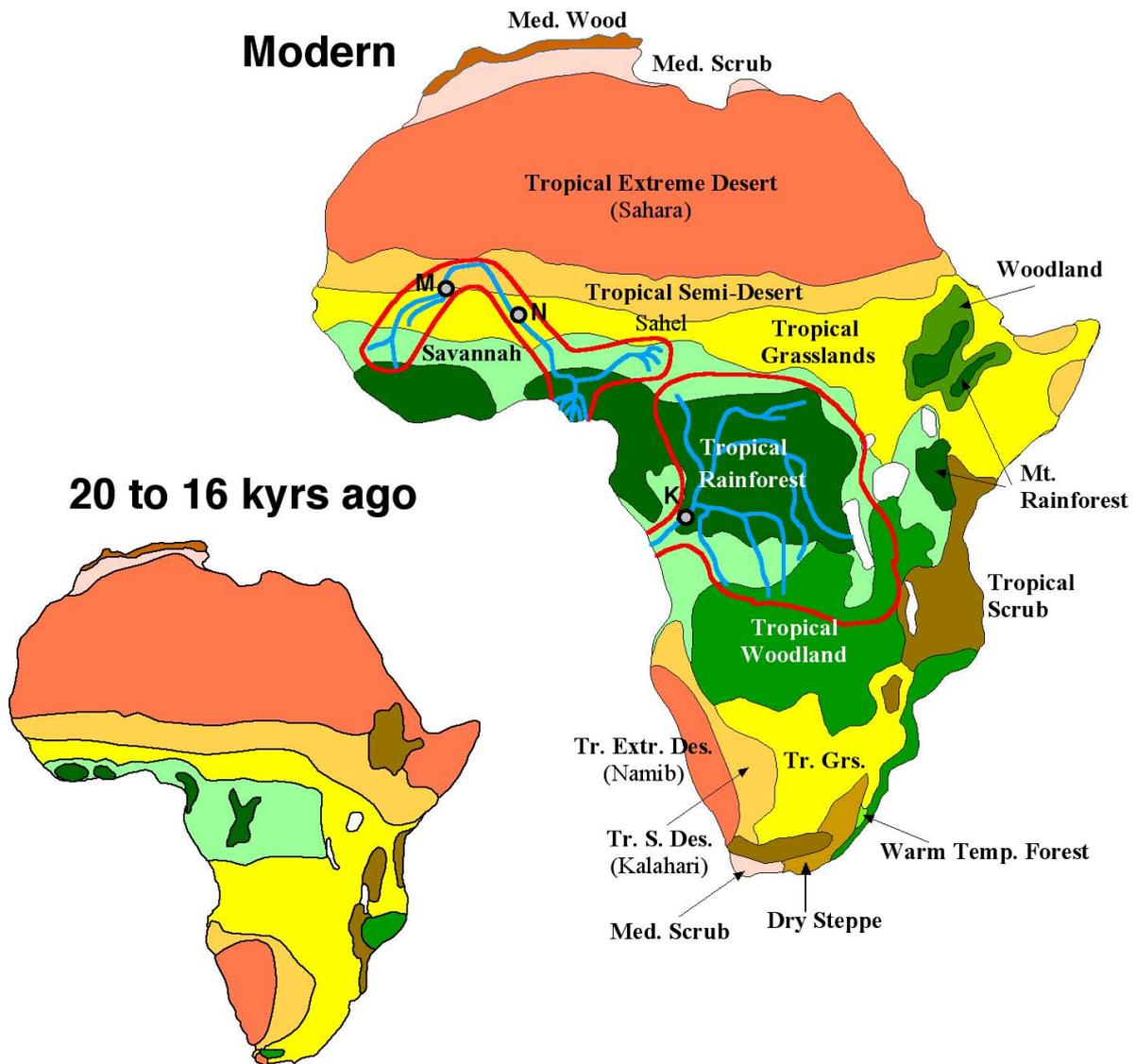
### *1.3.3 Modern and past vegetation of the Congo and Niger catchments – C<sub>3</sub> and C<sub>4</sub> plant habitats*

Prior to the description of plant habitats in the Congo and Niger catchment areas, one has to know an essential criterion of plant classification that has a fundamental impact on the interpretation of organic geochemical data:

Most vascular land plants are classified as C<sub>3</sub> plants according to their first product from photosynthesis, 3-phosphoglycerate, containing 3 C-atoms (Calvin-Benson cycle of carbon fixation). Some plants however use a different pathway of carbon fixation. As their first product of photosynthesis is oxaloacetate containing 4 C-atoms they are called C<sub>4</sub> plants (Hatch-Slack cycle). The C<sub>4</sub> metabolism is advantageous especially under dry and warm climate conditions and enhanced concentrations of CO<sub>2</sub> in the atmosphere. Most tropical grasses (Gramineae), e.g. in the African savannah belts, are C<sub>4</sub> plants. Characteristically, C<sub>4</sub> plants are enriched in <sup>13</sup>C resulting in a “heavy” isotope signature (bulk  $\delta^{13}\text{C}_{\text{org}} = -12 \text{ ‰}$ ) relative to C<sub>3</sub> plants (-27 ‰). This striking difference enables the reconstruction of vegetation habitats in the continental environment, e.g. when investigating paleosoils. On the other hand, it severely complicates the interpretation of isotopic data of limnic or marine sediments as a 1 to 1 mixture of C<sub>3</sub> and C<sub>4</sub> plant matter, for example, reveals an isotopic signature referring to 100% marine OM (average  $\delta^{13}\text{C}_{\text{org}}$  value  $\approx -19 \text{ ‰}$ ).

Today, two-thirds of the tropical Congo basin is covered by rainforest (C<sub>3</sub> habitat), one third by tree savannah (C<sub>3</sub> + C<sub>4</sub> vegetation) and grasslands (C<sub>4</sub> domains; Fig. 1.4, next page). The Niger crosses the tropical as well as the subtropical zone of western Africa and the types of vegetation reach from tropical rain forest around the Niger delta to semi desert in the northernmost part. The dominating types of vegetation within the catchment are tree savannah and grasslands.

During the Quaternary, the African vegetation cover changed considerably in response to orbitally forced climate variations. Stronger aridity during cooler climates (glacials) supported an expansion of the C<sub>4</sub> plant habitat (Jolly and Haxeltine, 1997; Cerling et al., 1997; Huang et al., 1999b). As a result the rainforest areas of the Congo basin were largely replaced by tree savannah. Furthermore, the grasslands in southern Africa expanded dramatically, largely replaced the tropical woodlands, and became an important element at the outer parts of the Congo basin (Fig. 1.4). Within the Niger catchment rainforests disappeared, semi-desert and desert areas expanded towards the south, and grass-rich vegetation took the lead (Dupont et al., 2000).



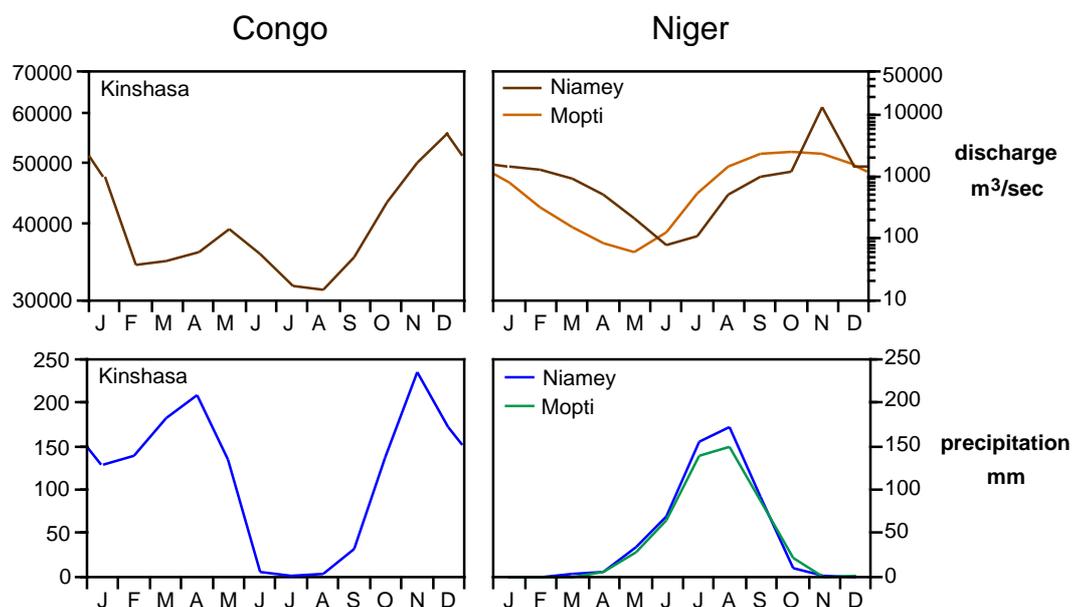
**Figure 1.4:** African vegetation zones during modern and glacial climate conditions (modified from Adams, 1995: [www.soton.ac.uk/~tjms/afpres.gif](http://www.soton.ac.uk/~tjms/afpres.gif) for present potential vegetation, [www.esd.ornl.gov/projects/gen/nercAFRICA.html](http://www.esd.ornl.gov/projects/gen/nercAFRICA.html) for glacial vegetation). Under glacial climate conditions grass and tree savannah expanded considerably while the relative share of tropical rainforest especially within the catchment of the Congo was strongly reduced. Catchment areas are defined by the red lines; Med. = Mediterranean, Mt. = Mountain, Temp. = Temperate, Tr. Extr. Des. = Tropical Extreme Desert, Tr. Grs. = Tropical Grasslands, Tr. S. Des. = Tropical Semi-Desert, K = Kinshasa, M = Mopti, N = Niamey.

#### 1.3.4 River discharge to the eastern equatorial Atlantic continental margin

The Congo (Zaire) River with a total length of ~ 4700 km is the second largest stream in the world with respect to its outflow (after the Amazon) and drains an area of approximately  $4 \cdot 10^6$  km<sup>2</sup>. The catchment of the Niger River (length: 4160 km) is considerably smaller, i.e.  $1.54 \cdot 10^6$  km<sup>2</sup> or less than half of the Congo catchment. However, following Ludwig et al. (1996) the basin area of a river has no significant influence on the flux rate of organic carbon to the oceans. Instead, the main factors controlling organic carbon export are drainage intensity and specific sediment fluxes that are related to the moisture regime (e.g. rainfall

intensity) and the steepness of the basin. Fluvial run-off is closely related to the seasonal distribution of precipitation.

*Discharge:* The Congo River exposes maximum discharge during the austral summer. Elevated discharge also occurs during May following the northern monsoon season (Fig. 1.5). The average annual precipitation within the Niger catchment is lower compared to the Congo basin, 1068 mm versus 1520 mm, respectively. The spatial distribution of rainfall, however, exhibits extreme regional differences with >4000 mm along the southern coast of west Africa but only 500 to 750 mm in northern Nigeria, and 200 mm at Timbuktu (Mali). In contrast to the Congo system, precipitation reveals a pronounced seasonality in the Niger catchment with only one maximum per year. Accordingly, the high flow period of the Niger lasts from July to December (Boeglin and Probst, 1998; Fig. 1.5). A special feature modifies the discharge, namely an inland delta close to the northern “turning point” of the river. It prolongs the seasonal flows as the flood crest takes up to 3 months to pass through the marshes, lakes, and channels of the delta. The Niger was profoundly influenced by late Quaternary climatic changes. During the last glacial maximum (around 18 ka), intensified trades and reduced summer precipitation effectively shifted the Saharan arid zone southwards into the present Sahel zone. Active sand dunes effectively blocked the Niger River near modern Timbuktu. In consequence of additionally reduced fluvial discharge the upper Niger temporarily terminated at its inland delta (Baker, 1986).



**Figure 1.5:** Yearly patterns of precipitation and river discharge of the Congo and the Niger. Within the tropics (Congo basin) there are two annual maxima of rainfall whereas there is only one within the Niger catchment during boreal summer. Maximum discharge generally follows precipitation maxima about one month in Kinshasa (Dem. Rep. of Congo) and in Mopti (Mali, see Figure 1.4 for geographical positions). However, peak discharge of the Niger downstream the inland delta, e.g. in Niamey (Niger), lags further 1-2 months due to the storing capacity of the delta and its dynamic buffering (precipitation data of Mopti and Niamey from the NOAA National Climatic Data Center, <http://www.ncdc.noaa.gov/oa/ncdc.html>; for Kinshasa from Müller, 1983; discharge data from the Global Runoff Data Centre, <http://www.grdc.sr.unh.edu>).

*Sediment load:* The Congo carries at most 70 million tons of suspended material per year towards the eastern tropical Atlantic. The concentration of suspended matter, however, is low (50 mg/l) compared to other major rivers (Amazon, Yang Tse Kiang, and Mississippi: 100 to 1400 mg/l; Eisma et al., 1978). This is attributed to the Malebo Pool, a basin 560 km upstream covering 830 km<sup>2</sup>, where large amounts of coarse particles are deposited before reaching the estuary. Therefore, the river load entering the estuary is diminished and contains mainly fine-grained material. According to Eisma et al. (1978) it consists largely of kaolinite (26 %), quartz (22 %), and ironhydroxides (10 %) as well as of substantial amounts of organic matter (32 %). Less than 5 % of the suspended material in the river finally reaches the deep sea and most particles are smaller than 18 µm (Eisma et al., 1978). Consequently, the sediments of the deep-sea fan are dominated by terrigenous clay whereas significant river-born sand and silt fractions are missing. The amount of fine-grained matter from dust supply is considered very low compared with the fluvial input (Jansen et al., 1984). The Congo discharges  $13 \cdot 10^6$  t/a of organic matter to the eastern equatorial Atlantic, which corresponds to 3.9 % of the global annual supply to the oceans (Martins and Probst 1991). Eisma et al. (1978) observed large amounts of plant fragments and fibres within the suspended organic fraction. This corresponds fairly well with the finding that the Congo exposes elevated concentrations of particulate organic carbon (POC) related to the total sediment flux when compared to other major rivers (Ludwig et al., 1996). Nevertheless, the transport rate of total organic carbon (export of dissolved and particulate organic carbon from the entire drainage area) is low compared e.g. to the Amazon ( $3.1 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$  vs.  $7.3 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$ ; see Ludwig et al., 1996 and references therein). The modern sediment export rate of the Niger is three times higher than is the case for the Congo: 33 versus  $11 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$ . However, the export of terrigenous OM is considerably less efficient: 1.0 versus  $3.1 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$  (Ludwig et al., 1996).

#### **1.4 Geochemical properties of marine and terrigenous organic matter**

For the scope of this study it is essential to quantify the amounts of autochthonous marine and allochthonous terrigenous OM or at least to detect changing proportions through time. Specific organic geochemical properties characterizing each organic compound are introduced in the following.

Terrigenous vegetable biomass differs significantly from primary organic matter produced in the ocean, or in aquatic environments in general (algae, zooplankton), regarding its (i) elemental composition, (ii) isotopic signature, (iii) biochemical stability (determining its bioavailability, i.e. the susceptibility towards microbial decomposition), and (iv) hydrocarbon generation potential. These differences can be used to recognize the contribution of terrigenous OM to the bulk sedimentary OM pool.

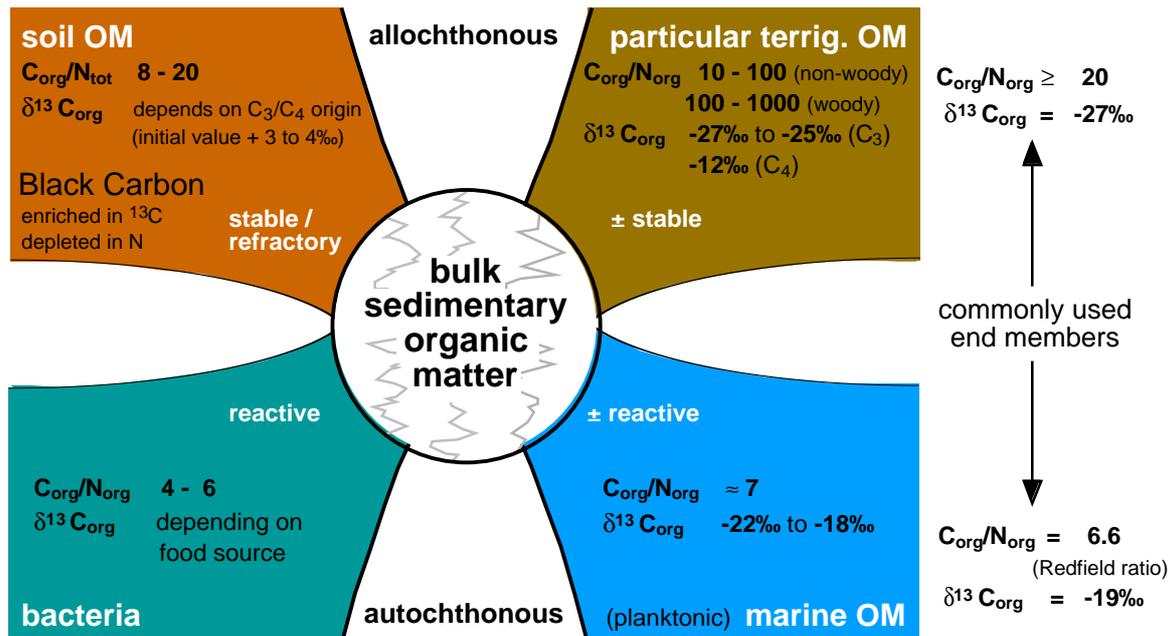
Compared to organic matter produced in marine or limnic settings terrigenous biomass generally is depleted in nitrogen due to the protein richness of algae. Additionally, cellulose, a nitrogen-free major compound of vascular land plants, is absent in organisms of aquatic environments. C/N ratios of bulk sedimentary OM therefore to some extent document varying relative shares of marine and terrigenous OM. Commonly used end-member values

are 7 for marine OM, as C/N ratios of algae range from 4 to 10, and ratios greater 20 for terrigenous OM (Emerson and Hedges, 1988; Meyers, 1994).

Also the isotopic ratio of bulk OM (bulk  $\delta^{13}\text{C}_{\text{org}}$  vs. PDB) is often used to estimate marine and terrigenous proportions as marine biomass reveals isotopic ratios of -20 ‰ to -18 ‰ whereas the vast majority of terrigenous biomass ( $\text{C}_3$  vegetation) generally exposes lighter (more negative) isotopic ratios, -27 ‰ on average (Meyers, 1997). However, contribution of isotopically heavy  $\text{C}_4$  plant matter (-12 ‰ on average) may lead to a significant underestimation of terrigenous OM in marine deposits if only a two-end-member model (marine vs.  $\text{C}_3$  OM) is applied.

Degradation of bulk OM may severely modify C/N ratios and  $\delta^{13}\text{C}_{\text{org}}$  values of bulk OM. For example, C/N ratios may increase during the sinking of algal OM particles through a suboxic water column under high-productive oceanic areas due to preferential microbial decay of nitrogen-rich proteinaceous matter (Twichell et al., 2002). In the terrestrial environment, two major processes significantly change both parameters: (i) humification and mineralization of plant litter and roots in soils and (ii) thermal degradation of biomass by vegetation fires. These processes result in self-contained terrigenous OM components: soil OM (SOM) and dead carbon or black carbon. Stalled plant matter is strongly altered by aerial weathering (e.g. leaching) and massive microbial degradation in humus and soils (humification = formation of humic substances, i.e. humic acids, fulvic acids, humin; mineralization = formation of inorganic substances, e.g.  $\text{CO}_2$ ,  $\text{CH}_4$ ). Humification and mineralization processes considerably lower the C/N ratios (e.g. Sorensen, 1981; Schmidt et al., 2000) and enhance the  $\delta^{13}\text{C}_{\text{org}}$  values (e.g. Balesdent, 1987; Mariotti and Peterschmitt, 1994) of the original biomass. Incomplete combustion of plant matter produces a broad variety of more or less inert oxidized residuals (charred material, charcoal, ash) that are summarized as black carbon (BC). Due to the different levels of oxidation the BC fraction reveals variable geochemical signatures, which rules out a specific end-member definition other than by its refractory character. However, it is typically strongly depleted in volatiles (incl. nitrogen-containing compounds), enriched in carbon, and is most resistant against microbial decomposition (for details on BC see Goldberg, 1985, and the review by Schmidt and Noack, 2000). Export of SOM and BC (or BC-containing SOM) to aquatic settings may therefore essentially bias the bulk geochemical and isotopic properties of marine and limnic sediments and complicate their interpretation. Both pre-oxidized OM compounds furthermore reveal best chances to become relatively enriched in the sediments due to selective decay of labile, non-degraded OM.

Figure 1.6 summarizes the various OM fractions that contribute to the bulk sedimentary OM and gives ranges for C/N ratios and  $\delta^{13}\text{C}_{\text{org}}$  values (see next page).



**Figure 1.6:** Autochthonous (marine) and allochthonous (terrigenous) contributors to bulk sedimentary OM. Black carbon is a common OM compound in soils but may also contribute to the particulate terrigenous fraction as part of the eolian dust load. Ranges are compiled following Fry & Sherr (1984), Hedges et al. (1986), Balesdent (1987), Zech et al. (1989), Müller et al. (1994), Goñi and Hedges (1995), Hedges et al. (1997), Ruttenberg and Goñi (1997).

Given the large number of potential terrigenous contributors it may be expected that marine organic-geochemical records with continental influence are seriously modified by a number of factors and mechanisms, e.g. (1) different types of source material depending on vegetation (and soil), (2) burning, (3) intermediate storage and alteration in soils and sediments, (4) reworking, (5) long-range transport, and (6) sorting in grain size. It is this heterogeneity of terrigenous OM that is hardly constrained and requires systematic investigation.

Sedimentary OM of terrestrial origin that survived the transport to the deep ocean to a great extent is pre-oxidized and is expected to be more resistant against microbial degradation, especially, if it is physically protected by clay minerals. The degree of degradation after burial and the reactivity of the residual OM thus provide further possibilities to detect terrigenous OM contribution.

Higher land plants contain large amounts of carbohydrates (e.g. glucose/cellulose) and lignin, both forming supporting tissues and together accounting for up to 75 % of the total biomass of higher land plants (Killops and Killops, 1993). In contrast, biomass produced in aquatic environments contains more aliphatic structures. Terrigenous OM thus is more aromatic and enriched in oxygen compared to marine (or lacustrine) OM resulting in lower ratios of hydrogen to carbon (1.3 to 1.5 versus 1.7 to 1.9) and higher ratios of oxygen to carbon ( $> 0.2$  vs.  $< 0.1$ ). Marine OM therefore generally produces higher quantities of hydrocarbons (HC) and less oxygen containing compounds like  $\text{CO}_2$  when pyrolysed. These differences in composition and chemical reactivity can be detected by pyrolytic methods, for example by

Rock-Eval pyrolysis, a quick method designed to characterize the kerogen (=insoluble fraction of bulk OM) by its HC and CO<sub>2</sub> generation pattern (see Chapter 1.5.2) established by Espitalié et al. (1977). Related to the TOC contents the amounts of released HC and CO<sub>2</sub> are given as hydrogen index (HI) and the oxygen index (OI). Kerogen in consolidated sediments (e.g. black shales and coals) is typically classified in four types with regard to its sources. Following Delveaux et al. (1990) this classification is also possible using HI and OI values. This concept has been transferred to unconsolidated aquatic sediments (Liebezeit and Wiesner, 1990; Wagner and Henrich, 1994; Tyson, 1995; Wagner and Dupont, 1999).

*Type I-kerogen* is of lacustrine origin and exposes very high initial HI (>600 mgHC/gTOC, Taylor et al., 1998) and low OI (<50 mgCO<sub>2</sub>/gTOC) values. It comprises high proportions of lipids that derive from algal and/or bacterial biomass whereas the content of polyaromatic nuclei and heteroatomic compounds (containing N, S, and O) is very low (Tissot and Welte, 1984). The maceral corresponding to kerogen type-I is liptinite.

*Type II-kerogen* (related to the exinite maceral group) has relatively high HI (350-600 mgHC/gTOC) and low OI (<100 mgCO<sub>2</sub>/gTOC) values. Compared to type I, polyaromatic nuclei and heteroatomic compounds are more abundant. Type II is related to marine settings where autochthonous biomass (phytoplankton, zooplankton, bacteria) is deposited under reducing conditions (typical oil-prone black shale facies).

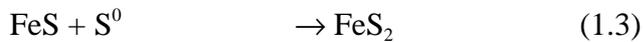
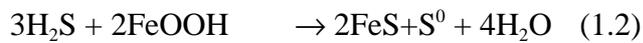
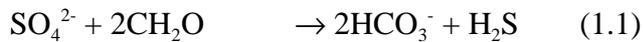
*Type III-kerogen* is characterized by much lower HI (100-350 mgHC/gTOC) and initially elevated OI (>100 mgCO<sub>2</sub>/gTOC) values compared to types I and II. It derives essentially from continental plants and thus contains important proportions of polyaromatic nuclei, heteroatomic compounds, and carboxylic acid groups whereas aliphatic groups are subordinate constituents. The corresponding macerals predominantly belong to the vitrinite group.

*Type IV-kerogen*, the “residual type” (Tissot and Welte, 1984), has extremely low HI values (<100 mgHC/gTOC) and high OI values. Aliphatic chains are absent, thus the HC generation potential is minimum. This type of organic matter, corresponding to the inertinite maceral group, is mostly reworked and transported and generally derives from plant material that has been oxidized by subaerial weathering or microbial activity. As hydrogen-rich OM is the most labile organic fraction and easily metabolised by microorganisms the HI index also characterizes bulk OM reactivity or stability. Another parameter for the thermal stability of bulk kerogen is the temperature where maximum HC generation occurs: the so-called T<sub>max</sub> value during Rock-Eval pyrolysis.

While HI, OI, and T<sub>max</sub> document the composition and reactivity of the residual bulk sedimentary OM, degradation rates are a measure of the reactivity of the initial OM mixture. Degradation rates can be estimated using the sulfur contents of sediments:

At the Congo and Niger deep-sea fans, organic matter is buried rapidly under fine-grained sediments (clay/silt). These settings are favourable for the establishment of anoxic conditions right below the sediment surface and microbial sulfate reduction becomes the main degrading process for organic matter. Under anaerobic conditions bacteria win the oxygen they need to

decompose organic matter to CO<sub>2</sub> (respiration) from sulfate (SO<sub>4</sub><sup>2-</sup>) that is dissolved in the pore water (sulfate reducing bacteria, e.g. *Desulfovibrio*). Hydrogen sulfide (H<sub>2</sub>S) released from this process reacts with dissolved iron forming hydrotroilite and troilite which are slowly converted to pyrite (Goldhaber and Kaplan, 1974; Jørgensen, 1982; Tissot and Welte, 1984). Vetö et al. (1994) suggest that microbial sulfate reduction in non-bioturbated marine sediments accounts for almost the total early diagenetic loss of organic carbon. As sulfate reduction furthermore is the most important process of sulfur fixation, measured total sulfur contents (mainly referring to pyrite) are indicative for the degree of degradation of bulk OM when related to organic carbon concentrations. The following equations describe the consumption of organic carbon and the formation of pyrite (after Leventhal, 1983; Berner, 1984):



Accordingly, two moles of organic carbon are needed to produce one mole of reduced sulfur. Thus, the original content of organic carbon ( $C_{\text{org}}^*$  = sulfate reduction index) can be estimated using the equation (Littke et al., 1991):

$$C_{\text{org}}^* = C_{\text{org}} + 2 S * M_C/M_S \quad (2)$$

$C_{\text{org}}$ , S: measured organic carbon, sulfur content

$M_C$ : molar weight of carbon (12,01 g)

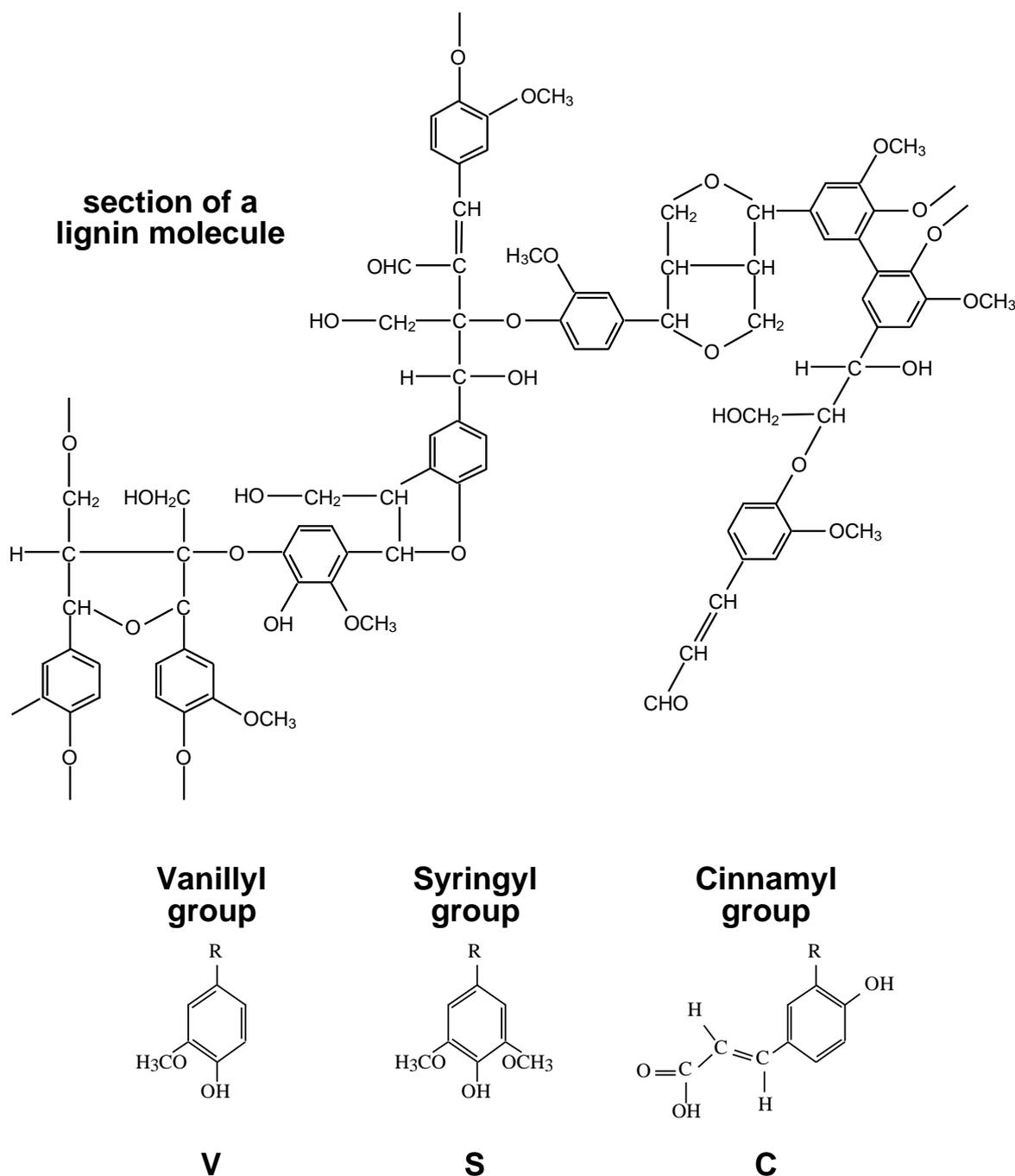
$M_S$ : molar weight of sulfur (32,06 g)

The ratio of calculated original versus measured organic carbon contents equals the degradation rate of bulk organic matter,  $C_{\text{org}}/C_{\text{org}}^*$ . It is a minimum estimate assuming that no H<sub>2</sub>S escapes from the sediment by diffusion. Elevated degradation rates indicate that either the sedimentary milieu became unsuitable for OM preservation or the initial bulk OM mixture contained enhanced amounts of labile OM (or both).

The described geochemical characteristics of marine and terrigenous OM allow conclusions on the composition of bulk OM whereas specific biomarkers (e.g., lignin phenols) and organic petrological investigations may directly document the presence of terrigenous OM as well as variations in its quality:

Lignin, an essential ingredient of vegetable biomass, stabilizes the plant tissue by its macromolecular structure. A section of the lignin molecule is shown in Fig. 1.7. The ratios of specific phenolic compounds of lignin can be used to identify the type of plant tissue the terrigenous organic fraction of sedimentary OM derives from (Hedges et al., 1979; Goñi and Hedges, 1992; see Fig. 1.7 for basic lignin phenol structures). All vascular land plants produce vanillyl phenols (V). Phenols of the syringyl group (S) characterize angiosperm tissues while they are absent in gymnosperms. Cinnamyl phenols (C) are a typical component of lignin in non-woody plant tissues (leaves, grasses). Thus, changing ratios of cinnamyl and vanillyl phenols (C/V) may indicate varying proportions of rain forest and grass savannah within a river catchment. Ratios of vanillic acid to vanillin,  $(\text{Ad/Al})_V$ , and syringic acid to

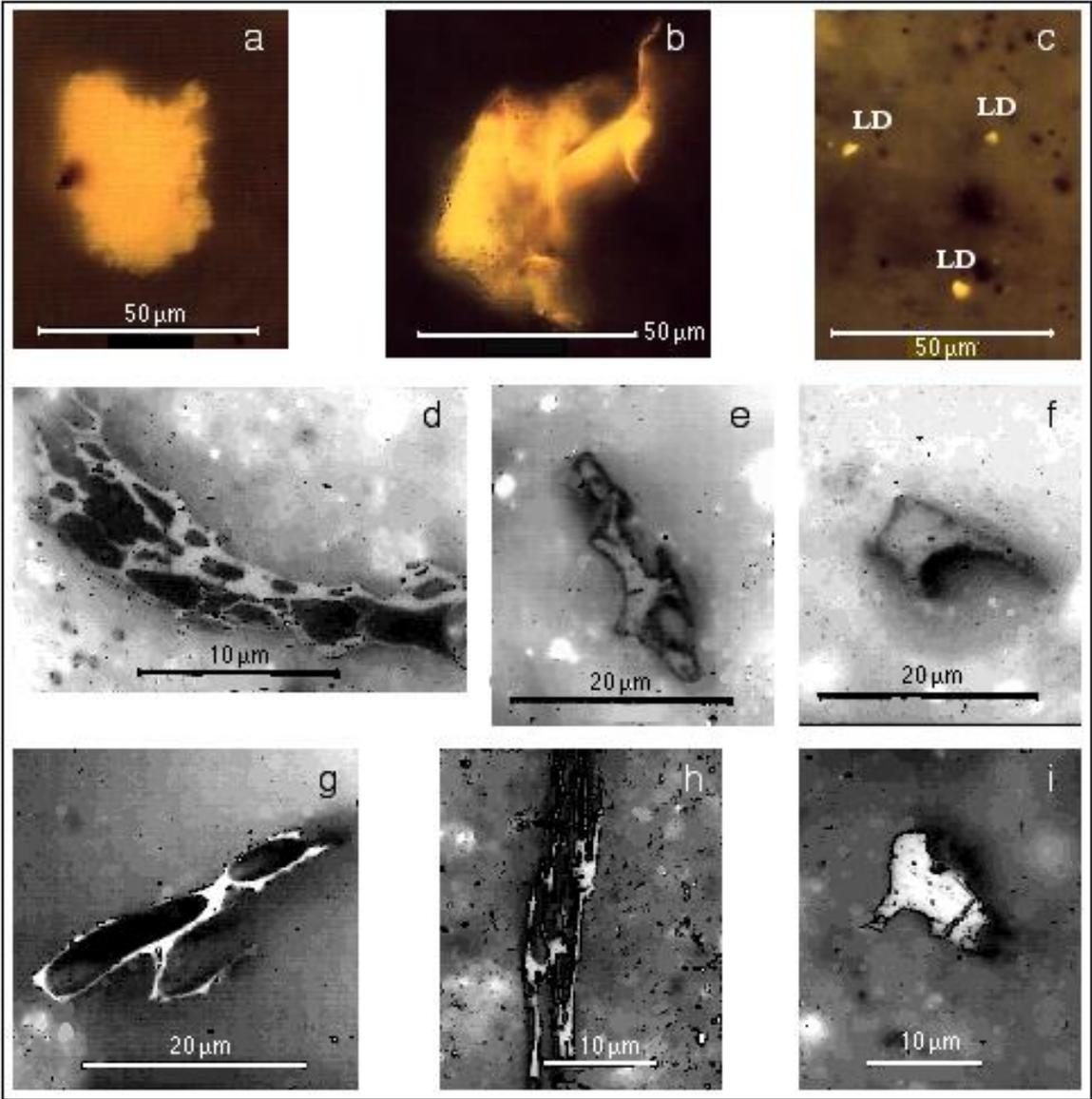
syringaldehyde, (Ad/Al)<sub>s</sub>, are sensitive to lignin alteration (Opsahl and Benner, 1995). The sum of all lignin phenols (A) may indicate varying terrigenous amounts. However, non-degraded particulate OM (“fresh” plant matter) reveals higher lignin contents than degraded SOM (e.g. Baldock et al., 1992; Dittmar and Lara, 2001). A values therefore do not represent terrigenous OM amounts if the proportions of these lignin sources are changing.



**Figure 1.7:** Section of a lignin molecule (from Tissot and Welte, 1984) and basic lignin phenols of the three investigated groups (from Killips and Killips, 1993).

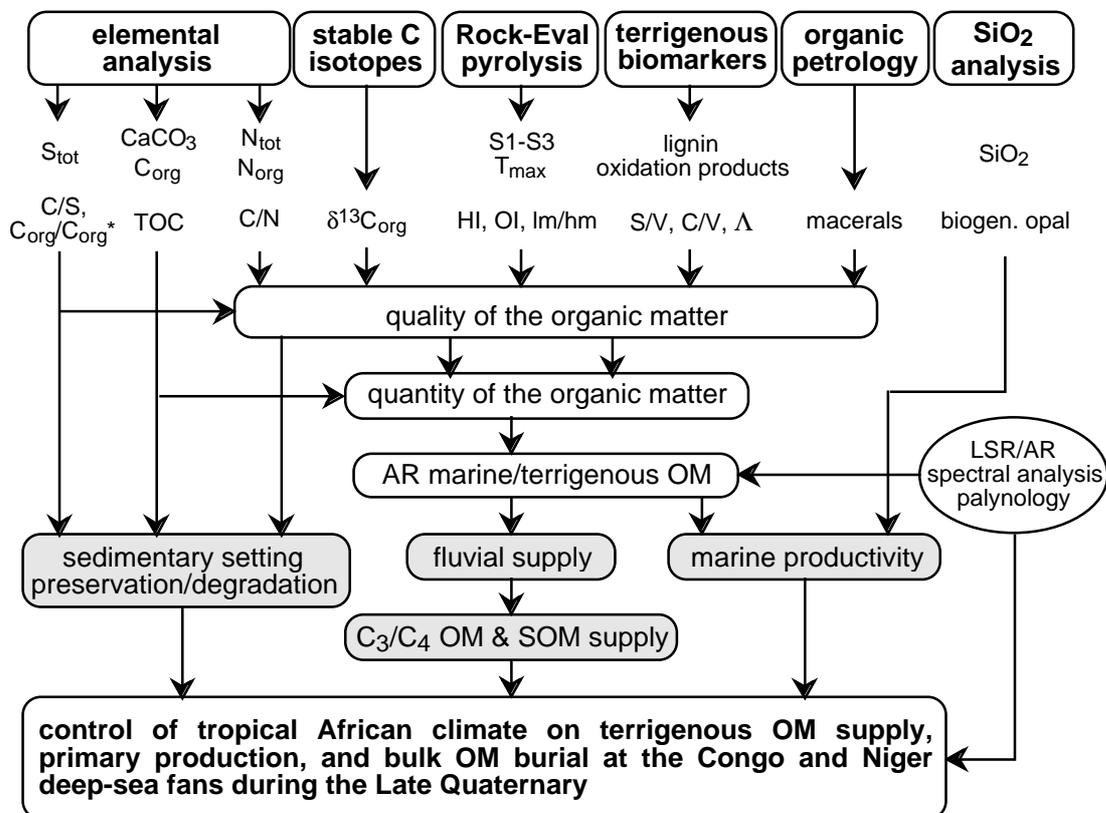
Organic particles can be identified and enumerated under the microscope by specific optical properties such as colour, shape, reflectance, and fluorescence. These characteristics depend on the origin (organism/tissue type) and the degree of degradation of the organic particles. They allowed the establishment of a descriptive system that classifies the various types of organic particles in coals and sediments as *maceral* types (detailed presentations e.g. in Stach et al., 1982 and Taylor et al., 1998; for application to modern and Quaternary marine sediments see Wagner, 1999a). Accordingly, three main groups of macerals are distinguished: vitrinites, liptinites, and inertinites. Vitrinites originate from lignin and cellulose of plant cell walls whereas liptinites derive from hydrogen-rich plant and algal remains, e.g. resins, waxes, fats. Inertinites result from biochemical or thermal degradation of vitrinites and liptinites and are poor in hydrogen contents (Taylor et al., 1998). Terrigenous macerals often show cell structures or fibrous shapes, whereas remains of (marine) algal cell walls often appear as organic linings. Chemical composition and macromolecular structure determine the optic characteristics of organic tissues or solids as, for example, the amount of incident light that is reflected from the surface of a maceral. Polished surfaces of terrigenous macerals (vitrinite, inertinite) reflect light to various degrees which makes them appear in different grey scales. Organic substances rich in lipids fluoresce under ultraviolet light. Lipid-rich marine OM therefore is characterized by its bright to moderate fluorescence whereas most terrigenous particles remain dark except, for example, lipid-rich remains of the protecting outer epidermis of leaves (cutinites). Examples of terrigenous and marine macerals are shown in Plate 1.1.

**Plate 1.1 (right):** Examples of marine and terrigenous macerals observed in late Quaternary sediments from the equatorial Atlantic (ODP Sites 663 and 959, taken from Wagner, 1999a). **a)** and **b)**: bright fluorescing algae bodies, *alginite* (liptinite maceral group); **c)** fluorescing fine-grained *liptodetrinite* (liptinite maceral group), the major marine maceral type in Niger and Congo deep-sea fan sediments; **d) - f)**: middle-grey reflecting *vitrinites* showing entire and broken cell lumina or 'bogen-structures'; P = bright reflecting pyrite; **g) - i)**: white reflecting oxidized *inertinites*. All photographs taken at 100- to 2000-fold magnification: a) - c) under UV-light excitation, d) - i) under white incident light (oil immersion).



## 1.5 Methods

A flow chart of the multi-parameter approach applied in this study is shown in Figure 1.8.



**Figure 1.8:** Methodological approach to investigate organic matter sedimentation at the Congo and Niger deep-sea fans. Terrigenous biomarkers were investigated only at the Congo deep-sea fan; extended maceral analysis (organic petrology) was performed only for Niger fan samples.

Sample material was freeze dried and homogenized prior to further investigations except for organic petrology.

### 1.5.1 Elemental analysis (C, N, S)

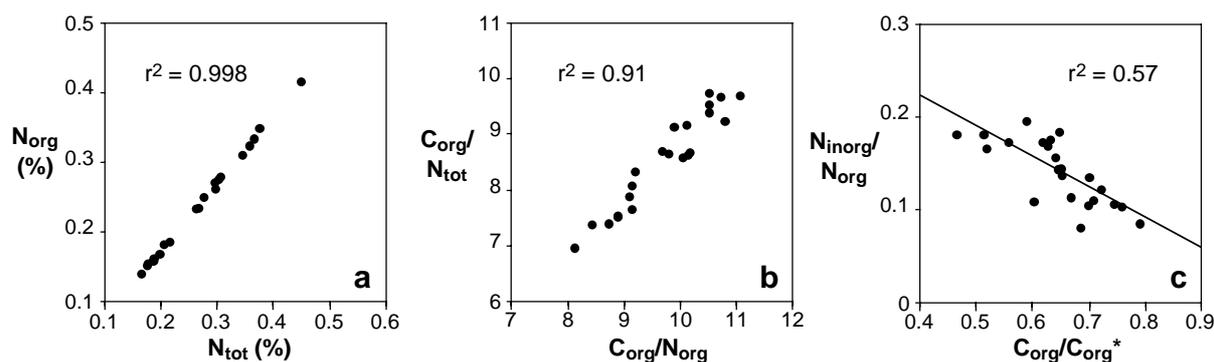
Total carbon (TC), total organic carbon (TOC), and sulfur contents of the Late Quaternary Congo fan sediments were measured at Bremen University using a Leco CS 300 (precision of measurement:  $\pm 3\%$ ). Carbonate contents were calculated from the difference of total carbon contents and organic carbon contents measured after using the equation:

$$\text{CaCO}_3 = (\text{TC} - \text{TOC}) * 8.33 \quad (3)$$

Factor 8.33 derives from the ratio of molecular/atomic weights of carbonate (100.09 u) and carbon (12.011 u).

Nitrogen was detected at the Max-Planck Institute for Marine Microbiology (Dept. of Biogeochemistry, Prof. B. B. Jørgensen), Bremen, using a Heraeus CNS Elemental Analyser

(precision of measurement:  $\pm 3\%$ ). As described above C/N ratios, the ratios of organic carbon and total nitrogen ( $C_{\text{org}}/N_{\text{tot}}$ ), to be precisely, are commonly used to assess marine and terrigenous shares of bulk OM. However, significant amounts of inorganic nitrogen ( $N_{\text{inorg}}$ ) may adulterate the  $C_{\text{org}}/N_{\text{tot}}$  ratios, as e.g. ammonium ( $\text{NH}_4^+$ ) that is released from OM destruction and fixed in clay minerals. To evaluate the potential influence of this factor a set of 23 samples from two time slices (586-519 ka and 330-213 ka) of ODP Site 1075 was examined for the content of inorganic nitrogen ( $N_{\text{inorg}}$ ). The samples were treated with a solution of KOBBr-KOH to convert all organic bound nitrogen into  $\text{N}_2$  (Silva and Bremner, 1966) and measured for residual inorganic nitrogen, again. The almost perfect fit of bulk and organic nitrogen ( $N_{\text{tot}}$  vs.  $N_{\text{org}}$ , Fig. 1.9a) and the very good correlation of  $C_{\text{org}}/N_{\text{org}}$  and  $C_{\text{org}}/N_{\text{tot}}$  ratios (Fig. 1.9b) allow to use the latter for a characterization of bulk OM. Those samples that have passed stronger alteration as indicated by their degradation rates ( $C_{\text{org}}/C_{\text{org}}^*$ , see above) tend to contain enhanced relative shares of inorganic nitrogen (Fig. 1.9c). However, this does not necessarily point to a causal relation as e.g. relative enrichment of inorganic nitrogen by selective diagenesis or uptake of released ammonium by clay minerals. The original bulk OM of samples with lower contents of inorganic nitrogen probably was more resistant against microbial attack or buried and sealed more effectively.



**Figure 1.9:** Relations of  $N_{\text{tot}}$ ,  $N_{\text{org}}$ ,  $C_{\text{org}}$ , and degradation rates of bulk OM ( $C_{\text{org}}/C_{\text{org}}^*$ ) of selected samples from the Congo deep-sea fan. Contents of organic and total nitrogen are strongly correlated (a). The good correlation of  $C_{\text{org}}/N_{\text{org}}$  and  $C_{\text{org}}/N_{\text{tot}}$  ratios justifies the application of  $C_{\text{org}}/N_{\text{tot}}$  ratios to characterize bulk OM (b). However, selective diagenesis after burial slightly increases the relative amount of inorganic nitrogen (c).

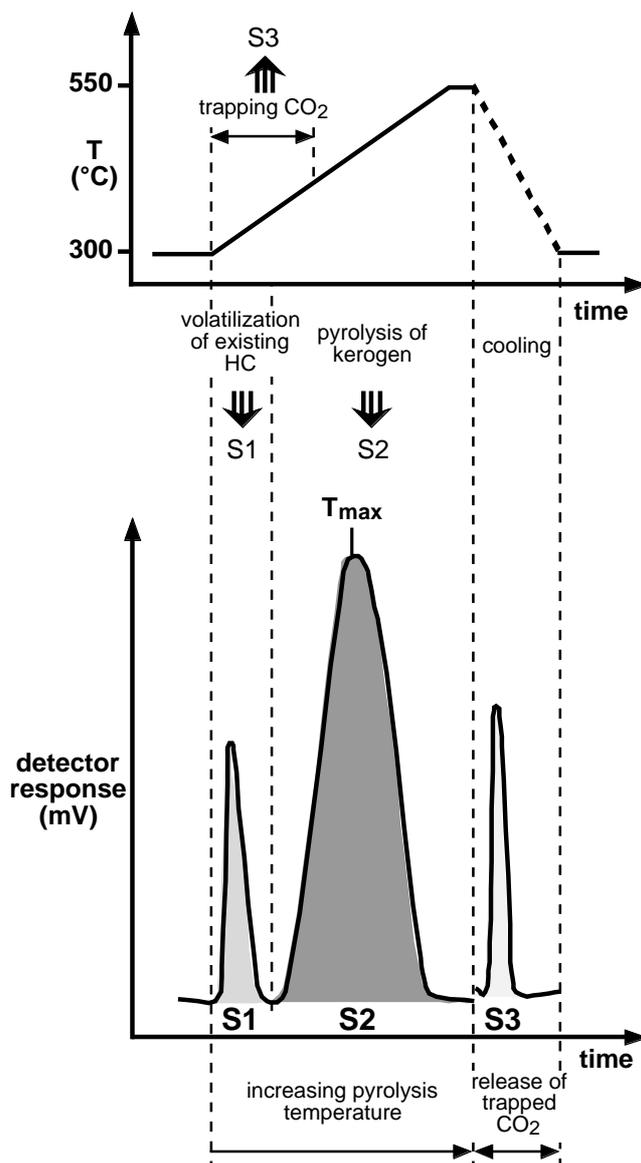
### 1.5.2 Determination of stable organic carbon isotopes (bulk $\delta^{13}\text{C}_{\text{org}}$ )

The isotopic composition of bulk sedimentary OM (bulk  $\delta^{13}\text{C}_{\text{org}}$  vs. VPDB) from site 1075 (Congo fan) was measured at the Alfred-Wegener-Institute in Potsdam (Dr. U. Wand) using a Heraeus Elemental Analyzer combined with a Finnigan MAT Delta S mass spectrometer (precision of measurements:  $\pm 0.2\%$ ). The Niger fan samples were investigated at Bremen University (Dept. of Marine Geology, Prof. G. Wefer) with a Finnigan MAT Delta E MS. Deviation from the isotopic ratio of the VPDB standard is calculated as follows:

$$\delta^{13}\text{C}_{\text{org}} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \quad [\text{‰}] \quad (4)$$

### 1.5.3 Rock-Eval pyrolysis (HI, OI, $T_{max}$ , Im/hm)

For this study the Rock-Eval II device at the Research Center Jülich (Institute of Chemistry and Dynamics of the Geosphere, Dr. B. Horsfield) was used. The principle: samples are smouldered under inert atmosphere (helium) during progressive heating from 300°C to 550°C (heating rate: 25°C/min). At moderate temperatures *existing* hydrocarbons are volatilised from the sediment, discharged by a helium stream, and measured by a flame ionisation detector (FID; S1 peak, Fig. 1.10). Hydrocarbons and hydrocarbon-like components that are *generated* from the kerogen fraction during increasing temperature are detected as S2 peak (Fig. 1.10). Between 300°C and 390°C oxygen containing volatiles, mainly CO<sub>2</sub> and water, are trapped. They are released during the cooling process and measured by a thermal conductivity detector (TCD; S3 peak, Fig. 1.10). The temperature of maximum hydrocarbon generation is recorded as  $T_{max}$ . The amounts of volatilised and generated hydrocarbons and CO<sub>2</sub> are calculated from FID and TCD responses, respectively, by means of a gas chromatographic integration system (VAX-Multichrom 2.2). Precision of measurement for hydrocarbon peaks S1, S2, and carbon dioxide peak S3 is  $\pm 5\%$ , for  $T_{max} \pm 1^\circ\text{C}$ .



**Figure 1.10:** Analytical cycle of Rock-Eval pyrolysis (modified from Tissot and Welte, 1984).

As will be described in Chapter 2 organic matter from late Quaternary sediments of the Congo deep-sea fan generates hydrocarbons within the S2-temperature window in two batches, at 385°C and at 530°C on average, resulting almost without exception in a distinct S2 double peak. Quantification of the partial peak areas ( $S2_{lm}$ ,  $S2_{hm}$ ; lm = low-mature, hm = high-mature) led to the establishment of a new proxy for OM reactivity, the "low-mature/high-mature ratio" (lm/hm ratio). As the bulk organic matter of the Congo fan sediments obviously is a mixture of two clearly different types of kerogen this proxy most likely illustrates the changing relative amount of type IV-kerogen

### 1.5.4 Analysis of lignin-oxidation products (S/V, C/V, $\Lambda$ , (Ad/Al)<sub>s,v</sub>)

Extraction and analysis of lignin phenols was carried out at the Max-Planck Institute for Marine Microbiology (Dept. of Biogeochemistry, Prof. B. Jørgensen) using a Hewlett Packard 6890 Series GC system. As the results from these investigations have been very conducive to the development of a model for OM sedimentation at the Congo deep-sea fan a more detailed description of the analytical procedure is given here.

