PERGAMON

Organic Geochemistry 33 (2002) 715–722

Organic Geochemistry

www.elsevier.com/locate/orggeochem

Significance of high C/N ratios in organic-carbon-rich Neogene sediments under the Benguela Current upwelling system

Shannon C. Twichell[a], Philip A. Meyers[a,*], Liselotte Diester-Haass[b]

[a]*Department of Geological Sciences, The University of Michigan, Ann Arbor, MI 48109-1063, USA*
[b]*Zentrum für Umweltwissenschaften der Universität, Universität des Saarlandes, 66041 Saarbrücken, Germany*

Received 18 July 2001; accepted 26 March 2002
(returned to author for revision 3 October 2001)

Abstract

$C_{organic}/N_{total}$ values change from ~ 5 in middle Miocene sediments deposited under the Benguela Current upwelling system to ~ 15 in latest Miocene and Pliocene sediments. Although the change appears to record a larger proportion of land-derived material in younger sediments, bulk $\delta^{13}C_{org}$ values indicate a predominance of marine origin for organic matter throughout the sequence. Marine paleoproductivity, as represented by mass accumulation rates of $CaCO_3$ and organic carbon, increased over this time interval. We postulate that the larger $C_{organic}/N_{total}$ values record a shift towards greater recycling rates of nitrogen-rich, relative to carbon-rich, organic matter components as the flux of total organic matter to the seafloor increased. Furthermore, we propose that high $C_{organic}/N_{total}$ values may record enhanced paleoproductivity in other sedimentary sequences dominated by marine organic matter.

1. Introduction

$C_{organic}/N_{total}$ ratios have been widely used as a proxy to identify changes in the proportions of sedimentary organic matter delivered from algal and land–plant origins (e.g. Prahl et al., 1980, 1994; Premuzic et al., 1982; Ishiwatari and Uzaki, 1987; Jasper and Gagosian, 1990; Meyers et al., 1996; Silliman et al., 1996; Ujiie et al., 2001; St-Onge and Hillaire-Marcel, 2001). The source distinction is based on the generalization that fresh algal organic matter typically has atomic C/N ratios between 5 and 8, whereas that from vascular land plants has C/N ratios of 20 and greater (Emerson and Hedges, 1988; Meyers, 1994). This fundamental difference in elemental compositions arises principally from (1) the paucity of cellulose in algae and its abundance in vascular plants, and (2) the protein richness of algal organic matter.

Selective degradation of organic matter components during diagenesis has the potential to modify the original C/N ratios of the organic matter that accumulates in sediments. A decrease in $C_{organic}/N_{total}$ ratios over time of burial below the seafloor has been reported in open-ocean settings (e.g. Müller, 1977; Waples and Sloan, 1980; Meyers et al., 1996), where it involves the absorption and retention of ammonia and the release of CO_2 and CH_4 from the sediment derived from decomposition of organic matter. In other cases, marine-derived organic matter in sediments has $C_{organic}/N_{total}$ values that are higher than typical algal values (Meyers, 1997). These high values typically occur in sediments rich in organic carbon, and they imply retarded loss of carbon relative to nitrogen in organic matter as it settles from areas of elevated surface productivity (Verardo and McIntyre, 1994). Examples of such preferential C-preservation and consequent relative N-depletion are documented in organic-carbon-rich sediments present in

* Corresponding author. Tel.: +1-734-764-0597; fax +1-734-763-4690.
E-mail address: pameyers@umich.edu (P.A. Meyers).

PII: S0146-6380(02)00042-6

light–dark color cycles on the Walvis Ridge (Meyers et al., 1983), in the Mediterranean Sea (Bouloubassi et al., 1999