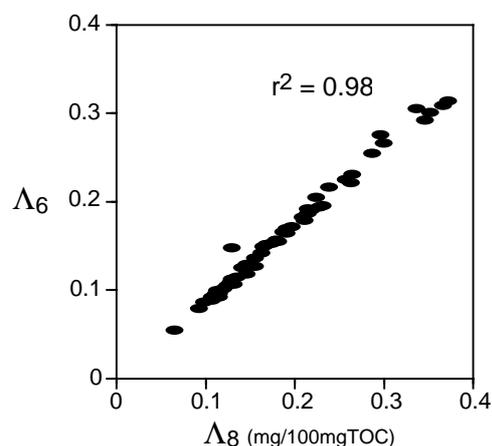
#### 1.5.4.1 Oxidation and extraction

Maximum 1g of sediment, 1g cupric oxide (CuO), and 100 mg iron(II)ammonium sulfate ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) are weighed into teflon cartridges. Under inert atmosphere ( $\text{N}_2$ ) 8 ml a 2M (8%) solution of sodium hydroxide (NaOH) are added and the cartridges are sealed. After efficient shaking the cartridges are placed in an aluminium block where the samples are heated to 155°C (max.) for three hours under permanent move (shaking table). Subsequent to oxidation and cooling of the samples 50  $\mu\text{l}$  of internal standard mix are added and the mixtures are transferred to teflon centrifuge tubes. With 15 ml of fresh 1M NaOH the samples are centrifuged (4500 rpm for 10 min) and the supernatant is transferred to separatory funnels. After this procedure is repeated twice 5 ml of ultrapure concentrated hydrochloric acid (HCl) are added to the separatory funnels. Reduction of the pH-value around or below 1 causes the precipitation of the humic acids. The fulvic acids (including the phenolic compounds) then can be extracted from the remaining solution by addition of ether (3\*20 ml) and the aqueous and ether layers are separated. Addition of small amounts of anhydrous  $\text{Na}_2\text{SO}_4$  to the ether fraction ensures that any water that has been carried over is removed. The ether extract is condensed to a volume of 1ml at low temperature (ca. 30°C) using a rotoevaporator. This residue is then transferred to drying columns containing anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and finally taken to dryness with a flow of  $\text{N}_2$ .

#### 1.5.4.2 Gas chromatography

For chromatography the extract is taken up with 100 $\mu\text{l}$  ultrapure pyridine. A split of 2  $\mu\text{l}$  is derivatized with 2  $\mu\text{l}$  N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 60°C to silylate all exchangeable hydrogens. The initial temperature of the injector is 100°C. The oven temperature is raised to 270°C with 4°C/min. Helium is used as carrier gas and the vaporised organic substances are detected by FIDs. CuO oxidation releases not only lignin phenols from the kerogen but countless other phenolic organic compounds which usually results in very complex traces and (sometimes) co-elution effects during gas chromatography. Therefore, two columns with different polarity of the stationary phases (J&W Scientific: db1 non-polar, db1701 polar; 30 m \* 0.25 mm, 0.25  $\mu\text{m}$  film) are used to separate the oxidation products and to ensure a good peak-resolution on at least one phase. The lignin phenols are quantified based on the yields of ethylvanillin. For the calculation of the lignin phenol yields and ratios generally the smaller quantities of each compound are taken from both columns. This provides minimum estimates and the risk of exaggerated yields due to co-elution effects is reduced. Opsahl and Benner (1995) demonstrate that *p*-coumaric acid and ferulic acid, forming the cinnamyl group, are the lignin components most susceptible to degradation

processes. They suggest the use of only the sum of the syringyl and vanillyl phenols ( $\Lambda_6$ ) instead of the “classical“  $\Lambda$  that sums syringyl, vanillyl, and cinnamyl phenols ( $\Lambda_8$ ). In fact, quantification especially of ferulic acid turned out to be problematic as the peaks were often affected by co-elution. However,  $\Lambda_6$  and  $\Lambda_8$  in this study show a very good correlation (Fig. 1.11) indicating that *p*-coumaric and ferulic acid are not more strongly degraded after deposition than other lignin components. The lignin phenol yields presented in this study therefore are given as  $\Lambda_8$ .



**Figure 1.11:** Relation of  $\Lambda_8$  (S+V+C) and  $\Lambda_6$  (S+V) in Late Quaternary sediments of the Congo deep-sea fan (ODP Site 1075). Apparently, *p*-coumaric and ferulic acid, the cinnamyl group (C), could be quantified properly resulting in an extremely good correlation of  $\Lambda_8$  and  $\Lambda_6$ .

Duplicate CuO oxidation, extraction, and GC analysis of lignin phenols were performed on 16 samples from the Congo deep-sea fan (Site 1075). Mean deviations for lignin parameters are:

$\Lambda_8$ :	16 %,
$\Lambda_6$ :	14 %,
S/V:	7 %,
C/V:	13 %,
(Ad/Al) <sub>V</sub> :	17 %
(Ad/Al) <sub>S</sub> :	14 %.

**Calibration mix and relevant lignin phenols:**

Benzoic acid	
<i>p</i> -OH-benzoic acid	
<i>p</i> -OH-acetophenone	
<i>p</i> -OH-benzaldehyde	
<i>m</i> -OH-benzoic acid	
3,5-di-OH-benzoic acid	
<hr/>	
Vanillin	
Acetovanillon	<b>V</b>
Vanillic acid	
<hr/>	
Syringaldehyde	
Acetosyringone	<b>S</b>
Syringic acid	
<hr/>	
<i>p</i> -coumaric acid	
Ferulic acid	<b>C</b>
<hr/>	
Hexadecanedioic acid	
16-OH-hexadecanoic acid	

**Internal standard:**

Ethylvanillin (3-ethoxy-4-OH-benzaldehyde)
Cinnamic acid
1,11-undecanedioic acid
12-OH-octadecanoic acid (12-OH-stearic acid)
Tricosanoic acid
3,4-dimethoxybenzoic acid
3,4-dimethoxybenzaldehyde
4,4-di-OH-benzophenone

### 1.5.5 Organic petrology

Selected bulk sediment samples were embedded in a low-viscosity resin, then ground and polished using a Logitech PM 2A (grain size of polish: 1/3  $\mu\text{m}$ ). Organic petrological investigations were performed using a Zeiss Axiophot with additional mercury lamp (HBO 100W/2) for fluorescence observations.

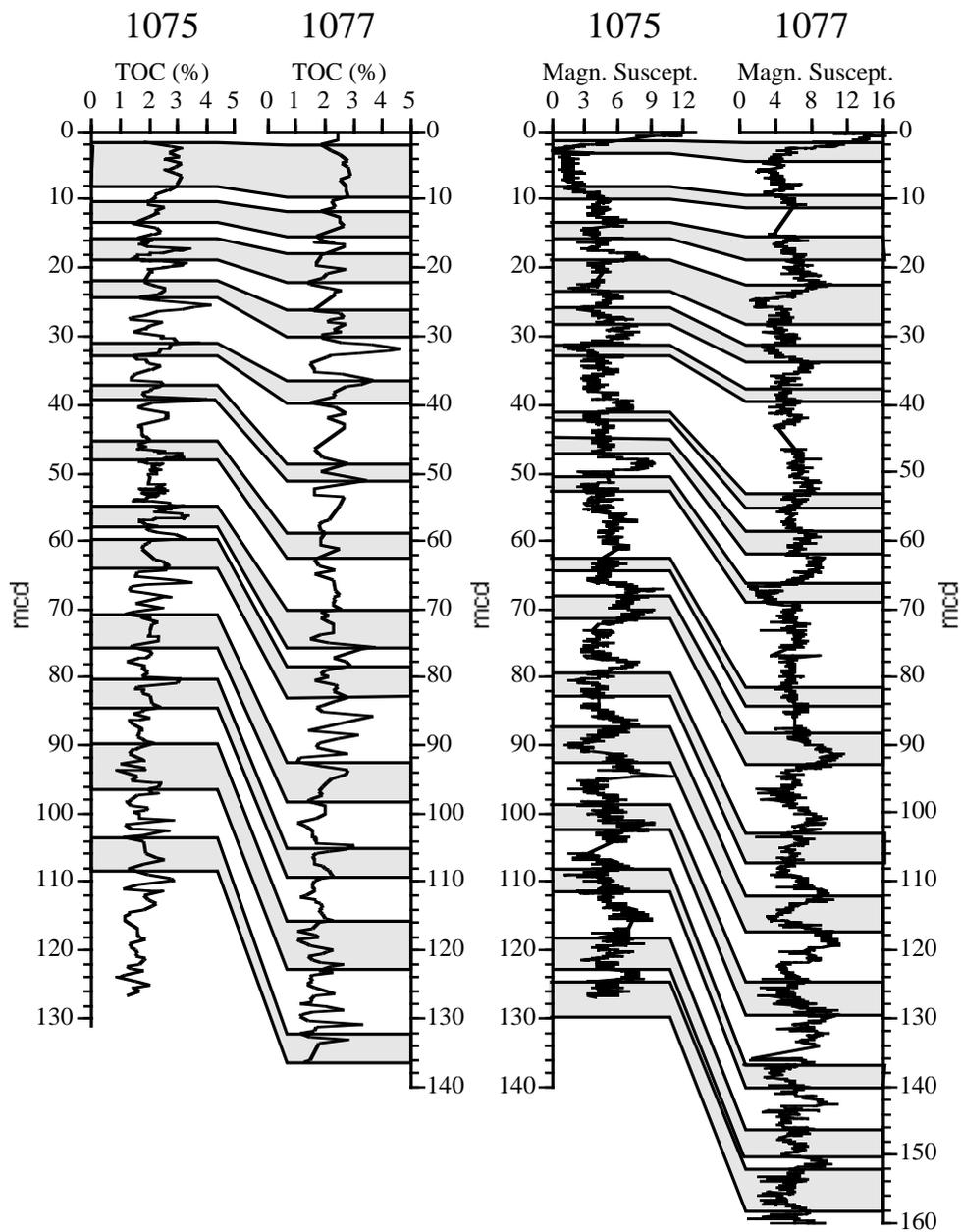
For statistical relevance 500 particles per sample were counted. The organic particles were sorted by grain size in 4 classes:  $<5\mu\text{m}$ , 5-10 $\mu\text{m}$ , 10-20 $\mu\text{m}$ , and  $>20\mu\text{m}$  and identified following the classifications for macerals of Stach et al. (1982) and Taylor et al. (1998). For estimation of terrigenous and marine proportions vitrinites and inertinites were rated as terrigenous particles whereas fluorescing liptinite particles (alginites, AOM, inner coatings of foraminifera) were counted as marine OM. Liptinites of terrigenous origin (e.g. cutinites) were extremely rare.

### 1.5.6 Determination of biogenic opal

Biogenic opal concentrations of selected samples from the Niger deep-sea fan were measured at Bremen University (Dept. of Marine Geology, Prof. G. Wefer) applying a sequential leaching technique (DeMaster, 1981) modified and automated by Müller and Schneider (1993). Opal is completely mobilized from the samples by treatment with 1 M NaOH for one hour at 85°C. Concentration of released  $\text{SiO}_2$  is simultaneously detected by continuous flow analysis with molybdate-blue spectrophotometry (precision of measurement:  $< 2\%$ ).

## 1.6 Stratigraphy of ODP Site 1075

Dupont et al. (2001) established a first stratigraphical model by correlation of the magnetic susceptibility records of sites 1075 and 1077 (see Fig. 2.1 for core position) that is used in Chapter 2. The measurement of TOC contents at Site 1077 enabled to develop a complementary stratigraphy based on the correlation of the TOC records ( $r^2 = 0.74$ ) of both sites that is used in Chapters 4 and 5. The TOC profiles and the assignment of TOC minima and maxima are shown in Figure 1.12.



**Figure 1.12:** TOC and magnetic susceptibility profiles of ODP Sites 1075 and 1077. Correlation of TOC records according to Holtvoeth et al. (2003): high-frequency cyclicality of both TOC records allows sound peak assignments (regression factor  $r^2 = 0.74$ ); correlation of magnetic susceptibility records following Dupont et al. (2001).

## 2. Late Quaternary supply of terrigenous organic matter to the Congo deep-sea fan (ODP site 1075): implications for equatorial African paleoclimate

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### 2.1 Abstract

Late Quaternary sections (about 1 Ma) from the Congo deep-sea fan (ODP Leg 175, site 1075) were used to reconstruct the terrigenous organic matter supply to the easternmost equatorial Atlantic Ocean. Variations in quantity and quality of the riverine organic matter reflect the interaction between the paleoclimatic development within the continental catchment area and the paleoceanographic conditions in the Congo river plume. To characterize the delivery of organic matter from terrigenous and marine sources, we used elemental and bulk carbon isotopic analyses, Rock-Eval pyrolysis, lignin chemistry, and organic petrology. High-amplitude fluctuations occurring about every 15-25 ka reveal a mainly precessional control on organic sedimentation. Results from Rock-Eval pyrolysis indicate a mixed kerogen type-III/II, as would be anticipated in front of a major river. Fluctuations in  $T_{\max}$  from Rock-Eval pyrolysis demonstrate pronounced cyclic changes in the delivery of low- and high-mature organic matter. Contribution of the low-mature organic fraction was strongest during warm climates supporting enhanced marine production offshore of the Congo. Organic petrological observations confirm the existence of abundant terrigenous plant tissues, both non-oxidized (vitritinite) and oxidized (inertinite). Charcoal-like organic matter (fusinite) is attributed to periods of increased bush fires in the continental hinterland, and implies more arid climatic conditions. Results from ratios of specific phenolic lignin components suggest that terrigenous organic matter in late Quaternary sections of site 1075 mainly derives from non-woody angiosperm tissue, i.e. grasses and leaves. Correlation between the amount of specific lignin phenols ( $\Lambda$ ) and the bulk  $\delta^{13}\text{C}_{\text{org}}$  signature fosters the conclusion that an appreciable amount of the terrigenous organic fraction derives from  $\text{C}_4$  plant matter. This may cause an underestimation of the terrigenous proportion of bulk organic matter when assessments are based on bulk carbon isotopic signatures alone.

## 2.2 Introduction

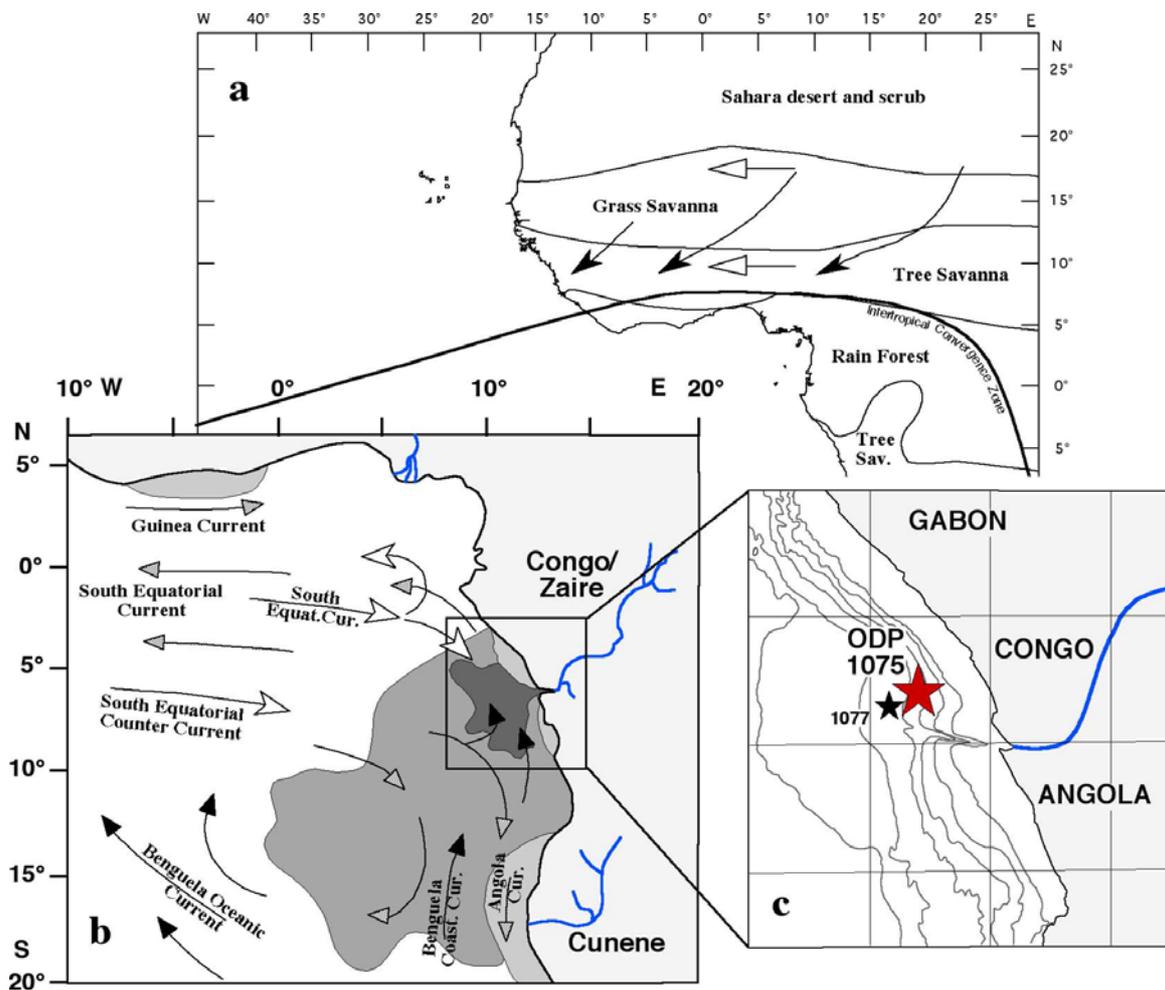
Investigations of sediments off major river mouths have shown that the fluvial systems make a more important contribution to the supply and accumulation of terrigenous organic carbon in deep-sea settings than has commonly been considered (e.g. Meyers, 1997; Goñi et al., 1998). In view of the modern and past glacial/interglacial global carbon budget, the lateral displacement of depositional areas in response to orbitally forced sea-level fluctuations (Schlünz et al., 1999) and dust deposition (Wagner, 2000) appear to be key mechanisms which are not yet well constrained. Accordingly, deposition of terrigenous organic matter occurs mainly in the shelf areas during interglacial sea-level highstands whereas a large proportion of the riverine organic matter is transported through channels or canyons beyond the continental slope to the associated deep-sea fans during glacial sea-level lowstands. The Amazon Fan (ODP Leg 155) and the adjacent Ceara Rise is a well-studied example in the western equatorial Atlantic where the dramatic effect of glacial sea-level lowstands on the downslope entrainment of terrigenous organic carbon to distal areas of the deep-sea fan, and even further eastwards has recently been demonstrated (Rühlemann et al., 1996; Schneider et al., 1997b; Schlünz et al., 1999).

The Congo river drains the second largest catchment area of the world with more than one third ( $1300 \text{ km}^3/\text{year}$ , equivalent to 38 %) of the yearly run-off from Africa (N’Koukou and Probst, 1987). The Congo contributes 3.9 % (about  $13 \cdot 10^6 \text{ t C/year}$ ) to the global annual supply of terrigenous organic carbon into the ocean (Martins and Probst, 1991), thereby strongly influencing nearshore sedimentation in the eastern equatorial Atlantic. In contrast to other major rivers, e.g., the Amazon or the Mississippi, the sediment supply through the Congo is characterized by 11 to 17 times lower suspension loads (Ludwig et al., 1996). This drainage property is attributed to the flat morphology of the catchment area, and the consistent distribution of precipitation on both sides of the equator (Eisma, 1982; N’Koukou and Probst, 1987). Because of the exceptionally narrow continental shelf in front of the Congo mouth (approximately 50 km) and the presence of a canyon which begins within the estuary of the river (Fig. 2.1), part of the riverine terrigenous organic matter may be transported directly to the deep sea even during modern and past interglacial sea-level highstands. It is therefore anticipated that climate-induced changes in the supply of terrigenous lithogenic and organic matter are well preserved in late Quaternary sediments of the Congo deep-sea fan.

Today, the vegetation in the catchment area of the Congo is dominated by tropical rainforest whose productivity is governed by the West-African monsoon (Ning and Dupont, 1997; Fig. 2.1a). In response to late Quaternary insolation changes, the equatorial African paleoclimate fluctuated between more arid conditions during cold glacial and interglacial periods and more humid conditions associated with their warm counterparts. Within the Congo catchment area, there is evidence that the savannah belt expanded and replaced the tropical rainforest as the dominant type of vegetation during dryer climatic conditions (Frédoux, 1994; Ning and Dupont, 1997; Jahns et al., 1998). The central African savannah is distinguished by an inner, mainly tree-covered belt and extended grasslands which dominate at the transition zone to full desert conditions (Fig. 2.1a). Under such dry conditions,  $C_4$  plants exhibit better growth

compared to C<sub>3</sub> plants (Tyson, 1995). Additionally, decreasing concentrations of CO<sub>2</sub> in the atmosphere can lead to expansion of the C<sub>4</sub> plant habitat (Jolly and Haxeltine, 1997; Cerling et al., 1997; Huang et al., 1999b). Consequently, the amount and composition of terrigenous organic matter which was exported by the Congo river may have fluctuated considerably during the development of Late Quaternary glacial-interglacial climates.

For a better understanding of the role and importance of upwelling regimes within the global ocean carbon cycle, ODP Leg 175 drilled 13 sites along the West African continental margin within a latitudinal corridor between 5° and 32°S (Wefer et al., 1998). Site 1075, situated in the northern part of the Congo deep-sea fan, was chosen to study the late Quaternary (0-1.2 Ma) supply of terrigenous organic carbon to the eastern equatorial Atlantic (Fig. 2.1c).

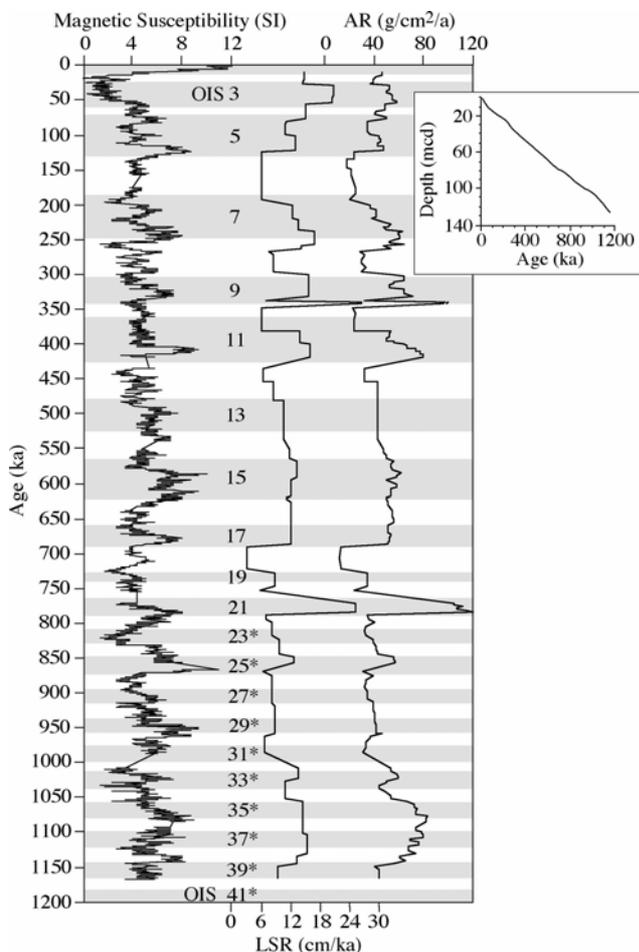


**Figure 2.1:** (a) Locality map of central and northern Africa showing major vegetation belts and general characteristics of the modern atmospheric circulation (modified after Ruddiman et al., 1989a). Black arrows indicate surface trade winds, open arrows the mid-level African Easterly Jet and the Saharan Air Layer. (b) Surface and subsurface currents, and highly productive areas in the eastern Equatorial Atlantic (modified after Schneider et al., 1994). Black arrows identify cold surface currents, open arrows warm surface currents, and hatched arrows undercurrents. High-productivity areas are marked by different shades of grey: dark – river plume with river-induced upwelling; medium – oceanic upwelling with shallow thermocline, thermal domes and fronts; light – coastal upwelling. (c) Core locations of ODP-sites 1075 and 1077 in the Congo deep-sea fan off the Congo river (after Wefer et al., 1998).

Characterization of sedimentary organic matter with regard to its marine and terrigenous origins was performed using organic geochemical methods (elemental analysis, stable carbon isotope analysis, Rock-Eval pyrolysis, lignin chemistry) and organic petrology (maceral analysis). In particular, evidence for the contribution of C<sub>4</sub> plant material to the bulk organic matter was sought to provide further information on variations in grasslands resulting from orbitally forced aridity/humidity cycles.

### 2.3 Stratigraphy, linear sedimentation rates and bulk accumulation rates

The persistently low carbonate contents in late Quaternary sections of site 1075 (see carbonate record presented below) exclude the establishment of a high-resolution stratigraphy based on stable oxygen isotopes (OIS = oxygen isotopic stage). Instead, the stratigraphic framework of site 1075 was set up by correlation of high-resolution magnetic susceptibility records from site 1075 and neighbouring site 1077 (Dupont et al., 2001; see Fig. 2.1c for core position). As carbonate contents are sufficiently high at Site 1077 to produce an oxygen isotope record, a high resolution stratigraphy based on *Globigerina ruber pink* was acquired by Dupont and coauthors. The magnetic susceptibility records of both sites reveal pronounced minima and maxima which parallel each other and apparently follow typical glacial/interglacial patterns (Fig. 2.2). Accordingly, interglacial intervals are characterized by generally higher contents of magnetizable minerals compared to glacial ones. Figure 2.2 displays this stratigraphic framework, including corresponding linear sedimentation and accumulation rates for site 1075.



**Figure 2.2:** Late Quaternary records of magnetic susceptibility of site 1075 (after Wefer et al., 1998), linear sedimentation rates (LSR) and accumulation rates (AR). The stratigraphy is based on correlation of magnetic susceptibility records of sites 1075 and 1077 (Dupont et al., 2001). Oxygen isotopic stages (OIS): Imbrie et al. (1984), \*Ruddiman et al. (1989b)

## 2.4 Methods

Total carbon, total organic carbon (TOC) and sulfur contents were analyzed using a Leco CS 300 (precision of measurement  $\pm 3\%$ ). The total amount of nitrogen was measured with a Heraeus CNS (precision of measurement:  $\pm 3\%$ ). As  $C_{\text{org}}/N_{\text{tot}}$  ratios were unexpectedly low with regard to the core position in front of a major river, selected samples were examined for their inorganic nitrogen content. These samples were treated with a solution of KOBBr-KOH to convert all organic bound nitrogen into  $N_2$  (Silva and Bremner, 1966).

Assuming that microbial sulfate reduction is the main degradation process for sedimentary organic matter in the Congo fan deposits, we estimated the original content of organic carbon according to Littke et al. (1997) following the equation  $C_{\text{org}}^* = C_{\text{org}} + 2S * M_C/M_S$  ( $S$  = measured sulfur content,  $M_C$  = molecular mass of carbon,  $M_S$  = molecular mass of sulfur). The degradation rate of organic carbon is expressed as the ratio of the measured to the estimated original organic carbon contents ( $C_{\text{org}}/C_{\text{org}}^*$ ).

Kerogen typing and determination of organic matter maturity were conducted according to Espitalié et al. (1977) using a Rock-Eval II instrument (precision of measurement for HI, OI:  $\pm 5\%$ ; for  $T_{\text{max}}$ :  $\pm 1^\circ\text{C}$ ; Espitalié et al., 1985). The yields of hydrocarbons and  $\text{CO}_2$  generated during pyrolysis were calculated from FID and TCD responses, respectively, by means of a gas chromatographic integration system (VAX-Multichrom 2.2). Hydrogen indices ( $\text{HI} = S_2 * 100/\text{TOC}$ ) and oxygen indices ( $\text{OI} = S_3 * 100/\text{TOC}$ ) were calculated using measured TOC values. Hydrocarbons and hydrocarbon-like components which are generated from the kerogen fraction of the bulk sediment are quantitatively detected within the  $S_2$  temperature window. The  $T_{\text{max}}$  value defines the temperature of maximum hydrocarbon generation rate within the  $S_2$  window, and is commonly used as a thermal maturity parameter. We point out, however, that  $T_{\text{max}}$  above all is a primary measure for the thermal stability of organic matter (OM), considering that some types of kerogen are inherently stable, e.g., from non-reactive OM. The  $T_{\text{max}}$  value is automatically attributed to the highest response of the detector.

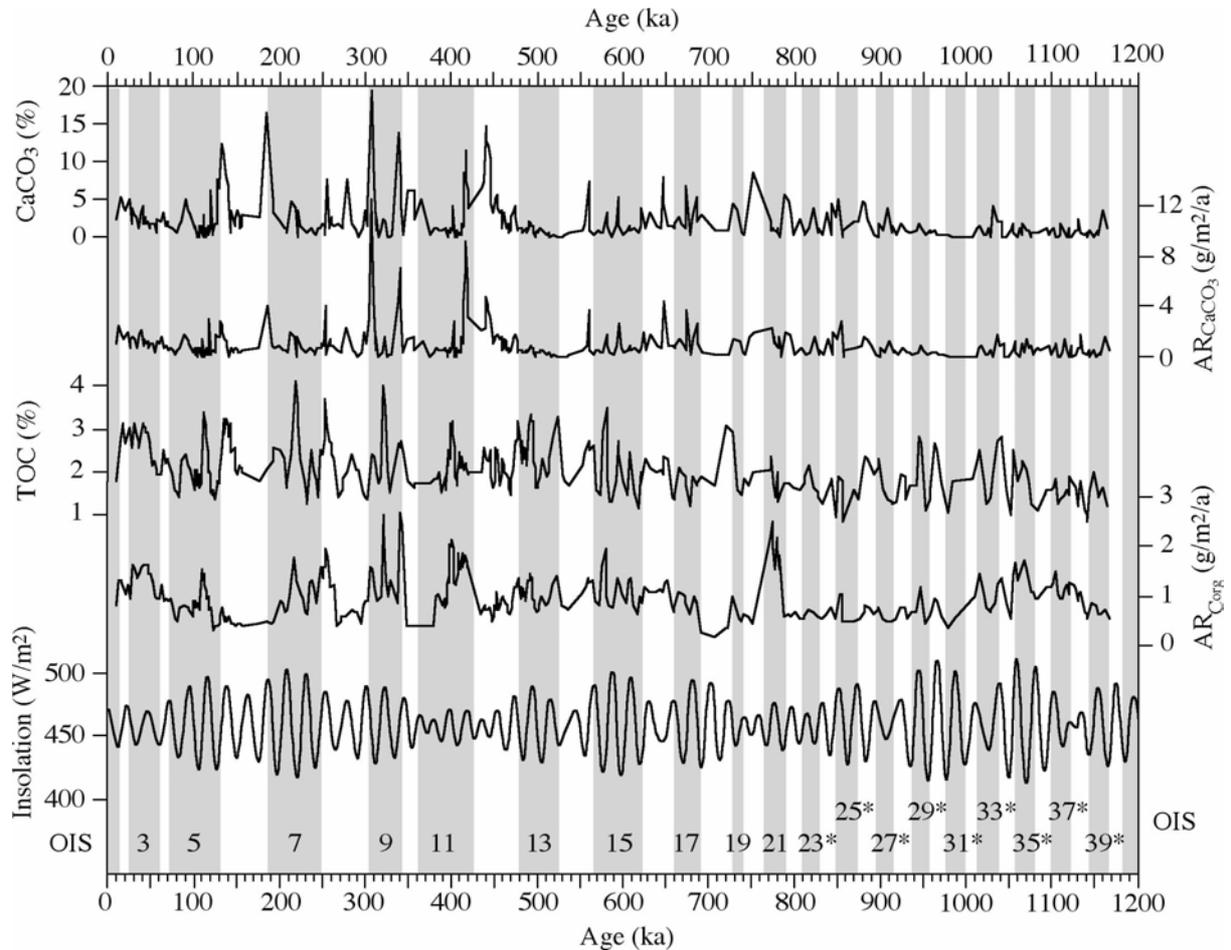
Organic petrological analysis was performed using a Zeiss Axiophot. Bulk sediment samples were embedded under vacuum in a low viscosity resin. After 24 hours specimens were ground and polished using a Logitech PM 2A (for details see Wagner, 1998). The macerals distinguished during these first qualitative investigations were huminite, vitrinite, semifusinite, fusinite and alginite. Also, amorphous organic matter was observed.

The stable carbon isotopic composition of bulk sedimentary organic carbon ( $\delta^{13}\text{C}_{\text{org}}$  vs. VPDB) was measured using a Heraeus Elemental Analyzer combined with a Finnigan MAT Delta S mass spectrometer (precision of measurement:  $\pm 0.2\%$ ).

Terrigenous biomarkers (lignin phenols) were measured using a Hewlett Packard 6890 Series GC system. The analytical procedure (CuO-oxidation) is based on the fundamental approach established by Hedges and Mann (1979a,b), and was carried out according to Goñi and Hedges (1992; precision of measurement:  $\pm 10\%$ ). Two parallel capillary columns (J&W Scientific db1 non-polar, db 1701 polar; 30 m \* 0.25 mm, 0.25  $\mu\text{m}$  film) were used for chromatography.

## 2.5 Results

Time series of TOC and  $\text{CaCO}_3$  from site 1075 are displayed as percentages and accumulation rates in Fig. 2.3. The record of insolation for  $15^\circ\text{S}$  is added, illustrating the precessional frequency.



**Figure 2.3:** Time series of TOC and  $\text{CaCO}_3$  contents and accumulation rates (AR) from site 1075. The TOC record shows a high variability with repeated minima and maxima (at 15-25 ka time intervals), indicating a mainly precessional-controlled organic sedimentation (compare with record of insolation for  $15^\circ\text{S}$  from Berger and Loutre, 1991).

Carbonate contents remain generally low except for various short-term spikes ( $>10\%$ , max.  $19\%$ ) which occur in the time intervals 455 to 300 ka (oxygen isotopic stages (OIS) 12 to 8), and 200 to 130 ka (OIS 6 to 5). Corresponding accumulation rates are  $1.0\text{ g/m}^2\text{ a}$  on average, and reach maximum values ( $>6\text{ g/m}^2\text{ a}$ ) during OIS 11 and 9.

The TOC record shows a general decreasing downcore trend which is attributed to long-term diagenetic effects. Within the uppermost core section, the TOC decreases from average values of 2.7 to 2.2 %, then fluctuates around 2.2 % between OIS 16 and 4, and finally decreases to an average level of 1.5 % at the bottom of the profile. Maximum values (3.3 to 4.3 %) and highest amplitudes appear during OIS 15, and especially during OIS 9 and 7. The calculated

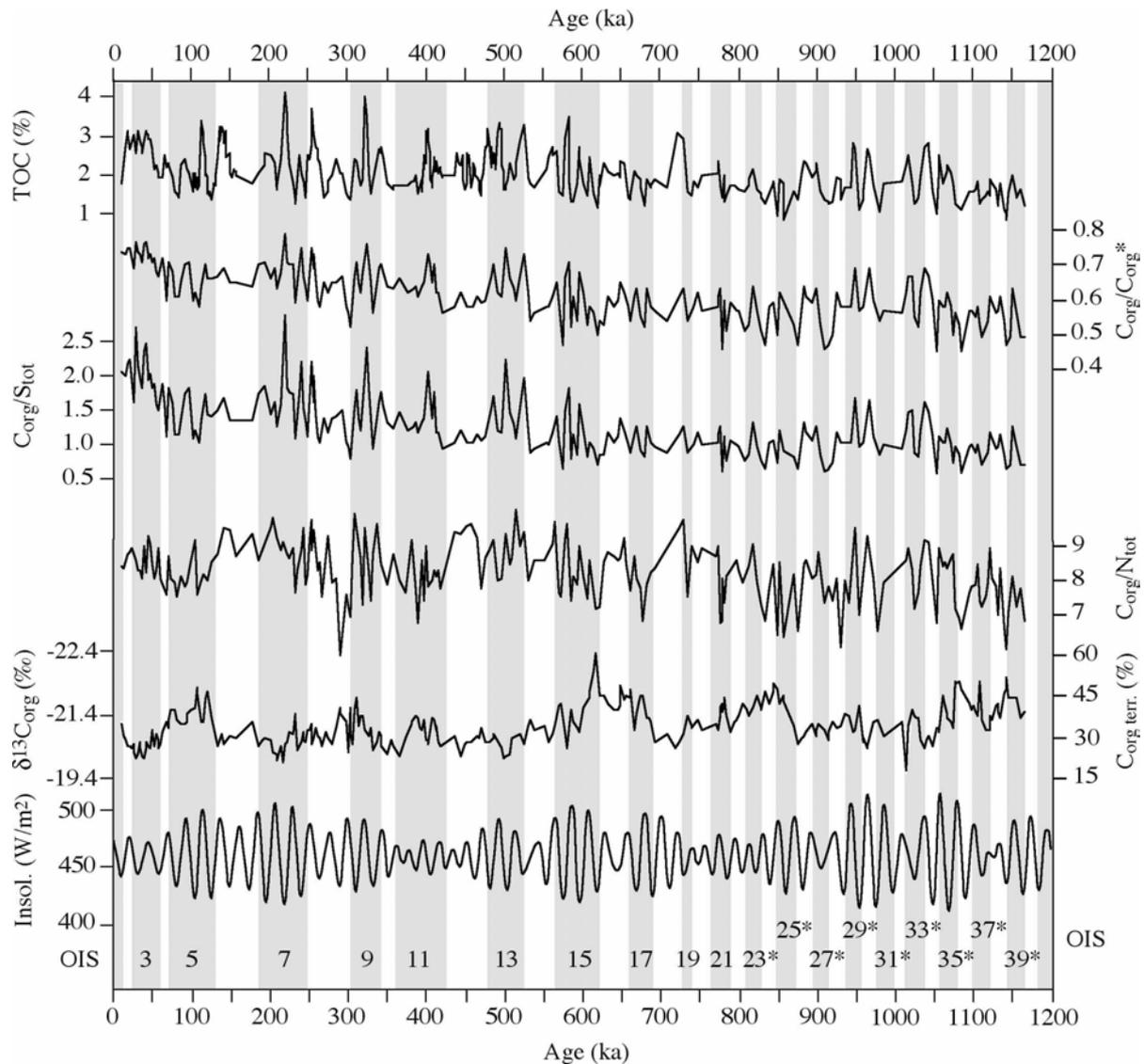
accumulation rates of organic carbon express this tendency even more clearly within the younger core sections, showing highest amplitudes and values exceeding  $1.5 \text{ g/m}^2/\text{year}$  during the interglacial stages 35, 21, 15, and 11 to 3 (Fig. 2.3).

Figure 2.4 illustrates the elemental geochemical and bulk isotopic records for site 1075. The nitrogen content is strongly correlated to total organic carbon ( $r^2 = 0.91$ ).  $C_{\text{org}}/N_{\text{tot}}$  ratios therefore show a relatively low variability (range from 6 to 15), and reveal no significant information about changes in the supply of terrigenous organic matter. As  $C_{\text{org}}/N_{\text{tot}}$  ratios may be lowered by ammonium bound to clay minerals (Müller, 1977), we removed organic nitrogen from 23 samples with exceptionally high or low TOC values, and then measured the inorganic nitrogen content (data not shown). On average, only 12.3 % of total nitrogen are of inorganic origin, implying that  $C_{\text{org}}/N_{\text{org}}$  ratios are not significantly higher than  $C_{\text{org}}/N_{\text{tot}}$  values.

Due to microbial sulfate reduction of sedimentary organic matter, the  $C_{\text{org}}/S_{\text{tot}}$  ratios decrease significantly from 2.1 to 1.6 within the uppermost core section, and then gradually level off to reach low values around 1.0 at approx. 650 ka (OIS 16). A remarkable lowering of the amplitudes is observed within the older sections.

For the focus of this study, the use of sulfur contents to estimate the original content of organic carbon prior to the onset of early diagenetic processes in the benthic boundary layer (Littke, 1993) has a high potential. The  $C_{\text{org}}/C_{\text{org}}^*$  ratio (Fig. 2.4) shows a generally decreasing downcore trend resulting from progressive diagenesis. In addition, there are repeated high amplitude fluctuations which document changes in the quality of the organic matter (marine vs. terrigenous), as terrigenous organic matter usually contains less reactive components and is therefore more resistant against microbial attack (Emerson and Hedges, 1988; Jansen et al., 1984).

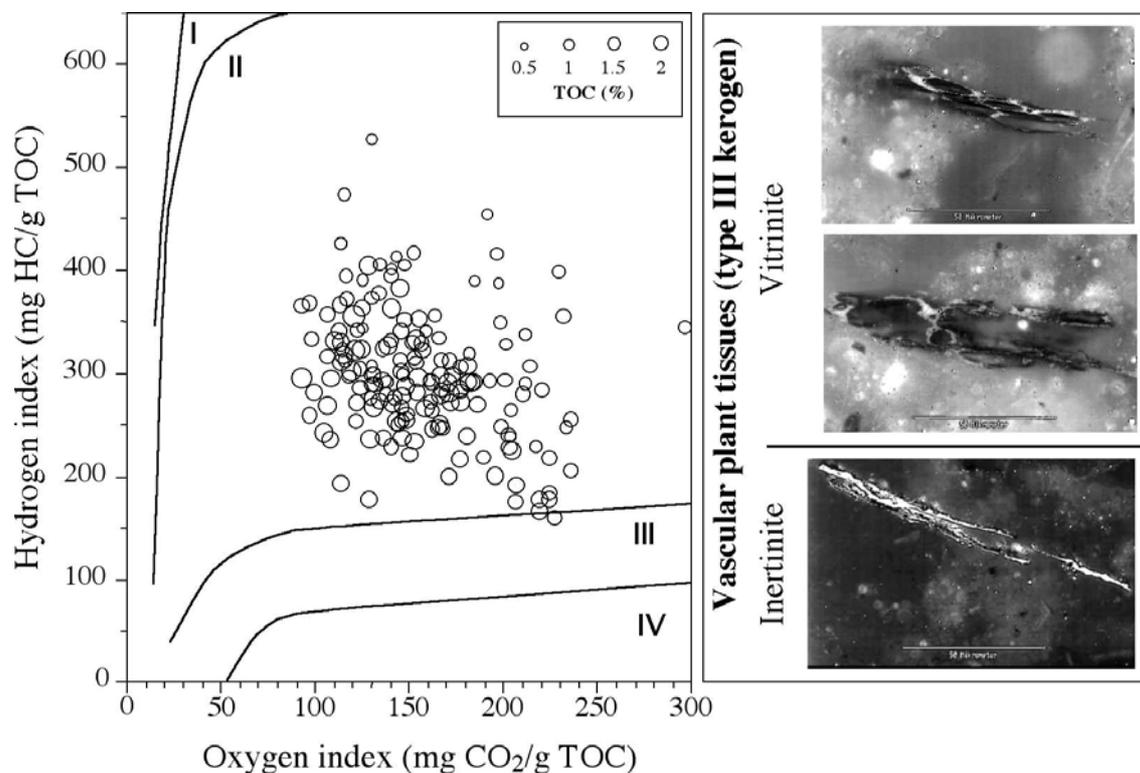
The carbon isotope signature of the bulk organic matter varies in a manner similar to that recorded for the other geochemical parameters (Fig. 2.4). Like the  $C_{\text{org}}/C_{\text{org}}^*$  ratio, high-frequency variations of the isotopic signals indicate changes in the primary composition of the sedimentary organic matter. Furthermore, the average isotopic signature becomes progressively lighter with increasing depth (from  $-20.8$  to  $-21.4$  ‰). Three effects are considered responsible for lowering the bulk  $\delta^{13}\text{C}_{\text{org}}$  signal with the onset of diagenesis or when changes in organic matter supply occur: (I) the relative enrichment of isotopically lighter terrigenous organic compounds, (II) the polycondensation and insolubilization of biogenic constituents, leading to the formation of fulvic and humic acids as well as humin (Tissot and Welte, 1984), and/or (III) the temporal admixture of isotopically heavy  $\text{C}_4$  plant matter.



**Figure 2.4:** Results from elemental (C, N, S) and stable carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ) analyses of late Quaternary sections from site 1075. The  $\text{C}_{\text{org}}/\text{C}_{\text{org}}^*$  ratio represents the degradation rate of organic carbon, and it was calculated based on the assumption that microbial sulfate reduction is the most important degradation process. Application of a binary mixing equation for marine and terrigenous organic matter using end-member values of -18 and -27 ‰ for marine and terrigenous organic fractions, respectively, results in  $30 \pm 5$  % of terrigenous compounds ( $\text{C}_{\text{org terr.}}$ ) in the bulk organic matter.

Kerogen typing by Rock-Eval pyrolysis exhibits a broad scattering between kerogen type III (mainly terrigenous) and type II (mainly marine, Fig. 2.5). Organic petrological investigations of selected samples reveal the presence of two organic terrigenous fractions which differ distinctly in their degree of oxidation, e.g., non-oxidized (vitrinite) and oxidized (inertinite) terrigenous particles. Both frequently show well-preserved plant tissue structures, especially in larger particles ( $>30 \mu\text{m}$ ), which are well known from higher terrestrial plants (Taylor et al., 1998). Furthermore, their abundance is consistent with the proximal position of site 1075 close to the Congo river mouth. Marine organic particles were identified as bright yellow fluorescent, thready alginite macerals or fragments thereof. Also non-fluorescent organic particles ("organic linings") were observed and assigned to the marine fraction. Amorphous

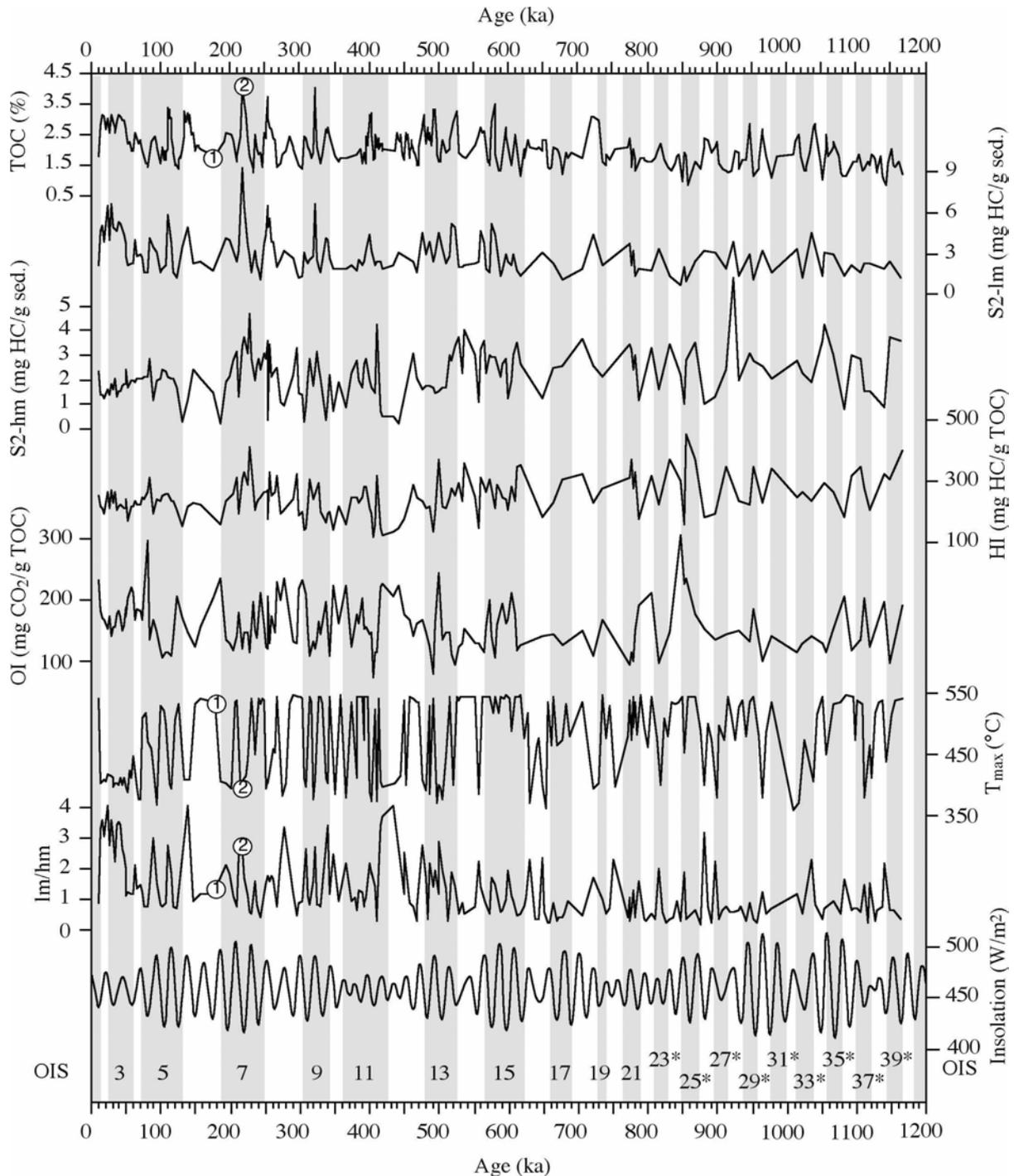
organic matter and a weak fluorescence of the matrix indicate intense degradation of the labile organic fraction (mainly liptinites), which is also documented by the occurrence of dispersed framboidal pyrite.



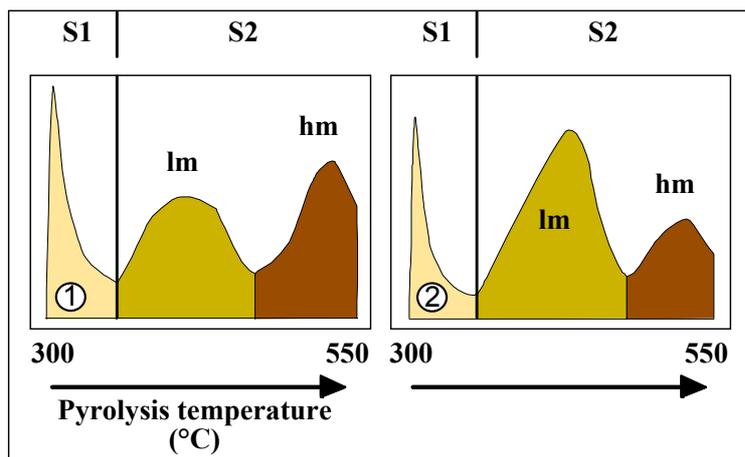
**Figure 2.5:** Kerogen types of late Quaternary deposits from site 1075. Note the presence of well-preserved plant tissues which are clearly distinguished by their level of oxidation (vitrinite/inertinite).

Time series from Rock-Eval pyrolysis (Fig. 2.6) also reveal a pronounced cyclicality which is most clearly shown by the  $T_{\max}$  signature. The extremely high amplitude of this record is explained from examination of the pyrograms obtained during the analytical cycle. Two contrasting pyrograms are shown in Fig. 2.7. Both traces show a pronounced double peak within the S2 window but with changing proportions of the partial peaks. As noted above,  $T_{\max}$  measures the thermal stability of kerogen rather than the thermal maturity *sensu strictu*. For most kerogen types there is a progressive increase in  $T_{\max}$  with increasing maturity, but some kerogens are inherently stable. Nevertheless, maturity and stability in our study may be regarded as synonymous on the basis of evidence from organic petrology. The presence of oxidized organic particles suggests that the generation of hydrocarbons and hydrocarbon-like components at high temperatures is related to this specific type of organic matter and therefore is mainly maturity controlled. Following this approach,  $T_{\max}$  values exceeding 430°C characterize generation from high-mature organic matter whereas  $T_{\max}$  values below 430°C mark hydrocarbons and hydrocarbon-like components from low-mature OM. The second partial peak occurring around 500°C therefore documents the fluctuating supply of a more stable and probably high-mature (or even over-mature) organic compound. Variations in the relative share of hydrocarbons generated from low-mature and high-mature organic matter reflect the patterns documented for the other elemental and pyrolytical parameters. This is illustrated by the ratio of the S2 partial peak areas ( $S_{2lm}/S_{2hm}$ ), in the following termed the

”lm/hm index“ (Fig. 2.6). Apart from the high variability, the lm/hm record shows a decreasing downcore trend suggesting a relative enrichment of the high-mature organic fraction in older sections.

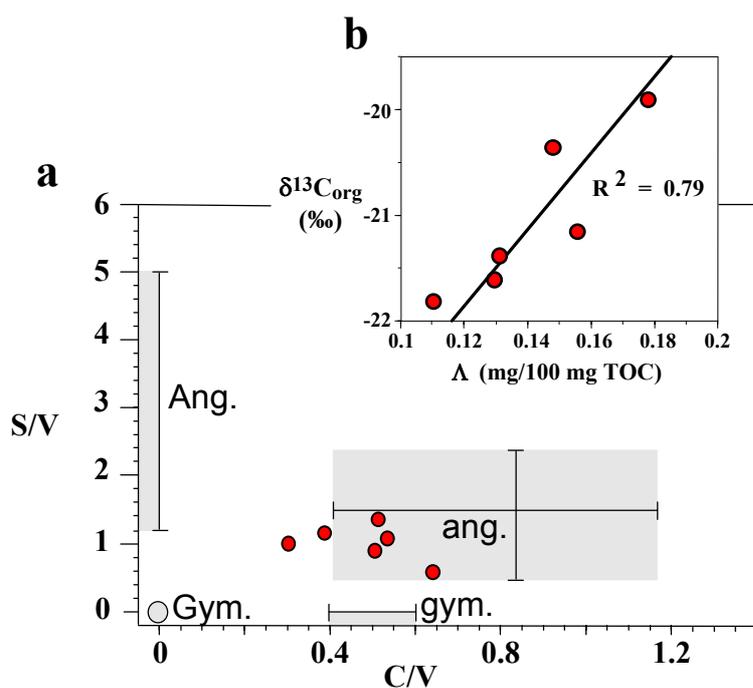


**Figure 2.6:** Downcore profiles of results from Rock-Eval pyrolysis covering late Quaternary sections from site 1075. Similarly to elemental and isotopic records (see Figs. 2.3 and 2.4), pyrolytic parameters show a high variability with regular cycles of about 15-25 ka. The  $T_{max}$  record shows repetitive (probably precessional-controlled) fluctuations in low-mature and high-mature organic matter. Hydrocarbons from the kerogen fractions were separated according to low (300-430°C; S2-lm) or high (430-550°C; S2-hm) maturity. The corresponding ratio is displayed as lm/hm index. Numbers (1) and (2) indicate the samples used for the pyrograms in Fig. 2.7.



**Figure 2.7:** Rock-Eval pyrograms from a TOC-rich and a TOC-poor sample, showing distinct fluctuations in the bimodal character of the S2 peak.

First results from lignin chemistry suggest a dominant non-woody angiosperm source of terrestrial plant matter (Fig. 2.8a). Note that the relative contents of lignin-derived phenols ( $\Lambda$ ) are positively correlated ( $r^2 = 0.79$ ) with the bulk  $\delta^{13}\text{C}_{\text{org}}$  signature of the sediments (Fig. 2.8b).



**Figure 2.8:** (a) Ratios of specific lignin phenols (S/V, C/V) of late Quaternary deposits from site 1075, indicating terrigenous organic matter mainly from non-woody angiosperm tissues (a), i.e. grasses and/or leaves (after Hedges et al., 1988).

V = vanillin + acetovanillone + vanillic acid (mg/100 mg TOC), S = syringaldehyde + aceto-syringone + syringic acid (mg/100 mg TOC), C = *p*-coumaric acid + ferulic acid (mg/100 mg TOC). Gym. = woody gymno-sperms; gym. = non-woody gymnosperms; Ang. = woody angiosperms; ang. = non-woody angiosperms.

(b) Relationship between the relative amount of lignin-derived phenols ( $\Lambda = V + S + C$ ) and bulk  $\delta^{13}\text{C}_{\text{org}}$ . The positive correlation supports the conclusion that  $\text{C}_4$  plant material (presumably from the African grass savannah belt) is preferentially admixed when total lignin supply is enhanced.

## 2.6 Discussion and conclusions

Geochemical records of late Quaternary sections of site 1075 clearly evidence that organic matter supply to the Congo deep-sea fan is closely linked to precessional insolation changes which caused cyclic variations in the intensity of the low-latitude African monsoon and trade wind system. Preliminary spectral analysis indicate that precessional forcing is superimposed

by lower frequency orbital variations (e.g., obliquity, excentricity). Orbital-forced fluctuations in the atmospheric circulation primarily controlled upwelling and productivity along the West African equatorial margin as well as continental aridity/humidity cycles which ultimately caused a displacement of vegetation zones and influenced the export of terrigenous material by the Congo river. This intimate link between African climate, river drainage and marine sedimentation has also been shown in high-resolution geochemical records from an adjacent piston-core site located in the southern part of the Congo deep-sea fan (GeoB 1008, Schneider et al., 1994, 1997a). The reliance of equatorial African vegetation patterns on precipitation, and thus on the monsoon system, has been demonstrated by various marine pollen records from the eastern equatorial Atlantic (e.g., Frédoux, 1994; Ning and Dupont, 1997; Jahns et al., 1998). In addition, Giresse and Barousseau (1989) concluded that glacial/interglacial sea-level fluctuations had a major influence on the stability of sedimentary units along the shelf break and upper slope off many West African river systems. Accordingly, they found evidence for enhanced gravity-induced sedimentation during glacial sea-level lowstands along the Congo fan.

At site 1075, the organic geochemical records document repeated short-term changes in the primary composition of sedimentary organic matter. Based on the late Quaternary  $C_{org}/S_{tot}$  record, a generally suboxic depositional setting is proposed (Berner, 1984; Leventhal, 1983), although Emeis and Morse (1993) have pointed out that the interpretation of  $C_{org}/S_{tot}$  ratios in modern high-productivity upwelling areas is problematic. The establishment of suboxic conditions on the Congo deep-sea fan probably relates to the extensive supply of riverine nutrients and a high surface productivity in the river plume. Despite increasing  $C_{org}/S_{tot}$  ratios, higher accumulation rates of organic carbon during more humid phases and, at the same time, increased fine-grained riverine sediment export may be explained by better preservation conditions as the organic matter burial rates are strongly increased. Considering that highest organic carbon accumulation rates mainly occurred during interglacial periods we conclude that enhanced fluvial discharge of nutrients compensates or even exceeds the reduced nutrient supply related to weakened continental upwelling.

A quantification of marine and terrigenous organic proportions using organic geochemical methods is problematic considering the presence of two different terrigenous organic components which are clearly distinguished by their thermal stability and chemical properties. Application of a binary mixing equation for marine and terrigenous organic matter, using end-member values of -18 and -27 ‰ for marine and terrigenous organic compounds, respectively (Müller et al., 1994; Schneider et al., 1994), suggests that the terrigenous organic fraction comprises  $30 \% \pm 5 \%$  of the bulk organic matter, which appears to be quite low considering the position of site 1075. Though persistent low C/N ratios ( $8 \pm 2$ ) at first sight would support a mainly marine origin of organic matter in the Congo fan deposits, results from Rock-Eval pyrolysis and organic petrology strongly favour higher terrigenous proportions, as indicated by kerogen type III and abundant terrigenous macerals. The new lm/hm index rather fosters the conclusion that terrigenous organic matter of different thermal maturity contributes to the bulk organic pool. Notably, the amount of hydrocarbons generated from the high-mature terrigenous organic fraction often exceeds the one from fresh marine and potentially fresh terrigenous organic material (lm/hm < 1). The pyrolytic character

of this high-mature component is not well constrained yet and obviously needs further investigation. Based on the present data, three types of organic matter are distinguished: (I) a low-mature marine source, (II) a low-mature terrigenous source (probably associated to the vitrinite fraction), and (III) a high-mature terrigenous fraction (related to inertinite).

The supply of  $C_4$  plant material provides one reason to believe that the bulk  $\delta^{13}C_{org}$  signal underestimates the proportions of the terrigenous component of the bulk organic matter. Notably,  $C_4$  plant matter typically reveals a distinctively heavier isotopic composition (on average  $-12\text{‰}$ , Gearing, 1988) than marine organic matter (see Tyson, 1995; Wagner and Dupont, 1999). Mariotti et al. (1991) have estimated a terrigenous content of  $44 \pm 14\%$  in late Quaternary sediments off the Congo estuary at 2000 m water depth, using stable carbon isotopes and specifically discuss the problem of end-member definition with regard to changing  $C_3/C_4$  ratios. On one hand, they warn of an overestimation of the terrigenous organic fraction because marine organic matter is more susceptible to degradation whereas, on the other hand, they emphasize that the presence of  $C_4$  material may easily lead to misinterpretations when using the classical isotope balance during mixing of two organic matter end-members. It has to be mentioned, however, that the importance and fate of terrigenous organic matter in the ocean still remains one of the biggest mysteries in the global carbon cycle, as only a small fraction of the organic matter dissolved in seawater and preserved in marine deep-sea sediments appears to be land-derived (Hedges et al., 1997). Recent geochemical studies from the central Equatorial Atlantic (ODP sites 663, 664) bear evidence for pronounced fluctuations in wind-born terrigenous organic matter (26-55 %) with minor admixture of  $C_4$  plant debris (up to 16% of the bulk organic fraction; Wagner, 2000). Goñi et al. (1998) recently re-evaluated the importance and sources of land-derived organic matter in surface sediments of the Gulf of Mexico using bulk and molecular level sedimentary compositions. They conclude that the terrigenous organic fraction has been significantly underestimated in earlier studies (e.g. Hedges and Mann, 1979b; Prahl et al., 1994), and that more than 50 % of the lignin from land-derived organic carbon originates from  $C_4$  plants being eroded from grasslands of the Mississippi river drainage basin. Bird et al. (1994) demonstrate that the isotopic ratio of bulk organic matter exported by the Sanaga River (Cameroon) has changed by more than 7 ‰ since the last glacial maximum as a result of changing percentages of  $C_4$  vegetation within the catchment of the river.

The ratios of specific lignin phenols from preliminary biomarker analyses clearly indicate that the organic terrigenous fraction at site 1075 mainly derives from non-woody angiosperm tissue, i.e. grasses or leaves. In particular, the positive correlation between the percentage of lignin phenols and bulk  $\delta^{13}C$  corroborates the conclusion that an appreciable amount of the terrigenous organic fraction may be derived from  $C_4$  plant matter. Therefore, a precise knowledge of the relative share of both terrigenous organic fractions is important.

The amounts of the specific lignin phenols ( $\Lambda$ ) measured in late Quaternary sediments from the Congo fan (0.110 - 0.178 mg/100 mg TOC, core position at 2995 m water depth) are two to three times higher than those reported from the Niger deep-sea fan (around 0.05 mg/100 mg TOC; Wagner, 1999b). These contrasts underline the dominant role of the Congo river regarding the supply of terrigenous organic carbon into the easternmost equatorial Atlantic. When compared with lignin data from the literature, it is evident that  $\Lambda$  values from site 1075

are within the same range as those reported from Quaternary sediments from the Indus fan (0.057 - 0.260 mg/100 mg TOC at 775 m and 0.048 - 0.293 mg/100 mg TOC at 2109 m water depth; Schubert, unpubl. data) but three to five times lower than in modern sediments off the Mississippi delta (0.46 - 1.40 mg/100 mg TOC; Goñi et al., 1998). It has to be noted, however, that the data from the Gulf of Mexico were partly collected closer to the river mouth and in considerably shallower waters (74 - 2250 m).

Observations of severely oxidized plant fibres show features which are typical of fusinite or charcoal (Taylor et al., 1998). The origin of (pyro-)fusinite is mainly attributed to forest or bush fires (Jones and Chaloner, 1991; Jones et al., 1991). As continental aridity repeatedly increased during past cool (mainly glacial) climates and caused an expansion of the savannah belts in central and southern Africa (Ning and Dupont, 1997), bush fires should have increased, too. Pokras and Mix (1985) proposed that African hyperarid conditions were established due to enhanced glacial wind speeds which, in turn, caused and fueled extensive natural bush or savannah fires. Therefore, a changing supply of charcoal-type organic matter likely indicates more arid climatic conditions in the catchment area of the Congo. Jansen et al. (1984) observed burnt plant fragments in smear slides of glacial samples from the Congo fan, and drew a similar conclusion.

Assuming that the late Quaternary magnetic susceptibility record of site 1075 overall reflects the run off-driven supply of terrigenous magnetizable minerals, some co-variation between this record and the lm/hm index is anticipated. Indeed, the lm/hm index and magnetic susceptibility show a perceptible negative correlation ( $r^2 = 0.59$ ) within the upper core section (215 - 10 ka). This correlation deteriorates and finally disappears with increasing depth ( $r^2 = 0.02$  at the bottom of the profile) because, in contrast to the magnetic mineral fraction, the low-mature organic matter is progressively affected by microbial degradation. However, the negative relationship between the lm/hm index and magnetic susceptibility suggests an enhanced supply of high-mature organic matter during more humid (interglacial and warm glacial) periods, a pattern which is contrary to expectations. Another argument in this context is the co-variation between the carbonate content and the lm/hm index which can be recognized in the upper core section (215 - 10 ka) of the record, and is visible down to the transition of OIS 12 to 11. Below, the correlation becomes weaker due to diagenetic degradation of the low-mature organic fraction and the relative enrichment of the high-mature organic compounds. Furthermore, the lm/hm index shows a strong positive correlation with TOC ( $r^2 = 0.83$ ), especially within the younger core section (215 - 10).

Considering these observations, we contend that the lm/hm index does not reflect fluctuations in the supply of high-mature terrigenous organic matter - as would be anticipated at first sight - but instead is mainly determined by variations in the low-mature (terrigenous and/or marine) organic fraction. It therefore remains a target of further studies to quantitatively assess either the marine or the low-mature terrigenous fraction. Combined with quantitative organic petrological data, the lm/hm index may provide a new proxy parameter to reconstruct changes in the relative contributions of different types of terrigenous organic matter, which finally reflect changes in the continental climate.

### **3. Terrigenous signals in sediments of the low latitude Atlantic – Implications for environmental variations during the Late Quaternary:**

#### **Part I: Organic carbon**

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#### **3.1 Abstract**

The established view of a marine-dominated organic signature of modern and late Quaternary deep ocean sediments is challenged by recently performed organic geochemical, petrological, and palynological investigations. This study reviews multidisciplinary concepts that were developed over the last decade in Bremen and have been successfully applied to modern and late Quaternary sediments from the low latitude Atlantic. Relative proportions and compositional variations of terrigenous OM are deduced from macerals (organic particles), freshwater diatoms, phytoliths, pollen grains, lignin signatures, and carbon isotopic compositions of bulk organic matter as well as from higher plant-derived long-chain *n*-alkanes. For their variety of depositional settings and their close location next to each other the dust-influenced central Equatorial Atlantic and the West-African continental margin are examined. To assess environmental variations during the late Quaternary, terrigenous organic records from the central Atlantic to the low latitude West-African continental margin and the Congo deep-sea fan are discussed with regard to the paleoclimatic evolution of central African dust source areas, continental run off and vegetational changes in the Congo catchment area. Additionally, the influence of degradation processes and/or selective preservation, both on short and long time scales, of non-reactive (mostly terrigenous) organic matter is investigated.

#### **3.2 Introduction**

One of the still poorly constrained elements in the global carbon cycle concerns the importance and fate of terrigenous organic matter (OM) in the deep ocean. Flux estimates of terrestrial particulate OM in front of major rivers suggest that about 65 % of the total particulate organic matter (POM) that enters the ocean is refractory (Ittekkot, 1988) probably being more resistant to degradation. Knowledge of quantitative proportions and composition of terrestrial OM in oceanic settings is essential since climate-driven fluctuations in total sedimentary organic carbon (TOC) have been widely used as a proxy for paleoproductivity, especially beneath oceanic and continental upwelling regions (see Sarnthein et al., 1992 for

review). This fundamental application appears to be supported by the general statement that only a very small fraction of the OM preserved in marine deep-sea sediments is land-derived (Hedges et al., 1997). On the other hand, terrigenous OM in organic-carbon-poor marine environments remains difficult to quantify mainly because of its broadly dispersed distribution, its potential sub-fossil age and its low analytical response (see Tyson, 1995; Hedges et al., 1997; Wagner and Dupont, 1999 for discussion).

The established view of a marine-dominated organic signature of modern and late Quaternary deep ocean sediments is challenged by improvements from collaborative geoscientific research at Bremen (e.g. Rühlemann et al., 1996; Schlünz et al., 1999; Wagner and Dupont, 1999; Huang et al., 2000; Wagner, 2000; Holtvoeth et al., 2001; for a complete list of contributions from Bremen with regard to the topic of this review see Wagner and Zabel, 2003) and from many other investigations reported in the literature (e.g. Prahl and Muehlhausen, 1989; Stein, 1991; Schubert and Stein, 1996; Eglinton et al., 1997; Bauer and Druffel, 1998; Goñi et al., 1998, 2000; Knies and Stein, 1998; Stein and Fahl, 2000; Raymond and Bauer, 2001).

Based on a broad variety of analytical techniques, all these studies recommend a re-evaluation of the assumption that the deposition of terrigenous organic carbon is restricted to deltas and continental margins, and rarely occurs beyond the shelf-slope boundary (e.g. Hedges and Keil, 1995). The most important mechanisms invoked for the entrainment of terrigenous OM to the deep ocean are (I) eolian supply (Gagosian and Peltzer, 1985; Gagosian et al., 1987; Huang et al., 2000; Wagner, 2000), (II) sea level controlled displacement of main depositional areas in front of major rivers (Schlünz et al., 1999; Stein and Fahl, 2000; Bauch et al., 2001), (III) redistribution and gravitational downslope transport from continental margins (Bauer and Druffel, 1998) likely associated with long-range lateral advection (Walsh, 1989; Gough et al., 1993), and (IV) sea ice transport at high latitudes (Wagner and Hölemann, 1995; Schubert and Stein, 1996).

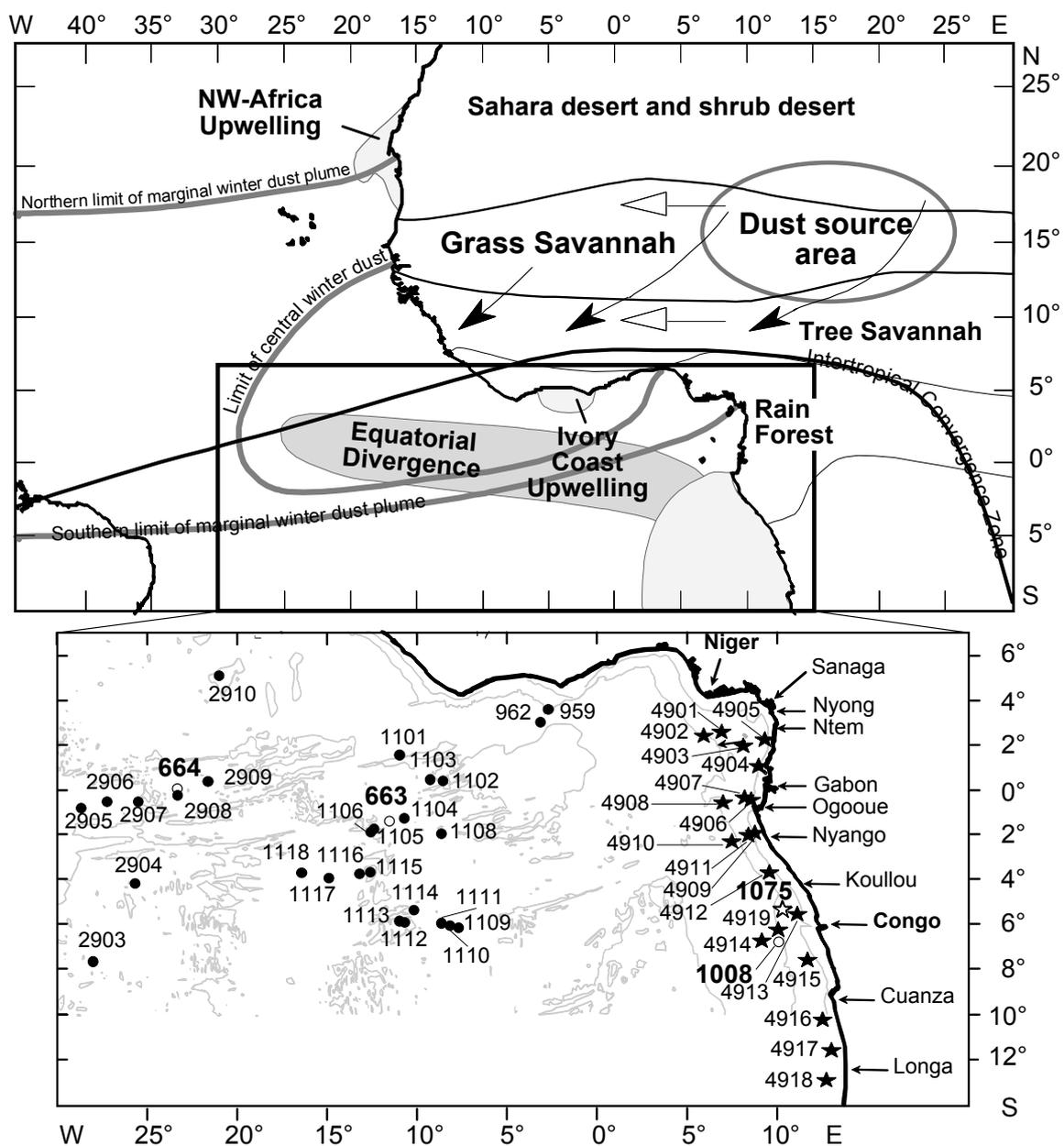
In this study we review multidisciplinary concepts that were developed over the last decade in Bremen and were successfully applied to modern and late Quaternary sediments from the low latitude Atlantic. Due to the variety of depositional settings and their proximity to one another, this review will focus on the dust-influenced central Equatorial Atlantic and the West-African continental margin, where riverine supply has build up extensive deep-sea fans in front of the Congo and Niger. Related aspects concerning the export of lithogenic matter to the low latitude Atlantic are reviewed in a separate contribution (Zabel and Wagner, 2003).

### **3.3 The low latitude Atlantic: A key area to study lateral and spatial processes controlling organic carbon deposition**

One key area in environmental research is the low latitude Atlantic. Here the interaction of atmospheric and oceanic circulation is well documented and controls on organic carbon production and preservation are reasonably well understood. Numerous marine records from the central and eastern low latitude Atlantic as well as the corresponding Indian Ocean document that modern climatic and oceanographic boundary conditions have repeatedly changed in response to orbitally-forced Quaternary glacial-interglacial cycles (e.g. Sarnthein et al., 1994; DeMenocal, 1995; Verardo and McIntyre, 1994; Raymo et al., 1997; Schubert et al., 1998) to produce distinct cycles and spatial relationships in many proxy parameters. Funk

et al. (2003), for example, present spatial and temporal trends in various continental and marine proxy records covering large areas of the low latitude Atlantic that convincingly demonstrate the close interaction of African dust export and marine carbon sedimentation in association with late Quaternary African aridity-humidity cycles and the history of oceanic upwelling along the equator.

There is a distinct asymmetry between the western and central to eastern sectors of the low latitude Atlantic with regard to source areas, transport mechanisms and distances, and flux rates. Areas of special interest are the dust-influenced oceanic upwelling zone along the Equatorial Divergence and the fluvial-induced high productivity areas in front of the Congo, Niger, and Amazon rivers (Fig. 3.1). These three river systems supply about 10 % of the annual global terrigenous organic carbon run-off into the Equatorial Atlantic and 28 % of the total annual run-off for the Atlantic Ocean (Ludwig et al., 1998). Giant deep-sea fans seaward of these rivers testify to the local burial of huge amounts of terrigenous matter on the continental margins.



**Figure 3.1** (previous page): Generalized map of the Equatorial Atlantic showing main coastal and oceanic upwelling areas, major African vegetation zones, and approximate boreal winter positions of source and corresponding depositional areas for atmospheric dust. Black arrows indicate surface trade winds, open arrows the mid-level African Easterly Jet (AEJ) and the Saharan Air Layer. Position of surface sediments and West-African rivers between 14°S and 6°S are shown in the inset map (filled circles mark locations along the open ocean E-W transect, stars of surface sediments from the near-continental N-S transect). Cores discussed in this review are highlighted in bold and indicated by open symbols.

In the central low latitude Atlantic, in contrast, terrigenous OM is mainly introduced by eolian transport. The trade and Harmattan wind systems are well known to carry huge amounts of lithogenic dust from arid African source areas to the deep Atlantic Ocean (e.g. Sarnthein et al., 1982; de Menocal, 1995; Ratmeyer et al., 1999). Indicators of wind-borne OM in pelagic low latitude Atlantic sediments are pollen and spores (e.g. Dupont et al., 1998; Frédoux, 1994), phytoliths (Pokras and Mix, 1985; Ruddiman and Janecek, 1989), fresh water diatoms (Pokras and Mix, 1985; Pokras and Ruddiman, 1989; deMenocal et al., 1993), charcoal (*sensu* Verardo and Ruddiman, 1996), and fragments of higher plant tissue (terrigenous macerals; Stein et al., 1989; Wagner, 1998, 1999a, 2000). Geochemical studies have utilized the ratio of organic carbon to total nitrogen (Stein et al., 1989; Westerhausen et al., 1993; Verardo and McIntyre, 1994; Wagner, 1998), the hydrocarbon yield from kerogen as determined by Rock-Eval pyrolysis (Stein et al., 1989; Wagner and Dupont, 1999; Wagner, 2000), the isotopic signature of bulk organic carbon (Westerhausen et al., 1993; Müller et al., 1994; Rühlemann et al., 1996; Wagner and Dupont, 1999; Wagner, 2000), the amount and isotopic composition of elemental carbon (Verardo and Ruddiman, 1996; Bird and Cali, 1998) and other terrigenous biomarkers (e.g. concentration and isotopic signatures of longchain *n*-alkanes, sterols, *n*-alkanols and lignin; Westerhausen et al., 1993; Huang et al., 2000; Eglinton et al., 2002; Schefuß, 2002) to separate allochthonous from autochthonous organic carbon. Mixing of wind-blown with riverine terrestrial OM is documented oceanward of the main African rivers (Westerhausen et al., 1993). For an introduction to concepts, limitations, and perspectives of each individual proxy parameter we refer to Wagner and Dupont (1999).

### **3.4 Modern distribution and sources of sedimentary terrigenous organic matter - Contrasts between the central pelagic and eastern near-continental equatorial Atlantic**

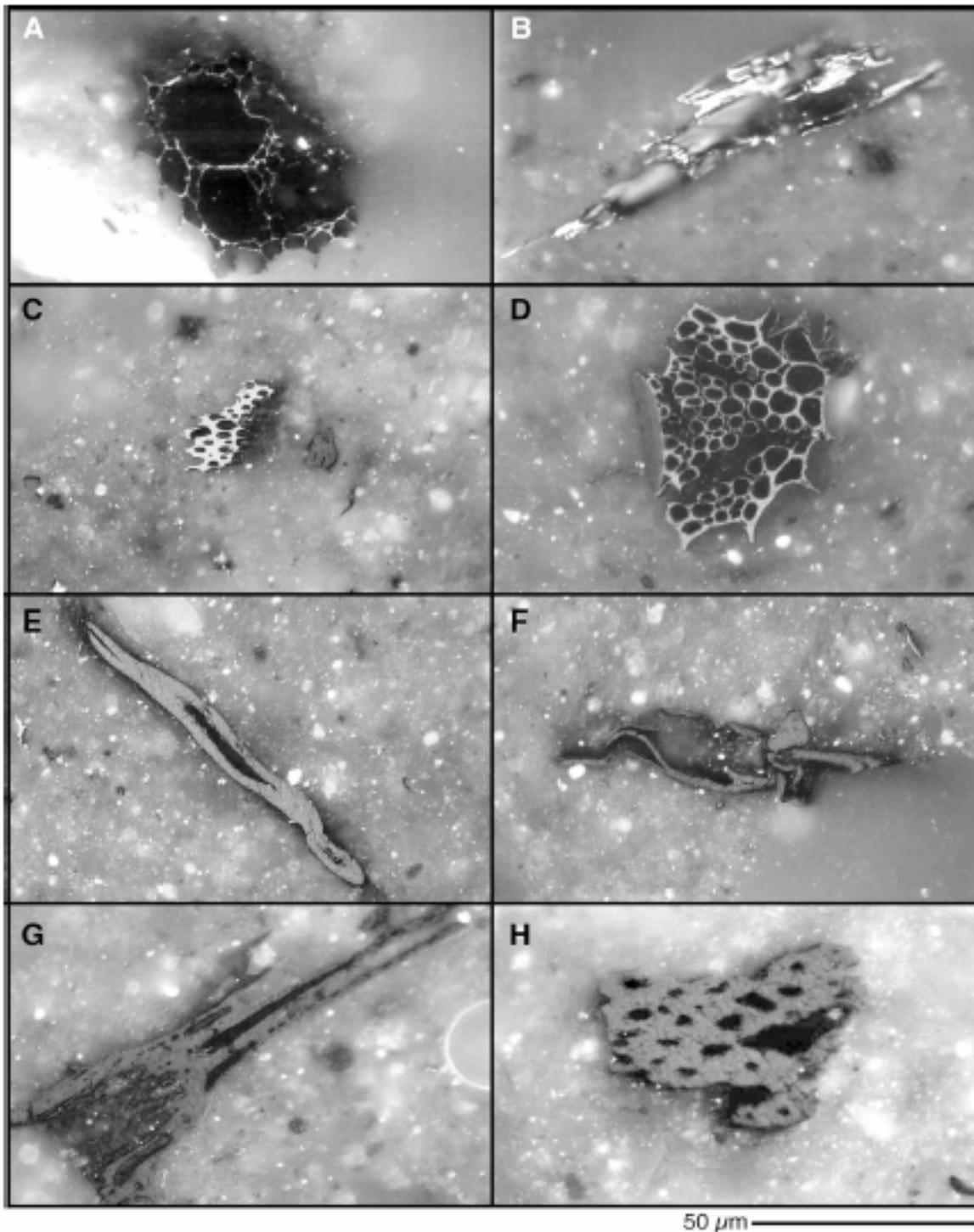
The first comprehensive investigation on the modern distribution of terrigenous OM along the Equatorial African margin was presented by Westerhausen et al. (1993). Employing elemental, isotopic, and molecular records they quantified terrigenous organic carbon and further distinguished an eolian and river-borne fraction. They concluded that terrigenous organic carbon comprise >60 % of bulk TOC on the modern shelves off Liberia, Ivory Coast and Gabon whereas proportions drastically decrease below 20 % along the upper continental slope. Subsequent studies extended further north and west using samples from eolian dust, sediment traps and the ocean floor from as far as 35° north and 32° west (e.g. Hooghiemstra

et al., 1986; Dupont and Agwu, 1991; Wagner and Dupont, 1999; Huang et al., 2000; Dupont and Wyputta, 2002; Romero et al., 1999; Zhao et al., 2003). In these studies, relative proportions and compositional variations of terrigenous OM were deduced from macerals (organic particles), freshwater diatoms, phytoliths, pollen grains, lignin signatures, bulk isotopic data ( $\delta^{13}\text{C}_{\text{org}}$ ), and carbon isotopes derived from longchain *n*-alkanes. Application of such a multiparameter approach confirm differences in quantity and composition of terrigenous organic matter between near-continental and open ocean settings of the central and eastern Equatorial Atlantic and further north (Huang et al., 2000; Romero et al., 1999).

### 3.4.1 Organic petrology and stable carbon isotopic composition of bulk OM

Accordingly, terrigenous OM in surface and Quaternary deposits of the low latitude Atlantic is composed of the two main groups huminite/vitrinite and inertinite, both originating from vascular land plants, whereby inertinite is stronger oxidized and less reactive being indicative of plant burning and more arid climatic conditions ("fusinite" or "charcoal", Taylor et al., 1998; Fig. 3.2). The distribution of the inertinite-vitrinite ratio (I/V) in the low latitude Atlantic is displayed in Figure 3.3a. Apparently, I/V ratios separate the two contrasting depositional settings with low values along the African continental margin and a gradual advance with increasing distance to the continent. This observation is in favour with preferential long-range eolian transport of pre-oxidized terrigenous plant matter from African grassland-covered dust source areas (Wagner and Dupont, 1999; Wagner, 2000).

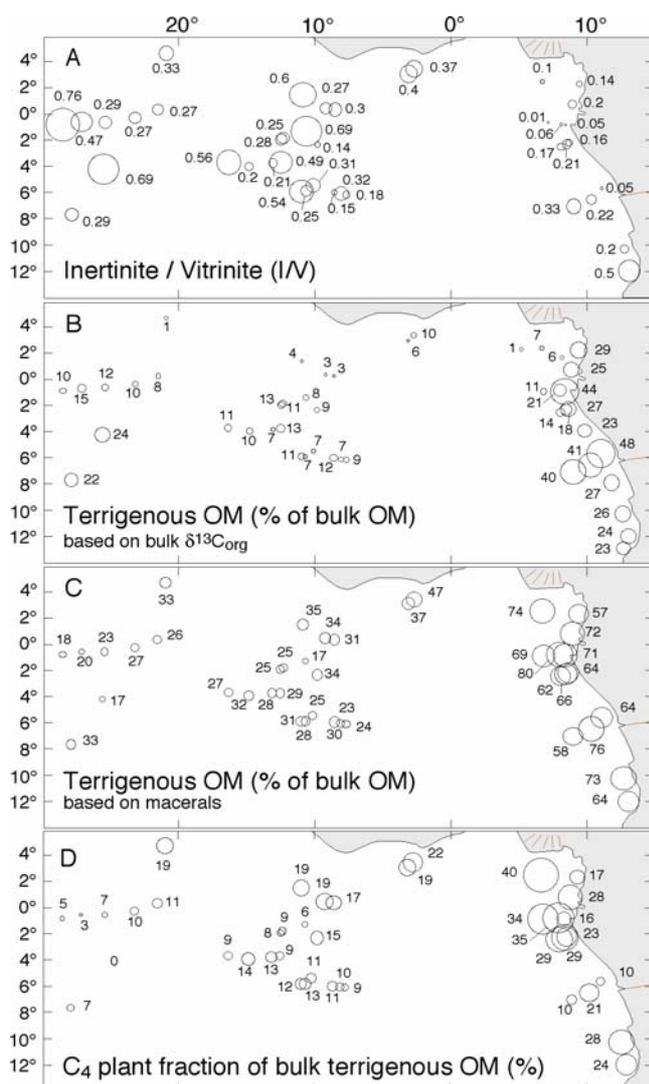
Along the West-African continental margin between 4°N and 13°S (Cameroon to northern Angola), contribution of terrigenous organic carbon is dominated by river discharge including channeled downslope transport on the Congo deep-sea fan. The modern distribution of terrigenous organic carbon as depicted from  $\delta^{13}\text{C}_{\text{org}}$  in comparison to estimates based on maceral analysis is shown in Figure 3b,c. Application of a simple two-component mixing model to bulk  $\delta^{13}\text{C}_{\text{org}}$  signatures of marine deposits has been extensively applied to estimate marine and terrigenous fractions of organic carbon, although various other factors may influence the bulk isotopic signal (see Tyson, 1995; Wagner and Dupont, 1999 for reviews). In fact, near-continental settings in the Equatorial Atlantic need to be considered at least as three-component systems, taking into account that supply of sub-fossil organic matter or dead carbon from continental peat and swamp areas and erosion of older strata, all of them with barely unknown and probably wide-ranging isotopic compositions, may considerably modify the isotopic composition of the bulk organic matter in the marine sediments. For the main types of African vegetation, the contrasting isotopic signatures of C<sub>3</sub> and C<sub>4</sub> land plants are of special relevance. Terrigenous OM derived from vascular C<sub>3</sub> plants (representing more than 95 % of the present day terrestrial biomass) reveal depleted values between -25.5 to -29.3 ‰ with an average endmember signature of -27 ‰, whereas <sup>13</sup>C-enriched carbon from terrestrial C<sub>4</sub> plant matter, including many grasses, range from -8 to -19 ‰ (average -12‰, Gearing, 1988). Accordingly, temporal variations in admixture of C<sub>4</sub> plant matter may influence the bulk  $\delta^{13}\text{C}_{\text{org}}$  signature of marine sediments. Elevated proportions of C<sub>4</sub> plant matter would result in higher <sup>13</sup>C values which, in turn, would lead to an underestimation of the terrigenous organic fraction if a simple two-endmember mixing model (marine versus C<sub>3</sub> plants) is applied.



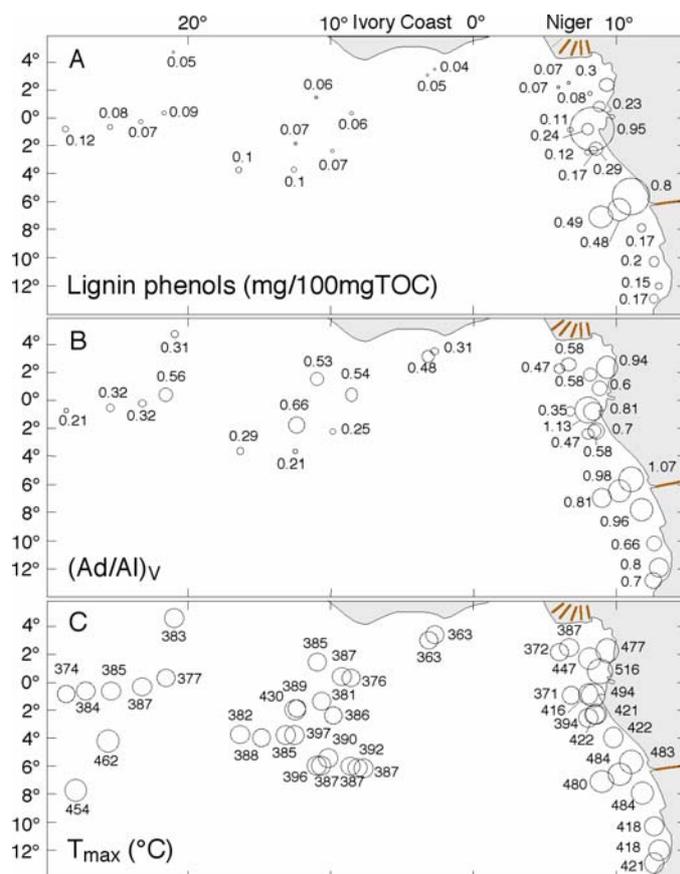
**Figure 3.2:** Terrigenous organic matter (macerals) in modern sediments from the Equatorial West-African continental margin. **(a-d)** Various types of highly oxidized organic matter (inertinite, fusinite) revealing elongated, thick-walled, often-pitted structures of vascular bundles (tracheids). Severe oxidation may be caused by terrestrial plant burning resulting in "charcoal-type" OM. **(e-h)** Non-oxidized terrigenous organic particles (huminite/vitrinite) with partly filled cell lumina documenting cross-sections through parts of plant vascular systems (tracheids). 200-500 fold magnification on polished surfaces under white incident light (oil). **((a-b)** GeoB 4901; **(c-f)** Geob 4917; **g)** GeoB 4907; **h)** GeoB 4918).

### 3.4.2 Lignin phenols

The importance of deep-sea fans in front of major rivers with respect to the entrainment of allochthonous organic carbon and deep-sea carbon budgets is evident from an almost 60 % terrigenous organic fraction based on petrographical assessment at the base of the Congo fan (3970 m water depth, Fig. 3.3c). A pronounced northward decrease in organic carbon concentrations along the continental slope (from 2.5 % off northern Angola to 0.63 % on the Niger fan) is mainly attributed to high productivity conditions within and south of the Congo river plume. To derive additional information on the type and source organic matter, lignin chemistry was investigated (Holtvoeth et al., 2001, 2003). Lignin, a principal component of terrestrial plant tissue, has been used to assess the contribution and composition of terrigenous OM in riverine suspended particles as well as modern and late Quaternary deposits from various lacustrine and marine environments (e.g. Hedges et al., 1986; Miltner and Emeis, 2000; Goñi et al., 1998, 2000; Keil et al., 1998). Following the fundamental studies by Hedges and Parker (1976) and Hedges and Mann (1979a,b) quantification of eight specific phenols allows for characterization of plant tissues that contribute to the terrigenous organic compound of bulk organic carbon. The ratios of syringyl phenols to vanillyl phenols (S/V) and of cinnamyl phenols to vanillyl phenols (C/V) are commonly employed to distinguish gymnosperm or angiosperm, woody or non-woody vascular plant tissues.



**Figure 3.3:** Distribution of **a)** the ratio of oxidized to non-oxidized terrigenous organic matter (Inertinite/Vitrinite), terrigenous organic carbon estimates based on **b)** bulk  $\delta^{13}C_{org}$  and **c)** maceral analysis and **d)**  $C_4$  plant fractions of bulk sedimentary organic matter in surface sediments of the central and eastern Equatorial Atlantic.



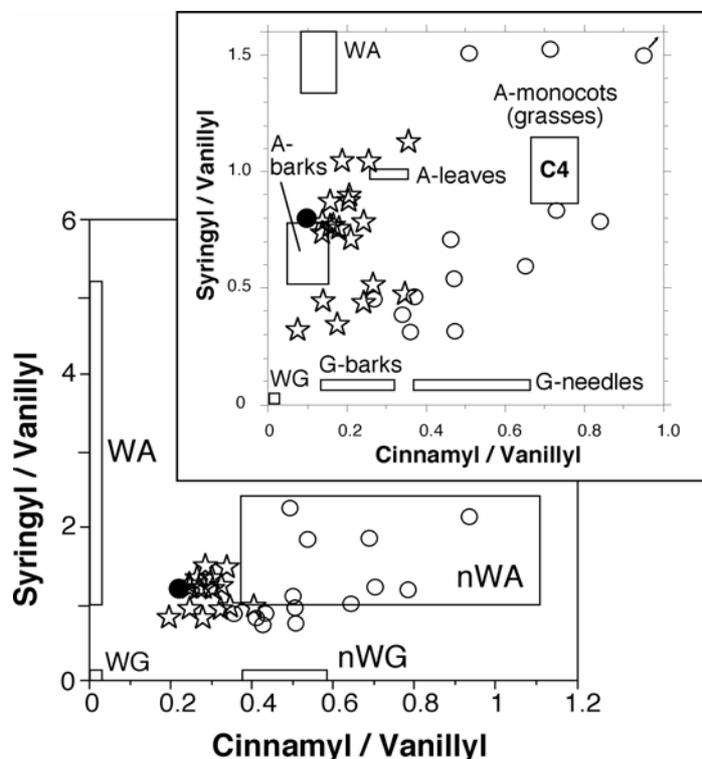
**Figure 3.4:** Distribution of **a)** lignin phenol concentration normalized to total organic carbon (in mg/100mg TOC), **b)** the vanillyl acid to aldehyde ratio ( $(Ad/Al)_v$ ), and **c)**  $T_{max}$  signatures (in  $^{\circ}C$ ) as obtained from Rock-Eval pyrolysis in surface sediments of the central and eastern Equatorial Atlantic.

In the modern low latitude Equatorial Atlantic results from lignin chemistry and organic petrology demonstrate a support non-oxidized (huminitic/vitrinitic) angiosperm origin of terrigenous organic matter along the West-African continental margin. Here, the sum of the eight specific lignin phenols (A) broadly scatters from 0.07-0.95 mg/100gTOC depending on the distance from the various river mouths (Fig. 3.4a). Notably, the Ogooué river north of Cape Lopez at about  $0.5^{\circ}S$  results in the most pronounced lignin signature followed by the Congo river which apparently supplies considerable amounts of lignin and bulk terrigenous OM (76 to 58 % according to maceral analysis) as far as the distal base of the deep-sea fan. Similar or higher lignin phenol concentrations are reported from various other continental shelf and slope environments, e.g. from the Washington coast (0.81-3.19 mg/100gTOC, Hedges and Mann, 1979b; Keil et al., 1998), the NW-Atlantic Shelf (Louchouart et al., 1999) or the Beauford Shelf in the Canadian Arctic (0.44-1.22 mg/100gTOC, Goñi et al., 2000; Table 3.1). The corresponding concentration of lignin phenols in the central Equatorial Atlantic is much lower (0.04-0.12 mg/100mgTOC) but is similar to pelagic sediments from the North Atlantic (0.01-0.12 according to Gough et al., 1993, Table 3.1). The lignin phenols in African continental margin sediments are dominated by a mixture of woody angiosperm tissue (mainly barks) and non-woody angiosperm tissue (e.g. leaves) as indicated by the ratios of Syringyl vs. Vanillyl (S/V) and Cinnamyl vs. Vanillyl (C/V) (Fig. 3.5). Studies of the lignin chemistry of Amazon river suspension load exhibit comparable compositions of higher plant tissue (see filled circle in Figure 3.5, Hedges et al., 1986) and apparently characterizes terrigenous plant matter from both tropical Equatorial Atlantic areas. A southward increase in S/V ratios along the African continental slope is attributed to a gradually increased admixture of leaf plant material, which is likely to be related to a stronger release of eolian dust from southern Africa. Low C/V ratios occurring along the African continental margin exclude any

Setting	Area	Sample	L* (mg/100mgOC)	SV	C/V	(Ad/Al) <sub>v</sub>	(Ad/Al) <sub>s</sub>	Reference
Open ocean	NE-Atlantic	1	0.01-0.12	0.14-0.70	0.09-0.77	0.37-2.92	0.46-2.44	Gough et al., 1993
	Central Equatorial Atlantic	1	0.04-0.12	0.32-1.98	0.27-0.84	0.21-0.66		this study
Marginal ocean basin	S-Baltic Sea	1	2.1-7.6	0.42-0.65	0.16-0.3	0.29-0.37	0.3-0.42	Milner & Emeis, 2000
	Mediterranean Sea	1	0.5-3.0	0.16-0.55	0.04-0.32	0.37-2.98	0.33-3.72	Gough et al., 1993
	Gulf of Mexico (US)	1	0.4-1.4	1.6 av.	0.5 av.			Goñi et al., 1998
Shelf/ Slope	Beauford Shelf	1	0.44-1.22	0.54-1.17	0.15-0.24	0.55-0.80	0.46-1.33	Goñi et al., 2000
	Atlantic Shelf (Canada)	1	0.6	0.92	0.83	2.09-		Louchouart et al., 1997, 1999
	Middle Atlantic Bay	1	0.05-0.11	0.37-0.49	0.24-1.1	0.52-1.45		Mitra et al., 2000
	Lake Washington (USA)	1	1.05 av.	0.44 av.	0.21 av.			Hedges & Mann, 1979b
	Washington Coast (USA)	1	0.23-6.5	0.16-0.31	0.03-0.49			Hedges & Mann, 1979b
	Washington Coast (USA)	1	3.19 (mid-shelf)/ 0.81 (slope)	0.29/0.32	0.06/0.12	0.35/0.64	0.24/0.38	Keil et al., 1998
	SW-African Margin (14°S-2°N)	1	0.07-0.95	0.36-1.15	0.06-0.35	0.35-1.13		this study
	Congo fan (ODP 1075)	3	0.07-0.37	0.47-1.38	0.15-0.39	0.47-1.74	0.26-1.94	Holtvoeth et al., 2003
	Peru shelf	2	0.58	2.66-	0.49	1.0		Bergamashi et al., 1997
	Pakistan Margin Arabian Sea	3	0.03-0.20	0.66-2.49	0.01-0.66	0.09-0.66	0.01-0.68	Schubert, unpubl. results
Estuarine/	Pakistan Margin (OMZ)	3	0.06-0.26	0.33-2.84	0.05-0.81	0.05-0.55	0.06-0.74	Schubert, unpubl. results
	Mackenzie Delta (Canada)	4	0.54-1.43	0.42-0.52	0.13-0.15	0.46-0.80	0.44-1.23	Goñi et al., 2000
	Saanich Inlet (Canada)		857-2707**					Hamilton & Hedges, 1988
	Rhone Delta (France)	1	1.29-2.08	0.45-0.66	0.08-0.20	0.25-0.43	0.3-0.46	Gough et al., 1993
Riverine	Caeté Estuary (Brazil)	5	12.9***	1.25-	0.16	0.56	0.4	Dittmar & Lara, 2001
	Arctic rivers	4	0.2-5.2	0.1-0.77	0.07-0.58	0.08-86		Lobbes et al., 2000
	US rivers	4	1.33 av.	0.82 sv.	0.12 sv.	0.5 av.		Onstad et al., 2000
Lacustrine	Amazon River (Brazil)	6	7.31 (coarse)/ 2.15 (fine)	0.78/0.85	0.07/0.1	0.23/0.44	0.19/0.25	Hedges et al., 1986
	Lake Baikal (Siberia)	3	30-1143****	0.1-1.2	0-0.8	0-12		Orem et al., 1997
	Lake Biwa (Japan)	3	330-1570					Ishiwatari & Uzaki, 1982

**Table 3-1:** Compilation of lignin data from various modern and Late Quaternary terrigenous and marine environments (sample material: 1=surface sediment; 2=near-surface sediment (10-15cm); 3 = Quaternary sediment; 4 = suspended POM; 5 = mangrove sediment; 6 = river suspension; \* = S+C+V; \*\* = (µg/l); \*\*\* = mmol/molOC; \*\*\*\* = V+S+C+P).

major supply of non-woody material, except at the southernmost and northernmost sectors of the transect, where C/V ratios approach slightly elevated values (0.34 on the Niger deep-sea fan and 0.35 off northern Angola). In these settings, riverine supplies from the Niger river and eolian transport from savannah-covered vegetation belts in southern Africa are probably responsible for the enhanced entrainment of non-woody plant matter.



**Figure 3.5:** Plot of cinnamyl to vanillyl (C/V) versus syringyl to vanillyl (S/V) phenol ratios of surface sediments from the central and eastern Equatorial Atlantic. Compositional ranges of major vascular plant tissues according to Goñi and Hedges (1992). Tissue abbreviations: WG gymnosperm wood; WA angiosperm woods; nWG non-woody gymnosperm; nWA non-woody angiosperm.

### 3.4.3 Supply of aged terrestrial organic matter as suggested by degradation and reactivity proxies

Apart from the main equatorial African rivers, the Congo and Niger, there is a number of smaller rivers, e.g. the Sanaga in Cameroon or the Gabon and Ogooue in Gabun, that contribute to the bulk export of terrigenous matter to the African shelf (Fig. 3.1). Since most of these tropical African rivers drain extensive swamp and peat areas in the hinterland, it is reasonable to expect that they supply different types of terrigenous OM, i.e. fresh and reactive plant litter representing the modern vegetation cover of the catchment area and diagenetically altered, older OM originating from eroded swamp and peat environments. The presence of a labile organic fraction associated with river discharge is indicated by the non-oxidized character of particulate OM (huminite/vitrinite; in Figure 3.3a expressed as low inertinite-vitrinite ratios) and steeply enhanced hydrogen indices (up to 560 mgHC/gTOC, Wagner, personal communication) in surface sediments of the Congo fan and at shallow sites off Gabun and Cameroon. By comparison, the TOC-enriched sediments off northern Angola receive higher amounts of oxidized terrigenous OM (I/V ratio up to 0.5, Fig. 3.3a) and reveal considerably lower hydrogen indices (240-305 mgHC/gTOC, Wagner, personal communication). The importance of supply and redistribution of allochthonous swamp and peat deposits along the coast of deltaic and estuarine systems has been documented for the Orinoco, Congo, Amazon, Mississippi, and Mahakam deltas (Stach, 1975; McCabe, 1984;

Wagner and Pfefferkorn, 1997) and in southern Florida (e.g. Cohen, 1970). The occurrence of such reworked terrigenous OM in marine sediments should be detectable e.g. by degradation and reactivity proxies. Enhanced contribution of non-reactive, sub fossil OM is notable along the shallow water corridor by elevated  $T_{\max}$  signatures  $>480^{\circ}\text{C}$  as obtained from Rock-Eval pyrolysis ( $T_{\max}$  depicts the temperature of maximum hydrocarbon generation from the kerogen fraction (S2) being a measure of reactivity and thermal maturity of sedimentary OM), which follow the African continental margin north of the Congo river and across the Congo fan to the deep-sea (Fig. 3.4c). This conclusion is further supported by overall elevated  $(\text{Ad}/\text{Al})_{\text{V}}$  ratios of lignin components which scatter around 1.0 north of the Congo river and approach highest levels of 1.13 on the slope north of the Ogooue river (Fig. 3.4b). Such high ratios suggest large input of degraded particle-bound OM to the modern slope and deep-sea fan deposits. Since the most efficient lignin-degrading organisms (e.g. soft-rot fungi, Nelson et al., 1995) are confined to terrestrial ecosystems (e.g. soils, Erikson et al., 1990), it is most probable that lignin-decay took place prior to river-discharge and marine deposition. The range of  $(\text{Ad}/\text{Al})_{\text{V}}$  ratios along the modern African continental margin is comparable to or slightly higher than  $(\text{Ad}/\text{Al})_{\text{V}}$  ratios reported from other modern shelf-slope environments (Table 3.1), e.g. the Middle Atlantic Bay (Mitra et al., 2000), the Peru shelf (Bergamashi et al., 1997), or the Beauford Shelf (Goñi et al., 2000), and corroborates the recent implication of enhanced riverine export of aged terrestrial OM to the deep ocean (Eglinton et al., 1997; Ludwig, 2001; Raymond and Bauer, 2001).

In the central Equatorial Atlantic, by comparison, the consistently low  $T_{\max}$  signatures and  $(\text{Ad}/\text{Al})_{\text{V}}$  ratios in surface sediments suggest that subfossil OM is not present at higher proportions, except for the northern Brazil Basin, where some advection of non-reactive OM from southern (probably South-American) source areas is assumed.

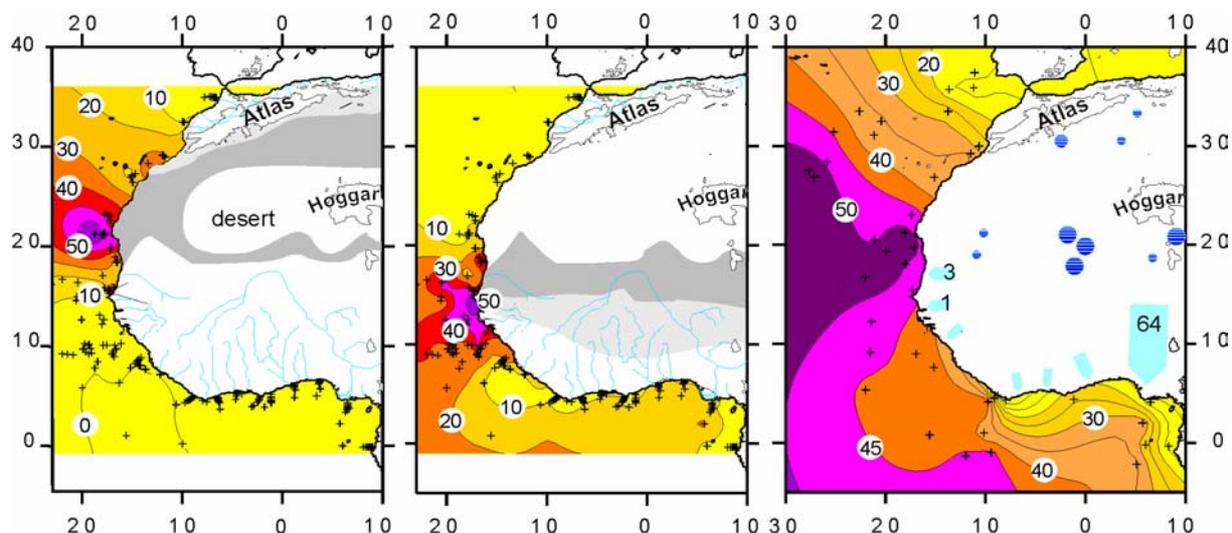
#### *3.4.4 African dust source areas and support for $C_4$ plant contribution*

As noted above, transport of terrigenous OM to the central Equatorial Atlantic is mainly attributed to eolian supply from African source areas. Due to the very fine grain size of eolian dust in that remote pelagic area (modal grain size of terrigenous silt ranges from 6-9 $\mu\text{m}$ , Rath et al., 1999) it remains difficult to distinguish laterally advected from windborn material. The composition of terrigenous OM in open ocean surface sediments is different from that on the African continental margin. The S/V and C/V ratios of lignin phenols and results from organic petrology confirm enhanced contribution of oxidized (inertinite), non-woody gymnosperm tissue (S/V 0.32-1.98, C/V 0.27-0.84; Fig. 3.4). Taking Lake Chad and the Sahel Zone as source areas of eolian dust (Ruddiman and Janecek, 1989; Bonifay and Giresse, 1992) terrigenous OM probably derives partly from  $C_4$  plant grass vegetation. Under modern climatic conditions, this area is mainly covered by savannah which is dominated by  $C_4$  grass plants (Giresse et al., 1994; Figure 3.1). Terrestrial  $C_4$  plants, including many grasses, exhibit optimum photosynthesis at temperatures about  $10^{\circ}$  higher than vascular  $C_3$  plants and are thus common in warm tropical and dry to arid climates. Due to their specific  $\delta^{13}\text{C}_{\text{org}}$  signatures, the contribution of  $C_4$  plant matter to marine sediments needs to be assessed as precise as possible usually requiring a combination of methods including palynology and carbon isotopes on land plant waxes.

Maceral analysis, bulk  $\delta^{13}\text{C}_{\text{org}}$ , (Figs. 3.3b,c) and palynology were employed to assess and evaluate the potential influence from  $\text{C}_4$  plant matter in the low latitude Atlantic results. Accordingly, maceral-based estimates for proportions of terrigenous OM range from 62-80 % along the African continental margin and 18-35 % in the central Equatorial Atlantic. The continental-slope estimates are consistent with former approximations by Westerhausen et al. (1993). Corresponding proportions derived from bulk  $\delta^{13}\text{C}_{\text{org}}$  are generally lower ranging from 6-48 % along the African continental slope and 1-13 % in the central Equatorial Atlantic. The largest discrepancies between maceral-based and isotopebased estimates are evident along the continental margin off Cameroon and Nigeria (up to 67 %) but gradually decrease south and west to approach smallest values (5-9 %) in the central Equatorial Atlantic at 29°W. Considering admixture of  $\text{C}_4$  plant matter to be responsible for these observed differences it is estimated that 3-40 % (1-30 %) of the terrigenous (bulk) organic fraction is composed of  $\text{C}_4$  plant matter (Fig. 3.3d) with strongest contribution on the Niger deep-sea fan and the adjacent continental margin off Cameroon and Gabon.

Recent biomarker and pollen studies on dust and sediment trap material and surface sediments from the eastern low latitude Atlantic support the presence of significant  $\text{C}_4$  plant material (Huang et al., 2000; Eglinton et al., 2002). Mapping the abundance of  $^{13}\text{C}$  in leaf-wax components in surface sediments recovered from the seafloor off northwest Africa (0-35°N) reveals a clear pattern of  $\delta^{13}\text{C}$  distribution, indicating systematic changes in the proportions of terrestrial  $\text{C}_3$  and  $\text{C}_4$  plant input (Fig. 3.6). They conclude that  $\text{C}_4$  plant derived terrigenous leaf-waxes achieve highest proportions (>50 %) off the NW-African coast at about 20°N. Notably,  $\text{C}_4$  plants still contribute about 40-50 % of total leaf-waxes to the central Equatorial Atlantic. These proportions gradually decrease towards the tropical African continental margin to account for less than 20 % off Niger and Cameroon. High  $\text{C}_4$  contributions, apparently carried by January trade winds, also extend far into the equatorial Gulf of Guinea. Similar distributions are obtained if summed pollen counts for the Chenopodiaceae-Amaranthaceae and the Poaceae are used as an independent  $\text{C}_4$  proxy. Huang et al. (2000) conclude that the specificity of the latitudinal distribution of vegetation in North West Africa and the pathways of the trade and Sahara Air Layer wind systems are responsible for the isotopic patterns observed in the surface sediments. Using a comparable analytical approach, Schefuß (2002) recently determined the relative amounts of  $\text{C}_4$  plant lipids of the bulk eolian lipid yield in dust samples that were collected along a transect from 33°N to 12°S along the African west coast. Employing endmember values of -36.0 ‰ and -21.5 ‰ for  $\text{C}_3$  and  $\text{C}_4$  plant leaf lipids, respectively, eolian  $\text{C}_4$  contribution was determined to be around 50% or higher off NW-Africa and northern Angola (8-10°S). Along the equatorial African coast (10°N to 7°S) these concentrations decrease to 30-35 % due to the greater contribution of aerosols from  $\text{C}_3$  plant matter.

All these lines of evidence indicate that deposition of  $\text{C}_4$  plant matter in the central and eastern low latitude Atlantic may well be substantial. It may therefore be expected that the impact of this specific type of terrigenous OM on quantitative estimates of marine versus terrigenous OM is also of relevance for other low latitude, dust-influenced ocean basins.



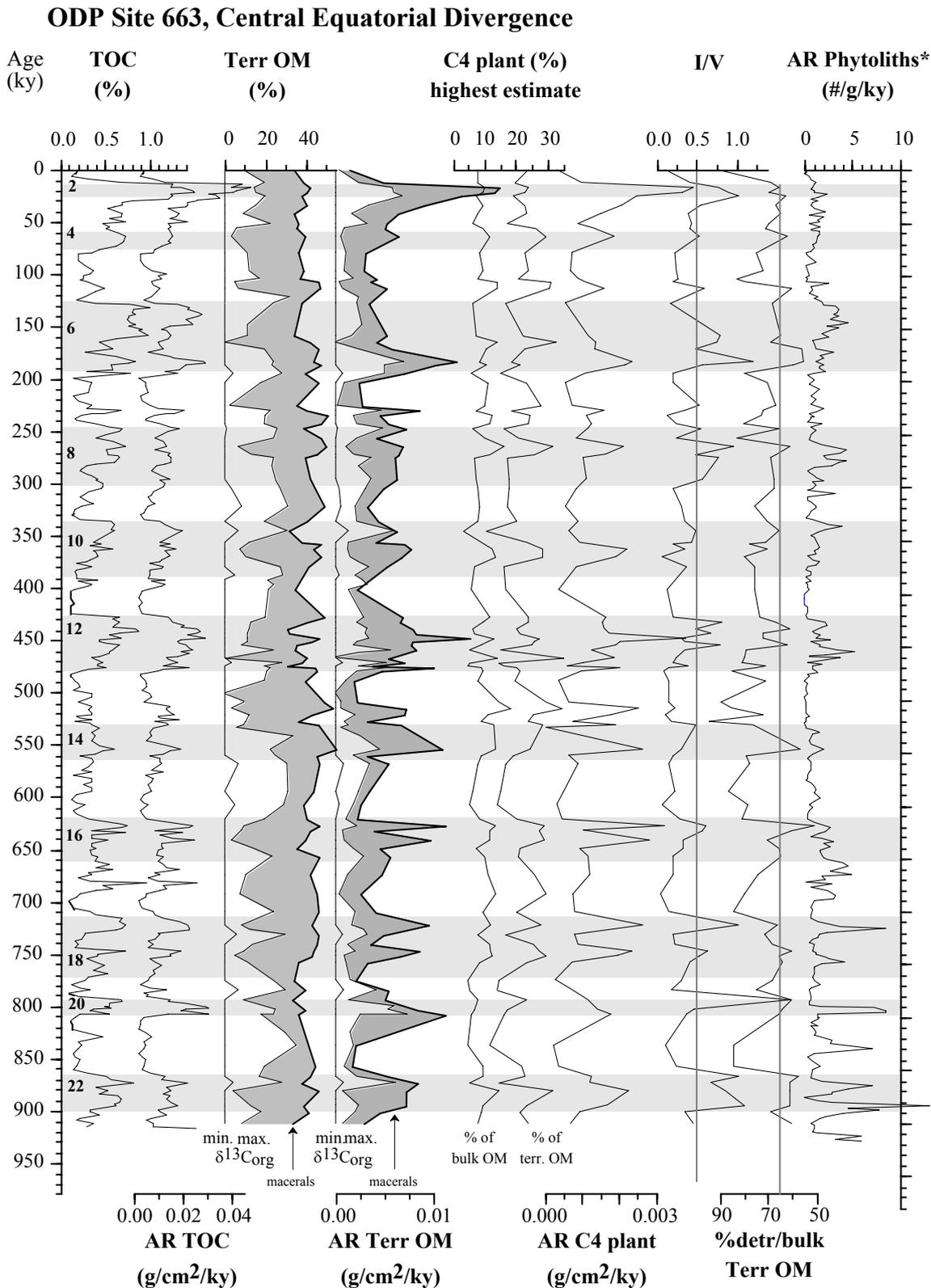
**Figure 3.6:** (adapted after Huang et al., 2000): Source areas of C<sub>4</sub> plant material distributed in the eastern tropical Atlantic. **Left:** Isopol contours (percentage of total pollen) of ChenoAms pollen in marine surface sediment samples (Hooghiemstra et al., 1986) and the main source areas of Chenopodiaceae and Amaranthaceae (ChenoAms) pollen on the continent (Sahara desert and semi-desert areas). **Middle:** Isopol contours of Gramineae pollen in marine surface sediments (Dupont and Agwu, 1991; Hooghiemstra et al., 1986) and the main source areas of grass pollen (Gramineae) on the continent (Sahel and savannah). **Right:** Distribution of C<sub>4</sub> plant wax (% of total C<sub>3</sub> and C<sub>4</sub>) in marine surface sediment samples, calculated from values of  $\delta^{13}\text{C}_{n\text{-alkanes}}$  using a two-component mixing equation with end member values of -34 and -19 ‰, respectively (Rieley et al., 1993; Collister et al., 1994). Circles indicate major source areas for dust deflation, such as Holocene lake deposits (Petit-Marie, 1991) (N.B. not shown but to east of map is another major source area around Lake Chad, centred on ca. 14° N 11° E). Arrows mark major river inputs of particulate terrigenous organic carbon ( $10^4$  tonnes·y<sup>-1</sup>) (Ludwig et al., 1996). (+) Sampling sites.

### 3.5 Environmental variations during the Late Quaternary

#### *The terrigenous organic record of the central equatorial Atlantic: Implications for the paleoclimatic evolution of African dust source areas*

Various paleoclimatic studies have shown that fluctuations in African aridity corresponded to changes in high latitude ice volume and North Atlantic sea surface temperatures (SST, Sarnthein et al., 1982; Street-Perrott and Perrott, 1990; Tiedemann et al., 1994). In addition, DeMenocal et al. (1993) proposed that African terrestrial climate responded most sensitively to high latitude SSTs during peak glacial conditions when precessional forcing in the tropics was lowest. Both controls were considered to promote stronger African aridity and enhanced dust transport due to an intensification of the trade winds at low latitudes. As a consequence, African climate should be preconditioned for aridity during high latitude ice growth and full glacial periods.

Aridity/humidity cycles in terrestrial African climate were inferred from palynological (Pokras and Mix, 1985; Hooghiemstra, 1989; Dupont and Hooghiemstra, 1989; Lezine, 1991; Hooghiemstra et al., 1992; Dupont, 1993; DeMenocal et al., 1993; Frédoux, 1994; Giresse et



**Figure 3.7:** Time series of ODP site 663 percentages and accumulation rates of organic carbon (TOC), terrigenous OM as determined by maceral analysis and isotopic measurements, and highest C<sub>4</sub> plant estimates (shown as percentages of bulk and terrigenous OM). Elevated I/V ratios are attributable to periods of enhanced aridity in dust source areas and vegetation fires similar to the phytolith record (from deMenocal et al., 1993). Late Quaternary variations in the percentage of the detrital terrigenous organic fraction (< 5 μm) relative to the total terrigenous organic fraction document changes in the transport energy of dust-carrying winds (from Wagner, 2000).

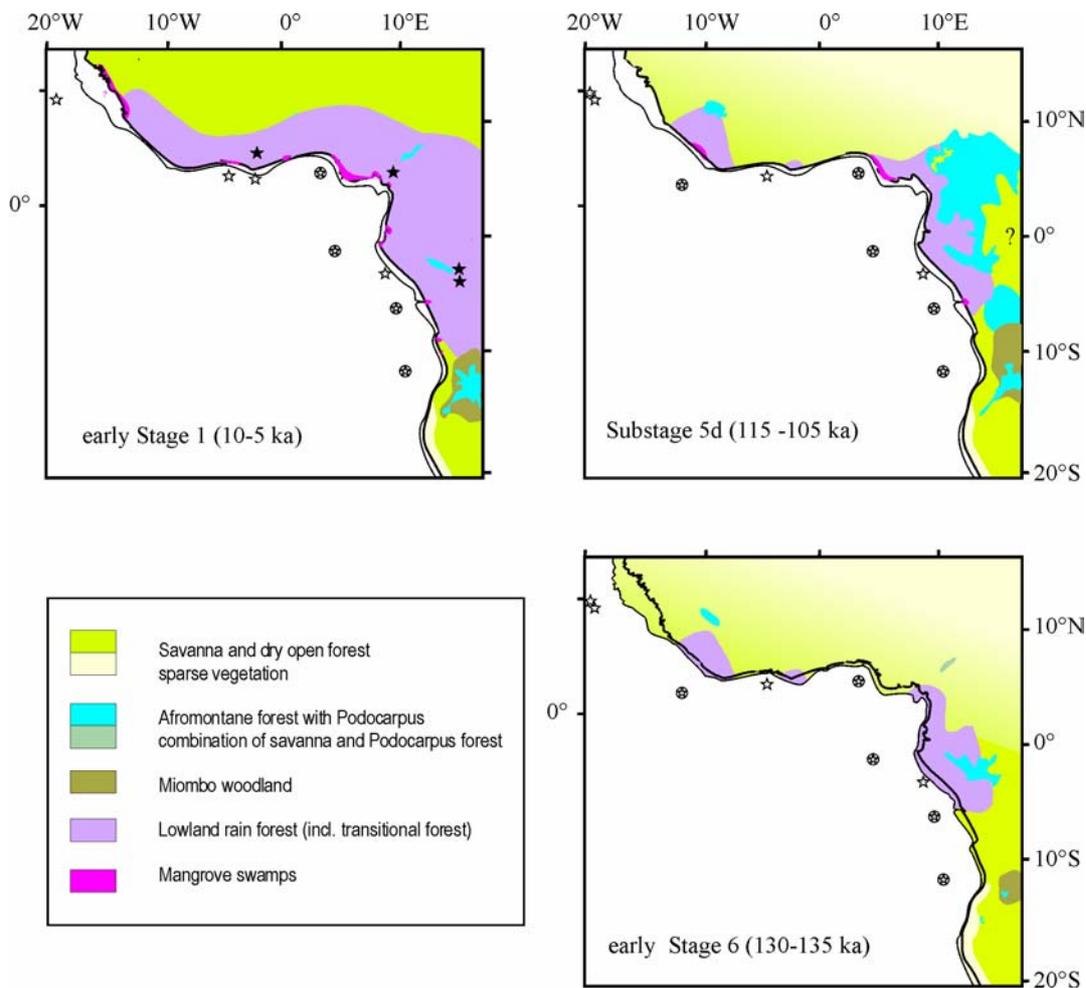
al, 1994; Dupont et al., 2000) and geochemical (e.g. Verardo and Ruddimann, 1996; Bird and Cali, 1998; Zabel et al., 1999, 2001) data. Most of them note enhanced eolian supply and an equatorward displacement of African vegetation zones during full glacial conditions. The one million year terrigenous organic records from Site 663 in the central Equatorial Atlantic provides evidence which supports fluctuations in African aridity (Fig. 3.7, from Wagner, 2000). Accordingly, estimates for terrigenous OM range between 26-55 % based on petrologic studies and 0-46 % from the isotopic signal. Both records suggest that terrigenous OM supply not simply responded to glacial-interglacial cycles but was restricted to short time intervals during glacial periods (except for two exceptions during interglacial stages 15 and 7) when terrigenous fluxes were almost twice as high compared to glacial background and interglacial conditions.

At site 663, changes in the composition of the terrigenous organic fraction were also deduced from fluctuations in C<sub>4</sub> supply, the I/V ratio, the percentage of the detrital fraction (<5 µm) of the bulk terrigenous OM (% detr/bulk Terr OM), and the flux of phytoliths (DeMenocal et al., 1993). Typically, maximum glacial accumulation of terrigenous OM coincided with peaks in C<sub>4</sub> debris and the inertinite/vitrinite ratio, whereas the relative proportion of detrital terrigenous particles approached lowest percentages. Wagner (2000) suggested that such constellations likely represent short time periods when eolian supply of larger and more highly oxidized organic particles containing an elevated portion of C<sub>4</sub> debris was enhanced. Glacial background and interglacial sections, in contrast, reveal almost entirely detrital terrigenous OM with very low dilution of C<sub>4</sub> plant debris or oxidized OM.

Wind-blown inertinite may be regarded as an indicator of vegetation fires in African source areas, equivalent to charcoal (Verardo and Ruddiman, 1996), phytoliths (Pokras and Mix, 1985; DeMenocal et al., 1993), or black/dead carbon (Bird and Cali, 1998). Pokras and Mix (1985) proposed that African hyperarid conditions were established due to enhanced glacial wind speeds which, in turn, caused and fueled extensive natural bush or savannah fires. Huge amounts of burned plant material were injected into the atmosphere and transported to the tropical Atlantic. The terrigenous organic record of Site 663 supply supporting evidence for changes in aridity of source areas over the past one million years. Increased glacial supply of C<sub>4</sub> debris to the tropical Atlantic is also indicated by Gramineae and Cyperaceae pollen records from the Gulf of Guinea (Frédoux 1994; Dupont and Weinelt, 1996; Dupont et al., 1998; Jahns et al., 1998), and has been proposed based on the carbon isotope signature of eolian black carbon for the Sierra Leone Rise (Bird and Cali, 1998). The general covariance of C<sub>4</sub> plant estimates with the inertinite/vitrinite record of Sites 663 favours a common aridity-driven control (Wagner, 2000). It should be emphasized, however, that the proposed C<sub>4</sub> plant supply only contributes a small fraction, never exceeding one quarter of the bulk terrigenous organic fraction (14 % with respect to the total organic matter).

Enhanced glacial dryness likely stimulated the expansion of the African grass-savannah covered vegetation belt and should be documented in marine palynological records. For example, in a recent study, Dupont et al. (2000) used marine and terrestrial palynological records from the eastern low latitude Atlantic to draw detailed vegetation maps of equatorial West Africa for eleven time slices over the last 150,000 years (Fig. 3.8). Accordingly, rain forest was widespread during interglacial stages 1 and 5, but strongly reduced during glacial

stages 3 and 4 and especially during 2 and 6 when open, grass-rich vegetation prevailed. During the extreme glacial conditions of stage 6 savannah and open dry forest covered large areas along the northern coast of the Gulf of Guinea and the southern Saharan desert reached far to the south and the Namib desert far to the north. The area of rain forest was restricted to the southwest of the Guinean mountains and along the eastern coast of the Gulf of Guinea, while mangrove swamps were strongly reduced and the area of *Podocarpus* forest fluctuated. In contrast, rain forest was widespread and mangroves were extensive along the coast during the last interglacial (Substage 5e). *Podocarpus* forest area strongly extended during Substages 5d and 5b. In Substages 5c and 5a, rain forest reclaimed areas it had lost in the previous substages (5d and 5b respectively). Mangrove swamps were less widespread in the later substages of Stage 5 than during Substage 5e. During Stage 4, the rain forest area was again strongly reduced, and recovered only slightly during the following Stage 3. Also the mangrove swamp area was reduced except along the Ivory Coast and along the northwestern coast of the Gulf of Guinea. *Podocarpus* forest only occurred in Angola and may be in Congo during Stage 4. Again forest was much reduced during Stage 2 and open vegetation types covered large parts of equatorial West Africa. Mangrove swamps must have been rare. At the beginning of the Holocene, mangrove swamps had recovered and reached their largest extension. Also the rain forests area increased in the early Holocene and Guinean and Congolian rain forests were probably not separated by a savanna corridor now existing in Togo and Benin.

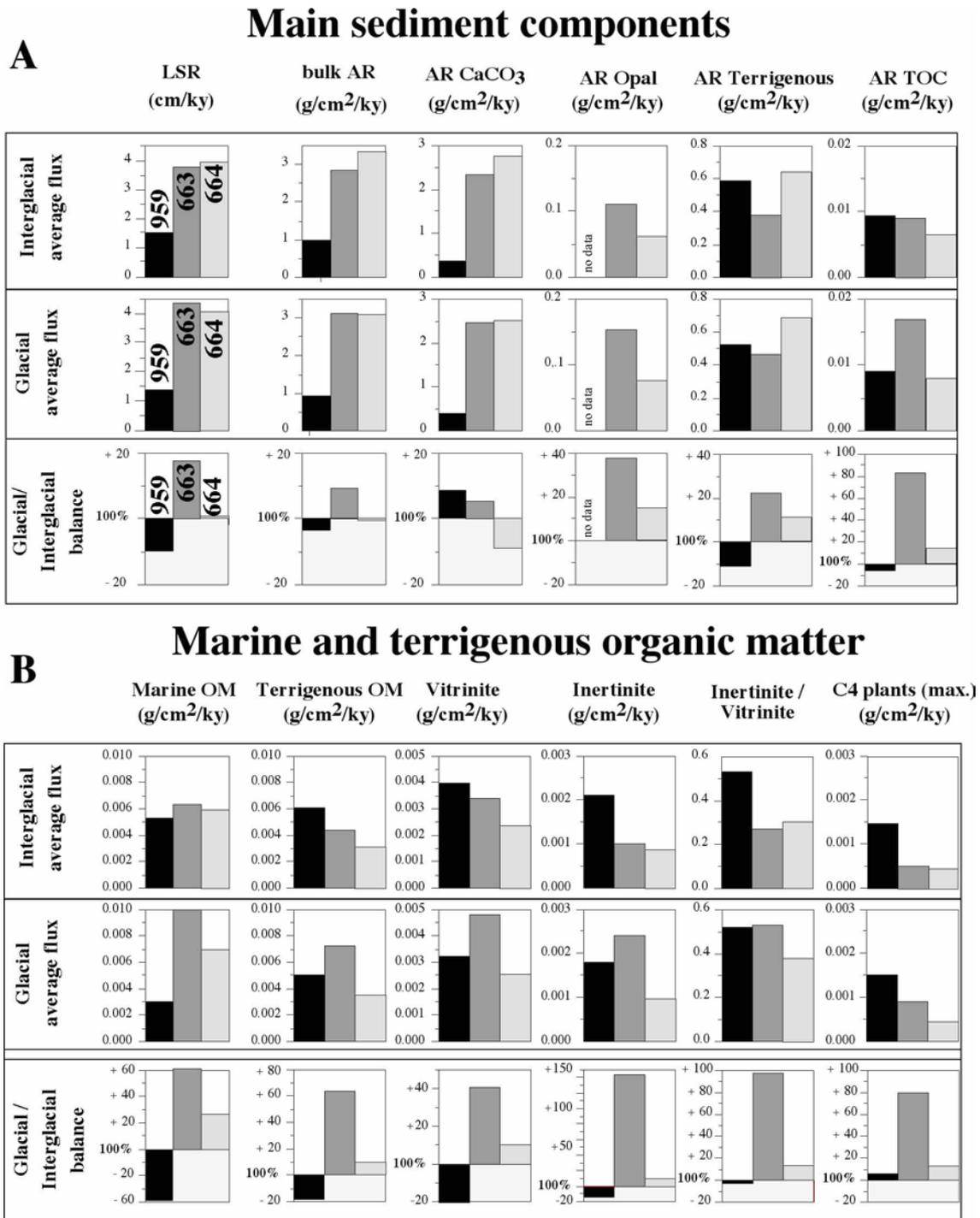


**Figure 3.8:** Time slice reconstructions of African vegetation (adapted after Dupont et al. 2000).

### 3.6 Towards a glacial-interglacial balance of OM accumulation along the central and near-continental low latitude Atlantic

It has been shown that surface water production beneath the Equatorial Divergence and dust supply from African source areas created late Quaternary changes in OM sedimentation. These relations allow the assessment of more general sedimentation patterns that link pelagic areas of the low latitude Atlantic to the African continent over the past 1 million years. Wagner (2000) presented average glacial and interglacial flux rates and glacial-interglacial balances of main sediment components (Fig. 3.9a, see following page) and marine and terrigenous OM (Fig. 3.9b) for sites 663, 664 and 959 (for location see Fig. 3.1).

Late Quaternary glacial-interglacial patterns of calcium carbonate, biogenous opal, terrigenous matter, and TOC clearly distinguish the central Equatorial Divergence (site 663) from the other areas. Here, glacial-interglacial balances are consistently positive, reaching highest offsets for biogenic opal (+ 40 %) and TOC (+ 80 %) closely coupled to enhanced supply of terrigenous matter (+ 20 %). Carbonate accumulation, in contrast, is not enhanced during glacials (+ 5 %) probably reflecting the influence of moderate and mainly productivity-driven calcite dissolution (see Funk et al., 2003 and Henrich et al., 2003 for further discussion on carbonate dissolution). Stronger carbonate dissolution due to enhanced contribution of corrosive deep waters from the southern ocean (Raymo et al., 1997) may be assumed from negative balances for carbonate accumulation (- 10 %) further west at site 664. The positive balance in TOC accumulation rates (+ 20 %) probably document slightly enhanced glacial upwelling in the western Equatorial Divergence. Off the equatorial West-Africa (site 959), glacial-interglacial accumulation was continuously low and constant throughout the past 1 Ma. The minor decrease in glacial deposition and accumulation (- 9 % and - 3 %, respectively) probably relate to persistent winnowing on top of the exposed transform margin (Wagner, 1998; Giresse et al., 1998; Giresse and Wiewióra, 2001). Distinct changes in accumulation of marine and terrigenous OM are evident when glacial average flux rates are considered. Due to enhanced dust supply to the central Equatorial Atlantic terrigenous organic components at site 663 consistently reveal pronounced positive balances during glacials that amount to a 1.6-fold increase compared to interglacial periods. The proposed enhancement of African dust source aridity and/or wind strength during glacials is reinforced by almost 2.5-fold higher accumulation rates of inertinite and a doubling of the estimated C<sub>4</sub> plant matter. A comparable change in glacial supply of terrigenous OM is not observed at sites 664 and 959. Probably stimulated by enhanced eolian deposition, glacial accumulation of marine OM increased by about 20 % to 60 % below the Equatorial Divergence in comparison to interglacial conditions. Assuming that these pronounced changes in marine OM accumulation are mainly related to productivity rather than to preservation, they suggest considerably stronger oceanic upwelling during late Quaternary glacial periods.



**Figure 3.9:** Late Quaternary average interglacial and glacial flux rates (950 ka) and glacial-interglacial balances of **a)** main sediment components and **b)** marine and terrigenous OM from ODP sites 664, 663 and 959 (from Wagner, 2000). Balances illustrate the relative increase or decrease of each individual component between glacial and interglacial periods at each position. Carbonate and biogenous opal data according to deMenocal et al. (1993; site 663) and Ruddiman and Janecek (1989, site 664). Data from site 959 as reported in Wagner (1998, 1999a).

### 3.6.1 *The terrigenous organic record of marine deep-sea fans: Land-ocean interaction and influence of selective degradation – Aspects from the Congo fan*

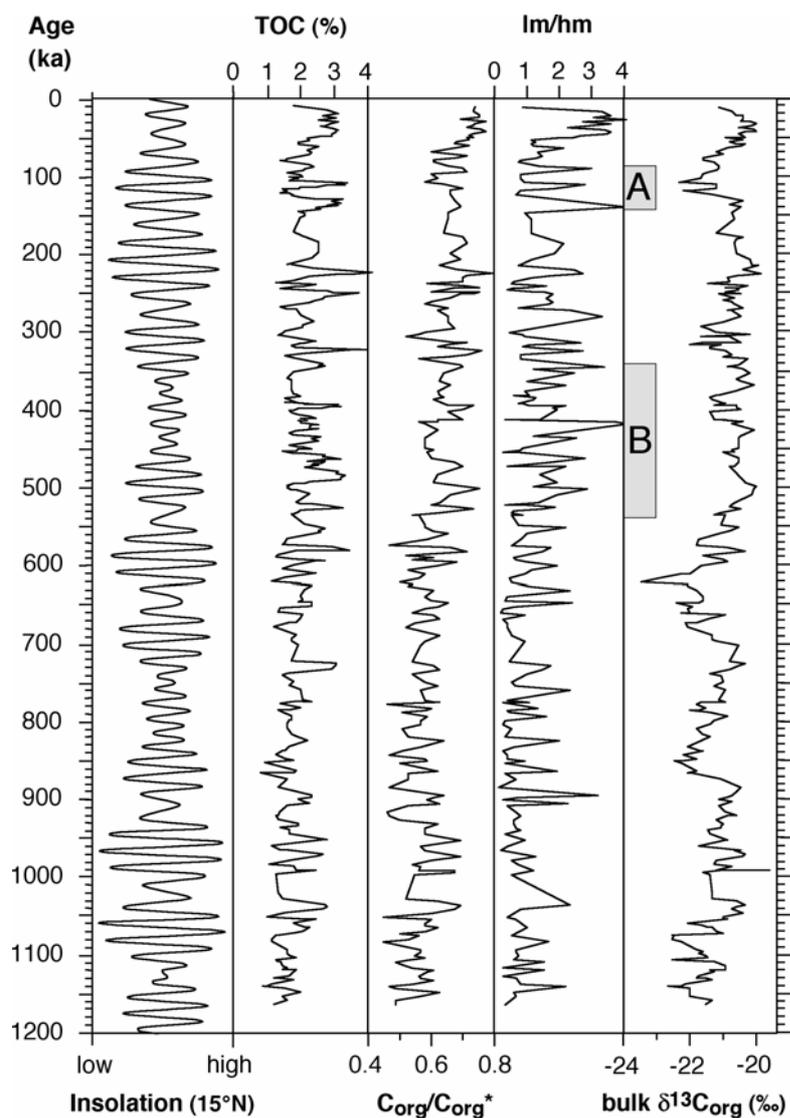
In contrast to the broad dispersal of terrigenous OM by eolian transport, the export of organic carbon through rivers is more confined to continental margins (e.g. Hedges et al., 1997).

Ludwig

et al. (1996) estimated the average global river carbon flux to the ocean to account for  $392 \cdot 10^{12}$  g per year ( $205 \cdot 10^{12}$  g/y dissolved organic carbon, DOC, and  $187 \cdot 10^{12}$  g/y particulate organic carbon, POC).

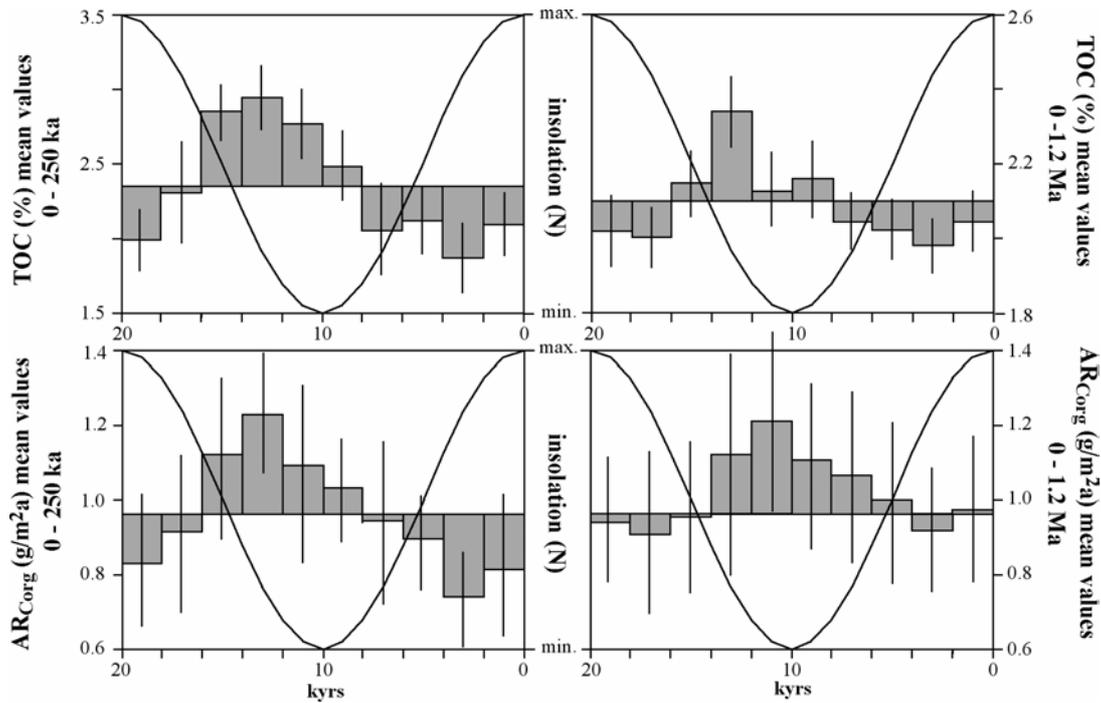
On a global scale, organic carbon in modern continental shelf sediments may be composed of nearly the same amounts of marine and terrestrial organic carbon (Schlünz and Schneider, 2000) although this view is challenged by other studies (e.g. see Hedges and Keil, 1995; Hedges et al., 1997 for reviews). Results from the Amazon Fan have shown the dramatic effect of glacial sea level lowstands on the downslope transport of riverine organic carbon to distal areas of the deep-sea fan (Schneider et al., 1997b; Schlünz et al., 1999; Schlünz and Schneider, 2000) and the adjacent western Equatorial Atlantic (Rühlemann et al., 1996). Estimates based on isotopic data from this area suggest that 15-40 % of the total OM is of terrigenous origin. At present it is not well constrained how much of that riverine OM is laterally advected by ocean currents to settle over vast areas of the deep Atlantic basins (for shallow current advection see implications by Zabel et al., 1999). Goñi et al. (1998) emphasized the importance and sources of land-derived OM in surface sediments of the Gulf of Mexico using bulk and molecular level sedimentary compositions. They conclude that the terrigenous organic fraction may have been significantly underestimated in earlier studies (e.g. Hedges and Mann, 1979b; Prahl et al., 1994) and that more than 50 % of the lignin from land-derived organic carbon originated from  $C_4$  plants being eroded from grasslands of the Mississippi river drainage basin. These results imply that the terrigenous organic fraction may be underestimated in pelagic sediments where river-induced  $C_4$  plant matter contribute to the bulk organic carbon pool, especially during past glacial conditions (Bird et al., 1994).

Considering that vegetation zones covering the catchment areas of the two main tropical African rivers, i.e. the Congo and the Niger, are intimately linked to precessional-forced fluctuations in the West-African monsoon system it appears appropriate to expect considerable fluctuations in the supply and composition of river-borne OM to the easternmost Equatorial Atlantic. The importance of monsoon-driven variations in sediment load and fluvial nutrient supply on late Quaternary paleoproductivity within the Congo and Niger river plumes and the adjacent areas has been demonstrated by Schneider et al. (1997a,b) and Zabel et al. (2001). To further address this topic the following discussion will focus on three aspects, (i) general controls on organic sedimentation including a distinct pyrolytic feature (Holtvoeth et al., 2001), (ii) evidence from palynology and (iii) implications from lignin chemistry for selective degradation as preserved in sediments from the Congo fan (sites 1008 and 1075, Fig. 3.1).



**Figure 3.10:** Organic geochemical records of bulk organic matter from late Quaternary sediments of the Congo deep-sea fan (ODP Site 1075, from Holtvoeth et al, 2001). High-amplitude fluctuations of bulk geochemical records are linked to the summer insolation curve at 15°N. TOC maxima are dominated by marine organic carbon. Down-core trends point to a relative enrichment of a more stable (terrigenous) organic compound with a remarkable shift between 700 and 600 ka in TOC, lm/hm, and bulk  $\delta^{13}\text{C}_{\text{org}}$  records. A and B indicate sections selected for more detailed lignin analysis (see Figures 3.15 and 3.16).

Applying detailed organic geochemical investigations on the nature and reactivity of OM, Holtvoeth et al. (2001) recognized high amplitude fluctuations for various geochemical proxy records which are linked to the record of summer insolation at 15°N (Fig. 3.10). This can be illustrated with a simple method of data processing. For each sample the specific time interval to the next insolation maximum in the core profile is determined and converted to an equivalent within an idealized insolation cycle that covers 20 kyrs and is subdivided into 10 classes (corresponding to 2 kyrs intervals). Mean values of TOC content and accumulation rates of all samples within each individual class are calculated and compiled in a diagram (41 samples per class on average). The close link of TOC concentration and accumulation to the insolation cycle showing maximum values during periods of enhanced trade wind intensity, dry African climate and low continental run-off (insolation minima) is clearly recognizable (Fig. 3.11).



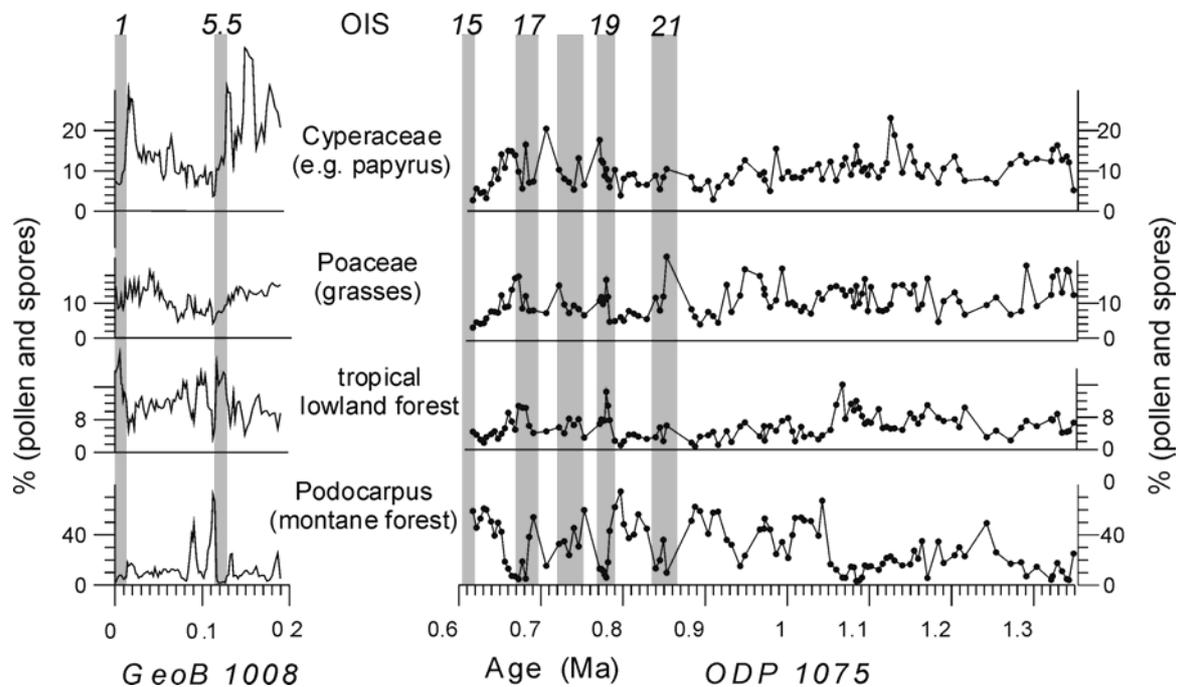
**Figure 3.11:** Mean values of TOC contents and accumulation rates from 0 to 250 ka and from the whole record of ODP site 1075 within idealized cycle. For the last 250 kyrs insolation can be clearly identified as the driving force for organic sedimentation at the Congo deep-sea fan. Over the whole time span of 1.2 Ma the relation becomes blurred due to long term diagenesis and changes in the system control (e.g. mid Pleistocene transition).

The observed amplitudes for total organic carbon (TOC) within the profile (Fig. 3.10) range from 0.8 to 4.1% and from 0.2 to 4 for the ratio of low-mature to high mature OM (lm/hm). The latter parameter was recently established as new OM-reactivity proxy and is based on the relative share of hydrocarbon yields from low-mature (reactive) and high-mature (lessreactive) organic fractions during Rock-Eval pyrolysis. Based on the data, Holtvoeth et al. (2001) distinguish three general types of OM, (i) a lowmature marine source, (ii) a low-mature terrigenous source (lm; probably to some extent corresponding to the huminite/vitrinite fraction), and (iii) a high-mature terrigenous fraction (hm; related to inertinite), although it remains a target of further studies to better assess chemical and physical properties of the low-mature terrigenous fraction. Combined with quantitative organic petrology, the lm/ hm ratio may serve to improve the reconstruction of changes in the relative contributions of these different types of terrigenous OM. Figure 3.10 further shows the degradation rate profile of bulk OM ( $C_{org}/C_{org}^*$ ). Assuming that microbial sulfate reduction is the main degradation process for sedimentary organic matter in the Congo fan deposits, a minimum estimate of the original content of organic carbon ( $C_{org}^*$ ) was calculated according to Littke et al. (1997) following the equation  $C_{org}^* = C_{org} + 2S * M_C/M_S$  ( $S$  = measured sulfur content,  $M_C$  = molecular mass of carbon,  $M_S$  = molecular mass of sulfur). The degradation rate of organic carbon is expressed as the ratio of the measured to the estimated original organic carbon contents ( $C_{org}/C_{org}^*$ ). Finally, bulk  $\delta^{13}C_{org}$  signatures are presented which range from -20 to -23.5 ‰ throughout the past 1.2 million years at site 1075 (Fig. 3.10). Application of a simple binary mixing model considering marine and terrigenous endmember values of -18 ‰ and -27 ‰, respectively, result in terrigenous organic fraction in the order of 25-30 %. It should be noted, however, that this approach ignores any influence

from C<sub>4</sub> plant matter and aged terrigenous OM, and thus most likely underestimates of the terrigenous organic fraction. To further address general fluctuations in supply from African vegetation belts including the admixture of C<sub>4</sub> plant matter to the Congo Fan some key palynological results are discussed.

### 3.6.2 Palynological results from the Congo deep-sea fan

Pollen and spores found in the Congo Fan deposits have their sources in the Congolian rain forest area and are mainly transported by the river. Additional aeolian pollen from the Angolan highlands are found (Dupont and Wyputta, 2002). The record of ODP Site 1075 (5°S 10°E) located north of the Congo deep-sea canyon shows slightly more aeolian influence than the one of GeoB Site 1008 (7°S, 10°E) taken south of it (Van Iperen et al., 1987). Relative abundances of pollen of rain forest elements, *Podocarpus* (from the Afromontane forest), Poaceae (grasses and bamboos), and Cyperaceae (sedges, rushes, papyrus, and others), record changes in the lowland rain forest, woodland, Afromontane forest, swamp forest, and open swamps of the Congo Basin (Fig. 3.12).



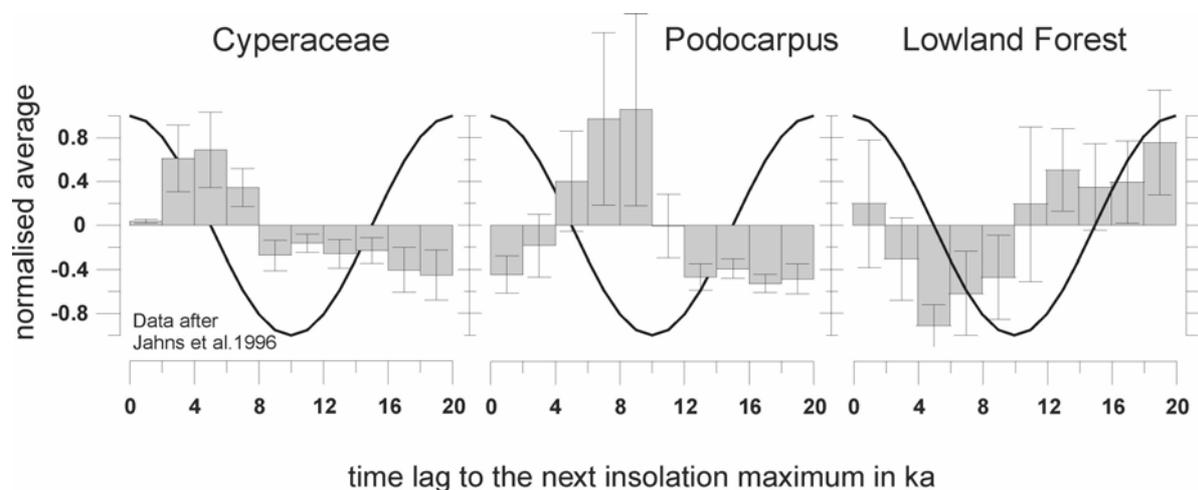
**Figure 3.12:** Selected pollen taxa of Sites GeoB 1008 (left; Jahns 1996) and Ocean Drilling Program Site 1075 (right; Dupont et al. 2001) expressed in percent of the total of pollen and spores. Warm stages are shaded; odd-numbered interglacial isotope stages are indicated on top. OIS is Oxygen Isotope Stage.

The early Pleistocene pollen record of ODP Site 1075 shows a strong rise in the percentages of *Podocarpus* pollen concomitant with a reduction of woodland and lowland forest pollen, 1.05 Ma ago (Dupont et al., 2001). It indicates the extension of the Afromontane forest belt toward lower altitudes and suggests lower temperatures during (even-numbered) glacial stages. From the pollen record, it is inferred that *Podocarpus* forest was common during the glacial stages between 1.05 and 0.6 Ma, suggesting that the climate in equatorial Africa became cooler, but remained humid. Interglacials (odd-numbered isotope stages) between 0.9 and 0.6 Ma, in contrast, exhibit large variations in African vegetation comprising lowland

rain forest, woodland, swamps, and some mountain forest. A trend to more open swamps is indicated within those mid-Pleistocene interglacial periods. The development of swamps in the Congo basin might be the result of reduced lake areas, which would suggest rather dry interglacial conditions.

The late Pleistocene pollen record of GeoB Site 1008 indicates the expansion of more open vegetation types, such as open swamps with grasses and Cyperaceae, during glacial Stages 6 and 2 (Jahns, 1996). This pattern specifically holds true during periods in which the insolation at the Northern Hemisphere tropics increased. During periods with open woodland (more grass pollen) and open swamps (more Cyperaceae pollen), the proportion of the  $C_4$  plants in the vegetation cover must have been larger than during periods with dense forests. However, in terms of biomass, the  $C_3$  trees probably remained the dominant source of terrigenous organic matter.

During the late Pleistocene climate cycles, the influence of the precession becomes more obvious. Several short-time fluctuations during Stages 6 and 5 underline the importance of precessional variation of the monsoon climate corroborating findings of Kutzbach (1987), Schneider et al. (1997a), and others. Spectral analysis of the GeoB 1008 record indicate that the response of the rain forest follows the pace of the Northern Hemisphere precession with a time lag of about  $90^\circ$ , equivalent to about 5 ka (Dupont et al., 1999). The timing of the relative abundance of selected pollen types within the precession dominated insolation cycle is illustrated in Figure 3.13.



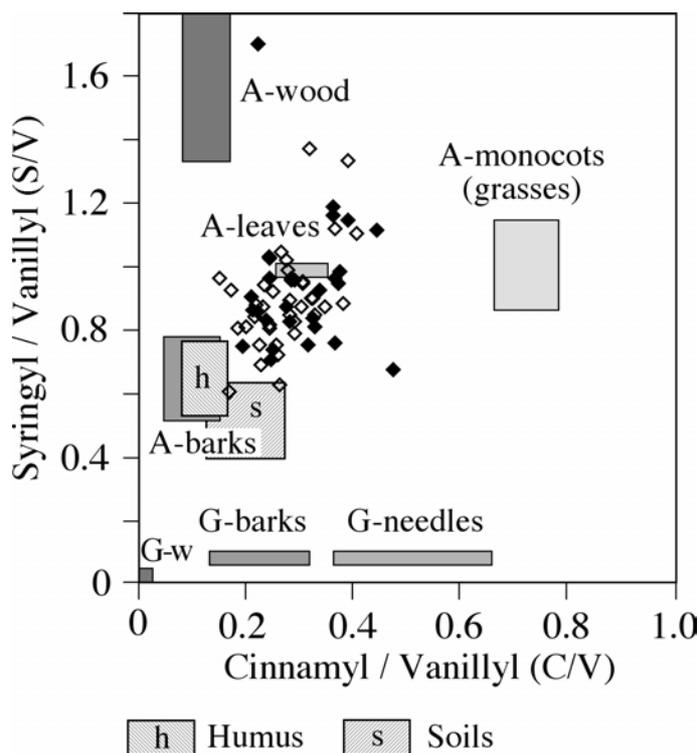
**Figure 3.13:** Samples of GeoB 1008 (dated between 0 and 190 ka) are grouped according to the time lag after the last insolation maximum (insolation at  $15^\circ\text{N}$ ) in classes of 2 ka. All cycles are normalised to 20 ka length. For each class the normalised average pollen percent of Cyperaceae (left), *Podocarpus* (middle), and sum of lowland forest elements (right) is plotted. The error bars are calculated by dividing the standard deviation of the class samples by the standard deviation of all samples. The line schematically depicts the insolation variation.

### 3.6.3 Primary supply versus selective degradation of organic matter: Implications from lignin chemistry

It is generally accepted that terrigenous OM is less susceptible to microbial attack than marine OM. Therefore, variations in initial composition of bulk OM should result in a changing susceptibility to OM degradation. In that respect the records of degradation of bulk

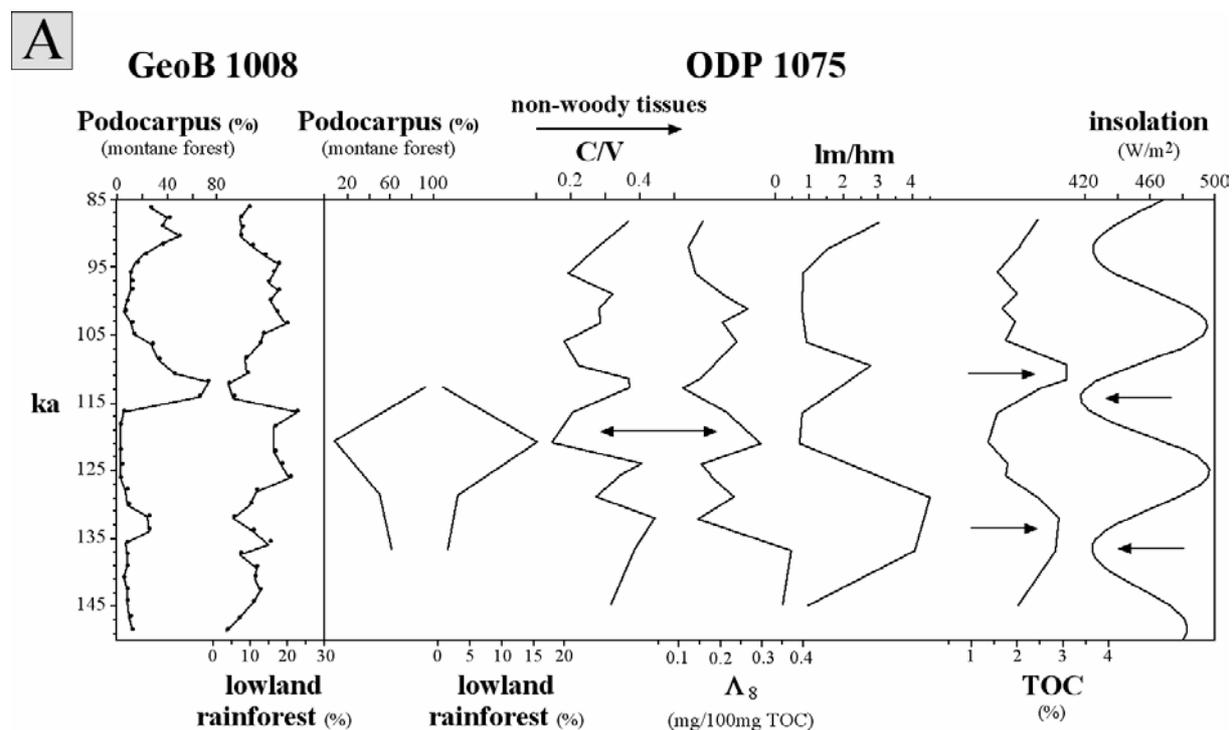
OM ( $C_{org}/C_{org}^*$ ), the lm/hm ratio, and bulk  $\delta^{13}C_{org}$  at site 1075 are of interest (Fig. 3.10) since there are distinct, short term fluctuations in all parameters, which likely are attributable to changes in primary supply. Typically, insolation minima are followed with a delay of 2-7 kyrs by peak TOC (Fig. 3.11), minimum degradation rates, high lm/hm ratios, and generally heavier isotopic signatures. These trends suggest enhanced marine productivity and sedimentation (and/or preservation) of labile (mainly marine) OM in response to stronger wind-driven upwelling. This pattern is reversed during insolation maxima, when humid climate conditions over tropical Africa resulted in enhanced river discharge but lower marine productivity due to reduced upwelling and lower organic carbon deposition. Such conditions apparently favoured the preservation of a less reactive (probably more terrigenous) OM in the sediments. Superimposed on these short-term fluctuations in primary composition of sedimentary OM, a longterm down-core trend is evident (Fig. 3.10). Accordingly,  $C_{org}/C_{org}^*$  and lm/hm ratios decrease with burial depth supporting the general conclusion that a more stable (and probably terrigenous) organic fraction is selectively enriched with increasing burial depth. In addition, an offset towards lower values is observed between 600 and 700 ka, most clearly documented in the TOC and lm/hm records. At the same time, bulk  $\delta^{13}C_{org}$  signature shifts to slightly lighter values. Up to now it is not clear whether these shifts preserve direct response of the ecosystem in response to climatic change or secondary (sedimentary or diagenetic) adjustments of the depositional system.

To investigate variations in terrigenous OM composition and selective degradation two time slices (150-85 ka (A) and 540-340 ka (B), see indication in Figure 3.10) were studied in detail. The projection of the S/V and C/V ratios obtained from lignin chemistry according to Goñi and Hedges (1992) shows that terrigenous OM in late Quaternary deposits of the Congo fan mainly originates from angiosperm leaves and barks with variable admixture of angiosperm wood and grass tissues (Fig. 3.14). Apparently, there is no clear distinction in lignin composition that supports the existence of two simple terrestrial endmembers that reflect glacial or interglacial depositional conditions.

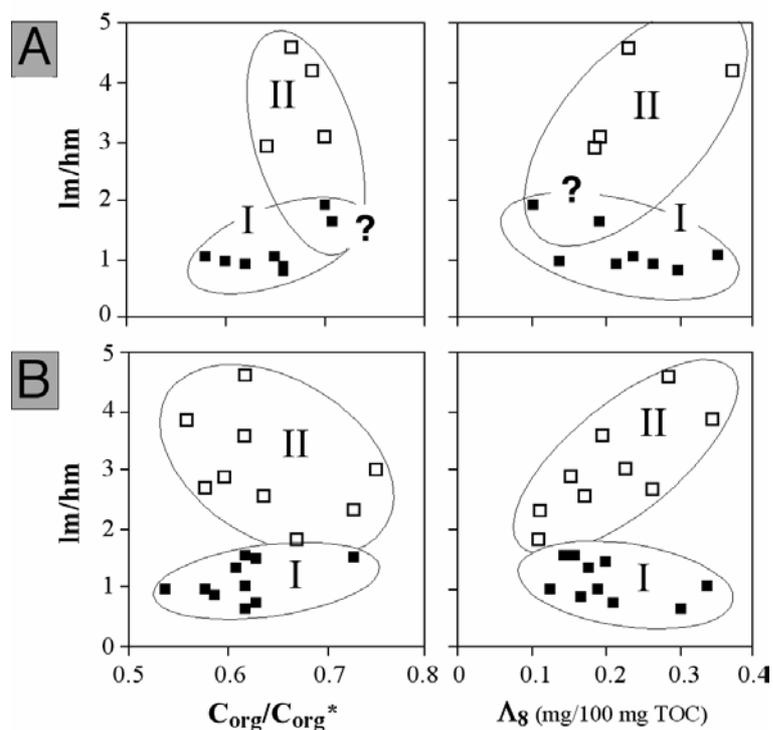


**Figure 3.14:** S/V and C/V ratios obtained from lignin chemistry of selected samples from site 1075 (from Holtvoeth et al. 2003). Terrigenous OM in the sediments of the Congo fan mainly derives from barks and leaves with admixture of angiosperm wood and grass. Gw = gymnosperm wood, open/ filled symbols: samples from insolation minima/maxima. Assignment of soil and humus OM according to Farella et al. (2001).

In addition to the general positive correlation of insolation minima to maxima in TOC and  $l_m/h_m$  ratios, the lignin parameters  $\Lambda$  and  $C/V$  reveal a negative correlation, as for example observed between 97-140ka (time slice A, Figure 3.15). This pattern may either be explained by a better preservation of woody plant tissues (indicated by low  $C/V$  ratios) compared to non-woody tissues, by enhanced primary supply of woody material, or by processes related to hydrodynamic sorting (Goñi et al., 1997). Fluctuations in primary supply is likely to have occurred during humid (interglacial) climates when the African tropical rain forest expanded over most of the Congo catchment area. Palynological data compared to the  $C/V$  ratios from four samples between 111 and 139 ka indicate that higher amounts of woody terrigenous OM occur during (warm and humid) stages with extended lowland rainforest whereas supply of mainly non-woody terrigenous OM is concomitant with enhanced pollen records from montane forests. It may therefore be assumed that tropical grasslands expanded together with montane forests during the latter (cooler) climate stages. These observations clearly favour a varying primary composition causing the  $C/V$  record although diagenetic and transport effects can not be ruled out. To address this alternative mechanism, proxies indicative for degradation ( $C_{org}/C_{org}^*$ ), reactivity ( $l_m/h_m$ ), and composition (bulk  $\delta^{13}C_{org}$ ,  $\Lambda$ ) of the OM are considered. Correlation of these parameters reveal two general groups of samples (Fig. 3.16), one reflecting the relative enrichment of high-mature terrigenous OM due to selective diagenesis (group I, degradation line) and one representing mainly differences in primary composition of the OM (group II, combined mixing/degradation line).

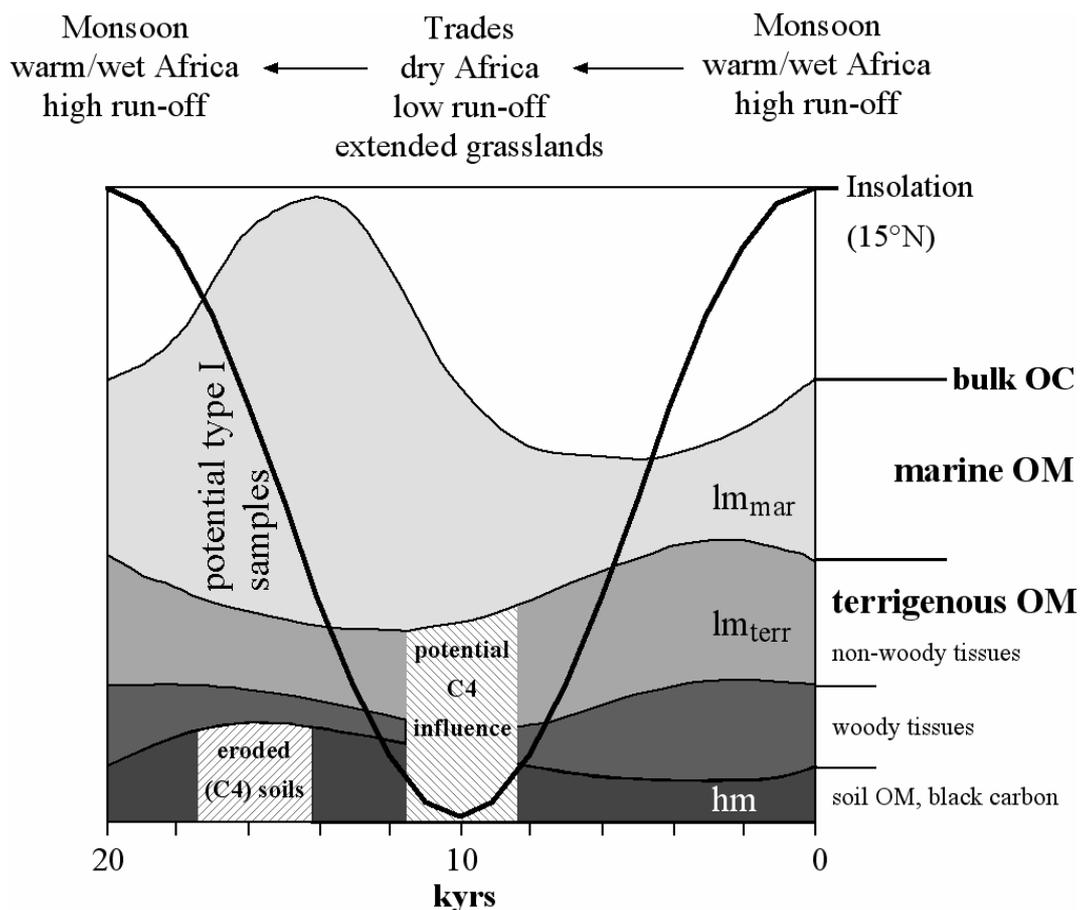


**Figure 3.15:** Lignin data compared to bulk organic parameters (150 - 85 ka, from Holtvoeth et al., 2003), insolation record, and palynological data (GeoB 1008 from Jahns et al., 1996) for time interval A see Fig. 3.10. A significant negative correlation of  $C/V$  ratios and  $\Lambda$  values between 140 and 97 ka either indicates enhanced supply of woody plant tissues during humid stages with extended rainforest (supported by palynological results) and reduced primary production or a better preservation potential of woody plant tissues.



**Figure 3.16:** Cross plots of proxies indicative for degradation ( $C_{org}/C_{org}^*$ ), reactivity (Im/hm) and composition ( $\Lambda_g$ ) of bulk OM in late Quaternary sediments from the Congo Fan (site 1075) for time intervals A and B see Fig. 3.10. Assignment of group I reflects the relative enrichment of high-mature terrigenous OM due to selective diagenesis while group II mainly documents differences in primary composition of OM (modified from Holtvoeth et al., 2003).

Group I samples have low Im/hm signatures indicating generally lower proportions of reactive OM. Therefore, decreasing  $C_{org}/C_{org}^*$  and increasing  $\Lambda$  document the progressive enrichment of a high mature terrigenous organic component due to diagenetic processes. In comparison, group II samples reveal a broad range for all proxies reflecting a combined mixing/degradation line according to their variable primary nature. Since reactive OM may originate from marine and terrigenous sources their relative affiliation to the degree of degradation may help to distinguish the two groups. Enhanced proportions of reactive, terrigenous OM may thus be indicated by high  $\Lambda$  and Im/hm but low  $C_{org}/C_{org}^*$  signatures, assuming that low mature terrigenous OM is more resistant to degradation compared to its marine counterpart. This model includes selective degradation of the most labile (marine) organic fraction, which likely was deposited in conjunction with fresh terrigenous OM. Enhanced supply of reactive terrigenous OM probably represents stronger river discharge during humid climatic conditions when tropical rain forests covered the catchment area. A schematic model summarizing the observed time relationships of insolation, organic carbon burial and the three organic components with indication of potential  $C_4$  plant and degradation influence is presented in Figure 3.17.



**Figure 3.17:** Schematic model summarizing time relationships of insolation, organic carbon burial, and the three organic components with indication of potential C<sub>4</sub> plant and degradation influence as documented in late Quaternary sediments from the Congo fan (ODP Site 1075).

### 3.7 Concluding Remarks

Various organic geochemical and palynological studies performed on modern and late Quaternary sediments from the central to eastern Equatorial Atlantic address the fundamental question of how terrigenous OM can be traced and quantified in TOC-poor deep-sea deposits. The application of multiparameter concepts combining macerals (organic particles), freshwater diatoms, phytoliths, pollen grains, lignin phenols, bulk isotopic data ( $\delta^{13}\text{C}_{\text{org}}$ ), and carbon isotopes derived from longchain *n*-alkanes to modern and late Quaternary near-continental and open ocean settings of the central and eastern Equatorial Atlantic provide evidence for spatial and temporal variations in quantity and composition of terrigenous organic matter. Most important, a growing body of data support the presence of significant and variable quantities of isotopically heavy C<sub>4</sub> plant-derived OM from arid, grass-covered African source areas in deposits from the central Equatorial Atlantic and along the NW-African continental margin. The spatial and temporal distribution of C<sub>4</sub> plant input is determined by climate-driven fluctuations in eolian dust export from the African continent. Terrigenous organic matter in sediments from the Congo deep-sea fan, in contrast, mainly originates from the C<sub>3</sub> plant dominated catchment area of the Congo River, although

palynological data indicate a minor riverine supply of C<sub>4</sub> plant to the deep-sea fan during past dry climate conditions. To validate these results and to improve the data base, additional research efforts utilizing molecular isotopic approaches are suggested.

Based on results from combined pyrolysis, lignin and isotope chemistry three general types of organic matter were distinguished in Congo fan sediments, i.e. (i) a highly reactive (low-mature) marine source, (ii) a reactive (low-mature) terrigenous source (probably associated to the huminite/vitrinite fraction), and (iii) a low-reactive (high-mature) terrigenous fraction (related to inertinite). Differences in selective degradation of the two reactive components apparently have a strong influence on organic geochemical attributes of individual samples and may lead to considerable fluctuation in the relative shares of the three organic components. Such diagenetic processes compete with primary fluctuations in supply of organic matter and may therefore complicate the interpretation of organic geochemical proxy records in a paleoenvironmental context. At present, the interplay of these complex processes are not well understood. It therefore remains a primary target for further studies to better assess chemical and physical properties of reactive organic matter, both of terrigenous and marine origin.

#### 4. Organic matter in river-influenced continental margin sediments: the land-ocean and climate linkage at the Late Quaternary Congo fan (ODP Site 1075)

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##### 4.1 Abstract

Late Quaternary sections (1.2 Ma) of ODP-Site 1075 from the Congo deep-sea fan are investigated to reconstruct variations of terrigenous organic matter supply to the eastern equatorial Atlantic. To characterize the organic matter (OM) with regard to marine and terrigenous amounts we used elemental analysis (C, N, S), stable carbon isotopes (bulk  $\delta^{13}\text{C}_{\text{org}}$ ), Rock-Eval pyrolysis, and terrigenous biomarkers (lignin phenols from CuO oxidation). The records of total organic carbon (TOC) contents,  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios, bulk OM degradation rates ( $\text{C}_{\text{org}}/\text{C}_{\text{org}}^*$ ), and the ratios of hydrocarbons (HC) from low-mature versus HC from high-mature OM (lm/hm) reveal pronounced cyclic changes in OM abundance, preservation, and reactivity that are closely related to the precessional controlled record of insolation, and thus, to variations in upwelling intensity and fluvial run-off. Primary productivity off the Congo is stimulated by both, enhanced nutrient supply in response to trade-induced upwelling during arid African climates (insolation minima) and fluvial nutrient delivery during humid stages (following insolation maxima), especially due to the contribution of dissolved silica that is taken up preferably by diatoms. However, results stemming from a multi-parameter approach reveal that the fluvial supply of degraded OM and black carbon (BC) associated with fine-grained sediments from soil erosion is a decisive factor for the preservation of marine OM and, in addition, significantly influences the geochemical signature of bulk and terrigenous OM. Riverine and eolian supply of  $\text{C}_4$  plant matter, as well as enhanced concentrations of BC, during arid and arid-to-humid transitional climate stages, may lead to a severe underestimation of terrigenous organic carbon, if its amount is calculated from bulk isotopic ratios using binary end-member models. During the humid stages, it is the massive supply of  $^{13}\text{C}$ -enriched soil OM with low  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios that may suggest a mainly marine composition of bulk OM. In fact, terrigenous OM governs bulk OM geochemical signatures in the sediments of the Congo deep-sea fan, a result that is contradictory to earlier studies, especially to the conventional interpretation of the bulk  $\delta^{13}\text{C}_{\text{org}}$  signal.

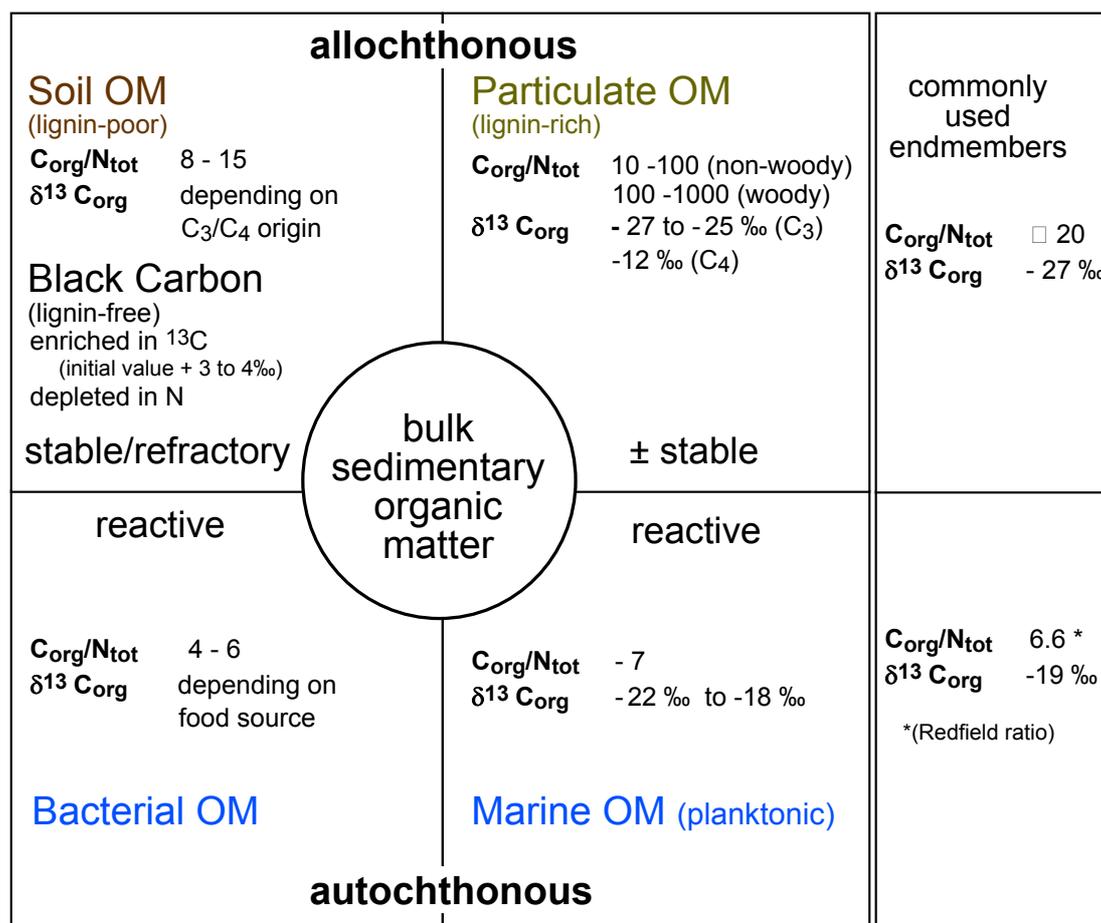
## 4.2 Introduction

The significance of terrigenous OM in the contemporaneous ocean (see Eglinton and Repeta, 2003, for review) and in deep-sea sediments is an important yet currently poorly constrained aspect of the global organic carbon cycle. Several recent studies argue that supply of riverine and eolian organic matter (OM) plays a greater role in bulk organic carbon accumulation in deep-sea basins than is commonly considered (e.g., Verardo and Ruddiman, 1996; Meyers, 1997; Goñi et al., 1998; Wagner and Dupont, 1999; Onstad et al., 2000; Stein and Fahl, 2000; Wagner, 2000; Stein and McDonald, 2003; Wagner et al., 2003). Moreover, the influence of climate variations on the quantity and quality of terrigenous OM exported to the ocean is not well understood. The conventional assumption is that deposition of terrigenous OM is restricted to the shelf and upper slope during periods of high sea-level stand (e.g., Jones, 1983). Together with generally elevated marine productivity, continental margins are considered primary sites for modern organic carbon production, burial, and export (Bauer and Druffel, 1998). The established view of a deep ocean devoid of significant terrigenous OM contributions is challenged by investigations on the modern Congo fan (Müller et al., 1994; Wagner et al., 2003) that clearly identify this deep-sea fan as a corridor where terrigenous OM escapes the shelf and is transported to the abyssal eastern tropical Atlantic Ocean. The dramatic effect of glacial sea-level lowstands on the downslope entrainment of terrigenous organic carbon has been shown for the Late Quaternary Amazon Fan (Schneider et al., 1997b, Schlünz et al., 1999). There, it has been proposed that part of the terrigenous OM from the Amazon reaches as far as the Ceará Rise (Rühlemann et al., 1996) and may even be advected to the deep Atlantic basins (Zabel et al., 1999).

The Congo River is the most important source of terrigenous organic carbon in the modern eastern Equatorial Atlantic (Showers and Angle, 1986). Previous high-resolution geochemical studies at site GeoB 1008 on the southern Congo deep-sea fan (Schneider et al., 1994, 1997a) suggest that organic sedimentation over the last 200 kyrs was governed by orbital-forced fluctuations in atmospheric circulation that triggered upwelling and marine productivity along the western equatorial African continental margin as well as continental aridity-humidity cycles (Pokras and Mix, 1985; deMenocal, 1995). The dominance of precessional-forced insolation changes on African climate and thus on the distribution of vegetation zones has been confirmed by numerous marine pollen records from the eastern equatorial Atlantic (e.g., Frédoux, 1994; Ning and Dupont, 1997; Jahns et al., 1998; Dupont, 1999; Dupont et al., 2000). The general link between organic sedimentation and orbital forcing persisted over the past 1.2 Myrs on the Congo deep-sea fan (Holtvoeth et al., 2001). The frequency in orbital forcing, however, experienced a fundamental change from dominant obliquity cycles to the large-amplitude eccentricity cycles of the Milankovitch chron (past 0.7 my) associated with the Mid-Pleistocene Revolution (Dupont et al., 2001). This general transition in climate forcing was characterized by prominent changes in atmospheric moisture content that controlled aridity on the African continent via fluctuations in sea-surface temperature and strength of the African monsoon (Scheffuß et al., 2003).

In addition to fluctuations in quantity and composition of bulk sedimentary OM in sediments from the late Quaternary Congo Fan, Holtvoeth et al. (2001) also identified pronounced cyclic variations in reactivity of the bulk OM at ODP Site 1075. These “bulk OM reactivity-cycles”

were attributed to changes in the relative proportions of oxidized versus non-oxidized terrigenous (mainly inertinite vs. vitrinite) and autochthonous (marine and bacterial) organic compounds. Since bulk OM reactivity is the primary factor determining microbial turnover rates in marine deposits (see reviews in Jørgensen, 1999; Rullkötter, 1999), it is essential to better assess and characterize the different sources and fate of reactive OM. In such cases a complex mixture of inputs from different additional sources must be considered. In addition to algal sources potential contributions include (i) particulate OM from relatively fresh vascular plant tissue (POM), (ii) pre-oxidized soil-derived OM, (iii) thermally altered (burned) OM (black carbon/BC, comprising a continuum of combustion products with decreasing reactivity from slightly charred biomass to char, charcoal and soot) (Schmidt and Noack, 2000), and (iv) OM from bacterial biomass (Figure 4.1). Variable admixture of this broad spectrum of continental, marine, and microbial OM and subsequent selective degradation of specific organic sub-fractions may result in a complex signature for the residual TOC in the geological record. This combination of inputs and degradation processes confounds attempts to establish conservative factors, such as changes in OM supply, climate or ocean properties.



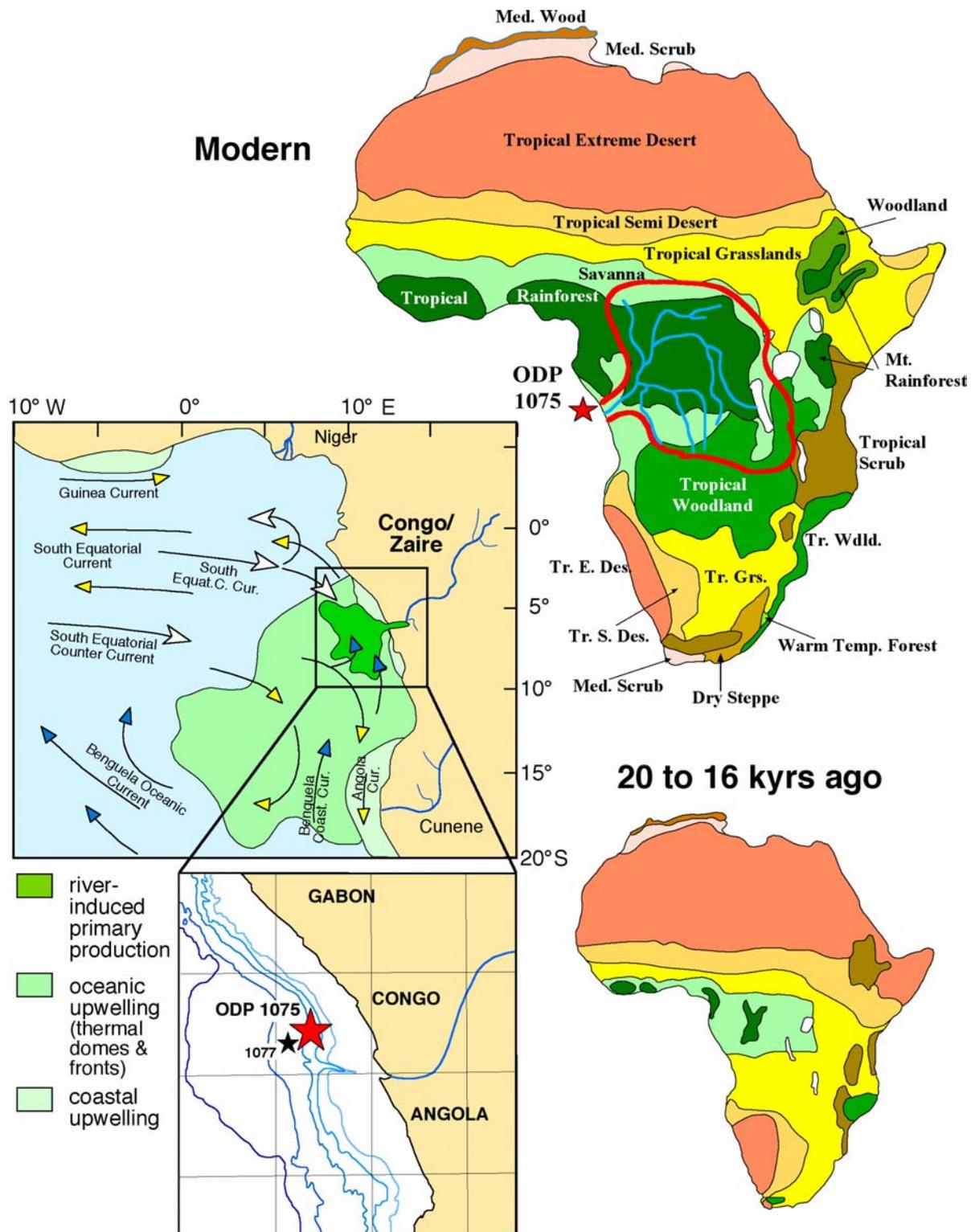
**Figure 4.1:** Sources of organic matter (OM) in river-influenced continental margin sediments and geochemical properties of selected, commonly used diagnostic parameters (according to Fry and Sherr, 1984; Hedges et al., 1986; Müller et al., 1994; Goñi and Hedges, 1995; Hedges et al., 1997; Ruttenger and Goñi, 1997).

In this study we combine established bulk organic geochemical parameters ( $\delta^{13}\text{C}_{\text{org}}$ ,  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$ ) and parameters sensitive to degradation (sulfate reduction index,  $\text{C}_{\text{org}}/\text{C}_{\text{org}}^*$ ) as well as reactivity of bulk OM (lm/hm ratio) with molecular parameters from lignin oxidation (S/V, C/V,  $\Lambda$ , acid/aldehyde ratios) to develop a model in an attempt to explain the record of organic carbon burial in river-influenced continental margin sediments. Although desirable, this study does not provide the properties for each of the individual organic compounds contributing to the bulk OM but addresses only the principle characteristics of the bulk OM. Our research area is the Congo deep-sea fan at ODP Site 1075 and the stratigraphic interval spans the past 1.2 million years (approximately 120 meters section).

### 4.3 Depositional setting and geological background

The Congo River drains the second largest catchment area of the world and contributes 3.9 % ( $13 \cdot 10^6$  t C/year) of the global annual supply of terrigenous organic carbon into the ocean (Martins and Probst, 1991). About 38% ( $1300 \text{ km}^3/\text{year}$ ) of the yearly run-off from Africa occurs through the Congo (N'Koukou and Probst, 1987). The strong influence of the river load on long-term marine sedimentation on the adjacent continental margin is evident from the existence of the Congo deep-sea fan. The Congo reveals 11 to 17 times lower suspended sediment loads than other major rivers (Schlünz and Schneider, 2000). This difference is attributed to the morphology of the catchment area and regional precipitation patterns (Eisma, 1982, N'Koukou and Probst, 1987). Due to the narrow (~50 km wide) continental shelf in front of the Congo mouth and the presence of a central canyon that begins within the estuary of the river (Figure 4.2), part of the riverine terrigenous OM is transported directly to the deep-sea even during modern and past interglacial sea-level high-stands. Therefore, late Quaternary changes in the supply of terrigenous OM should be well preserved in sediments of the Congo deep-sea fan.

The modern vegetation in the Congo catchment area is dominated by tropical rainforest whose productivity is governed by the West-African monsoon (Ning and Dupont, 1997). Late Quaternary insolation cycles strongly influenced African paleoclimate that fluctuated from arid conditions during cold glacial and interglacial periods to humid conditions associated with their warm counterparts. Marine palynological records show that the savannah belts on both sides of the equator expanded during dryer climatic conditions to replace the tropical rainforest as the dominant type of vegetation in the Congo catchment area (e.g., Frédoux, 1994; Jahns et al., 1998; Dupont et al., 2001). The African grass-savannah dominates at the transition to full desert conditions and exhibits better growth conditions for  $\text{C}_4$  plants (Tyson, 1995). Climate-driven changes in atmospheric  $\text{CO}_2$  concentrations caused a repetitive expansion or contraction of the  $\text{C}_4$  plant habitat (Jolly and Haxeltine, 1997; Cerling et al., 1997; Huang et al., 1999b). It is therefore expected that the amount and composition of terrigenous OM exported by the Congo river and supplied via eolian supply has fluctuated in response to the Late Quaternary glacial-interglacial cycles. Compound-specific carbon isotope data of terrigenous plant waxes (long-chain  $\text{C}_{25}$  to  $\text{C}_{35}$  odd-numbered  $n$ -alkanes) analysed in surface sediments of the eastern Angola Basin and in 1.2 to 0.45 Ma old sections at ODP Site 1077, located down-slope ODP Site 1075 on the Congo fan, confirm regional and temporal fluctuations in wind-transported terrigenous OM from  $\text{C}_4$  plant sources and thus African aridity (Schefuß et al, 2003).



**Figure 4.2:** African vegetation zones under modern and past glacial climatic conditions (Adams and Faure, 1995, [www.soton.ac.uk/~tjms/adams1.html](http://www.soton.ac.uk/~tjms/adams1.html)) with superimposed modern Congo catchment area (red line). (a) Surface and subsurface currents, and highly productive areas in the modern eastern Equatorial Atlantic (modified after Schneider et al., 1994). Black arrows identify cold surface currents, open arrows warm surface currents, and hatched arrows undercurrents. High-productivity areas are marked by different green tints: dark – river plume with river-induced upwelling; medium – oceanic upwelling with shallow thermocline, thermal domes and fronts; light – coastal upwelling. (b) Position of ODP Sites 1075 and 1077 on the Congo deep-sea fan (Wefer et al., 1998).

#### 4.4 Lithology, stratigraphy, and methods

Late Quaternary sections of Site 1075, situated on the northern part of the Congo deep-sea fan in 2996 m water depth, are a bioturbated monotonous sequence of greenish-grey clay containing relicts of diatoms and varying amounts of nannofossils, e.g. silicoflagellates, radiolaria, and foraminifera (Wefer et al., 1998). The stratigraphy of Late Quaternary sections of ODP Site 1075 was originally set up by correlation of high-resolution magnetic susceptibility records of Site 1075 and the neighbouring Site 1077 (see Figure 4.2b for core positions), where a stratigraphy based on oxygen isotope ratios of *Globigerina ruber pink* was established by Dupont et al. (2001). Both magnetic susceptibility records reveal pronounced minima and maxima, which parallel each other and apparently follow typical glacial/interglacial patterns. Generally, interglacial (more humid) stages are characterized by higher contents of magnetizable minerals compared to glacial (more arid) stages due to an enhanced riverine run-off during the former intervals. To accommodate the excellent visual correlation of the high-frequency (precessional) TOC records from both sites in sections younger than 1 Ma we refine the age model for ODP Site 1075 by correlation of the TOC profiles between 0 and 108.3 mcd (Table 4.1). Below, from 108.3 to 126.5 mcd, we used the stratigraphic framework of Dupont et al. (2001).

Depth 1077 (mcd)	Depth 1075 (mcd)	Age (ka)	Depth 1077 (mcd)	Depth 1075 (mcd)	Age (ka)
1,99	1,65	9,20	68,95	54,01	454,75
4,69	3,15	22,72	69,87	54,74	462,80
7,99	6,65	39,64	70,25	54,94	466,13
9,49	8,15	47,34	71,17	55,64	474,17
11,59	10,65	58,20	73,95	56,58	495,26
13,99	12,05	70,61	75,65	57,58	507,37
15,42	13,15	78,00	77,31	58,08	519,21
16,89	14,65	88,20	78,43	59,58	527,19
17,99	15,65	95,84	79,63	61,01	535,74
19,49	16,55	105,21	82,93	64,05	558,31
22,19	18,65	120,84	85,23	65,05	573,01
23,99	20,05	143,15	87,83	67,10	589,62
26,19	21,91	172,24	90,23	69,14	604,96
26,79	22,81	180,17	91,23	69,64	611,35
30,19	24,31	212,55	92,53	70,68	619,84
31,69	25,41	222,46	93,63	71,73	627,32
35,19	29,41	243,95	96,63	74,19	647,11
36,29	30,91	249,83	98,43	75,69	658,99
38,19	31,83	259,98	99,03	76,29	662,95
39,69	32,83	268,00	101,43	77,83	678,78
40,37	33,33	271,28	103,33	78,73	694,92
46,37	35,33	300,17	104,83	80,27	726,12
48,67	36,83	311,25	106,33	81,77	741,56
51,07	39,23	322,81	107,77	82,87	759,86
56,75	43,25	362,38	109,27	84,53	773,89
58,65	45,25	383,01	110,37	85,50	777,86
60,95	47,35	394,62	112,27	86,50	786,55
62,49	48,25	402,39	115,67	89,73	825,91
65,79	51,71	419,04	117,27	91,28	843,77
67,66	52,71	440,01	118,37	92,78	853,68
68,15	52,91	445,85	119,17	93,28	863,72
68,50	53,21	450,02	119,87	94,65	873,84

Depth 1077 (mcd)	Depth 1075 (mcd)	Age (ka)	Depth 1077 (mcd)	Depth 1075 (mcd)	Age (ka)
120,97	95,15	883,94	130,77	102,53	971,06
122,17	95,65	894,96	132,27	103,53	984,14
122,87	96,51	901,39	136,47	108,33	1020,77
123,27	97,01	905,06	140,48	111,29	1053,56
123,67	97,33	908,73	146,35	118,09	1101,00
125,17	98,33	922,23	150,45	122,84	1132,00
126,77	99,73	936,18	152,06	124,71	1146,01
127,87	100,65	945,78	158,15	129,76	1199,01
128,67	101,05	952,75			

**Table 4.1:** Refined age model for ODP Site 1075 on the Congo fan based on the correlation of TOC profiles from ODP Sites 1075 and 1077 and on previous studies (Dupont et al., 2001); mcd = meters composite depth.

Total carbon, total organic carbon (TOC) and sulfur contents were measured using a Leco CS 300 (precision of measurement:  $\pm 3\%$ ). Assuming that microbial sulfate reduction is the main degradation process for sedimentary OM in the Congo fan deposits, we estimated the original content of organic carbon ( $C_{org}^*$ ) according to Littke et al. (1997) following the equation  $C_{org}^* = C_{org} + 2S * M_C/M_S$  ( $S$  = measured sulfur content,  $M_C$  = molecular mass of carbon,  $M_S$  = molecular mass of sulfur). The degradation rate of organic carbon is expressed as the ratio of the measured to the estimated original organic carbon contents ( $C_{org}/C_{org}^*$ ). This approach provides minimum estimates, taking into consideration that diffusive escape of  $H_2S$  from the sediment results in reduced pyrite precipitation in situ and thus in lower sulfur contents. Furthermore, additional oxic degradation may play an important role for OM sinking to greater water depths and its contact to oxic bottom water (Hartnett et al., 1998; Schubert et al., 2001). However, the oxygen exposure time of sedimentary OM at the Congo deep-sea fan is expected to be relatively short due to high accumulation rates of fine-grained sediment. The total amount of nitrogen was measured using a Heraeus CNS analyzer (precision of measurement:  $\pm 3\%$ ). A set of 23 selected samples from two core sections (213 - 330 ka, 519 - 585 ka) was examined for inorganic nitrogen contents. The samples were treated with a solution of KOB $r$ -KOH to convert all organic bound nitrogen into  $N_2$  following the method of Silva and Bremner (1966). The stable isotopic composition of bulk sedimentary organic carbon ( $\delta^{13}C_{org}$  vs. VPDB) was measured using a Heraeus Elemental Analyzer combined with a Finnigan MAT Delta S mass spectrometer (precision of the measurements:  $\pm 0.2\%$ ). Kerogen was classified according to Espitalié et al. (1977) using the Rock-Eval II device at the Research Center Jülich (precision of measurement for hydrocarbon peaks S1, S2, and carbon dioxide peak S3:  $\pm 5\%$ ; for  $T_{max}$ :  $\pm 1^\circ C$ ; Espitalié et al., 1985). The yields of hydrocarbons and  $CO_2$  were calculated from FID and TCD responses, respectively, by means of a gas chromatographic integration system (VAX-Multichrom 2.2). Hydrocarbons and hydrocarbon-like components that are generated from the kerogen fraction of the bulk sediment were quantitatively detected within the S2 temperature window. Holtvoeth et al. (2001) observed that kerogen of samples from ODP Site 1075 generates hydrocarbons in two temperature sub-windows resulting in a distinct double peak of the bulk S2 peak. Variations in the relative proportions of hydrocarbons are generated from two principally different

organic sources, i.e. low-mature and high-mature OM. Quantification of the S2 partial peak areas ( $S2_{lm}/S2_{hm}$ ) resulted in the establishment of a new proxy for bulk OM reactivity, the "low-mature/high-mature ratio" (lm/hm ratio). This proxy was applied to Late Quaternary sections of ODP Site 1075 to infer climate-driven fluctuations in reactivity of bulk sedimentary OM (Figure 4.3). Though there are certainly differences in OM reactivity within the two major groups of low-mature and high-mature OM (e.g. POM compared to MOM in the low-mature fraction) further differentiation of their individual reactivity is not feasible using a standard Rock-Eval temperature program (heating rate: 25°C/min from 300°C to 550°C terminal temperature).

Organic petrological observations were performed using a Zeiss Axiophot. Bulk sediment samples were embedded in a low-viscosity resin, then ground and polished using a Logitech PM 2A (for details see Wagner, 1998, 1999a). The organic particles were sorted by grain size in 5 classes: <2 µm, 2-5 µm, 5-10 µm, 10-20 µm, and >20 µm. For the calculation of inertinite/vitrinite ratios (I/V) only particles larger 5 µm were used, as the determination of these maceral groups is often problematic for very small particles.

49 samples from three core sections (A: 150 to 85 ka, B: 270 - 210 ka, and C: 540 - 340 ka, see Figure 4.3) were selected for terrigenous biomarker studies (analysis of lignin oxidation products). Sections A and B both include transitions from glacial to interglacial climate stages (OIS 8-7, 6-5) at relatively high amplitudes of the insolation record and were therefore chosen for more detailed investigation. The third section C was sampled at lower time resolution from an interval with lower amplitudes of insolation to provide additional data for cross-relations. The analytical procedure (CuO-oxidation) was carried out according to Goñi and Hedges (1992). The extracted lignin phenols were analysed using a Hewlett Packard 6890 Series GC system. Two parallel capillary columns (J&W Scientific db1 and db 1701; 30 m \* 0.25 mm, 0.25 µm film) were used for chromatography. Opsahl and Benner (1995) demonstrate that the ester-bound cinnamyl phenols, *p*-coumaric acid and ferulic acid, are the lignin components most susceptible to degradation processes. To overcome that problem they suggested the use of only the sum of the six lignin-derived syringyl and vanillyl phenols ( $\Lambda_6$ ) instead of the "classical"  $\Lambda$  that sums syringyl, vanillyl, and cinnamyl phenols ( $\Lambda_8$ ). Indeed, the determination of peak areas turned out to be problematic for the ester-bound components because the latter was strongly affected by co-elution effects. The uncertainty of assignment of the ferulic acid signal results in a mean deviation of 16 % for the ratio of cinnamyl to vanillyl phenols (C/V). However,  $\Lambda_6$  and  $\Lambda_8$  in this study show a very good correlation ( $r^2=0.99$ ) indicating that coumaric and ferulic acid, forming the cinnamyl group, are not more strongly degraded after deposition than other lignin components. The lignin data presented in this study therefore are given as  $\Lambda_8$  and as the established ratios of individual groups C/V, S/V, (Ad/Al)<sub>v</sub>, and (Ad/Al)<sub>s</sub>. Duplicate CuO oxidation and extraction runs were performed for 16 samples and the obtained lignin phenols were analysed in different GC-runs. The resulting mean deviations of the lignin parameters range from 7 % for S/V, to 17% for (Ad/Al)<sub>v</sub> (Table 4.2). Regarding primary differences in lignin yields of the various terrigenous organic fractions (POM, soil OM, BC; compare Figure 4.1) we emphasize that  $\Lambda_8$  is not representative for the total terrigenous OM fraction and therefore can hardly be used to estimate marine versus terrigenous fractions of the bulk OM. Instead, variations in concentration and

accumulation of lignin result from a combination of various processes, in principle changing riverine supply of terrigenous OM and alternating relative shares of the lignin sources. All geochemical data presented in this study are available at <http://www.pangaea.de>.

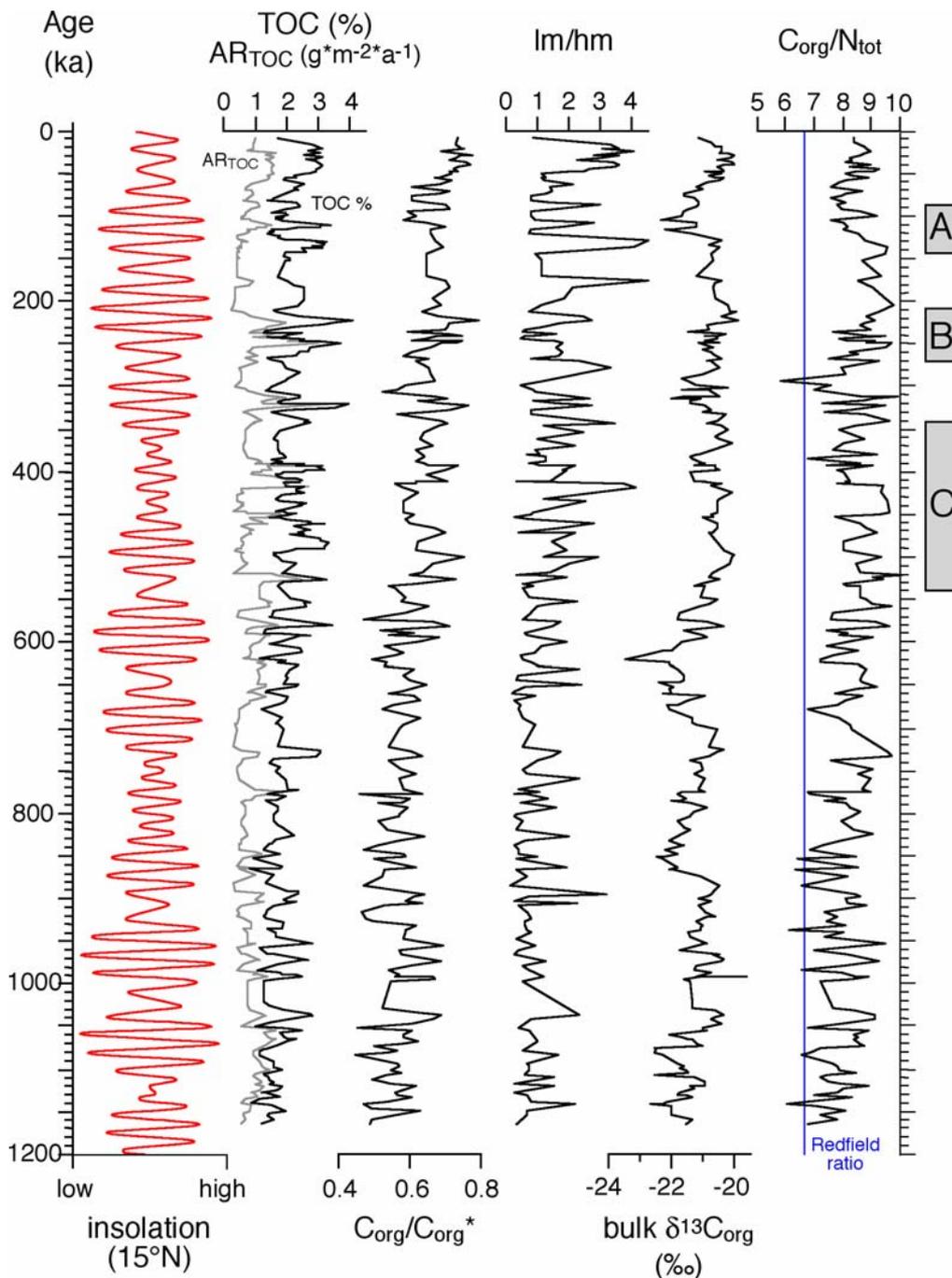
	$\Lambda_8$ (mg/gTOC)	$\Lambda_6$ (mg/gTOC)	S/V	C/V	(Ad/Al) <sub>v</sub>	(Ad/Al) <sub>s</sub>
<b>Range</b>	0.066 - 0.373	0.057 - 0.316	0.47 - 1.38	0.15 - 0.39	0.47 - 1.74	0.26 - 1.94
<b>Mean value</b>	0.151	0.130	0.87	0.28	0.72	0.46
<b>Mean deviation</b>	16 %	14 %	7 %	13 %	17 %	14 %

**Table 4.2:** Range, mean value, and mean deviation of parameters from lignin oxidation; S = syringaldehyde + acetosyringone + syringic acid, C = *p*-coumaric acid + ferulic acid, V = vanillin + acetovanillone + vanillic acid [mg/100mgTOC];  $\Lambda_8 = S + C + V$ ,  $\Lambda_6 = S + V$ ; (Ad/Al)<sub>v</sub> = vanillic acid/vanillin, (Ad/Al)<sub>s</sub> = syringic acid/syringaldehyde.

## 4.5 Results

### 4.5.1 Data

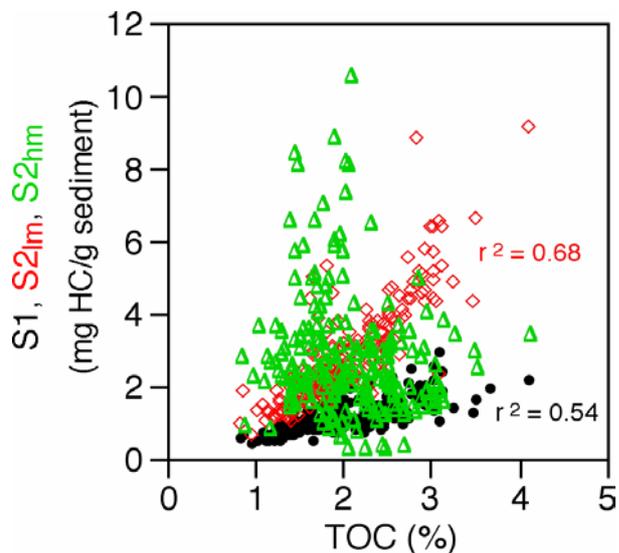
At ODP site 1075, late Quaternary sediments of the Congo deep-sea fan contain 0.8 to 4.2 % total organic carbon (average TOC is 2.1 %, Figure 4.3; Holtvoeth et al., 2001). Degradation rates ( $C_{org}/C_{org}^*$ ) indicate that (at least) 25-55 % of the organic carbon is mineralized under sulfate reducing conditions. The ratios of hydrocarbons released from low-mature (high-reactive) and high-mature (low-reactive) OM (lm/hm ratio) range from 0.2 to 4.5. The latter parameter was initially established as new bulk OM-reactivity proxy that bases on the relative proportions of hydrocarbon yields from low-mature (reactive) and high-mature (less-reactive) organic fractions obtained in the S2 temperature window during Rock-Eval pyrolysis (see Holtvoeth et al., 2001, for more details). Notably, there is a gradual decrease in baseline lm/hm values from about 1.0 at the core top to about 0.2 at 650 ka suggesting a progressive relative enrichment of a high-mature (more stable) organic compound with increasing depth. Bulk OM reactivity (lm/hm ratio) and TOC are generally positive correlated ( $r^2 = 0.4$ ) revealing the best correlation in the upper 20-30 m of the record (125-0 ka:  $r^2=0.93$ , 250-0 ka:  $r^2=0.70$ , respectively).



**Figure 4.3:** Records from elemental analysis (TOC,  $C_{org}/N_{tot}$ ), mass spectrometry (bulk  $\delta^{13}C_{org}$ ), and Rock-Eval pyrolysis (Im/hm) of Late Quaternary sections from ODP Site 1075 compared to the record of insolation at  $15^{\circ}N$  (from Holtvoeth et al., 2001).  $C_{org}/C_{org}^*$  shows the (minimum) degradation rate of bulk organic carbon, estimated based on microbial sulfate reduction only. Note that the  $C_{org}/C_{org}^*$  record differs from the record of  $C_{org}/S_{tot}$  ratios (range 0.6 to 2.9) only by its amplitudes as both parameters are strongly exponentially correlated ( $r_{exp.}^2 = 1$ ).

Figure 4.4 illustrates the relationship of TOC and the amount of hydrocarbons generated from immature ( $S_1$ ), low-mature ( $S_{2_{lm}}$ ), and high-mature OM ( $S_{2_{hm}}$ ). The data support the conclusion that variations in bulk TOC are mainly determined by the concentration of labile OM (represented by HC from  $S_1$  and  $S_{2_{lm}}$ ). Accordingly, progressive degradation of low-

mature OM results in decreasing TOC contents and relative enrichment of high-mature OM. Notably, the highest amounts of hydrocarbons are not released from the low-mature organic fraction at highest TOC concentration but instead are recognized in samples with less than 2% TOC (background level at Site 1075) and within the high-mature fraction. This observation is opposite to what may be expected, however, it confirms that the fraction of high-mature OM is not inert at all. We infer as for the low-mature organic fraction that high-mature OM in Congo fan deposits is composed of a variety of terrigenous organic sources. These sources may include contribution of reworked peat/soil/swamp OM and inert organic carbon (charcoal or dead carbon). Peak hydrocarbon generation in low TOC samples must be related to the presence of OM from these sources.

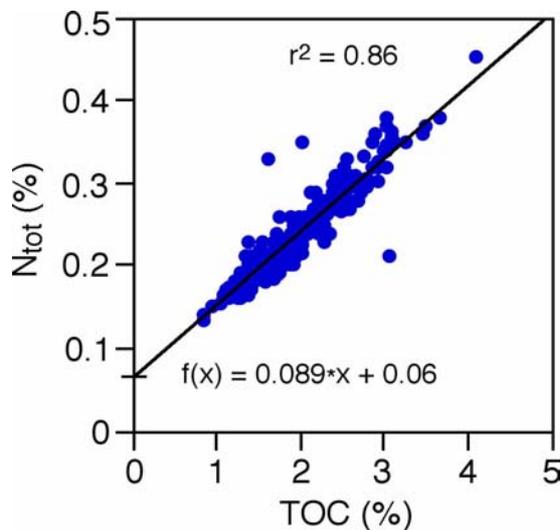


**Figure 4.4:** Hydrocarbon (HC) generation of ODP Site 1075 samples represented by S1 (black dots), S2<sub>lm</sub> (open diamonds), and S2<sub>hm</sub> (open triangles) yields relative to TOC contents. TOC is mainly shaped by low-reactive OM generating HC's in the S1 and S2<sub>lm</sub> temperature windows. Samples with low TOC are dominated by high-mature OM. Notably, this fraction generates astounding high HC quantities (S2<sub>hm</sub>) that are comparable to or even exceed those from low-mature OM. The HC generation capacity of the high-mature organic fraction supports the assumption that a variety of continental sources contributes to that fraction.

Bulk  $\delta^{13}\text{C}_{\text{org}}$  values range from -19 to -23.5 ‰ (Figure 4.3) (Holtvoeth et al., 2001). Application of a conventional binary mixing equation for marine and C<sub>3</sub> terrigenous organic matter (-18 ‰ and -27 ‰, respectively) suggests that between 18 % and 61 % (average 35 %) of the bulk OM is continental in origin assuming only the presence of a single isotopically light terrigenous organic fraction (C<sub>3</sub> plant remains). TOC contents correlate well with calculated amounts of the isotopically heavy end-member fraction (marine/bacterial OM, C<sub>4</sub> plant matter,  $r^2=0.94$ ) but not with the <sup>13</sup>C-depleted one ( $r^2=0.27$ ). Highest amounts of isotopically light terrigenous OM (> 40 %) occur only in samples with less than 2.5 % TOC, whereas samples with higher TOC (>2.5 %) typically imply less than 30 % light terrigenous OM.

$\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios range from 5.8 to 10.1 (8.3 on average) over the stratigraphic record (Holtvoeth et al., 2001). Organic carbon and total nitrogen yields are strongly correlated ( $r^2 = 0.86$ , Figure 4.5). The intercept point of the regression line for 0 % TOC at 0.06 %  $\text{N}_{\text{tot}}$  provides evidence for additional contribution of nitrogen from an inorganic source such as ammonium bound to clay minerals. Investigation of samples from sections B and C confirm the implications from  $\text{N}_{\text{tot}}/\text{TOC}$  relationships as they reveal that 8 % to 16 % of the total nitrogen content is inorganic. TOC and organic nitrogen show an excellent correlation

( $r^2=0.97$ ) for all samples.  $C_{org}/N_{org}$  ratios range from 8.1 to 11.1 (average 9.7) and thus are 14 % higher than the ratios of TOC and total nitrogen. Ratios of inorganic to organic nitrogen ( $N_{inorg}/N_{org}$ ) slightly increase from 0.14 to 0.16 with increasing depth. Extrapolation of this trend would result in approximately 20 %  $N_{inorg}$  of  $N_{tot}$  at the bottom of the profile. The good correlation of  $C_{org}/N_{org}$  with  $C_{org}/N_{tot}$  ratios ( $r^2=0.92$ ), however, justifies the use of total nitrogen contents to detect changes in bulk OM quality and degradation.

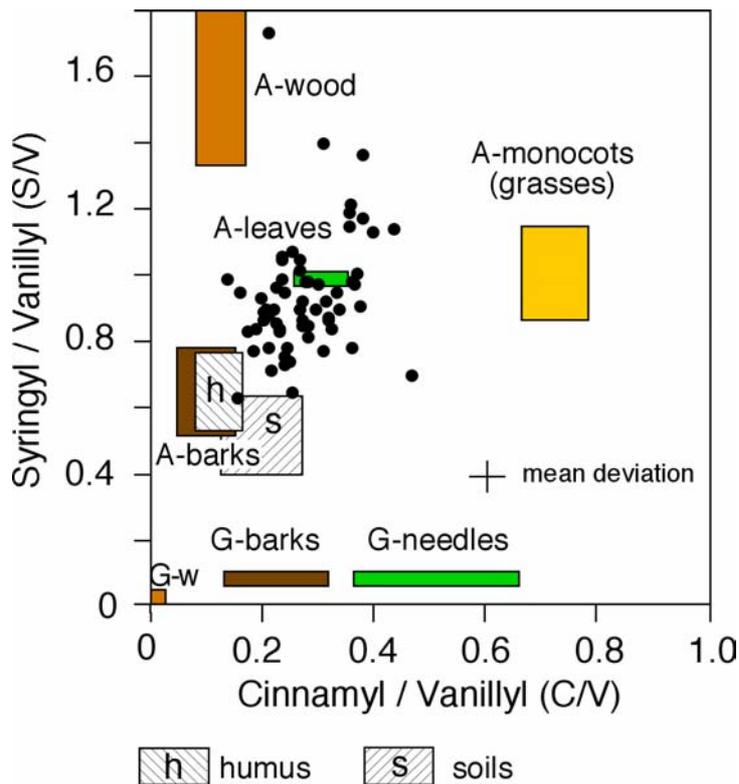


**Figure 4.5:** Relation of total organic carbon (TOC) and total nitrogen ( $N_{tot}$ ) in late Quaternary sections of ODP Site 1075; intercept of regression line at 0,06 %  $N_{tot}$  for zero TOC suggests that part of the total nitrogen is inorganic.

Superimposed on short-term fluctuations in primary composition of sedimentary OM long-term trends over the entire Late Quaternary record are observed (Figure 4.3). Specifically, TOC,  $C_{org}/C_{org}^*$ ,  $lm/hm$ , and  $C_{org}/N_{tot}$  ratios generally decrease with depth while bulk  $\delta^{13}C_{org}$  shifts to slightly lighter values. The consistency of these trends has been used to argue for the selective enrichment of a more stable terrigenous organic fraction in response to long-term diagenesis (Holtvoeth et al., 2001).

The C/V and S/V ratios (cinnamyl/vanillyl, syringyl/vanillyl) from lignin analysis range from 0.15 to 0.47 and from 0.61 to 1.71, respectively (Figure 4.6). The projection of these ratios in a general scheme to classify plant tissue (according to Hedges and Mann, 1979b; Goñi and Hedges, 1992; Farella et al., 2001) reveals that terrigenous OM in Late Quaternary deposits of the Congo fan mainly originates from non-woody angiosperm tissues with variable admixture of angiosperm wood (mainly barks) and soil or humus OM. Given the geographic and geological context of the Congo catchment area with its extensive rain forest and swamp areas, a preferential admixture of soil OM appears plausible.

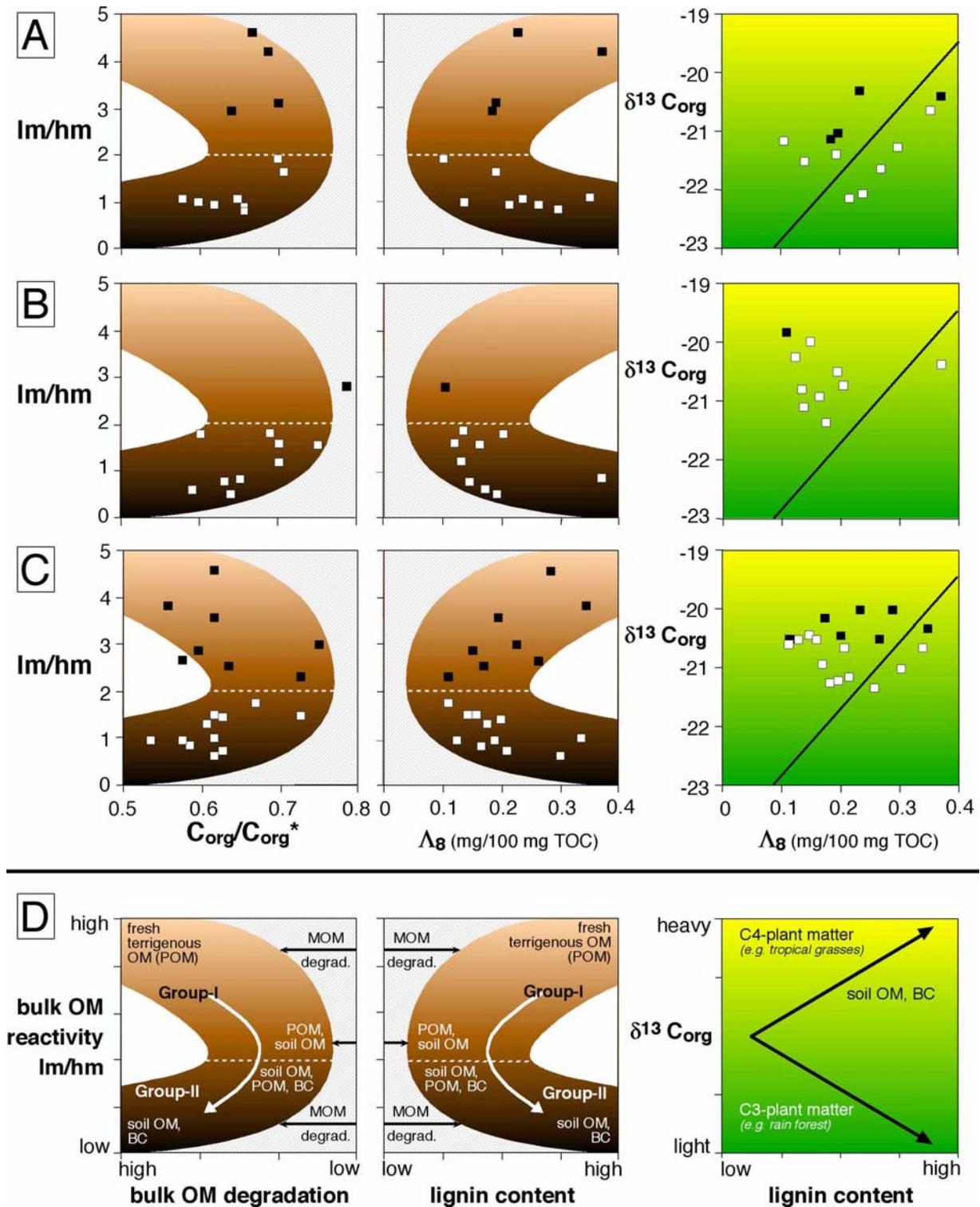
**Figure 4.6** (next page): Ratios of specific lignin phenols (S/V, C/V) from lignin chemistry of selected samples from ODP Site 1075. According to Goñi and Hedges (1992) and Farella et al. (2001), terrigenous OM in the sediments of the Congo fan mainly derives from angiosperm leaves and barks, or soil and humus with admixture of angiosperm wood and grass; V = vanillin + acetovanillone + vanillic acid in mg/100 mg TOC, S = syringaldehyde + acetosyringone + syringic acid in mg/100 mg TOC, C = *p*-coumaric acid + ferulic acid in mg/100 mg TOC; A = angiosperm, G(w) = gymnosperm wood.



#### 4.5.2 Relationship of bulk OM reactivity, degradation rates, and lignin phenol yields

The relationships of bulk OM reactivity ( $lm/hm$ ), degradation rates, and lignin phenol yields provide insights on primary differences in the composition of bulk OM and their corresponding susceptibility to degradation (Figure 4.7). The distribution of data from the Congo site reveals two different groups of samples, i.e. Group-I and Group-II. All samples represent residual mixtures of autochthonous (marine/bacterial) OM, fresh particulate terrigenous-derived OM (POM), and BC-bearing soil OM, the latter components being selectively enriched with diagenesis. Remarkably, there are no samples with low contents of lignin phenols and high ratios of both,  $C_{org}/C_{org}^*$  and  $lm/hm$ , a combination that would support a dominance of high-reactive, non-degraded autochthonous OM. This circumstance proposes that a large part of the primary autochthonous OM has already been selectively degraded, and thus does not contribute an important share to the bulk OM in Congo deep-sea fan sediments. Instead, variable fractions of fresh, degraded, and inert terrigenous OM determine the total organic signature. The main source of lignin in G-I samples is reactive POM (mainly tissue from fresh plants growing in the Congo catchment area). A decrease in this lignin-rich source goes along with a continuous increase in lignin-poor soil OM resulting a drop in bulk OM reactivity (expressed as  $lm/hm$  ratios) and lignin concentrations. At moderate bulk OM reactivity levels (corresponding to  $lm/hm$  ratios of about 2), a principle change of the main lignin source from POM to soil OM occurs. This transition leads to a progressive decline of POM while relative proportions of soil OM increase. Finally, the relative amounts of soil OM in G-II samples with lignin phenol concentrations comparable to those of G-I samples must significantly exceed the proportions of POM in G-I samples given the primarily low lignin yields of soil OM. Most likely, the described change from POM to

soil OM as the main lignin source is accompanied by a relative increase in BC associated with soil OM that reduces bulk OM reactivity to its minimum.



**Figure 4.7:** Relationship of bulk OM degradation ( $C_{\text{org}}/C_{\text{org}}^*$ ) and reactivity ( $\text{Im/hm}$  index), lignin concentration ( $\Lambda_{8/6}$ ), and bulk carbon isotopic signatures (bulk  $\delta^{13}\text{C}_{\text{org}}$ ) in samples from three time intervals of ODP Site 1075 (for assignment of time intervals A-C see Figure 4.3), and (D) a conceptual model derived from the data. Accordingly, the main source of lignin in relatively reactive Group-II samples ( $\text{Im/hm} > 2$ ) is particulate terrigenous OM (POM), whereas lignin derives mainly from

degraded soil OM in low-reactive ( $lm/hm < 2$ ) Group-II samples. Shaded grey areas represent variable relative proportions of marine OM that have been degraded (MOM degrad. = marine OM degradation, effectiveness illustrated by black arrows) leading to elevated degradation rates (low  $C_{org}/C_{org}^*$  values); white arrow indicates progressive change from POM- to soil OM-dominated river load, from upwelling- to river-controlled nutrient supply, respectively (see text for further explanation). In both extreme scenarios, degradation of labile MOM is very effective, only during the transitional stage ( $lm/hm$  ratios around 2) degradation and probably also primary production is reduced. Influence of  $^{13}C$ -enriched OM ( $C_4$  plant matter,  $C_4$  soil OM, BC) is indicated by positive correlation of lignin yields with bulk  $\delta^{13}C_{org}$  for samples either enriched in soil OM or with maximum amounts of POM (presumably from  $C_4$  habitats).

The results obtained are summarized in a conceptual model (illustration D in Figure 4.7). It is important to realize that two major processes determine the organic geochemical signature of bulk OM in the Congo deep-sea fan sediments: (i) the change of the primary composition in response to climate variability and (ii) microbial degradation of labile (mainly marine) biomass during and after deposition. The model proposes that maximum  $C_{org}/C_{org}^*$  ratios are related to conditions of massive supply of labile OM to the sediment, thus to enhanced marine primary productivity stimulated either by elevated upwelling- or river-induced nutrient supply. Accordingly, G-I samples (maximum  $lm/hm$  values, reactive POM) represent periods of minimum soil erosion and supply, likely in response to arid climate conditions in central Africa and reduced fluvial run-off. Enhanced trade intensity during these periods should have fostered primary productivity to produce elevated  $C_{org}/C_{org}^*$  ratios in the sedimentary record. In contrast, G-II samples (minimum  $lm/hm$  ratios) document periods of humid climatic conditions. These were associated with massive erosion and supply of soil OM from high-productive rainforest areas in tandem with enhanced fluvial nutrient supply forcing marine primary productivity and flux of labile OM. The transition from wind- to river-induced high-productivity is characterized by minima in marine primary production consequently leading to lowest degradation rates. Obviously, the proposed conceptual model of interrelated bulk OM primary composition and degradation on the Congo Fan is intimately linked to the temporal development of environmental conditions and climate, which is discussed below (e.g. see Figure 4.11).

The contribution of  $C_4$  plant matter, soil OM from  $C_4$  habitats, and BC adds terrigenous components to the bulk organic pool that may complicate the interpretation of the bulk OM isotopic signal due to the distinct enrichment of  $^{13}C$  especially in  $C_4$  plants ( $\delta^{13}C_{org} \approx -12$  ‰) but also in degraded soil OM and BC. In the absence of a dominant marine organic fraction,  $C_4$  plant matter from POM or soil OM as well as BC may at least be detectable from the bulk isotopic composition. Significant influence of  $^{13}C$ -enriched OM on the bulk  $\delta^{13}C_{org}$  signal is expected only for samples with highest contents of lignin, i.e. either from reactive POM (Group-I), from soil OM (Group-II), or for samples enriched in BC (Group-II,  $lm/hm \ll 2$ ). Indeed, the relationship of  $\Lambda_8$  as a gross indicator of the two principle types of terrigenous OM (POM, soil OM) and bulk  $\delta^{13}C_{org}$  reveal a positive correlation for the most lignin-rich samples supporting the presence of “fresh”  $C_4$  tissue (for  $\Lambda_8 > 0.3$ , filled symbols right of trend line in Figure 4.7) and of diagenetically altered, probably BC-containing soil OM with low  $lm/hm$  values ( $\Lambda_8 > \sim 0.2$ , open symbols right of trend-line in Figure 4.7). Over the entire Late Quaternary record of site 1075 samples with  $lm/hm$  values  $< 1.5$  (Group-II) tend to have

slightly lower bulk  $\delta^{13}\text{C}_{\text{org}}$  values (-21.3 ‰ on average) than Group-I samples (-20.5 ‰) with  $\text{lm/hm}$  values  $> 2.5$  probably indicating that soil OM originates mainly from  $\text{C}_3$  habitats while POM contains an enhanced proportion of  $\text{C}_4$  plant remains.

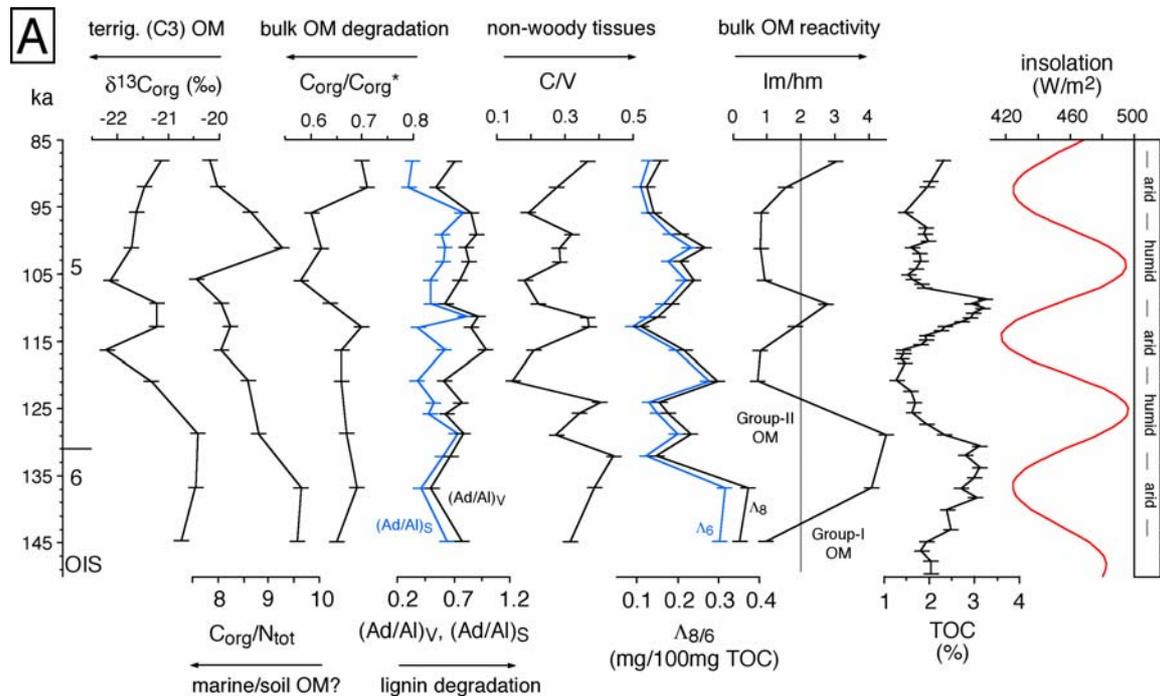
Results from organic petrological investigations strongly favour an important supply of fine-grained soil OM as almost 90 % of the non-fluorescent (terrigenous) macerals are smaller than 10  $\mu\text{m}$ , 67 % even smaller than 5  $\mu\text{m}$ . Though qualitative observations reveal the existence of terrigenous particles with distinct differences in the degree of oxidation (vitrinites and inertinites) a reliable quantification of these two terrigenous maceral groups is problematic due to the mean particle size. A more reliable estimation for the ratio of inertinite and vitrinite (I/V) is possible for terrigenous particles larger than 5  $\mu\text{m}$ . Accordingly, I/V ratios range from 0.24 to 1.0 (av. 0.56) indicating a predominance of moderately oxidized particles. The average I/V ratio is clearly lower for particles larger 10  $\mu\text{m}$  (I/V = 0.19) thus suggesting an increasing degree of oxidation with decreasing particle size. Indeed, the I/V ratio for particles smaller 5  $\mu\text{m}$  appears to be drastically increased (av. I/V = 0.95). However, this estimation is questionable for the reason mentioned above. Notably, high-fluorescent marine alginites and amorphous organic matter are rare in the Congo fan sediments. Instead, high-fluorescent particles of less than 2  $\mu\text{m}$  in size comprise almost 50 % of the observed marine and probably bacterial biomass. Based on organic petrology about 73 % on average of the bulk OM is terrigenous in origin, with minimum and maximum values of 83 % and 61 %, respectively.

To place the observed relationships of OM composition, degradation and reactivity in a stratigraphic and environmental context and to assess to which extend specific groups of lignin were selectively affected by degradation processes we next present the three proxy records together with other bulk geochemical and lignin-specific data for the two time slices with highest resolution (i.e. OIS 8 to 7 and OIS 6 to 5, Figures 4.8 and 4.9).

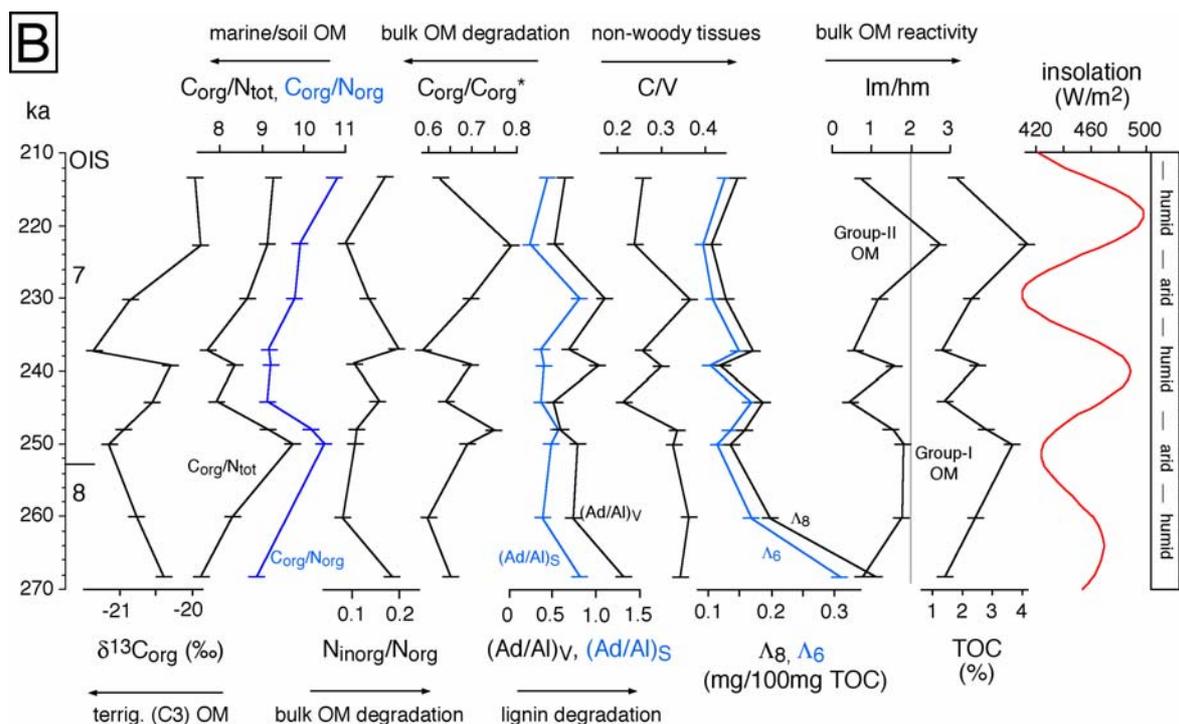
#### *4.5.3 Temporal and environmental context of OM variations (OIS 8 to 7 and OIS 6 to 5)*

During both time intervals the TOC record as well as the ratio of low-reactive to high-reactive OM ( $\text{lm/hm}$  ratio) run parallel (except for one single data point at 240 ka, Figure 4.8) and reveal a close relation to the precessional-forced record of insolation. This positive relationship already suggests a link between OM composition and abundance and climate-related depositional processes. Characteristically, maxima in TOC and bulk OM reactivity post-date insolation minima by about 3 - 5 kyrs (Figures 4.8 and 4.9). This time delay is a robust feature of the entire stratigraphic interval investigated as has been shown for the general phase relation between insolation and TOC content and accumulation over the past 1.2 million years (Wagner et al., 2003, Figure 4.10). Determining the specific time interval to the next insolation maximum for each sample and assigning each sample to 2-kyrs-time-windows as part of an idealized insolation cycle of 20 kyrs, the data from Congo Site 1075 clearly reveals a systematic coupling of bulk OM sedimentation or preservation with insolation. With increasing depth, however, the correlation fades-out due to long-term diagenesis and potential changes in the prominent orbital frequencies (e.g. associated with the mid-Pleistocene transition). The synchrony of  $\text{lm/hm}$  with TOC indicates that reactive OM

dominates slightly following insolation minima, while the relative share of more stable OM is preferentially linked to periods of highest or decreasing insolation.

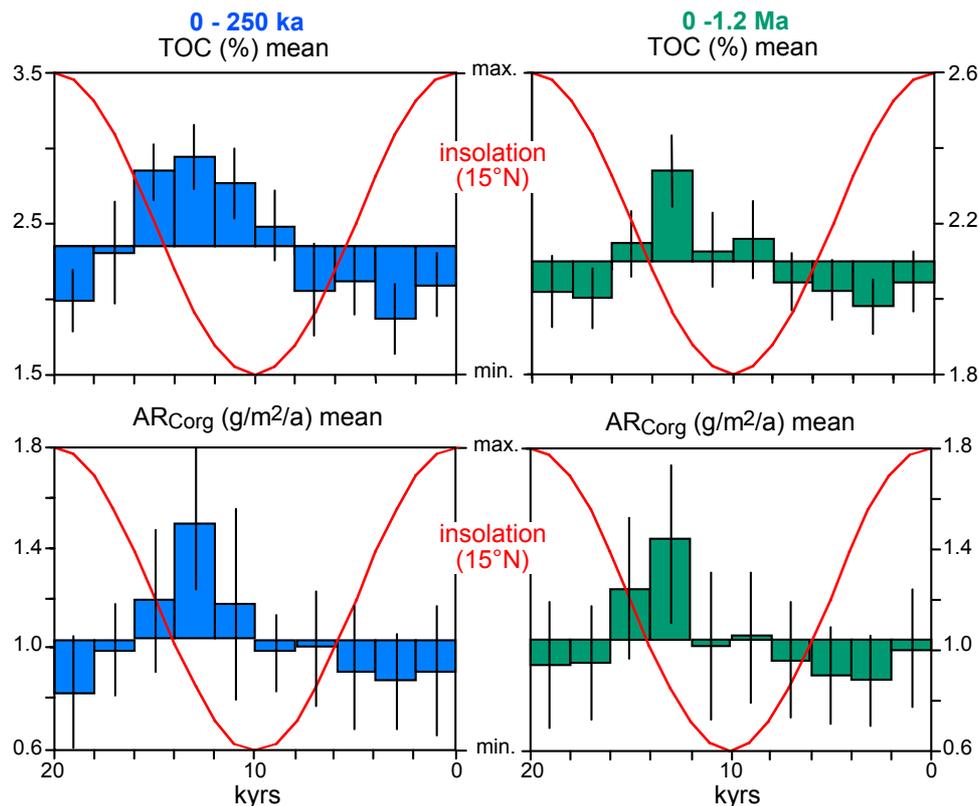


**Figure 4.8:** Time series of bulk organic geochemical and biomarker records from time section A (147-85 ka, OIS 6-5) at ODP Site 1075 compared to the insolation record at 15°N. Note close relation of TOC and lm/hm records to insolation with maxima in reactive (marine and terrigenous) OM occurring 2-5 kyrs following insolation minima due to depressed supply of low-reactive soil OM during arid African climates. The distinct relation of C/V and lignin yields ( $\Delta_{8/6}$ ) suggests that elevated concentrations of lignin are attributable to enhanced amounts of either woody plant tissue or soil OM.



**Figure 4.9:** see next page

**Figure 4.9:** Time series of bulk organic geochemical and biomarker records from time section B (270–210 ka, OIS 8-7) at ODP Site 1075 compared to the insolation record at 15°N. Almost all samples belong to Group-II samples. At least during the interglacial stage (OIS 7) the consistency of all parameters suggests that soil OM from C<sub>3</sub> habitats is a major terrigenous fraction that dilutes reactive marine OM and thus determines bulk OM reactivity, C<sub>org</sub>/N<sub>tot</sub> and C<sub>org</sub>/N<sub>org</sub> ratios, as well as bulk δ<sup>13</sup>C<sub>org</sub>. The highest relative enrichment of soil OM is indicated at 244 and 237 ka whereas enhanced supply of soil OM from former C<sub>4</sub> habitats may be deduced from heavier bulk δ<sup>13</sup>C<sub>org</sub> around 244 ka.



**Figure 4.10:** Mean values of TOC contents and accumulation rates in 2 kyr time increments of an idealized insolation cycle (10 classes comprising 20 kyr) displayed for samples of the upper section of ODP Site 1075 (0–250 ka, n=11/class) and from the entire record (0–1.2 Ma, n = 41/class) (modified from Wagner et al., 2003).

The detailed records from lignin analysis ( $\Lambda_{8/6}$  and C/V) for OIS 6-5 (Figure 4.8) and 8-7 (Figure 4.9) do not follow this relatively simple and systematic pattern. Moreover, they reveal some significant differences between the two time slices. Whereas  $\Lambda_{8/6}$  shows no clear relation to TOC during OIS 6-5, it is negatively correlated with TOC during OIS 7-8. For both time slices a distinct negative co-variation of  $\Lambda_{8/6}$  with C/V is also recognizable suggesting that terrigenous OM contains enhanced proportions of non-woody plant tissues and probably less soil OM in samples with low lignin concentrations than in their lignin-rich counterparts.

The profiles of bulk OM degradation (C<sub>org</sub>/C<sub>org</sub>\*) imply almost constant preservation during OIS 6 and parts of OIS 5 followed by slightly elevated indices between about 110–90 ka (covering about one insolation cycle) (Figure 4.8). In the older interval (Figure 4.9), bulk OM

degradation is in the same range (0.6 to 0.8) but more variable through time. Poorer preservation ( $C_{org}/C_{org}^*$  below 0.6) is indicated close to the insolation maxima at about 237 ka. The corresponding lignin-specific degradation index  $(Ad/Al)_{V/S}$  is generally more variable than bulk OM degradation (ranges between 0.26 and 1.3 for OIS 6-5 and OIS 8-7, respectively) and suggests that degradation of bulk and terrigenous OM is not necessarily synchronous and coupled, which may be expected in continental margin sediments where only the more residual organic fraction is left for further degradation.

The ancillary records of  $C_{org}/N_{tot}$  and  $N_{inorg}/N_{org}$  (the latter determined for OIS 8-7 only) do not show any clear relation to any of the parameters presented, except for OIS 7. There,  $N_{inorg}/N_{org}$  closely follows the bulk OM degradation rate indicating that carbon-nitrogen relationships reflect degradation (i.e. fixation of released ammonium in clay minerals) rather than qualitative changes in the OM. Elevated  $N_{inorg}/N_{org}$  ratios, on the other hand, may also support the presence of ammonium-rich soil material. Enhanced  $C_{org}/N_{tot}$  ratios of almost 10 are observed at 101 ka (OIS 5) or at 250 ka (OIS 8/7), and may also be attributed to enhanced proportions of BC, as this component is typically depleted in nitrogen.

The bulk  $\delta^{13}C_{org}$  signatures are about 0.5 -1.5 ‰ enhanced in glacial stage 6 (about -20.5 ‰) than in interglacial stage 5 (-21 to -22 ‰) indicating slightly higher relative proportions of marine OM or a greater admixture of  $C_4$ -plant matter during glacial conditions (Figure 4.8). In the older interval (OIS 8-7) the isotopic ratios co-vary during OIS 7 with TOC,  $lm/hm$ , and  $C_{org}/C_{org}^*$  ratios and oppose the  $\Lambda_{8/6}$  record indicating higher amounts of autochthonous OM for TOC maxima. During OIS 8 these relations are reversed. Elevated proportions of soil OM from a  $C_4$  habitat around 270 ka and eolian supply of black carbon at 250 ka can explain these changes.

Following the general assignment of two different groups being separated according to their bulk OM reactivity ( $lm/hm$  of 2, Figure 4.7), Group-I samples (corresponding to fresh terrigenous and autochthonous OM, and soil OM) characterize periods of peak TOC deposition and thus periods of rapid change from dry to humid climate (the transition from insolation minima to maxima). This pattern is consistent throughout both time slices investigated in detail, except for one TOC maximum at the transition from glacial stage 8 to interglacial stage 7 (250 ka, Figure 4.9) where OM reactivity remains below that threshold. In contrast, a dominance of soil OM with variable enrichment of BC (Group-II samples) is linked to low TOC and humid or transitional climatic conditions (insolation maxima and transition to insolation minima).

## 4.6 Discussion

### 4.6.1 Assessing the nature of sedimentary organic matter in marine sediments using conventional bulk parameters ( $C_{org}/N_{tot}$ , bulk $\delta^{13}C_{org}$ ) and lignin – principles and pitfalls relevant to this study

OM from marine or lacustrine production and from terrigenous vascular land plant sources display sharp general contrasts in their isotopic signature (bulk  $\delta^{13}C_{org}$ ) as well as in their ratios of organic carbon and total nitrogen ( $C_{org}/N_{tot}$ , Figure 4.1). Since both parameters are easy to

analyse, they are frequently used to estimate contributions of autochthonous (marine or lacustrine) versus allochthonous (terrigenous) OM in aquatic sediments. Numerous investigations have demonstrated the utility of these parameters for continental paleoecological reconstructions using limnic sediments from different climate zones (e.g., Orem et al., 1997; Meyers and Lallier-Vergès, 1999; Hu et al., 1999; Filley et al., 2001). Compared to oceanic settings, lakes and their surroundings form more or less closed regional ecosystems where geochemical signals corresponding to changes in vegetation type and primary production in response to climate variations are directly transferred to sedimentary OM due to high accumulation rates and short transport distances. In contrast, interpretation of bulk  $\delta^{13}\text{C}_{\text{org}}$  values and  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios in marine settings is generally not as straightforward (Tyson, 1995; Meyers, 1997; Wagner and Dupont, 1999; Twitchell and Meyers, 2002). However, there are a number of applications providing plausible results within their individual geological context using this approach, e.g. from the Congo deep-sea fan (Müller et al., 1994), the Washington margin (Prahl et al., 1994), and the Gulf of Mexico (Hedges and Parker, 1976). Interpretation of both parameters in the marine geological record, however, is more problematic due to potentially severe modifications of both parameters related to the heterogeneous multi-component nature of the OM, varying susceptibilities to degradation, and specific characteristics of the sedimentary setting (e.g. grain sizes of lithogenic and organic particles or the influence of benthic fauna). The latter factors usually change considerably as climate and depositional conditions evolve, adding uncertainty to the definition (or recognition) of appropriate end-members. Goñi et al. (1998), for example, suggest that terrigenous OM in surface sediments from the northwestern Gulf of Mexico may have been significantly underestimated in previous studies when  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios and bulk  $\delta^{13}\text{C}_{\text{org}}$  signatures were used to define marine and terrigenous end-members. They found that a significant part of the terrigenous OM derives from  $^{13}\text{C}$ -enriched  $\text{C}_4$  plant matter that results in a terrigenous OM signature that is virtually indistinguishable from marine OM. A recently published study on surface sediment samples from the inner Louisiana shelf imposingly demonstrates that massive supply of soil OM (and  $\text{C}_4$  plant matter) through the Atchafalaya River masks actual terrigenous OM proportions when two-end-member mixing models are applied on  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios and bulk  $\delta^{13}\text{C}_{\text{org}}$  values (Gordon and Goñi, 2003). The authors found that soil derived OM in fact is the dominating organic compound in deltaic, inshore and offshore sediments, and conclude that a two-end-member model underestimates the amount of terrigenous OM by 40 to 85%. A similar, although less pronounced effect may be assumed for sediments deposited along the continental margin between the Congo and the Niger, considering that both rivers drain parts of the main African  $\text{C}_4$ -plant habitat (Adams, 1995, [www.soton.ac.uk/~tjms/afpres.gif](http://www.soton.ac.uk/~tjms/afpres.gif); Giresse et al., 1994).

Apart from isotopic shifts related to a varying primary composition of bulk OM, selective microbial degradation may also bias the bulk isotopic signal. Freudenthal et al. (2001) for example observed increasing bulk  $\delta^{13}\text{C}_{\text{org}}$  values with increasing diagenesis in sediments from the eastern subtropical Atlantic and point to the highly problematic estimation of marine and terrigenous amounts of bulk OM if both end-members are modified by fractionation. Comparable to the isotopic composition,  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios may also shift upon diagenesis, both prior to and post sedimentation. According to Hedges et al. (1986), degradation of terrigenous OM occurs primarily within the terrestrial environment. Dittmar and Lara (2001) observed

sharply reduced  $C_{\text{org}}/N_{\text{tot}}$  ratios ( $\sim 18$ ) of particulate OM in mangrove sediments compared to fresh plant litter fall ( $C_{\text{org}}/N_{\text{tot}} = 70$ ) and postulate a relative enrichment of nitrogen during earliest degradation of leaf litter before its deposition.  $C_{\text{org}}/N_{\text{tot}}$  ratios are not only determined by the relative proportions of terrigenous and marine OM (and their different susceptibilities to microbial degradation) but are additionally closely related to the grain size of both organic matter and sediment matrix (Hedges et al., 1997; Farella et al., 2001). Ammonium released by microbial degradation of organic compounds (e.g. amino acids) can be fixed in the sediments when bound to clay minerals, while organic carbon is lost after respiration as  $\text{CO}_2$  or  $\text{CH}_4$ . Schubert and Calvert (2001) also demonstrated the significant impact of nitrogen linked in the form of ammonium to clays of Arctic Ocean sediments leading to very low  $C_{\text{org}}/N_{\text{tot}}$  ratios. This ammonium has been bound to the clays on land i.e. before the introduction to the aquatic environment as could be confirmed by isotopic measurements.

Poirier et al. (2002) investigated a tropical ancient soil from the Congo and indeed detected refractory OM and black carbon particles from incomplete combustion associated with fine-grained minerals. Although some minor degradation may occur, BC potentially persists over long time spans in soils and sediments and thus has great potential to enter the geological record (Bird et al., 1999; Schmidt and Noack, 2000; Masiello and Druffel, 2001, 2003; Czimeczik et al., 2003). The  $C_{\text{org}}/N_{\text{tot}}$  ratio of the bulk fine fraction ( $< 50\mu\text{m}$ ) in the Congo samples is 12.8 while the refractory material (BC) is depleted in nitrogen ( $C_{\text{org}}/N_{\text{tot}} \approx 20.1$ ) (Poirier et al., 2002). Bird et al. (1999) investigated samples of burned and unburned savannah soils from Zimbabwe. They observed increasing bulk  $\delta^{13}\text{C}_{\text{org}}$  values with decreasing particle size in both sample types, whereas in unburned samples the isotopic ratio was always 3-4‰ lower. Verardo and Ruddiman (1996) conclude that charcoal supply to deep-sea sediments of the tropical Atlantic reduces previous estimates of marine organic carbon burial fluxes by 50% (compare estimates in Wagner, 2000, for same area). In surface sediments of the northwestern Gulf of Mexico, Goñi et al. (1998) observe  $C_{\text{org}}/N_{\text{tot}}$  ratios of 8 in sites shallower than 605m water depth, and 6 to 5 in samples from deeper water. From the isotopic signatures of bulk OM the authors infer for significant supply of soil OM from the Mississippi drainage basin ( $C_{\text{org}}/N_{\text{tot}} = 10-13$ ), much of which is dominated by grasslands (prairie), an important source of  $\text{C}_4$  plant debris. Onstad et al. (2000) draw similar conclusions based on measurements of suspended POM in the Mississippi river and its tributaries. These authors also argue that  $^{13}\text{C}$ -rich and lignin-poor particulate OM from soils makes it difficult to distinguish terrigenous from marine OM inputs.

Ruttenberg and Goñi (1997) measured  $C_{\text{org}}/N_{\text{tot}}$  ratios in Amazon shelf sediments ranging from 5 to 7. As fine suspended matter from the Amazon river has  $C_{\text{org}}/N_{\text{tot}}$  values of 10 to 11 and furthermore important sorption of inorganic nitrogen (ammonium) by clay minerals was ruled out, the authors conclude that nitrogen must have been enriched *after* burial. They suggest a significant contribution of bacteria and their remains to the bulk organic pool. Bacteria have  $C_{\text{org}}/N_{\text{tot}}$  ratios of 4 to 6 (e.g., Goñi and Hedges, 1995) and thus may lower the  $C_{\text{org}}/N_{\text{tot}}$  values especially in fine-grained sediments where bacteria consuming organisms (e.g. protozoans) are less abundant. Additionally, bacteria have highly variable  $\delta^{13}\text{C}_{\text{org}}$  signatures, their isotopic composition tends to reflect their dominant food source (Fry and Sherr, 1984). Regarding these findings, Ruttenberg and Goñi (1997) conclude that two-end-

member models are not suitable for estimations of marine and terrigenous OM contributions in sediments from the Gulf of Mexico and the Amazon shelf. However, these parameters, when measured in parallel, may provide important information on the complex nature of sedimentary OM.

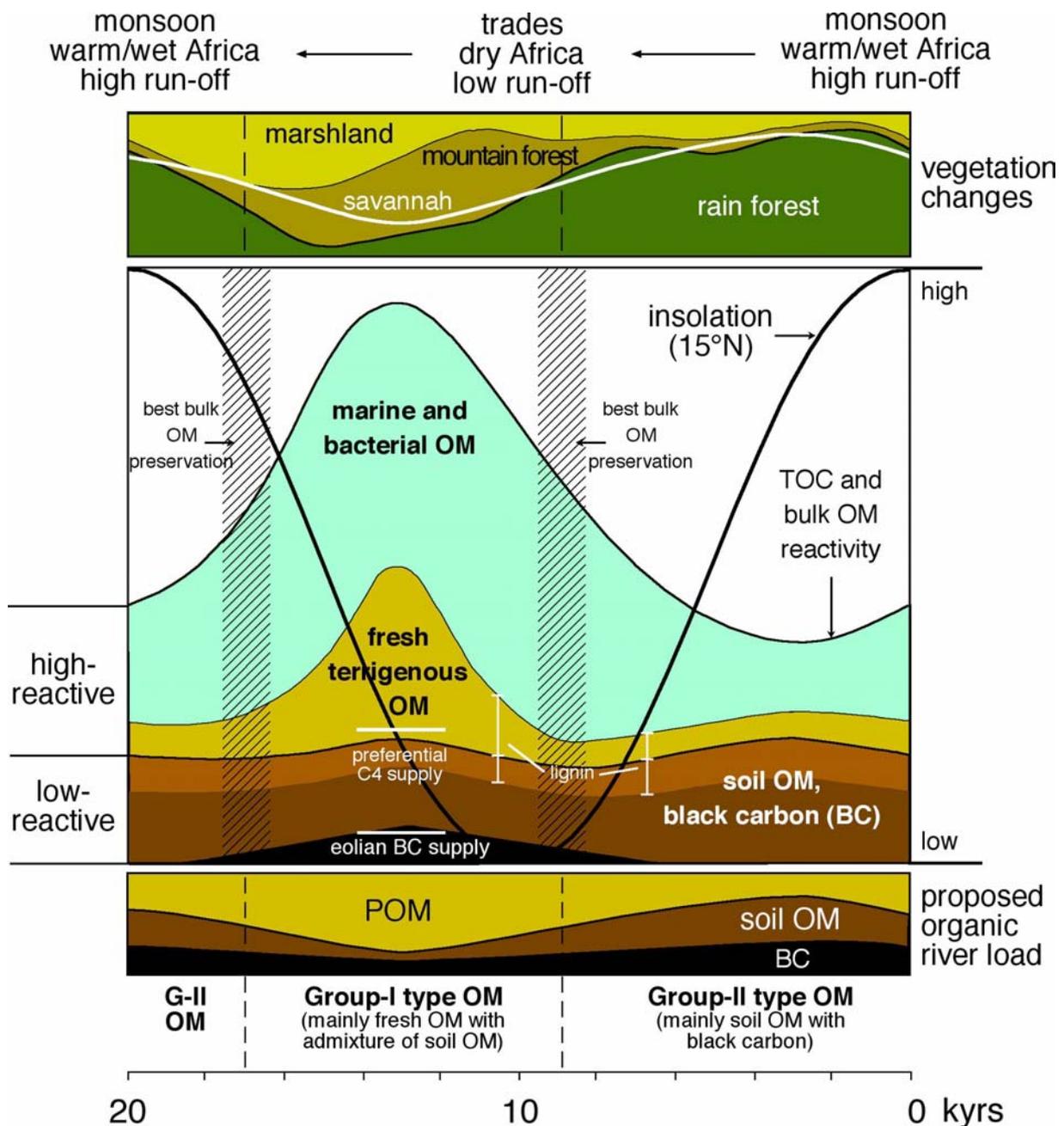
Lignin, a principle structural component of higher plant tissues, serves as a diagnostic tracer of terrigenous OM in marine environments and is commonly considered to be resistant to microbial degradation (e.g. Hedges and Mann, 1979b; Hedges and Ertel, 1982; Tissot and Welte, 1984). Furthermore, variations in the composition of eight specific lignin-derived phenols provide means to distinguish between the most important types of plant tissue and thus down-core variations may provide information about past vegetation and climate changes. Investigation of lignin phenols is progressively used in paleoenvironmental research since its early introduction (Hedges and Parker, 1976; Hedges and Mann, 1979a,b). The S/V and C/V ratios provide information on angiosperm or gymnosperm, non-woody or woody vascular plant tissues, respectively. Numerous investigations from different limnic and marine settings discuss lignin data (e.g. see list of selected applications to modern marine environments in Wagner et al., 2003). Some of them emphasize that lignin is sensitive to degradation, selective decay, and mild thermal stress (e.g. Ishiwatari and Uzaki, 1987; Opsahl and Benner, 1995; Cody and Sághi-Szabó, 1999; Dittmar and Lara, 2001) supporting the concept that the ratios of vanillic acid to vanillin,  $(Ad/Al)_V$ , and syringic acid to syringaldehyde,  $(Ad/Al)_S$ , are suitable to assess the degree of lignin degradation.

#### *4.6.2 The land-ocean and climate linkage on the Congo deep-sea fan*

The results from this study demonstrate the importance of terrigenous OM from different continental sources in late Quaternary sediments at ODP Site 1075 on the Congo deep-sea fan. They challenge the widely held assumption that TOC maxima in late Quaternary sediments from the equatorial Atlantic continental margin reflect maxima in primary production, the driving force being trade wind-induced upwelling and nutrient supply from intermediate waters (e.g. Schneider et al., 1997a). The latter interpretation, however, mainly stems from interpretations, assuming a binary mixing model for bulk  $\delta^{13}C_{org}$  data (i.e., marine versus terrigenous OM exclusively from  $C_3$  sources). Schneider et al. (1997a) identify riverine nutrient supply as the driving force for marine primary production in the Congo high-productivity area. It may therefore be reasonable to expect at least some admixture of OM from riverine sources in the sediments, and thus has been confirmed for surface sediments from the Congo fan and the adjacent upper continental margin between Congo and Cameroon (Wagner et al., 2003).

The observed relationships between compositional changes, level of reactivity and degradation of bulk OM, and their variability over time provide means to identify principle sources of OM and the definition of a succession of events that explains organic sedimentation at ODP site 1075 as a function of insolation forcing (Figure 4.11). The combination of data from lignin chemistry, bulk elemental analysis and pyrolysis, and bulk carbon isotopes indicates the presence of OM from at least three different sources: (i) marine (including bacterial) OM, (ii) fresh and reactive, lignin-rich terrigenous OM (POM), and (iii)

lignin- and black carbon-bearing soil OM. Fluctuations in the relative proportions of these primary contributors result in systematic fluctuations in TOC and bulk OM reactivity with overall variability being closely linked to insolation-driven environmental change in central Africa and the adjacent easternmost Equatorial Atlantic. The close relation of bulk OM reactivity and soil OM implicates riverine supply as a key mechanism that determines not only the nature of OM in the sediments but also continental nutrient supply and thus primary production along the eastern Equatorial Atlantic continental margin.



**Figure 4.11:** Conceptual model of organic matter sedimentation and preservation at the Congo deep-sea fan related to cyclic changes of insolation and vegetation. Palynological data from the Congo fan (Wagner et al., 2003) suggests expansion of savannah (white line in the top) and increasing aridity within the Congo catchment during and 2-6 kyr after the insolation minimum by reduced pollen from rain forest and elevated contribution from Afromontane forests. Enhanced proportions of pollen from marsh and swamp areas mark the transition to humid conditions. Maximum TOC content and bulk

OM reactivity is observed in sediments that accumulated during arid African climates at maximum savannah expansion, intense upwelling off the Congo, highest relative proportions of POM (fresh terrigenous OM) in the river suspension load, and minimum supply of soil OM (Group-I samples). Opposite, the highest concentration of soil OM occurs 2-4 kyrs following the insolation maximum and results from dilution of marine OM and terrigenous POM and intense degradation of these reactive fractions. During this interval humid conditions and greatest expansion of rain forest with enhanced soil formation, weathering, and runoff prevailed. Best preservation of bulk OM occurs during the transitional stages, mainly from river- and upwelling-induced to pure river-induced primary production, short time before the insolation extremes and probably due to optimum balanced relations of labile OM and fluvial sediment supply. Changes of the relative contents of BC within the soil OM fraction are based on literature data suggesting that BC production was enhanced during arid periods with extended savannah vegetation compared to humid stages. Accordingly, quantitative estimates of BC cannot be given.

#### *4.6.2.1 The transition from humid to arid African climate*

Relatively non-reactive, soil-rich OM (Group-II samples) and corresponding low TOC characterize warm and humid climates (insolation maxima and decreasing insolation) and the transitional stage from humid to arid climate conditions at Site 1075. These properties apparently correspond to warm and wet climatic conditions in central Africa. A strongly developed monsoonal system during this orbital configuration fostered extension of the Congo rain forest with its dominant  $C_3$  vegetation. The invigorated hydrologic cycle also enhanced run-off to the adjacent tropical African continental margin. Due to the enhanced continental nutrient supply, marine productivity should have been relatively high during these conditions. One of the most important nutrients for the dominant group of primary producers off the Congo, marine diatoms (van Bennekom and Berger, 1984), is dissolved silicate from river-outflow and/or upwelling supply (Schneider et al., 1997a; Uliana et al., *subm.*). Notably, marine taxa account for 95% of the siliceous microfossil assemblage (Uliana et al., 2001). On the other hand, the massive suspension load of the river deriving from intensive erosion of tropical soils probably hampered primary productivity by haze of the surface water in the river plume and a diminished translucence. At least, a stronger dilution of labile marine OM leading to a subdued productivity signal may be expected. It may also be speculated that degraded soil OM associated with the fine-grained lithogenic fraction was not a main nutrient source for marine primary producers (as e.g. dissolved silica) but may have favoured the development of benthic micro-fauna. In fact, most of the marine OM has apparently been degraded as indicated by highest levels of bulk OM degradation (i.e.,  $C_{org}/C_{org}^*$  as low as 0.55), leading to the observed dominant terrigenous organic signature in the sedimentary record and finally resulting in TOC minima. BC-bearing soil OM comprising the principle organic fraction in the sediments also determines the observed very low bulk OM reactivity (lm/hm ratios as low as 0.2). It has been shown that formation of BC is not only restricted to arid climate but also occurs during humid conditions as natural part of rain forest ecosystems (Schmidt and Noack, 2000). The relative proportions of BC in the soil fraction of Congo fan sediments may therefore be variable, depending on the type of vegetation they originate from ( $C_3$  versus  $C_4$ ), however, they are not quantified in this study. Kuhlbusch et al. (1996) estimate that 90% of the fire-derived BC remains on the ground. We therefore assume that most part of BC in Congo fan deposits is introduced as part of the fluvial soil OM fraction and

not from eolian transport. Nevertheless, elevated contents of BC within the soil fraction may only be expected during maximum expansion of the African savannah.

This study does not provide direct evidence or source-specific biomarkers for soil OM. However, the consistency of bulk OM parameters strongly supports the presence and importance of such an organic component. Fine-grained soil OM is often enriched in nitrogen ( $C_{\text{org}}/N_{\text{tot}} \approx 12$ ) compared to coarse-grained POM, mostly associated with fine-grained minerals, depleted in lignin, and the remaining lignin is severely degraded (Prahl et al., 1994; Hedges et al., 1986; Hedges and Oades, 1997; Keil et al., 1998). C/V ratios of lignin from soils are generally low, whereas degradation-sensitive  $(\text{Ad}/\text{Al})_V$  parameters are enhanced (Farella et al., 2001). It has been shown that a significant proportion of soil OM may be BC, especially, where the overlying vegetation is affected of periodic burning (Bird et al., 1999; Schmidt and Noack, 2000; Poirier et al., 2002). These burned components are depleted in nitrogen, enriched in the heavy carbon isotope, and have lowest concentration of lignin compared to bulk soil OM or POM. If soil OM with low or moderate contents of BC account for a significant proportion of the bulk OM in Congo fan sediments, low  $C_{\text{org}}/N_{\text{tot}}$  and C/V ratios but elevated  $(\text{Ad}/\text{Al})_V$  values may be expected. One example is clearly recorded at 106 ka (transition to full humid climate conditions, Figure 4.8). Here, very low  $C_{\text{org}}/N_{\text{tot}}$ ,  $\text{lm}/\text{hm}$  and C/V ratios but high lignin yields and light bulk isotopic ratios support the presence of soil OM from  $C_3$  vegetation as a main source of lignin and a major component of the bulk OM. A distinct shift to very high  $C_{\text{org}}/N_{\text{tot}}$  ratios during the following humid conditions (101 ka) in combination with heavier bulk isotopic signatures (caused by the inert fraction) and elevated C/V ratios and lignin contents suggest a progressive increase in soil-associated BC, as well as enhanced admixture of nitrogen-poor POM from rainforest vegetation at that time.

The observed relative enrichment of soil OM in Group-II samples is supported by low reactivity of the remaining bulk OM, elevated lignin yields, and low C/V and  $C_{\text{org}}/N_{\text{tot}}$  ratios (e.g. at 237 ka and 244 ka, Figure 4.9). The lighter isotopic ratios ( $\sim -21.5\text{‰}$ ) suggests the preferential supply of soil from  $C_3$  habitats at 237 ka, whereas the  $1\text{‰}$  heavier isotopic signature at 244 ka supports an origin of soil OM from  $C_4$ -type vegetation associated with the transition from arid to more humid conditions.

The environmental conditions changed rapidly with the progressive decrease in insolation and aridification of central Africa. According to the palynological data (see Wagner et al., 2003) rain forest cover receded and the relative supply of pollen from the Afromontan forests (dominated by *Podocarpus*) increased parallel to the expansion of savannah vegetation (Dupont et al., 2000). Synchronous with the transition from a monsoonal to a trade wind-dominated atmospheric circulation, upwelling was enhanced and stimulated marine productivity in the Congo high productive area, the main nutrient source for primary production changing from riverine supply to wind-induced upwelling about 6 to 8 kys following the insolation maximum. Notably, a short time before the insolation minimum, contributions of continental OM dropped to their lowest level (Figure 4.11). The diminished availability of reactive OM from marine primary production and/or terrigenous supply apparently suppressed microbial activity in the sediment, the result being enhanced preservation of marine OM as indicated by highest  $C_{\text{org}}/C_{\text{org}}^*$ .

#### 4.6.2.2 *The transition from arid to humid African climate*

During the phase of maximum savannah expansion, supply of soil OM approached its minimum whereas the amount of POM in the terrigenous organic fraction was relatively enhanced. Samples from arid climates are therefore dominated by Group-I OM. The bulk OM reactivity (expressed as the  $l_m/h_m$  ratio) and concentration (TOC) remains high during this interval, mainly due to significant amounts of POM and marine OM. While the supply of soil OM was relatively low under these conditions, its BC concentration may have approached highest proportions taking lower biomass production and a probably increased number of bush fires within the extended savannah areas into account. In view of enhanced aridity and stronger trade winds, an additional source of BC may have been the central and southern African  $C_4$  habitats, the primary transport mechanism being eolian supply (Verardo and Ruddiman, 1996). Eglinton et al. (2002) studied dust samples collected from off NW-Africa and Huang et al. (2000) mapped the abundance of  $^{13}C$  in leaf-wax components in surface sediments recovered from the seafloor off northwest Africa (0-35°N) both revealing a clear pattern of  $\delta^{13}C$  distribution, indicating systematic changes in the proportions of terrestrial  $C_3$  and  $C_4$  plant input. The latter authors conclude that  $C_4$  plant derived terrigenous leaf-waxes achieve highest proportions (>50%) off the NW-African coast at about 20°N. Using a comparable approach, Schefuß et al. (2003) found that more than 50% of *n*-alkanes from plant waxes in surface sediments of the Congo and Angola Basins derive from  $C_4$  plants and infer for an increased eolian supply of this material from southern African grasslands towards the northwest. In the Congo river, reduced amounts of fine-grained suspension from soil erosion and enhanced relative proportions of fresh POM within the river load in combination with strong upwelling along the Equatorial Atlantic continental margin effectively stimulated marine productivity off the Congo, as is documented by a pronounced maximum in TOC. Increasing humidity following full arid climatic conditions in central Africa was certainly accompanied by a major re-draining of the former savannah-covered habitats in the surrounding of the Congo catchment and the rain forest itself that should have resulted in an enhanced supply of POM from  $C_4$  habitats. Elevated relative amounts of Cyperaceae pollen (mainly sedges and rushes) go along with rising humidity. The presence of these pollen suggests more extensive marshlands and swamps in flat areas and along the rivers (Dupont et al., 2001). With further increasing insolation and humidity, the rainforests expanded again, and the influence of the monsoonal system on organic sedimentation on the Congo fan progressively recovered to its initial configuration. This general change in atmospheric circulation caused the recession of upwelling processes in the eastern tropical Atlantic. 2-4 kyrs before the insolation maximum reduced primary production and relatively low concentrations of reactive terrigenous OM (POM) in the river load are balanced with increasing soil supply resulting in reduced microbial activity in the sediments (comparable to the situation 2-4 kyrs before the insolation minimum). A better preservation of marine OM during this intermediate stage is indicated by high  $C_{org}/C_{org}^*$  ratios. Following a further increase of continental humidity, weathering, and run-off the sedimentation of lignin-rich soil OM primarily from  $C_3$  habitats (Group-II samples) one more time took the lead as a primary proportion of the bulk OM ~2 kyrs before the insolation maximum.

The data presented propose two maxima in primary productivity. One during stages of enhanced trade-forced upwelling (arid African climate) and a second during monsoonal stages and enhanced fluvial nutrient supply (humid African climate). This is consistent with results from investigations of modern (van Bennekom and Berger, 1984) and past (Schneider et al., 1997a; Uliana et al., 2001) productivity off the Congo. Accordingly, reactive marine OM is diluted by massive delivery of soils rich in low-reactive OM during the latter (humid) stage, which stimulated intensive microbial degradation and finally results in lowest TOC concentrations. This relationship may also explain the observed non-covariance between TOC and biogenic opal as productivity proxy for marine diatoms ( $r^2=0.002$  at Site 1075 and  $r^2=0.05$  at Site 1077, Holtvoeth, unpublished data).

#### 4.7 Conclusions

Primary productivity in the late Quaternary eastern equatorial Atlantic off the Congo is stimulated by strong nutrient supply in response to trade-induced upwelling during arid African climates and by massive fluvial nutrient delivery during humid climate stages, both resulting from precessional controlled changes of insolation and atmospheric circulation (monsoon vs. trade winds). However, the fluvial contribution of fine-grained lithogenic suspension from OM-rich soils appears to be a decisive factor for the concentration and preservation of autochthonous (marine) OM. This conclusion is supported by the observed 2-4 kyrs time shift of bulk organic geochemical signatures that corresponds to the delayed development of vegetation and soil with respect to atmospheric circulation and insolation. It may be speculated that the supply of clay-size lithogenic matter fostered scavenging effects and the interaction of mineral surfaces with the labile organic fraction. These mechanisms should have amplified the flux and burial rates of reactive OM but, on the other hand, should also have promoted the growth of benthic and bacterial communities and thus degradation of labile OM. Most favourable conditions for the preservation of bulk OM occurred during intermediate climate stages when moderate upwelling was combined with a balanced fluvial supply of soil material and POM.

The data reveal that varying organic geochemical properties in Congo fan sediments can neither be explained by changes in upwelling- and river-induced primary production, fluvial OM supply, and OM burial rates nor by the degree of selective OM degradation. Massive fluvial contribution of fine-grained soil material with significant amounts of low-reactive OM as well as BC is indicated by bulk parameters ( $C_{org}/N_{tot}$ ,  $lm/hm$ ) and results from lignin analysis ( $C/V$ ,  $\Lambda_8$ ,  $Ad/Al_V$ ). These components apparently strongly determine bulk OM composition, concentration, and preservation. In fact, the residual TOC profile records only one of two former maxima in primary production. Correlation with other productivity proxies, e.g. concentrations of biogenic opal, is therefore complicated or impossible.

Significant fluvial and/or eolian supply of soil OM, BC from  $C_4$  plant habitats especially during arid African climates may lead to a severe underestimation of terrigenous OM if binary mixing models are used for the interpretation of the bulk  $\delta^{13}C_{org}$  signal. Though ratios of stable carbon isotopes (bulk  $\delta^{13}C_{org}$ ) and  $C_{org}/N_{tot}$  values of bulk OM apparently are not suitable to directly assess marine and terrigenous amounts both parameters bear substantial

information on bulk OM quality and cyclic variations within the terrigenous fraction when combined with lignin data ( $\Lambda_{8/6}$ , C/V, and (Ad/Al)<sub>v,s</sub> ratios) and parameters characterizing bulk OM reactivity and degradation from Rock-Eval pyrolysis (Im/hm) and elemental analysis ( $C_{org}/S_{tot}$ ,  $C_{org}/C_{org}^*$ ).

## 5. Soil organic matter as an important contributor to late Quaternary sediments of the tropical West-African continental margin

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### 5.1 Abstract

Soil organic matter (SOM) is a fraction of bulk organic matter (bulk OM) in continental margin sediments that is largely ignored in most paleoceanographic investigations. There are various lines of evidence supporting the conclusion that SOM considerably modifies established proxies used to assess marine and terrigenous OM proportions in marine sediments, i.e. the isotopic composition ( $\delta^{13}\text{C}_{\text{org}}$ ) and  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios of the bulk OM. We present new data from organic geochemical (elemental analysis, Rock-Eval pyrolysis), isotopic (stable organic carbon isotopes), and organic petrological (maceral analysis) investigations of late Quaternary sediments (245 - 0 ka) from the Niger deep-sea fan and combine them with results from the Congo deep-sea fan. We demonstrate that  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios and isotopic signatures of bulk OM in both deep-sea fan deposits are essentially determined by supply of various types of SOM and particulate OM (partly of  $\text{C}_4$  origin) from the Niger and Congo catchments that changed in response to Late Quaternary African aridity/humidity cycles. On the Niger fan, supply of generally nitrogen-poor but  $^{13}\text{C}$ -enriched particulate terrigenous OM and SOM derived from  $\text{C}_4/\text{C}_3$  vegetation/Entisol domains (grass- and tree-savannah on young, sandy soils) increased  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios and bulk  $\delta^{13}\text{C}_{\text{org}}$  values (up to -17 ‰) during arid climate conditions. During humid climates, in contrast, drainage of combined  $\text{C}_3/\text{C}_4$  vegetation/Alfisol/Ultisol domains (forest and tree-savannah on older/developed, clay-bearing soils) caused lower  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  and bulk  $\delta^{13}\text{C}_{\text{org}}$  values (< -20 ‰). Different from the Niger system, sediments from the Congo fan contain a thermally stable organic fraction as detected by Rock-Eval pyrolysis. There is support that this thermally stable organic fraction derives from strongly degraded SOM of old and highly developed, kaolinite-rich ferallitic soils typical for the Congo basin (i.e., Oxisols). In contrast to the Niger fan, reduced contribution of this nitrogen-rich and  $^{12}\text{C}$ -depleted SOM type during arid climate conditions was compensated by enhanced proportions of marine OM from upwelling-induced primary production. This results in significantly smaller ranges and generally lower values of  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  and bulk  $\delta^{13}\text{C}_{\text{org}}$  ratios on the Congo fan. We argue that ignoring the presence of SOM may result in a severe underestimation of the terrigenous organic fraction and, thus, to erroneous paleoenvironmental interpretations. We finally conclude that fluvial SOM export towards the ocean and the burial of SOM in marine sediments represents a more important process of atmospheric  $\text{CO}_2$  lowering than commonly considered.

## 5.2 Introduction

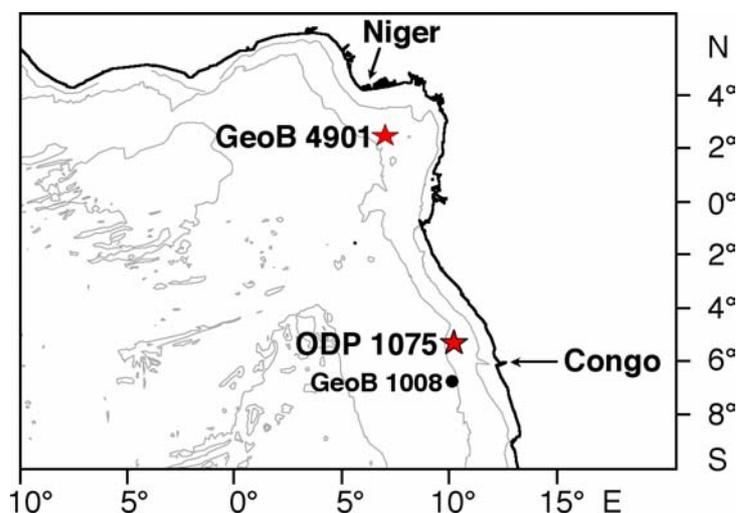
Organic geochemical investigations on the distribution, composition, and reactivity of bulk organic matter (OM) in modern and Late Quaternary sediments from Congo deep-sea fan (ODP Site 1075) and the adjacent tropical African continental margin have recently demonstrated that bulk organic geochemical properties may significantly be modified in presence of soil organic matter (SOM) eroded and supplied by rivers from the Congo catchment to the tropical African continental margin (Holtvoeth et al., 2003; Wagner et al., 2003). These studies have shown that established proxies in paleoceanography, e.g. the ratio of organic carbon versus total nitrogen contents ( $C_{\text{org}}/N_{\text{tot}}$ ) and the stable carbon isotope composition of bulk OM (bulk  $\delta^{13}C_{\text{org}}$ ) may be biased in presence of SOM that typically is enriched in nitrogen, depleted in  $^{12}C$  due to humification processes and microbial degradation occurring in the terrestrial environment (e.g. Hatcher et al., 1989; Christensen, 1996; Zech et al., 1989, 1997). These proxies are commonly used in paleoceanography to estimate the relative amounts of marine and terrigenous OM. Their application is based on the assumption that terrigenous OM is depleted in nitrogen and  $^{13}C$  relative to marine OM. The broader implication of the Congo studies is that SOM may be an important component in many other marine sediments that have been deposited in front of large river systems and along the adjacent continental margins. Ignoring the presence of SOM may result in a severe underestimation of the terrigenous organic fraction and erroneous paleoenvironmental interpretations. However, export and burial of terrigenous OM represent an important process of atmospheric  $CO_2$  lowering, thus have to be evaluated cautiously.

The central aim of this study is to detect changing quantities and qualities of terrigenous OM exported by the Niger River during the last 245 kyrs. In particular, we try to find evidence that supports the presence of SOM and  $C_4$  plant matter, and discuss their influence on bulk OM geochemical and isotopic properties. We present new high-resolution bulk organic proxy records from sediments of the lower Niger deep-sea fan (core GeoB 4901) and combine them with records from the Congo fan. This approach incorporates principle conclusions from previous studies performed on both tropical African river fans using inorganic geochemical data. Zabel et al. (2001) conclude that titanium/aluminium (Ti/Al) ratios of late Quaternary Niger deep-sea fan sediments are rather determined by the delivery of kaolinite, a weathering product of silicate rocks, than by varying supply of Ti-bearing heavy minerals. The authors therefore suggest that varying Ti/Al ratios reflect the hydrological cycle, the intensity of chemical weathering, and the export of different types of soils (kaolinite-rich vs. kaolinite-poor) depending on the climatic conditions and the vegetation cover in the Niger catchment. Schneider et al. (1997a) draw similar conclusions for sediments from the southern Congo deep-sea fan (core GeoB 1008). We need to point out that any change in humidity, chemical weathering, and runoff - all being essential elements of the tropical African hydrological (monsoonal) cycle - are intimately linked to vegetation growth, soil formation, and soil erosion. Consequently, inorganic continental proxy records from deep-sea fan sediments do not only document changes in chemical weathering intensity, the way they are typically discussed, but also provide a valuable although indirect record of soil erosion.

In this study we argue that climate-driven changes in supply of SOM and C<sub>4</sub> plant matter to a large extend determine bulk OM properties (TOC, C<sub>org</sub>/N<sub>tot</sub>, Hydrogen Index, Oxygen Index, T<sub>max</sub>, and bulk δ<sup>13</sup>C<sub>org</sub>) in late Quaternary sediments of the Niger fan. Based on the data from deep-sea fan sediments and on soil and vegetation patterns in central Africa we propose an alternative interpretation of established paleoenvironmental proxy records that can be tested on many other deep sea fan settings.

### 5.3 Study site, material, methods, and stratigraphy

Gravity core GeoB 4901 studied here was taken in 1997 during *RV Meteor* cruise 41/1 from the Niger deep-sea fan (2°40.7' N, 6°43.2' E) at 2184 m water depth (Schulz et al., 1998, Figure 5.1). The sediments consist mainly of dark greenish-gray, clay-bearing ooze containing remains of diatoms and foraminifera as well as terrestrial siliceous components. Between 13.6 and 19.3 meters below sea floor (mbsf) changing greenish black and dark olive colours reveal variable amounts of organic matter. No evidence was found for turbidites or contourites. The results from organic geochemical investigations on core GeoB 4901 are compared to results previously reported from the Congo deep-sea fan, i.e. ODP Site 1075 (Holtvoeth et al., 2001, 2003) and GeoB 1008 (Schneider et al., 1997a; Fig. 5.1 for site positions).



**Figure 5.1:** Positions of gravity cores GeoB 4901 (Niger fan, 2184m water depth), GeoB 1008 (Congo fan, 3124 m water depth), and ODP-Site 1075 (Congo fan, 2996 m water depth).

The samples were kept frozen until they were freeze-dried in the shore-based laboratory. Total carbon (TC), total organic carbon (TOC) and sulfur contents of the homogenized samples were measured using a Leco CS 300 (precision of measurement: ± 3 %). Carbonate contents were calculated as  $\text{CaCO}_3 = (\text{TC} - \text{TOC}) * 8.33$  with the latter factor as the ratio of molecular/atomic weights of carbonate and carbon. Assuming that microbial sulfate reduction is the main degradation process for sedimentary OM in rapidly accumulating fine grained river fan deposits, the original content of organic carbon (C<sub>org</sub><sup>\*</sup>) were estimated following the equation of Littke et al. (1997):  $C_{\text{org}}^* = C_{\text{org}} + 2S * M_C/M_S$  (S = measured sulfur content, M<sub>C</sub> = atomic weight of carbon, M<sub>S</sub> = atomic weight of sulfur). The degradation rate of bulk organic carbon is expressed as the ratio of measured and estimated original organic carbon

contents ( $C_{\text{org}}/C_{\text{org}}^*$ ). This approach provides minimum estimates, taking into consideration that diffusive escape of  $\text{H}_2\text{S}$  from the sediment results in reduced pyrite precipitation in situ and thus in lower sulfur contents. Furthermore, oxic degradation of OM particles sinking to greater water depths and the contact to oxic bottom water may play an important role for early OM decay prior to the transfer to anoxic environments (Hartnett et al., 1998; Schubert et al., 2001). Total amounts of nitrogen were determined using a Heraeus CNS analyzer (precision of measurement:  $\pm 3\%$ ).

The stable isotopic composition of bulk sedimentary organic carbon ( $\delta^{13}\text{C}_{\text{org}}$  vs. VPDB) was measured using a Heraeus Elemental Analyzer combined with a Finnigan MAT Delta S mass spectrometer (precision of the measurements:  $\pm 0.2\%$ ). Kerogen was classified according to Espitalié et al. (1977) using a Rock-Eval II (precision of measurement for hydrocarbon peaks S1, S2, and carbon dioxide peak S3:  $\pm 5\%$ ; for  $T_{\text{max}}$ :  $\pm 1^\circ\text{C}$ ; Espitalié et al., 1985). The yields of hydrocarbons and  $\text{CO}_2$  were calculated from FID and TCD responses, respectively, by means of a gas chromatographic integration system (VAX-Multichrom 2.2). Hydrocarbons and hydrocarbon-like components that are generated from the kerogen fraction of the bulk sediment were quantitatively detected within the S2 temperature window.

Organic petrological observations were performed using a Zeiss Axiophot. Selected bulk sediment samples were embedded in a low-viscosity resin, then ground and polished using a Logitech PM 2A (for details see Wagner, 1998). For statistical relevance 500 particles per sample were counted. The organic particles were sorted by grain size in 4 classes:  $<5\ \mu\text{m}$ ,  $5\text{-}10\ \mu\text{m}$ ,  $10\text{-}20\ \mu\text{m}$ , and  $>20\ \mu\text{m}$ .

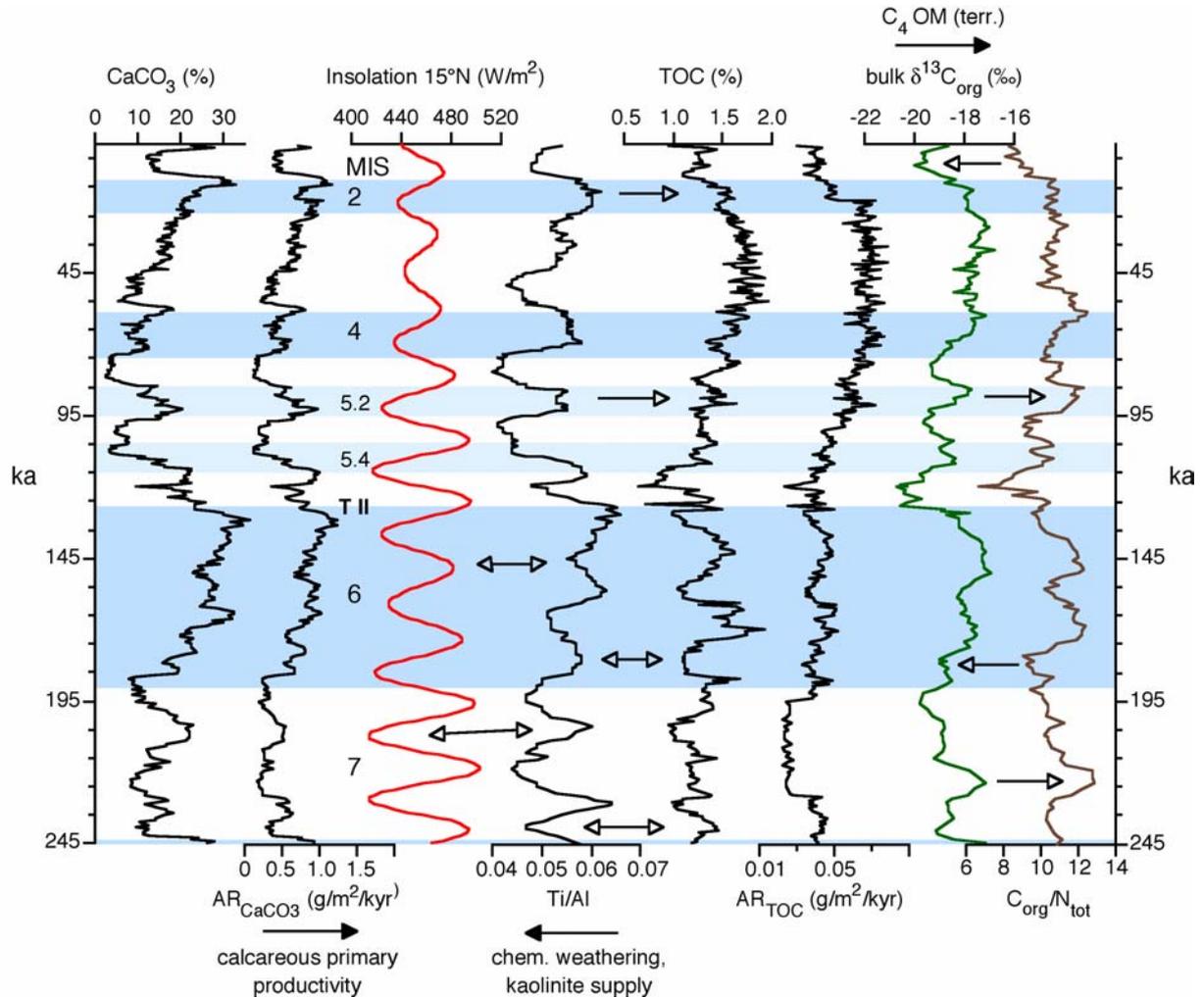
A set of 28 samples was selected for measurements biogenous opal contents. Biogenic opal was determined using a sequential leaching technique (DeMaster, 1981) modified by Müller and Schneider (1993). Opal was mobilized from the samples by treatment with 1 M NaOH for one hour at  $85^\circ\text{C}$ . Concentrations of silica were simultaneously detected by continuous flow analysis with molybdate-blue spectrophotometry (precision of measurement:  $\pm 0.5\%$ ).

The age model of core GeoB 4901 used in this study is taken from Zabel et al. (2001). These authors established the stratigraphy by visual comparison of the SPECMAP oxygen isotope stack with the  $\delta^{18}\text{O}$  record of the core measured at the benthic foraminifera *Cibicidoides wuellerstorfi* (Adegbie, unpublished data).

## 5.4 Results

Late Quaternary records from elemental analysis (TOC,  $\text{CaCO}_3$ ,  $C_{\text{org}}/C_{\text{org}}^*$ ,  $C_{\text{org}}/N_{\text{tot}}$ ) and stable carbon isotope ratios of bulk OM (bulk  $\delta^{13}\text{C}_{\text{org}}$ ) are shown in Figure 5.2. The geochemical and isotopic data are compared to the records of insolation at  $15^\circ\text{N}$  and Ti/Al previously reported by Zabel et al. (2001). These authors conclude that low Ti/Al ratios indicate more intense chemical weathering in the Niger catchment and thus enhanced supply of kaolinite-rich soil material during humid climate conditions (e.g., marine isotopic stages [MIS] 5.5, 5.3, 5.1, and 1) and vice versa (e.g., MIS 6, 4, and 2). The Ti/Al record shows a clear relation to northern hemisphere insolation ( $15^\circ\text{N}$ ) with maxima in chemical weathering intensity and kaolinite supply lagging insolation maxima by about 4.9 kyrs (Zabel et al.,

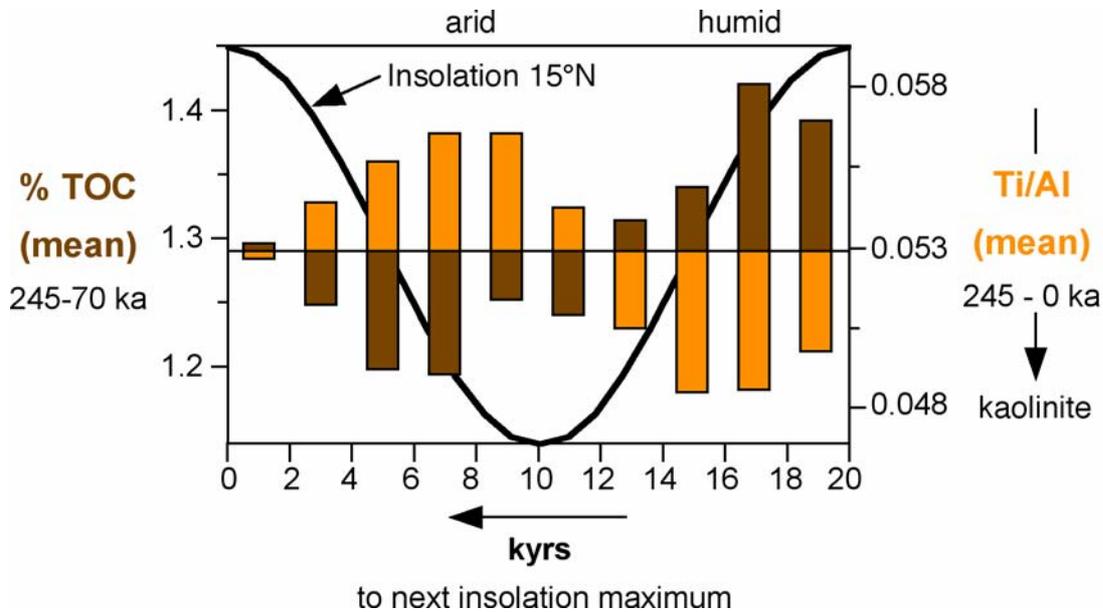
2001). A shift to lower Ti/Al ratios in sediments younger than 127 ka (Termination II) from average values of 0.055 to 0.051 supports the conclusion of generally more humid climatic conditions following the penultimate glacial-interglacial transition.



**Figure 5.2:** Organic geochemical records from elemental analysis and mass spectrometry of Late Quaternary sediments of the Niger deep-sea fan (GeoB 4901), compared to the records of insolation ( $15^{\circ}$  N) and Ti/Al ratios from inorganic geochemical investigations (Zabel et al., 2001). Low Ti/Al ratios parallel to insolation maxima indicate intense chemical weathering due to humid climate conditions in tropical Africa and enhanced supply of kaolinite-rich soils; MIS = marine isotopic stage, T II = Termination II (127 ka).

Total organic carbon contents (TOC) and accumulation rates ( $AR_{TOC}$ ) range from 0.65 to 1.95 % and 0.022 to 0.078  $g/m^2/kyr$ , respectively, with decreasing values down core. Notably, TOC increases by about 13 % and  $AR_{TOC}$  by 50 % to higher average values in sediments younger than Termination II (127 ka). In sediments older than Termination II a pronounced precessional cyclicity and a negative correlation with Ti/Al ratios is observed for TOC revealing highest OM concentrations during periods of enhanced riverine kaolinite supply. This relationship is also illustrated by the projection of mean Ti/Al and TOC values relative

to an idealized 20 kyrs insolation cycle. As evident from Figure 5.3 maxima in TOC and kaolinite occur synchronous and with a time delay of about 2-4 ka following insolation maxima. The observed relation between kaolinite supply and OM concentration disappears in sections younger than Termination II (Fig. 5.2) mainly due to the missing high-amplitude precessional frequency pattern of TOC. Notably, TOC tends to be slightly enhanced during cool and arid MIS 5.2 and 2, and in these cases corresponds to maxima of Ti/Al.



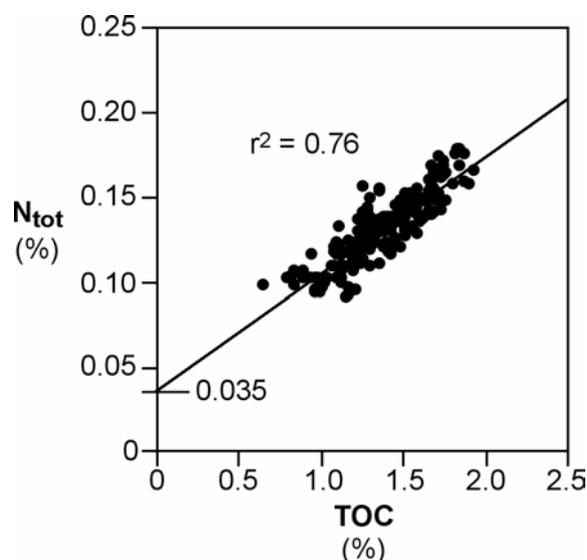
**Figure 5.3:** TOC and Ti/Al of Niger deep-sea fan sediments from core sections older than 127 ka (Termination II) projected to an idealized insolation cycle at 15°N. Mean values were calculated of all samples that correspond to a certain section of the insolation record and corrected for the idealized 20 kyrs insolation cycle (average number of samples per 2kyrs class: 41). OM concentrations in the Niger fan sediments apparently are closely related to riverine kaolinite supply. Both records reveal a 2-4 ka time delay relative to insolation maxima.

Degradation rates of bulk organic matter ( $C_{org}/C_{org}^*$ ) increase with burial depth proposing progressive decay of labile OM.  $C_{org}/C_{org}^*$  ratios around 0.72, i.e. 28 % of the original bulk OM content has been mineralised, characterize young sections (< 40 ka). In the older sediments bulk OM degradation rates decrease to average values of 0.56 (200 - 250 ka). Bulk OM degradation rates reveal no correlation with any other bulk parameter. We therefore assume that variations in TOC do not primarily result from changing intensity of microbial degradation but rather reflect primary changes in sedimentary OM supply and composition.

Concentrations and accumulation rates of carbonate range from 2.4 to 36.1 % and 0.11 to 1.23 g/m<sup>2</sup>/kyr, respectively (Fig. 5.2). Both tend to be enhanced during cool and arid climate stages, e.g. MIS 6, 5.2, 4, 2. Comparable to other bulk organic records a remarkable shift towards lower values after Termination II, i.e. from 20.9 to 13.7 %, is recognized.

Total nitrogen contents range from 0.09 to 0.18 % (average 0.13) being closely related to TOC ( $r^2 = 0.75$ , Fig. 5.4). The y-axis intercept of the regression line at 0.035 %  $N_{tot}$  for zero

percent TOC suggests that a certain amount of the total nitrogen is inorganic in nature, likely ammonium ( $\text{NH}_4^+$ ) released from OM degradation bound to clay minerals.  $C_{\text{org}}/N_{\text{tot}}$  ratios range from 6.6 to 12.9 (average 10.5, Fig. 5.2).



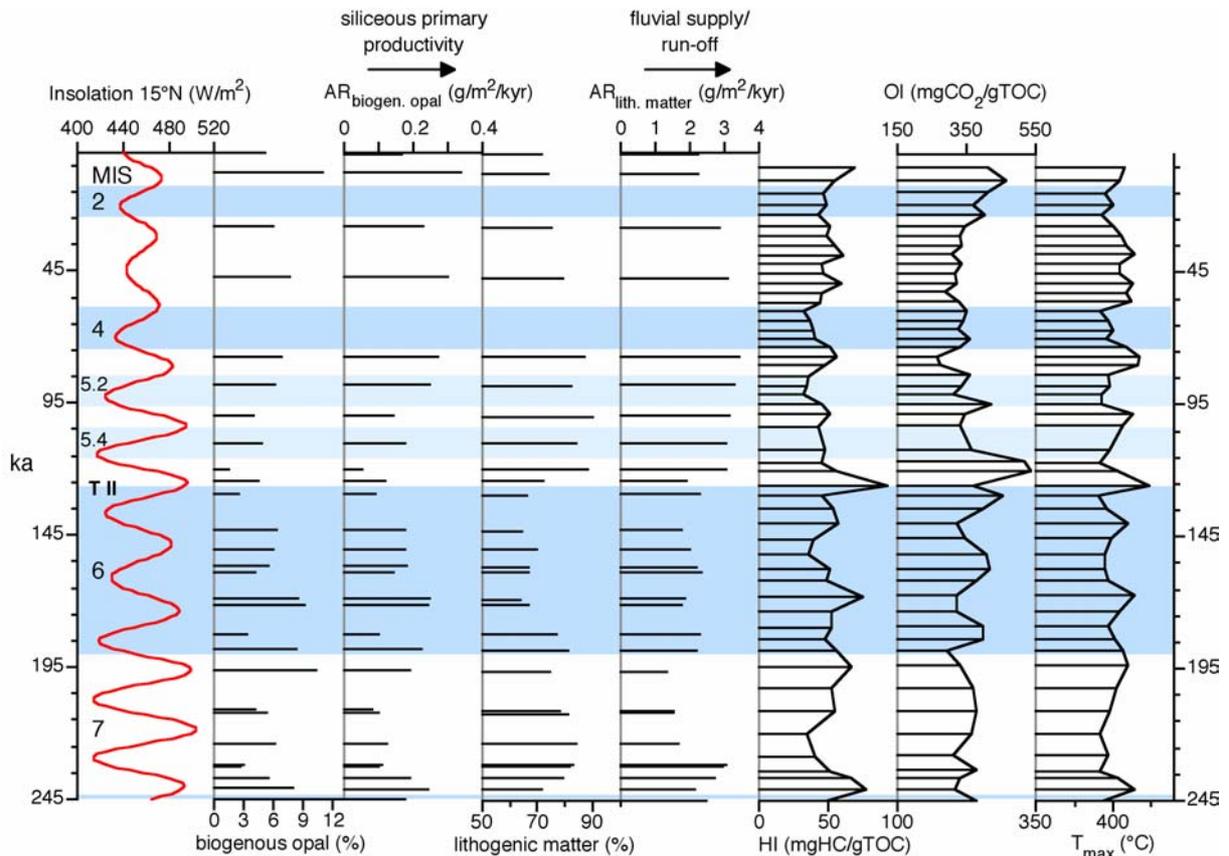
**Figure 5.4:** Relation of total nitrogen and organic carbon concentrations in sediments of the Niger deep-sea fan (GeoB 4901). Positive y-axis intercept of the regression line for zero percent TOC suggests certain amounts of inorganic nitrogen (ammonium).

Bulk  $\delta^{13}\text{C}_{\text{org}}$  values range from -20.7 to -16.8 ‰ (average -18.4 ‰, Fig. 5.2). They are generally more positive during more arid climate conditions, i.e. MIS 6 and sub-stages 5.2, 5.4. The more positive  $\delta^{13}\text{C}_{\text{org}}$  values may either be attributed to increased admixture of marine OM (values around -18 ‰ could be interpreted as entirely marine OM) or of terrigenous OM deriving from  $C_4$  plants (end-member values of about -12 ‰, Sackett, 1989). The latter may be supplied either directly as particulate OM or as part of the SOM fraction. The record of bulk  $\delta^{13}\text{C}_{\text{org}}$  values reveals a remarkable co-variation with the  $C_{\text{org}}/N_{\text{tot}}$  record.

Biogenous opal concentrations and accumulation rates range from 0.08 to 11.06 % and 0.05 to 0.34  $\text{g}/\text{cm}^2/\text{kyr}$ , respectively, with average values of 5.56 % and 0.17  $\text{g}/\text{cm}^2/\text{kyr}$  (Fig. 5.5). Comparable to the other geochemical records mean opal accumulation rates are lower before Termination II than afterwards, they shift from 0.16 to 0.20  $\text{g}/\text{cm}^2/\text{kyr}$ . As a maximum approximation of the non-biogenic (terrigenous lithogenic) matter fraction we assume that non-biogenic terrigenous matter equals the total sediment minus the concentrations of  $\text{CaCO}_3$ , TOC, and biogenous opal. Accordingly, ranges of terrigenous (lithogenic) matter may be as high as 64 to 90 % (average: 76 %). Despite the uncertainty of a terrigenous biogenous opal fraction these high numbers clearly argue for a dominant terrigenous (mainly riverine) nature of the deep-sea fan sediments. Further the accumulation rates of non-biogenic sediment increase from 2.1 to 2.8  $\text{g}/\text{cm}^2/\text{kyr}$  after Termination II probably due to elevated riverine sediment export.

Results from Rock-Eval pyrolysis support that bulk OM in the Niger fan sediments is immature with respect to hydrocarbon (HC) generation, taking  $T_{\text{max}}$  values between 365 and 424°C (average 401°C) into account (Fig. 5.5). Despite all over elevated TOC concentrations the amount of HC generated during pyrolysis remains low as evident by the HI that hardly reaches 90  $\text{mgHC}/\text{gTOC}$  but typically scatter around 50  $\text{mgHC}/\text{gTOC}$ . According to Tyson (1995) such low HI values from immature OM characterize *type IV* kerogen, representing

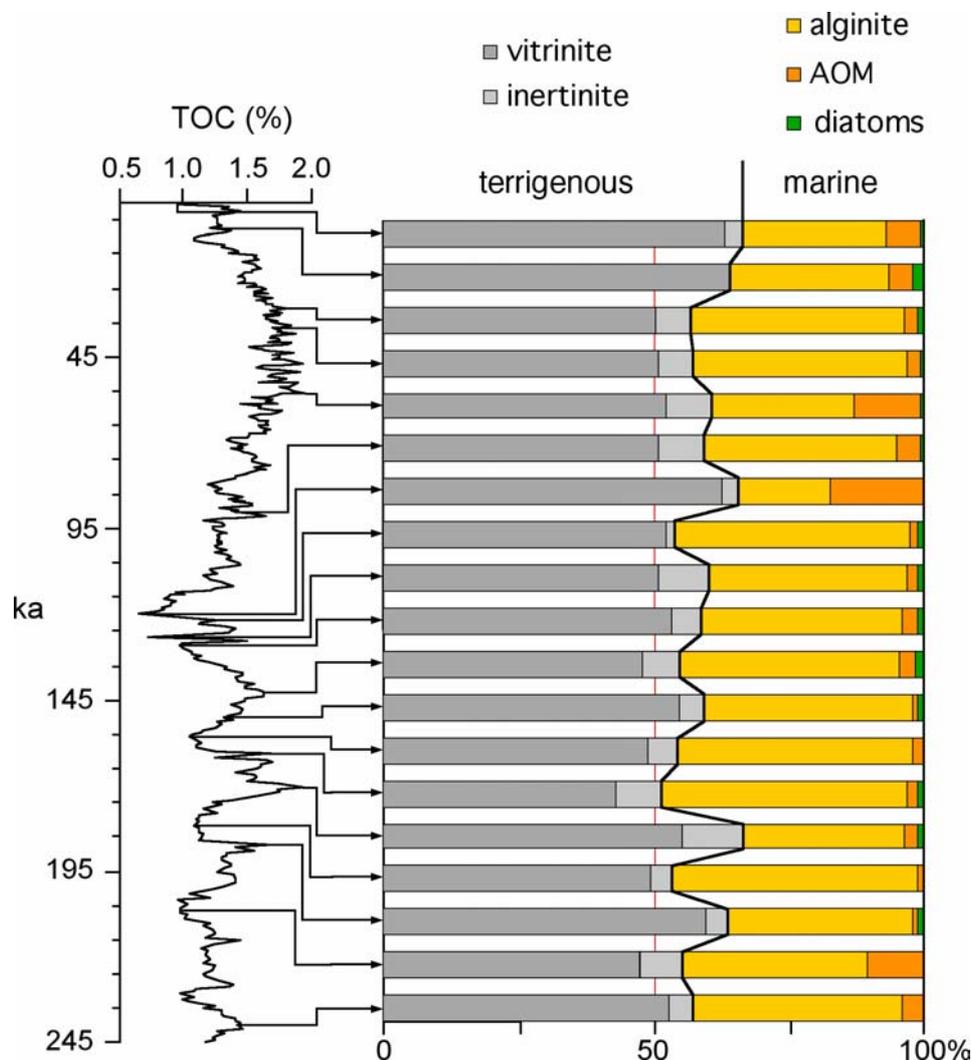
strongly oxidized OM preferentially from terrigenous sources. Opposite, the average  $\text{CO}_2$  release of 412 mg/gTOC (OI) is exceptionally high in the Niger sediments comparable to other young marine sediments containing immature OM (Tyson, 1995). Tissot and Welte (1984) define OM revealing abnormally low H/C ratios (corresponding to HI) associated with high O/C ratios (OI) as *residual type* of organic matter that may be reworked, oxidized inertinitic OM likely stemming from subaerial weathering or biologic oxidation in swamps and soils.



**Figure 5.5:** Contents and accumulation rates of biogenous opal and (terrigenous) lithogenic matter and Rock-Eval parameters of Late Quaternary sediments from the Niger fan (GeoB 4901). Enhanced accumulation rates of lithogenic matter after Termination II indicate a general shift towards more humid climate conditions with enhanced fluvial run-off.

Organic petrological investigations indicate that at least 50 % of the observed particulate OM is of terrigenous origin (Fig. 5.6). The relative amounts of terrigenous macerals (vitrinite, inertinite) range from 50 to 83 % (average 62 %) independent from climatic boundary conditions. Remarkably, 60 to 91% of the counted terrigenous particles are smaller than 10  $\mu\text{m}$  (average 74 %), i.e. the terrigenous OM fraction is generally fine-grained. Stable terrigenous OM stored and protected between clay minerals is invisible under standard reflected light microscopy whereas marine OM adsorbed to clay minerals should be recognizable as matrix fluorescence. However, fluorescence of the mineral matrix was not observed suggesting that OM of marine sources is rare both particulate and sub-microscopic.

We therefore emphasize that the proportions of terrigenous OM estimated from macerals analysis are minimum numbers that only represent the particulate fraction from plant litter and soils. This restriction implies that terrigenous proportions represent only a part of the total terrigenous OM, specifically in samples with elevated contents of clay-rich soils where a considerable contribution of detrital, terrigenous OM may be expected.



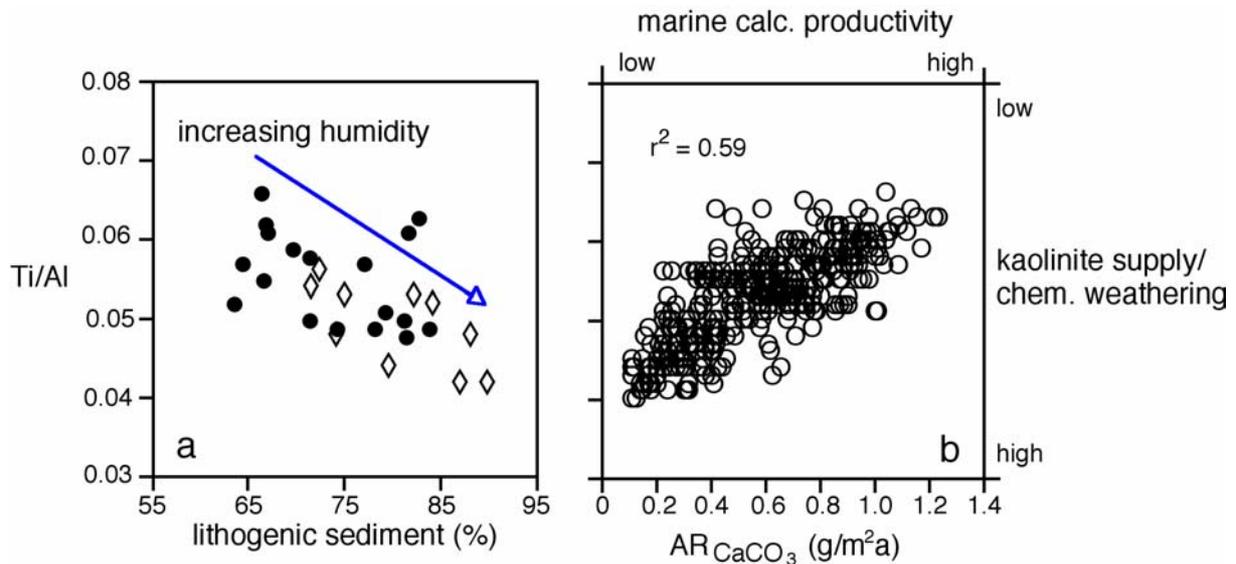
**Figure 5.6:** Results from maceral analysis of Late Quaternary of the Niger deep-sea fan sediments (GeoB 4901) illustrating that at least half of the particulate sedimentary organic matter originates from terrigenous plant matter with minor contribution of inert (oxidized) sources.

## 5.5 Discussion

### 5.5.1 Principle controls on late Quaternary marine sedimentation on the Niger fan

The Ti/Al record from the Niger core reveals a pattern that documents the principle effect of insolation-driven climate change. As shown by Zabel et al. (2001) elevated supply of kaolinite-rich terrigenous material is directly linked to humid African climate stages with a 5 kyrs delay following insolation maxima. The observed co-variation of non-biogenic sediment

with Ti/Al including the general shift after Termination II suggests that Ti/Al detects both, the concentration of kaolinite in the suspended river load and the history of riverine sediment supply (Fig. 5.7a).

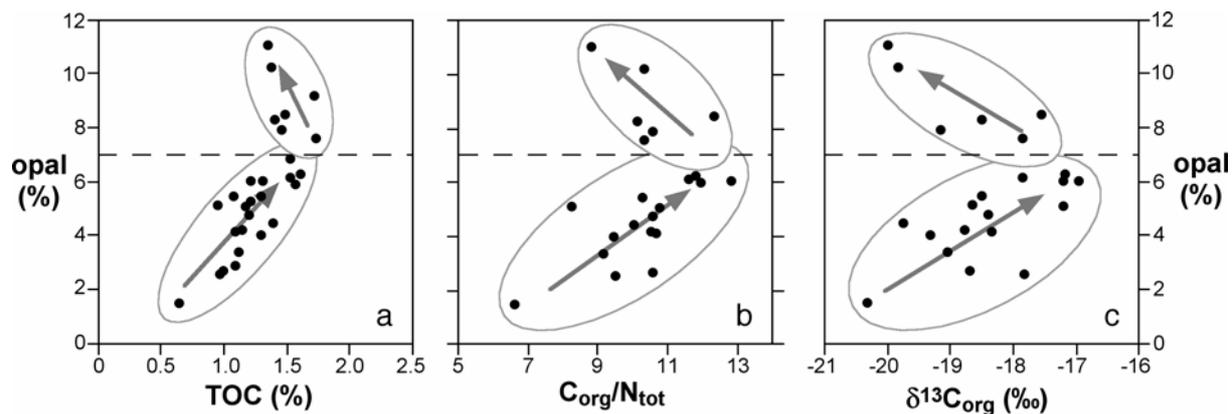


**Figure 5.7:** **a)** Relation of non-biogenic terrigenous sediment contents and Ti/Al ratios; different symbols represent samples from sediments deposited before (circles) and after (diamonds) Termination II. The general shift towards lower Ti/Al ratios and higher non-biogenic sediment contents in sediments younger than Termination II proposes elevated riverine export of kaolinite-rich material and thus more humid climate conditions. **b)** Co-variation of carbonate accumulation rates and Ti/Al ratios suggesting that calcareous marine production off the Niger was enhanced during more arid climate stages with diminished chemical weathering and erosion of kaolinite-rich soils. Apparently, calcareous marine productivity is not river-induced but controlled by other factors, e.g. nutrient supply from oceanic upwelling, sea surface temperatures, or salinity.

Notably, TOC and carbonate records from the Niger core are not correlated ( $r^2 = 0.05$ ) suggesting that Late Quaternary OM supply and burial was principally decoupled from calcareous primary production. Instead, a co-variation of carbonate accumulation with Ti/Al is recognized (Fig. 5.7b) proposing that calcareous production was primarily linked to other mechanisms of nutrient delivery (e.g. trade-induced upwelling along the tropical Atlantic continental margin) or basic ecological conditions (e.g. sea surface temperatures, salinity) rather than to riverine nutrient supply through the Niger.

A positive correlation of biogenous opal and TOC especially for opal concentrations below 7 % at the first glance suggests that OM sedimentation was related to siliceous primary production (Fig. 5.8). Given the parallel trends in  $C_{org}/N_{tot}$  and heavy bulk  $\delta^{13}C_{org}$  values of up to -17 ‰, however, we rather conclude that opal sedimentation increased synchronously with supply of nitrogen-poor C<sub>4</sub> plant matter. Opposite trends of  $C_{org}/N_{tot}$ , and bulk  $\delta^{13}C_{org}$  for opal contents above 7 % instead suggest increasing influence of marine OM on bulk organic geochemical signatures. The latter interpretation, however, contradicts with consistent low Hydrogen Indices determined for all sediment samples that exclude a major contribution of marine OM. Notably, a change of the main constituent of the terrigenous fraction from C<sub>4</sub>

plant matter to nitrogen-rich SOM of  $C_3$  plant habitats parallel to successively increasing run-off, nutrient supply, and opal production would have the same effect on the organic geochemical record. We therefore conclude that increasing continental humidity at first fostered effective drainage of  $C_4$  plant habitats and, at the same time, enhanced riverine nutrient export that stimulated siliceous primary production. With further increasing humidity and riverine nutrient export the relative amount of SOM from newly establishing  $C_3$  plant habitats and/or from areas with older soil systems that were not drained during arid climate stages progressively increases.



**Figure 5.8:** Biogenous opal concentrations compared to (a) TOC, (b)  $C_{org}/N_{tot}$ , and (c) bulk  $\delta^{13}C_{org}$ . Biogenous opal apparently increases synchronously with nitrogen-rich and  $^{12}C$ -depleted particulate terrigenous OM from  $C_4$  plant habitats. Nitrogen-rich SOM and particulate OM from  $C_3$  plant habitats exert influence on the geochemical signatures of bulk OM in samples with opal concentrations above 7%. The grey arrows follow changing OM quality during stages of increasing continental humidity.

Summarizing the observations on opal and carbonate contents and their individual accumulation rates and considering their non-relation ( $r^2 = 0.01$ ) we conclude that siliceous and calcareous production off the Niger River were principally governed by different mechanisms. We assume that opal production mainly depended on dissolved silicate from the Niger run-off. A comparable mechanism has been suggested to determine siliceous primary productivity off the Congo River (Schneider et al., 1997a).

### 5.5.2 Implications for a major shift in tropical African climate at Termination II

We so far argue that OM burial went along with riverine supply of kaolinite-rich soils, at least prior to Termination II. Following that pronounced climate transition average TOC contents are higher by 13%. Regarding the opposite shifts of Ti/Al and carbonate we assume a general shift to more humid conditions in central Africa, with enhanced erosion of kaolinite-rich soils and terrigenous OM following the transition to the penultimate interglacial.

The pronounced variability of TOC contents disappears for TOC accumulation rates. Actually, accumulation rates of TOC expose a positive correlation with bulk sediment accumulation rates ( $r^2 = 0.64$ ) whereas carbonate and opal accumulation rates do not ( $r^2 = 0.01$  and  $0.07$ , respectively). This observation appears reasonable given that a dominating part

of the OM varies in phase with the inorganic terrigenous material, both together making up at least three quarters of the bulk sediment. Changes of bulk OM contents prior to Termination II therefore presumably mainly reflect variations of terrigenous OM concentrations in the river load. The pronounced shift in most records after Termination II (e.g. enhanced accumulation rates of non-biogenic terrigenous matter and elevated kaolinite contents) supports a general change in climatic conditions to more humid climates and a stronger monsoon system in tropical Africa after the transition to the last interglacial.

### 5.5.3 *C<sub>4</sub> plant-derived particulate OM and SOM*

Results from Rock-Eval pyrolysis indicate that sedimentary OM in Late Quaternary sediments of the Niger deep-sea fan primarily consists of strongly degraded, hydrogen-poor but oxygen-rich terrigenous OM of type III to IV kerogen. Additionally, organic petrological investigations reveal a dominantly terrigenous origin of the recognizable macerals. These findings are not consistent with bulk  $\delta^{13}\text{C}_{\text{org}}$  signatures that suggest preservation mainly of marine OM assuming that  $\delta^{13}\text{C}_{\text{org}}$  signatures of -18 ‰ to -20 ‰ represent a pure marine origin. An alternative and more reasonable interpretation would be that enhanced input of *C<sub>4</sub>* plant matter and degraded, <sup>12</sup>C-depleted SOM of both, *C<sub>3</sub>* and *C<sub>4</sub>* habitats caused the observed shift in bulk  $\delta^{13}\text{C}_{\text{org}}$  signatures towards more positive values.

Vascular land plants are classified according to their type of metabolism during carbon fixation. Most of the higher plants use the Calvin-Benson cycle of carbon fixation (*C<sub>3</sub>* plants) that discriminates against the heavy carbon isotope (<sup>13</sup>C). The isotopic ratio of *C<sub>3</sub>* terrigenous OM therefore ranges from -23 ‰ to -34 ‰, with an average value of about -27 ‰ (Meyers, 1997; Guillaume et al., 1999). Tropical grasses like Poaceae and Cyperaceae that grow in open vegetation habitats, i.e. in tree and grass savannah, in contrast, are mostly *C<sub>4</sub>* plants using the Hatch-Slack cycle of carbon fixation that reveal isotopic ratios between -9 ‰ and -17 ‰ (average: -12 ‰; Gearing, 1988; Sackett, 1989).

To assess the influence of OM from *C<sub>4</sub>* plant sources we next consider the striking similarity in  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  and bulk  $\delta^{13}\text{C}_{\text{org}}$ . Their consistent trends in the Niger core (see Fig. 5.2) indicate that bulk OM with  $\delta^{13}\text{C}_{\text{org}}$  values above -18 ‰ is depleted in nitrogen. As terrestrial plant matter generally is nitrogen-poor compared to marine OM a good candidate to explain such a relationship is *C<sub>4</sub>* plant matter from savannah areas: the isotopic ratios of savannah type vegetation range from -12 ‰ to -18 ‰ depending on the relative proportions of *C<sub>3</sub>* and *C<sub>4</sub>* plants (Delègue et al., 2001). On the other hand, *C<sub>4</sub>* plant material may be supplied to the Niger fan as part of the eroded SOM fraction. The transformation of plant residues (leaf litter, roots) to SOM and its further mineralization in soils (humification) generally is accompanied by (i) loss of the light stable organic carbon isotope (<sup>12</sup>C) and (ii) relative enrichment of nitrogen. Delègue et al. (2001) report  $\delta^{13}\text{C}_{\text{org}}$  values up to -13 ‰ for SOM of natural savannah soils in Gabon and Congo. In contrast, Guillaume et al. (1999) detected average  $\delta^{13}\text{C}_{\text{org}}$  values of SOM in *C<sub>3</sub>*-dominated tiger bush-type vegetation of the Sahelian zone in Niger (Niamey) of -22.4 ‰ for bare areas (currently without vegetation cover) and -23.6 ‰ for vegetation-covered locations. In Central Africa,  $\delta^{13}\text{C}_{\text{org}}$  values of SOM from *C<sub>3</sub>* vegetation in deep soils typically are lower than -24.5 ‰ (Delègue et al., 2001).

Numerous studies of soil profiles report decreasing  $C_{org}/N_{tot}$  ratios with proceeding humification (e.g. Guggenberger et al., 1995; Christensen, 1996; Zech et al., 1997; Baldock and Skjemstad, 2000; Glaser et al., 2000; Solomon et al., 2000). Frankart (1960) investigated A1 horizons of savannah and rainforest soils in the north east of the Republic of Congo. There rain forest soils reveal average  $C_{org}/N_{tot}$  ratios of 8.6 and savannah soils of 13.3.  $C_{org}/N_{tot}$  ratios of SOM may even reach values below 8, as observed for example by Sahrawat (1995) in a soil profile from India. Thus, variable mixtures of particulate  $C_4$  plant remains and SOM from  $C_4$  and mixed  $C_3/C_4$  plant habitats may not only explain the full range of bulk  $\delta^{13}C_{org}$  values of the Niger deep-sea fan sediments, in fact they might even reveal  $C_{org}/N_{tot}$  ratios close to those reported as ‘typical’ for marine OM.

Regarding these observations and conclusions the conventional interpretation of bulk  $\delta^{13}C_{org}$  and  $C_{org}/N_{tot}$  ratios as means to determine riverine terrigenous OM in marine sediments has to be abandoned, at least for Late Quaternary sediments from the tropical West-African continental margin. The finding that elevated TOC concentrations occur during more humid climate conditions together with relatively enhanced supply of kaolinite-rich lithogenic material strongly supports the conclusion that bulk OM on the Niger deep-sea fan contains significant amounts of SOM. The influence of SOM on bulk organic geochemical signatures therefore requires a new approach to assess specific differences in SOM quality as well as temporal variations in supply.

#### 5.5.4 Soil organic matter in Late Quaternary Niger and Congo deep-sea fan sediments

The effect of SOM on bulk geochemical and isotopic properties in continental margin sediments so far has hardly been addressed in paleoceanography and paleoclimatology. We therefore discuss this specific type of terrigenous OM in African continental margin sediments in a broader context. This approach takes recent observations from the Congo deep-sea fan into account (Holtvoeth et al., 2003).

		TOC (%)	$C_{org}/C_{org}^*$	CaCO <sub>3</sub> (%)	bulk $\delta^{13}C_{org}$ (‰)	$C_{org}/N_{tot}$	Opal (%)	Ti/Al
Niger	Range	0.65 - 1.95	0.39 - 0.85	2.4 - 36.1	-20.7 to -16.8	6.6 - 12.9	0.1 - 11.1	0.04 - 0.066
	Mean	1.40	0.64	16.3	-18.4	10.5	5.6	0.053
	n	404	403	404	206	200	28	405
Congo*	Range	1.3 - 4.1	0.58 - 0.79	0.0 - 16.6	-22.3 to -19.9	7.6 - 9.8	1.4 - 14.3	0.037 - 0.05
	Mean	2.3	0.69	2.7	-20.8	8.6	9.7	0.043
	n	110	59	110	87	59	24	221

\* 250 - 0 ka (except Ti/Al: 200 - 0 ka from core GeoB 1008)

**Table 5.1:** Ranges and mean values of bulk organic parameters from the Niger fan compared to results from Congo fan (data from Holtvoeth et al., 2001, 2003). Ti/Al ratios from the Niger fan after Zabel et al. (2001); Ti/Al data of the Congo fan core GeoB 1008 according to Schneider et al. (1997a).

On average, late Quaternary sediments from the Niger fan contain less organic carbon than those from the Congo fan (Table 5.1). Bulk OM degradation rates ( $C_{org}/C_{org}^*$ ), by comparison, are similar however show a broader range for the Niger fan sediments. Niger fan bulk OM typically is poorer in total nitrogen with a much broader range of  $C_{org}/N_{tot}$  and significantly enriched in  $^{13}C$  compared to the Congo sediments. The offset in bulk  $\delta^{13}C_{org}$  in the order of 2 ‰ refers to the all over enhanced relative proportion of  $C_4$  plant matter supplied by the Niger River.

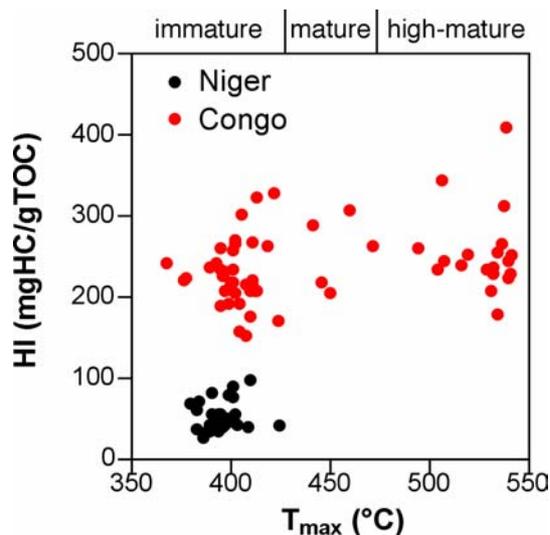
Pyrolytic properties reveal striking differences between the two river systems. Specifically, the amount of hydrocarbons generated from the kerogen is considerably higher in the Congo fan sediments as demonstrated by the HI values (Table 2) whereas OI values are significantly lower. The corresponding kerogen types are mixed II/III type for the Congo and III/IV for the Niger fan, respectively.

		HI	OI	$T_{max}$ (°C)	Kerogen Type
Niger	Range	23 – 157	192 - 828	380 - 424	III – IV
	Mean value n = 51	62	412	395	III
Congo*	Range	154 – 411	106 - 297	368 - 542	II – IV
	Mean value n = 59	238	164	385/531	II/III

\* 250 - 0 ka

**Table 5.2:** Ranges and mean values of parameters from Rock-Eval pyrolysis from the Niger fan compared to results from Congo fan (Holtvoeth et al., 2001). In addition to labile marine and terrigenous OM, kerogen from the Congo fan contains a stable, high-mature organic fraction that generates hydrocarbons at high temperatures (double peak within S2 temperature window) during pyrolysis as revealed by  $T_{max}$  values exceeding 450°C.

A conspicuous difference between both fan sediments is the temperature of maximum hydrocarbon generation from the kerogen,  $T_{max}$  (Table 5.2 and Fig. 5.9). As described by Holtvoeth et al. (2001, 2003) OM of the Congo fan consists of two organic fractions that are clearly distinguished by their reactivity (or thermal stability) resulting in a double peak within the S2-temperature window (at average  $T_{max}$  temperatures of 385°C and 531°C, respectively). Quantification of the sub-peak areas was used to develop a new proxy for bulk OM reactivity in marine sediments, the low-mature/high-mature ratio (lm/hm). To further assess specifically the origin of the low-reactive component in the Congo fan sediments, Holtvoeth et al. (2003) studied the relations and temporal variations of TOC, bulk OM degradation rates, lm/hm ratios,  $C_{org}/N_{tot}$  and  $C_{org}/N_{org}$  values, bulk  $\delta^{13}C_{org}$ , and lignin phenols. They conclude that samples with lm/hm ratios lower than 2 contain a highly degraded, stable, and nitrogen-rich organic source most likely from soils formed in the Congo catchment. Characteristically, this type of SOM is able to generate considerable amounts of HC during pyrolysis despite its high-mature nature.

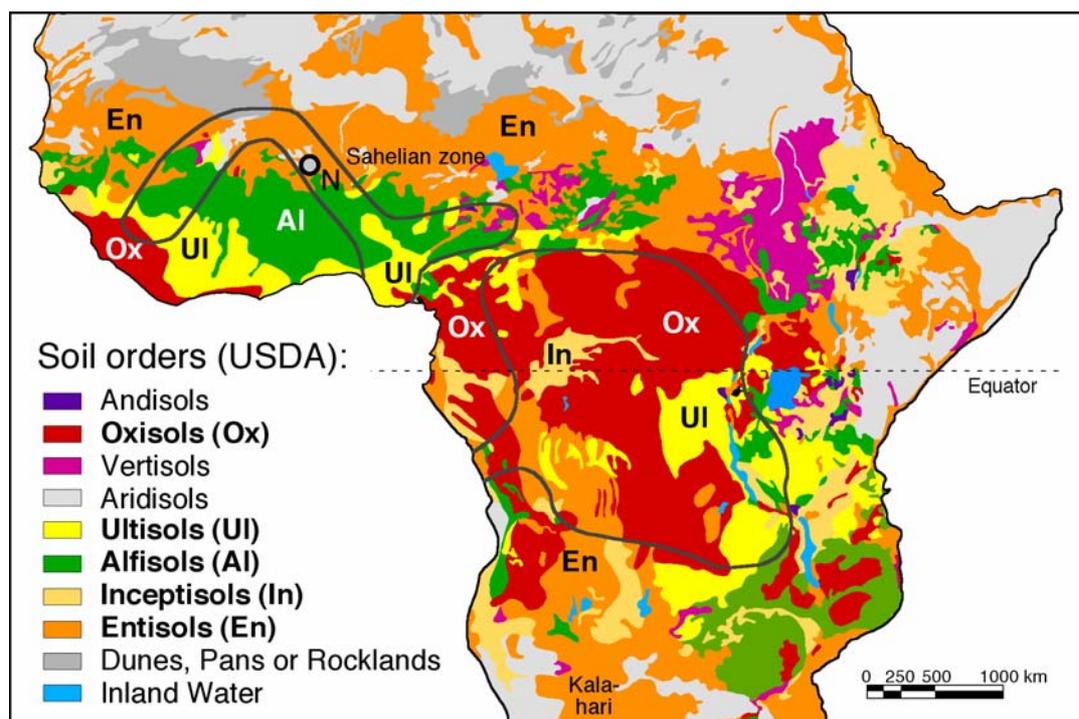


**Figure 5.9:**  $T_{\max}$  and HI values from Niger and Congo deep-sea fan sediments. Bulk OM from the Niger fan is immature and generates low amounts of hydrocarbons. In contrast, bulk OM from the Congo fan consists of two fractions with distinct different thermal stability (maturity). Both fractions generate considerable amounts of hydrocarbons.

Opposite to the Congo fan, OM of the Niger fan does not contain such a thermally stable/high-mature organic fraction. The conclusion, however, that export of SOM is restricted to the Congo fan is rash and requires a more detailed investigation of the different types and properties of soils that form in the catchment of the two river systems. It appears reasonable to assume that different types of soils or SOM/plant matter combinations, respectively, are exported through the Congo and Niger rivers.

#### 5.5.5 Soil orders in tropical Africa

The distribution of the main soil orders in central and subtropical Africa is shown in Figure 5.10. The classification of the soil orders follows the soil taxonomy of the United States Department of Agriculture (USDA; 2<sup>nd</sup> edition, available at <http://soils.usda.gov>).



**Figure 5.10:** see next page

**Figure 5.10:** Soil map of Africa (modified from Eswaran et al., 1997). The most important difference between the Congo and Niger catchments is the absence of Oxisols within the Niger catchment. Entisols in the western part of the Congo basin and Ultisols in the east cover ancient Oxisols. Dark grey lines mark the catchment areas; N = Niamey.

The dominating soils in the Niger catchment area are Entisols, Alfisols and Ultisols. The most important soil order in the rain forests of the Congo Basin and adjacent areas is Oxisol. According to Eswaran et al. (1997), many of ancient Oxisols are covered by more than 150 cm of Holocene sands and, consequently, are classified as Entisols, Alfisols, or Ultisols, with sandy topsoil and low activity clayey subsoil. This can be recognized for example in the southwestern part of the Congo basin where a tongue of sandy soils extends from the Kalahari northwards (Fig. 5.10). A similar feature is seen in the Alfisols in the Sahelian zone: eolian sand from the Sahara has buried many of the former Ultisols and Oxisols. The most conspicuous and important difference in the modern distribution of the soil orders in the Niger and Congo catchments is that there are almost no surface exposures of Oxisols in the first one.

There are significant differences in organic geochemical properties of the various tropical African soil types (Table 5.3). Generally, the carbon stocks of clay-rich developed tropical soils (Ultisols, Oxisols) are higher than those of undeveloped clay-poor soils (Entisols, Inceptisols).

	undeveloped (young) soils		developed (old) mineral soils		
	no/minimal horizon development, no illuvial horizons		humification, $C_{org}/N_{tot}$ ratios; clay/kaolinite content organic carbon stocks		
soil order	Entisol	Inceptisol	Alfisol	Ultisol	Oxisol
substratum	eolian sands, floodplains deltadeposits, steep slopes		Pleistocene or older surfaces in Central Africa typical for mid- to end-Tertiary plateaus <sup>1)</sup>		
moisture regime	arid/semi-arid	arid to humid	semi-humid/ semi-arid	humid	(warm) permanent humid
typical vegetation (in Africa)	savannah (e.g. Sahel zone, Kalahari)	wooded grasslands/ open woodlands	grassy woodlands/ open forests	forests	rain forest (e.g. Congo basin)
sand, clay	sandy ( $< 30\%$ clay in fine fraction)	sandy	basic argillic (clay-rich) B-horizon	clay-rich (illuvial argillic horizon)	clay-rich (kaolinite dominated, no illuvial clay-horizon)
special properties	$< 1\%$ SOM		$> 10\%$ weatherable minerals	$< 10\%$ weatherable minerals, more deeply weathered than Alfisol	extr. weathered, Fe/Al sesquioxides, SOM-rich/humic subgroups <sup>1)</sup> , stable SOM

<sup>1)</sup> Eswaran et al., 1997

**Table 5.3:** The main soil orders of tropical Africa and their most important characteristics. Apart from the status of soil development regarding age and clay content, the sequence of soil orders also reflects the development of SOM quality, i.e. progressive decomposition (humification) of SOM from Entisols to Oxisols. The general trend of decreasing  $C_{org}/N_{tot}$  ratios during humification is described by numerous studies (see references in the text).

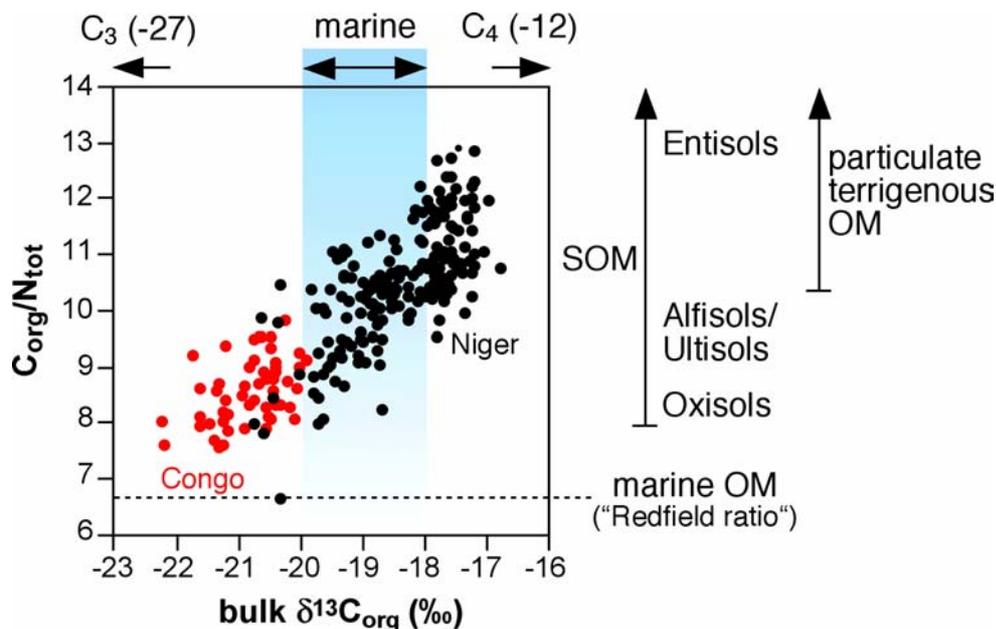
For example, soils from tropical rainforest in Liberia show higher carbon stocks than soils in semi-arid Africa (Zech et al., 1997), and sandy soils from Katanga (Democratic Republic of Congo) reveal clearly lower organic carbon contents than clay-rich soils of the same region (Sys, 1971). Clay minerals play a decisive role for both, degradation and mineralization of organic matter in soils as well as for protection and selective preservation of specific organic compounds. On the one hand, microbial decomposition of organic substrate and synthesis of humic acid-like polymers are more efficient in the presence of clays (Martin and Haider, 1986). On the other hand, large amounts of fine grained or dissolved SOM released from the topsoil litter and humus layers by eluviation can be bound to clay minerals and thus are protected against biological attack as demonstrated by numerous studies in soil sciences (e.g. Eusterhues et al., 2003; Zech et al., 1997; Guggenberger et al., 1995; Christensen, 1992; Spain, 1990; Theng et al., 1986). Protection of dissolved OM by clay minerals is most effective in the presence of iron and aluminium oxyhydroxides (or sesquioxides, e.g.  $\text{Al}_2\text{O}_3$ ). The metal oxyhydroxides work as a coupler between charged clay mineral surfaces and organic molecules. Dissolved OM rich in carboxyl/hydroxyl functional groups and hydrophobic aromatics sorbs more strongly to metal oxide surfaces than hydrophylic fractions like polysaccharides (Kaiser and Guggenberger, 2000; Gu et al., 1995). Sorption processes amplify the fractionation of bulk OM by relative enrichment of stable OM compounds while unprotected labile OM is preferentially degraded. OM of soils with maximum concentrations of oxyhydroxides (Oxisols) therefore becomes successively enriched in aromatic OM compounds with progressive OM decomposition (humification). As highly aromatic carboxylated humic material represents the chemically most stable soil carbon pool (Haumaier and Zech, 1995) we conclude that the high-mature terrigenous organic fraction observed in the Congo fan sediments is a typical component deriving from the Oxisol habitat of the Congo basin. In the Niger catchment, in contrast, Oxisols are almost absent and thus a stable (high-mature) SOM fraction does not occur in sediments from the Niger fan. Instead, relatively higher proportions of O-alkyl carbon from less degraded terrigenous particulate OM and SOM (e.g. from Entisols) may be expected. Such a component may be also responsible for the observed exceptionally high OI. Disnar et al. (2003) attributed unusually high OI values to initial organic matter oxidation that begins with dehydrogenation and is probably accompanied by oxygen uptake.

#### *5.5.6 An alternative interpretation of established bulk proxies in paleoceanography*

As described above  $C_{\text{org}}/N_{\text{tot}}$  ratios on average are higher for the Niger than for the Congo fan sediments (Table 5.1). This indicates that either SOM of the Niger catchment soils exposes a lower degree of humification and thus higher  $C_{\text{org}}/N_{\text{tot}}$  values or that relative amounts of particulate terrigenous OM are comparatively higher (or both). The broader range of  $C_{\text{org}}/N_{\text{tot}}$  ratios of the Niger fan sediments suggests distinct changes in the relative proportions of nitrogen-poor terrigenous OM (particulate OM, SOM from Entisols) and nitrogen-rich terrigenous OM (SOM from Ultisols and Alfisols) and thus reflect aridity humidity cycles.

The amount and the isotopic signature of SOM exported by the Niger and the Congo Rivers depend on the type of the vegetation cover within the catchment ( $C_3$  versus  $C_4$  plants) and on its degree of humification within the specific type of soil. The development of both, soil and

vegetation, is coupled to the moisture regime. During arid climate stages stronger dry northeasterly trades fostered the export of eolian sand from the Sahara desert across the Sahelian zone towards the south covering older soils like Alfisols and Ultisols within the Niger catchment. Contemporaneously, grass savannah vegetation expanded and largely replaced tree savannah and tropical woodlands whereas the rainforest cover was strongly reduced in tropical Africa as suggested by palynological records (e.g. Dupont et al., 2001; Jahns, 1996). Thus,  $C_4$ /Entisol domains largely replaced the  $C_3$ /Alfisol/Ultisol habitats within the Niger catchment and/or the effectiveness of drainage was strongly reduced. Consequently, the main compound of terrigenous OM exported by the Niger should have changed from nitrogen-rich degraded SOM of developed soils to nitrogen-poor particulate OM from undeveloped soils and enhanced proportions of ( $C_4$ ) plant remains. Eolian export of  $C_4$  plant matter probably increased simultaneously as suggested by enhanced supply of oxidized OM to the late Quaternary central Equatorial Atlantic (Wagner, 1999a). The proposed changes in central African vegetation and climate are supported by the late Quaternary  $C_{org}/N_{tot}$  and bulk  $\delta^{13}C_{org}$  records of the Niger fan as both parameters reveal higher values during more arid (cool) climate stages (Fig. 5.2). We therefore suggest that parallel trends in  $C_{org}/N_{tot}$  ratios and bulk  $\delta^{13}C_{org}$  primarily reflect contribution of SOM from different soil orders (Figure 5.11).



**Figure 5.11:** Relation of bulk  $\delta^{13}C_{org}$  values and  $C_{org}/N_{tot}$  ratios in Late Quaternary sediments of the Niger and Congo deep-sea fans. Co-variation of both parameters off the Niger indicates that bulk OM is more enriched in  $^{13}C$  than typical marine OM (-20‰ to -18‰) but nitrogen-poor, likely containing a significant amount of particulate OM from  $C_4$  plant habitats. Samples from the Congo fan instead reveal stronger admixture of  $C_3$  plant matter and contribution of highly degraded, nitrogen-rich SOM from Oxisols.

The Congo fan sediments do not reveal such a significant influence of nitrogen-poor particulate OM from a combined  $C_4$ /Entisol habitat. Though relative proportions of  $C_4$ /Entisol domains within the Congo basin considerably increased during arid climate stages (e.g. from

the Kalahari towards the north) the drainage of the Oxisol domain and contribution of highly degraded terrigenous OM persisted. Holtvoeth et al. (2003) have shown that TOC maxima off the Congo occurring during arid climate stages correspond to increased sedimentation (or better preservation) of labile marine OM. This nitrogen-rich organic fraction thus compensates reduced supply of nitrogen-rich SOM and relatively enhanced proportions of nitrogen-poor particulate OM. Therefore,  $C_{\text{org}}/N_{\text{tot}}$  ratios off the Congo do not reveal high-amplitude changes as observed off the Niger and remain on low levels. Summarizing, we conclude that bulk OM off the Niger contains less marine OM than off the Congo but larger proportions of particulate terrigenous OM either directly from plants or from undeveloped soils (Entisols).

A stronger influence of the Oxisol domain is not only reflected by organic geochemical properties of the Congo fan sediments but also by the generally lower Ti/Al ratios (Table 1). This observation is consistent with the assumption of Zabel et al. (2001) whereupon Ti/Al ratios mainly reflect varying contributions of different kaolinite-rich soils. After Termination II, no high-amplitude variations in Ti/Al are observed on the southern part of the Congo deep-sea fan (site GeoB 1008, Schneider et al., 1997a). This suggests that Oxisols established as the permanent and prominent feature within the Congo basin while erosion of kaolinite-poor, undeveloped soils (e.g. Entisols) from the catchment margins and their influence on bulk mineralogy of the deep-sea fan sediments was diminished.

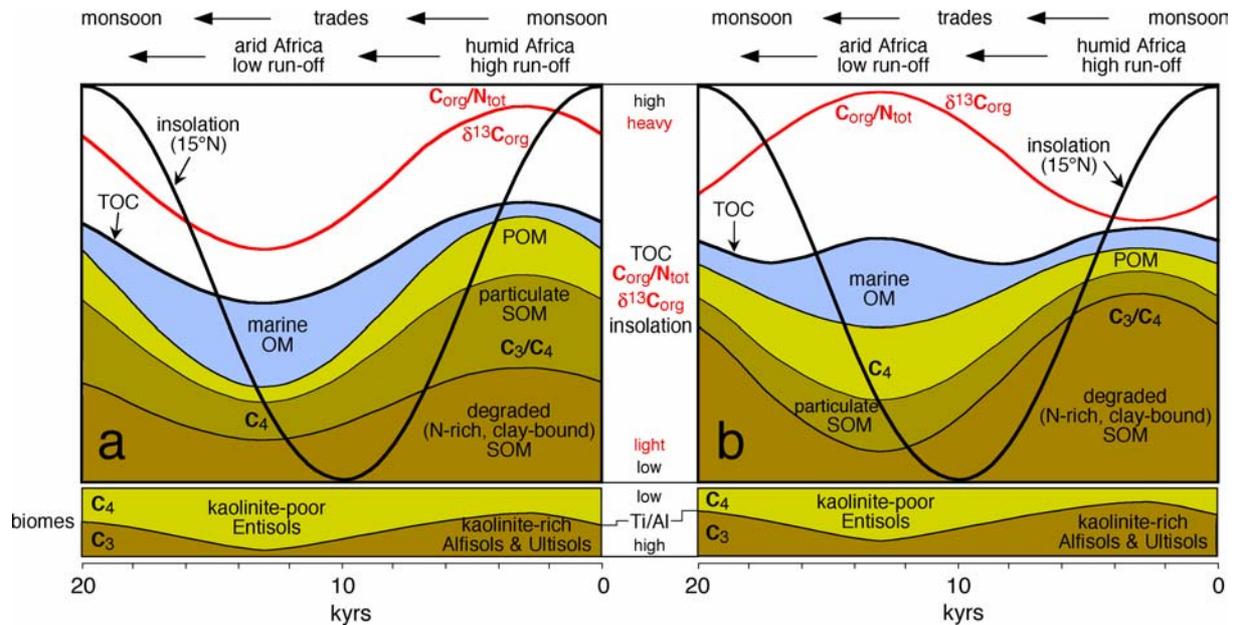
#### *5.5.7. A conceptual model linking climate changes and bulk OM composition*

Based on the observed relations of organic geochemical parameters, their patterns within the Quaternary records, and the information on soil and vegetation development, we propose a conceptual model that considers the influence of insolation-forcing on bulk organic matter composition of the Niger deep-sea fan sediments (Figure 5.12).

Prior to Termination II, under generally more arid climate conditions, variations in bulk OM composition are characterized by high-amplitude fluctuations of relative proportions of particulate OM that derives from less developed soils and plant litter (Fig. 5.12a). TOC contents,  $C_{\text{org}}/N_{\text{tot}}$  ratios, and bulk  $^{13}\text{C}_{\text{org}}$  were determined by SOM supply from both, undeveloped (Entisols) and developed soils (Alfisols, Ultisols), during more humid climate stages (insolation maxima) and by supply of particulate OM from  $C_4$  plant habitats, SOM from undeveloped soils (Entisols), and marine OM during arid climate stages (insolation minima). Relative amounts of particulate OM and SOM are diminished due to lowest carbon stocks of the sandy savannah soils and/or intermitted drainage of dry savannah areas.

Following Termination II, soils within the Niger catchment were more developed and/or persisting developed soil domains were better drained under generally more humid climate conditions. Variations of bulk OM composition in the fan sediments were mainly determined by high-amplitude fluctuations of relative proportions of nitrogen-rich SOM from clay-rich soils (Fig. 5.12b). Accordingly, TOC contents,  $C_{\text{org}}/N_{\text{tot}}$ , and bulk  $^{13}\text{C}_{\text{org}}$  were controlled by massive supply of SOM of developed soils (Alfisols, Ultisols) from  $C_3$  plant habitats during humid climates (insolation maxima) and by particulate OM from  $C_4$  plants and SOM of

undeveloped soils (Entisols) during arid climates (insolation minima). This model resembles the pattern of OM sedimentation on the Congo fan (Holtvoeth et al., 2003). There, the relative amount of particulate OM was even more reduced during humid stages (insolation maxima) due to the massive supply of highly degraded SOM from Oxisols (lm/hm ratios < 1), whereas marine OM was enhanced during arid stages (insolation minima) leading to elevated TOC contents and lm/hm ratios.



**Figure 5.12:** Conceptual model on the effect of insolation-forced climate changes on sedimentary bulk OM composition of Late Quaternary Niger deep-sea fan sediments.

**a) prior to Termination II:** During more humid climate stages (2-4 kyr after insolation maximum) elevated proportions of particulate terrigenous OM (plant litter) and particulate SOM of undeveloped soils (e.g. Entisols) from  $C_4$ -/ grass-rich vegetation lead to elevated  $C_{org}/N_{tot}$  ratios and isotopic signals ( $\delta^{13}C_{org}$ ). This OM fraction is reduced relative to marine OM and degraded SOM during most arid climate stages (2-4 kyr after insolation minimum) due to lowest carbon stocks of the sandy savannah soils and/or intermitted drainage of dry savannah areas. These compositional changes result in low  $C_{org}/N_{tot}$  and  $\delta^{13}C_{org}$  values. An analogous scenario can be seen in MIS 6 (Fig. 5.2).

**b) after termination II:** During most humid climate conditions (2-4 kyr after insolation maximum) the relative amount of nitrogen-rich SOM from developed soils under  $C_3$ /forest vegetation is strongly enhanced leading to low  $C_{org}/N_{tot}$  ratios and  $\delta^{13}C_{org}$  signatures. During arid climate stages (2-4 kyr after insolation minimum) marine OM and SOM from developed soils are minor fractions. Particulate and less degraded terrigenous OM dominates as  $C_4$ /savannah areas expanded but still are drained. Thus,  $C_{org}/N_{tot}$  and  $\delta^{13}C_{org}$  reveal elevated values. An analogous scenario can be found between 95 and 75 ka (MIS 5.2 and 5.1, Fig. 5.2).

Note that absolute amounts cannot be given, the chart illustrates relative changes only as concluded from organic geochemical signatures. The time shift of TOC contents is deduced from Figure 5.3; time shifts of vegetation and soil development are adopted from organic geochemical and palynological investigations on the Congo fan (Jahns, 1996; Holtvoeth et al., 2003; Wagner et al., 2003) assuming that (i) climate of both African regions (Congo basin and Niger catchment) changes contemporaneously and (ii) soils and/or drainage of various biomes develop parallel to vegetation cover. POM = particulate terrigenous OM/plant debris.

## 5.6 Conclusions

Results from organic geochemical and petrological investigations of late Quaternary sediments of the Niger deep-sea fan (core GeoB 4901) provide evidence that a dominant part of the bulk organic matter is of terrestrial origin. Low HI values from Rock-Eval pyrolysis characterize bulk OM as type IV or *residual* kerogen where labile (marine) OM has been degraded effectively. This conclusion is supported by average degradation rates ( $C_{\text{org}}/C_{\text{org}}^*$ ) of 0.64, estimating that at least one third of the original sedimentary OM has been mineralized after deposition. Maceral analysis reveals that more than half of the visible OM is of terrigenous OM origin and partly derives from soils as indicated by the small average grain size of the terrigenous particles. Regarding the observation that labile marine OM plays a minor role  $C_{\text{org}}/N_{\text{tot}}$  ratios of bulk OM appear fairly low for continental margin sediments in front of a major river system (7-13), especially during humid climate stages (e.g. 8.7 on average during MIS 5.5). Since furthermore TOC shows a positive correlation with fluvial kaolinite supply (deduced from Ti/Al ratios) we conclude that a significant part of the terrigenous organic fraction is nitrogen-rich SOM probably protected by clay minerals. Bulk OM with enhanced  $C_{\text{org}}/N_{\text{tot}}$  ratios tends to be relatively enriched in  $^{13}\text{C}$  and is supposed to contain significant proportions of  $C_4$  plant remains. The positive correlation of  $C_{\text{org}}/N_{\text{tot}}$  and bulk  $\delta^{13}\text{C}_{\text{org}}$  likely documents variable supply of nitrogen-poor particulate terrigenous OM from  $C_4$  plant habitats and nitrogen-rich SOM of  $C_3$  plant origin. Vegetation and soil cover in the Niger catchment change with the moisture regime in tropical Africa. Accordingly, high-amplitude variations in TOC on precessional frequencies and its close correlation with kaolinite supply reflect cyclic erosion of developed soils (Alfisols and Ultisols) rich in clay, nitrogen, and organic carbon during humid climate stages, and of undeveloped soils (Entisols) poor in these compounds during arid conditions.

Comparison of bulk OM properties of Niger and Congo deep-sea fan sediments expose striking differences. Most important, there is a stable, high-mature organic fraction supplied through the Congo River which is absent in the Niger river load. From the distribution of major African soil types and their chemical properties we conclude that the high-mature organic fraction in the Congo sediments represents strongly degraded SOM from Oxisols. This soil type, however, is almost absent in the Niger catchment where Alfisols and Ultisols dominate. Despite these differences in tropical African soil types, physical protection of SOM by clay minerals likely prevents its effective microbial degradation once the SOM is supplied to the continental margins. This finally favours the relative enrichment of terrigenous OM while labile marine OM is effectively degraded during early diagenesis.

Lower Ti/Al ratios and higher accumulation rates of non-biogenic (terrigenous) sediment matter recognized in the Niger fan sediments after Termination II indicate a general shift towards more humid climate conditions. Parallel to this general transition in climate Enhanced fluvial nutrient supply stimulated siliceous primary production as indicated by enhanced accumulation rates of biogenous opal. At the same time,  $C_4$ /Entisol domains were progressively replaced by  $C_3$ /Alfisols/Ultisols habitats that were better drained with increasing precipitation. These insolation-controlled environmental changes finally resulted in

reduced proportions of particulate OM within the SOM fraction of the river load and enhanced export of clay-bound, nitrogen-rich SOM.

The results from this study emphasize that terrigenous OM and especially SOM is a much more important organic compound in deep-sea settings near effective continental drainage systems than commonly assumed. Apparently it is easily underestimated when conventionally estimated from  $C_{org}/N_{tot}$  ratios or bulk organic carbon isotopes are applied. Furthermore, soils might represent a more effective  $CO_2$  sink than previously considered if significant amounts of SOM are transferred to the ocean and buried in marine sediments.

## 6. Conclusions, perspectives, and open questions

### 6.1 Conclusions

Organic and inorganic geochemical investigations as well as palynological studies of marine sediments from the eastern equatorial Atlantic have shown that the land-ocean linkage has a much stronger imprint on continental margin sediments than commonly assumed.

#### AFRICAN CLIMATE CONTROLS ORGANIC SEDIMENTATION ON THE CONTINENTAL MARGIN

The basic factor governing all processes related to organic carbon burial in eastern tropical Atlantic deep-sea settings is the changing solar irradiation in response to varying orbital parameters, especially to the precession of the Earth's rotational axis. Changing insolation determines the hydrological cycle on the African continent (humidity/aridity, ground-water resources, drainage intensity) which governs the extension and type of vegetation and soil cover, eolian dust export, and fluvial run-off, and thus the export of terrigenous organic matter, nutrients, and lithogenic sediment towards the deep sea. The hydrological cycle apparently lags the insolation record by about 4 kyrs as recognized in the late Quaternary records of TOC, bulk OM reactivity (lm/hm), Ti/Al, and pollen assemblages from the tropical West-African continental margin. This time delay is explained by the gradual adjustment of the continental ecosystem to the new atmospheric circulation pattern.

#### ABANDONING C/N AND $\delta^{13}\text{C}_{\text{ORG}}$ APPLICATION

It is a key result of this study that well-established proxies applied in paleoceanography to assess marine and terrigenous organic matter (OM) proportions, namely  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios and  $\delta^{13}\text{C}_{\text{org}}$  values of bulk OM, are virtually useless in deep-sea fan settings. Actually, the terrigenous fraction is far underestimated by these proxies. The reason for misleading interpretations is that both proxies are based on two end-member models for marine and terrigenous OM proportions. Terrigenous OM in oceanic sedimentary records however does not simply represent the land-derived counterpart to marine OM with well-defined organic geochemical end-member properties. Varying relations of stable/high-mature terrigenous OM and lignin phenol concentrations in sediments of the Congo deep-sea fan exemplify that land-derived OM is a complex mixture of plant remains from different sources, i.e.  $\text{C}_3$  and  $\text{C}_4$  vegetation or soils. Furthermore, terrigenous OM may experience a wide range of chemical modifications by microbial degradation (plant litter  $\rightarrow$  humus  $\rightarrow$  soil OM) and thermal oxidation (charred material  $\rightarrow$  charcoal = "black carbon"). This heterogeneity of terrigenous OM rules out the application of conventional two-end-member models for estimations of terrigenous and marine OM amounts, e.g. by  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  ratios or bulk isotopic signatures ( $\delta^{13}\text{C}_{\text{org}}$ ).

#### SOIL ORGANIC MATTER (SOM) AS MAJOR SEDIMENTARY OM COMPONENT

Results from this study strongly support the conclusion that soil organic matter (SOM) is a dominant fraction in marine deposits that has been largely ignored in previous studies of river-influenced deep-sea settings. This conclusion is of extreme importance as SOM masks true proportions of terrigenous OM in marine sediments. This is due to the fact that SOM partly exhibits geochemical characteristics which are commonly regarded to be typical for

marine OM, i.e. high nitrogen contents and depletion in  $^{12}\text{C}$ . SOM reveals significant differences in quality, especially in the nitrogen content that is directly related to the degree of SOM humification. Furthermore, the amounts of stable SOM from old and well-developed ferallitic soils (Oxisols) buried in Congo deep-sea fan sediments show high-amplitude variations during the late Quaternary whereas this specific fraction of SOM is absent in the Niger fan sediments. With decreasing influence of riverine OM in open ocean settings the relative contribution of wind-born terrigenous OM increases. This results in enhanced proportions of particulate terrigenous OM (especially from arid  $\text{C}_4$  source areas with open vegetation) and oxidized particles from vegetation fires (inertinite, black carbon) within the terrigenous OM fraction of open ocean sediments.

### TOC AS PALEOPRODUCTIVITY PROXY?

This study demonstrates that terrigenous OM apparently is a major or even the dominating fraction of the bulk OM in the Congo and Niger deep-sea fan sediments. The reversal of this conclusion implies that the bulk OM records (TOC) cannot be used as a proxy to reconstruct marine paleoproductivity as long as marine and terrigenous OM amounts are not determined quantitatively. Though compositional changes in the bulk OM were detected in this study, the basic problem of reliable quantification of terrigenous (and marine) OM still remains a major issue in marine biogeochemistry and paleoceanography. However, reevaluation of terrigenous contributions to the sedimentary organic carbon pool is essential for global carbon budgets and paleoclimate modelling.

## 6.2 Perspectives and open questions

### 6.2.1 How to assess terrigenous OM amounts?

Systematic studies on the source materials are essential to better assess and understand the integrated organic geochemical signal preserved in marine sediments. Prior to the application of bulk proxies like  $\delta^{13}\text{C}_{\text{org}}$  and  $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$  the relative proportions of particulate terrigenous OM, SOM, and  $\text{C}_4$  plant remains have to be estimated from multi-proxy investigations. For correct interpretations of  $\delta^{13}\text{C}_{\text{org}}$  signals it is most important to determine the ratios of  $\text{C}_3$  and  $\text{C}_4$  plant matter as these fractions represent the extremes of possible terrestrial organic carbon isotope compositions. Palynological studies are highly suitable to reconstruct changing vegetation in continental dust source areas and river catchments. Specific determination of organic carbon isotopes of well-defined OM compounds like long-chain  $n$ -alkanes from plant waxes or lignin phenols by GC-MS are appropriate methods to confirm and extend the interpretation of palynological findings.

### NEED OF SOIL AND SOM STUDIES

The mentioned approaches however cannot distinguish whether terrigenous OM was exported directly to the investigated sedimentary settings or stored in soils for a certain time. Thus, assessment of the ratio of SOM and “fresh” plant remains (addressed here as particulate OM) is inevitable for exact high-resolution reconstructions of paleovegetation. As plant matter is severely decomposed in humus layers and soils, parameters sensitive to plant matter degradation like  $(\text{Ad}/\text{Al})_{\text{s,v}}$  ratios from lignin analysis may help to recognize SOM

contributions. Also grain size distributions of terrigenous particles observed by organic petrology may help to assess supply of OM from eroded soils, as plant fragments decrease in size with progressive physical and biochemical destruction in the soils. However, particulate OM represents only a part of the SOM fraction, clay-bound SOM is not recognized by standard petrological methods. On the other hand, differences in the organic geochemical signatures of individual grain-size fractions (e.g.  $C_{org}/N_{tot}$ ,  $\delta^{13}C_{org}$ , lignin phenol concentration) provide important information on the relative amount of fine-grained SOM and coarse-grained particulate OM.

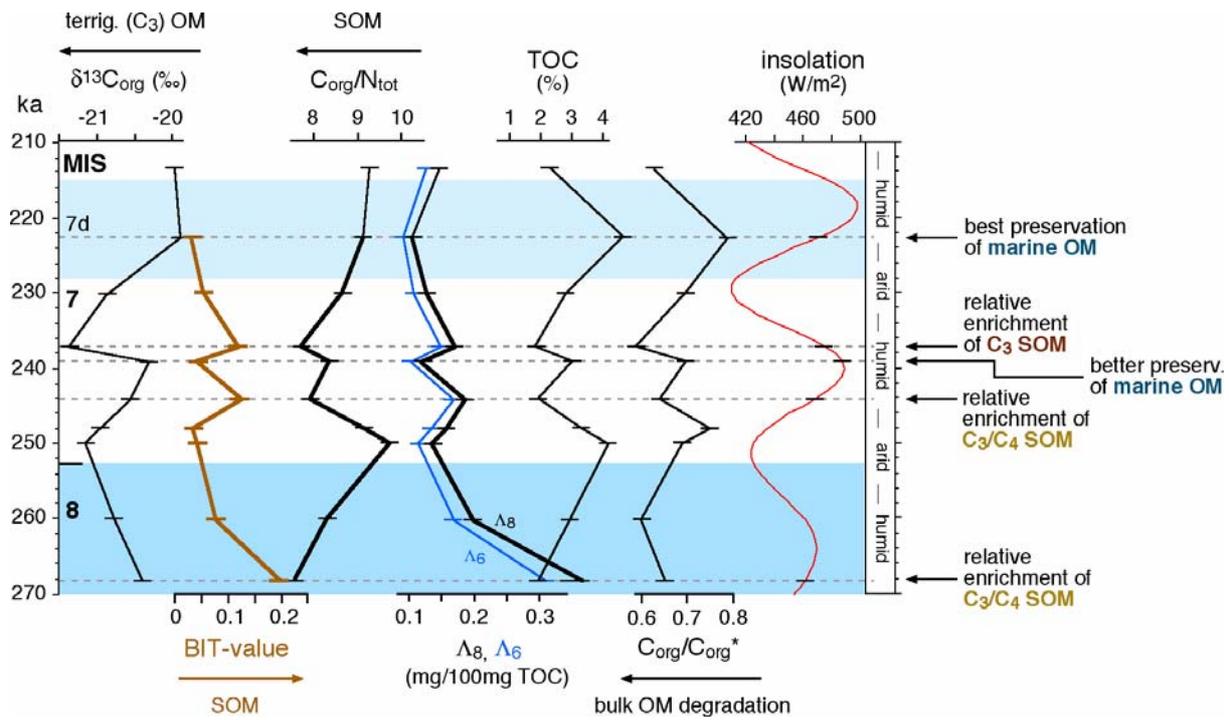
With progressive humification the aromaticity of SOM, especially of the clay-bound fraction, generally increases. A common method in soil science to detect the degree of SOM humification is NMR spectrometry that determines SOM aromaticity. Also low  $C_{org}/N_{tot}$  ratios may indicate the presence of SOM if significant contribution of nitrogen-rich autochthonous marine and bacterial OM can be excluded. This can be determined by pyrolytic properties of bulk OM characterizing origin (kerogen types from Rock-Eval pyrolysis) and reactivity ( $T_{max}$ , possibly  $Im/hm$ ) of bulk OM and by organic petrology from estimates of marine and minimum (visible) terrigenous OM amounts. In young sediments, aged OM that has been stored in soils may be discovered by  $^{14}C$  datings (AMS). This approach also helps to reconstruct the duration of climate related changes in the continental ecosystem.

#### FIRST INNOVATIVE STEPS

A new promising tool to detect the contribution of SOM to marine/aquatic sediments is the analysis of glycerol dialkyl glycerol tetraethers (GDGT's) by high performance liquid chromatography/atmospheric pressure positive ion chemical ionization mass spectrometry (HPLC/APCI-MS, method described by Hopmans et al., 2000). Isoprenoidal GDGT's are abundant in marine settings. In contrast, non-isoprenoidal (branched) GDGT's are known from soils but are absent in open ocean sediments. The ratio of branched versus isoprenoidal tetraethers (BIT value) thus is suggested to be sensitive for SOM supply (Weijers, Netherlands Institute for Sea Research, pers. comm.). One problem along the interpretation of BIT values is that the producers of branched GDGT's in the continental environment or the precursor substances, respectively, are not known until now. Furthermore, SOM of the various soil types might contain variable shares of GDGT's. Nevertheless, recent investigations strongly support significant influence of SOM on bulk organic geochemical signatures as the resulting BIT values correlate very well with  $C_{org}/N_{tot}$  ratios and lignin phenol concentrations at the Congo fan (Fig. 6.1, next page) and co-vary with Ti/Al ratios at the Niger deep-sea fan ( $r^2 = 0.56$ ) during generally more humid climate conditions after Termination II (Weijers, unpublished data).

#### NEED OF MULTI-DISCIPLINARY CONCEPTS (PALEOCEANOGRAPHY MEETS SOIL SCIENCE)

Though there are several tools to detect SOM in marine sediments, it appears inevitable to investigate the organic geochemical characteristics ( $C_{org}/N_{tot}$ ,  $\delta^{13}C_{org}$ , lignin yields, reactivity, aromaticity) of the soil inventory of terrestrial source areas. Only the knowledge of the organic geochemical properties of all potential contributors to bulk sedimentary OM allow accurate estimations of SOM amounts and assessment of its influence on terrigenous and bulk sedimentary OM geochemical signatures.



**Figure 6.1:** Bulk organic geochemical parameters from the Congo deep-sea fan compared to the BIT value (data from J. Weijers, NIOZ, Texel). Correlation of BIT value with  $C_{org}/N_{tot}$  ratios, lignin phenol concentrations ( $\Lambda_{8,6}$ ) and degradation rates ( $C_{org}/C_{org}^*$ ) exemplarily illustrates relative enrichment of lignin-bearing SOM after selective degradation of labile marine OM between 246 and 236 ka. Bulk  $\delta^{13}C_{org}$  values suggest combined C<sub>3</sub>/C<sub>4</sub> and mainly C<sub>3</sub> contribution during arid (244 ka) and humid (237 ka) climate stages.

### ... AND WHAT HAPPENS AFTER BURIAL?

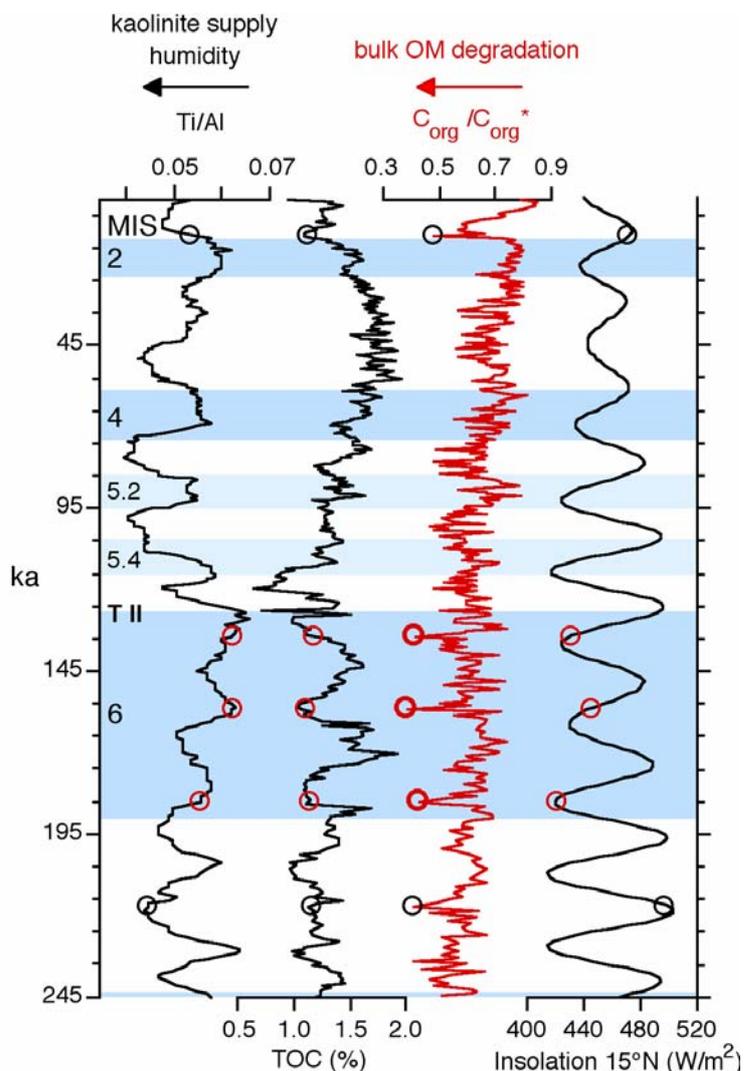
For paleoenvironmental interpretations of organic geochemical records it is necessary to determine the postsedimentary diagenetic stage of bulk OM as marine and terrigenous OM fractions reveal significant differences in bioavailability and thus are selectively degraded or relatively enriched. For sulfate reducing settings, like the fine-grained sediments of the Congo and Niger deep-sea fans, degradation rates of bulk OM calculated from C/S ratios ( $C_{org}/C_{org}^*$ ) emerged to be a very helpful proxy for bulk OM decay.

#### 6.2.2 A special feature of Niger sediment supply?

One interesting observation from organic geochemical investigations of the Niger deep-sea fan sediments has not been presented and discussed in this study until now: the record of (postdepositional) bulk OM degradation rates ( $C_{org}/C_{org}^*$ ) show some conspicuous spikes of maximum OM decay especially during glacial MIS 6 but also in MIS 7 and at 11.2 ka, immediately after the Younger Dryas climate event (Fig. 6.2). In MIS 6, these spikes always occur at or short time after insolation minima, thus prior to most arid climate conditions. Apparently, short-term specific changes of the sedimentary setting cause the massive decay of sedimentary OM. However, which short-term cyclic process might be the trigger?

A well-known special feature of the Niger river-system is the Niger inland delta. At least during the last glacial maximum, under arid climate conditions in tropical Africa, the upper Niger River ended at the inland delta near Timbuktu (e.g. Baker, 1986). However, a sudden cut of the Niger must have reduced run-off and sediment export dramatically. A relatively high amount of marine OM that has been produced proportionately to the level of riverine nutrient supply just before the break is not buried effectively, anymore. Thus, the labile OM fraction remains for a longer time in the uppermost sediment sections with highest microbial activity and may therefore be substantially degraded. Apparently, the system was balanced after short time.

$C_{org}/C_{org}^*$  minima during MIS 7 and after the Younger Dryas occur around insolation maxima, i.e. at the initial stages of full humid climate conditions. The opposite scenario, the flooding of the Niger inland delta and abruptly increased run-off, might be responsible for short-term changes of the sedimentary setting, again. However, the coherency with enhanced degradation of sedimentary OM is not clear.



**Figure 6.2:** Record of bulk OM degradation rates in late Quaternary Niger fan sediments compared to the Ti/Al ratios, TOC, and insolation changes. Distinct spikes indicating maximum bulk OM decay occur close to most arid climate condition during glacial marine isotope stage (MIS) 6 (red circles) or and at 11.2 ka immediately after the Younger Dryas climate event; evidence for short-term changes of the sedimentary milieu in response to the abrupt onset of Niger inland delta at strongest aridity?

The speculative theory about the effect of the Niger inland delta insertion on sedimentary records of the Niger deep-sea fan cannot be verified by this study. Future studies might get

indications for abrupt changes of drainage area extension and erosion intensity from grain-size analysis or clay mineralogy as these events surely caused drastic modifications of the river load. Investigation of such short-time events however needs highest time-resolution. So, research can go on!

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**Data resources on the web:**

- Climate data: <http://www.ncdc.noaa.gov/oa/ncdc.html>  
(NOAA National Climate Data Center)
- Core data: <http://www.pangaea.de>  
(Network for Geological and Environmental Data)
- <http://www-odp.tamu.edu>  
(Ocean Drilling Program)
- River data: <http://www.grdc.sr.unh.edu>  
(Global Runoff Data Centre)
- Soil orders: <http://www.nrcs.usda.gov/technical/worldsoils>  
(Natural Resources Conservation Service)
- USDA soil taxonomy: <http://soils.usda.gov/technical/classification/taxonomy>  
(United States Department of Agriculture)
- (Paleo-)Vegetation: <http://www.soton.ac.uk/~tjms/adams1.html>  
(Quaternary Environments Network)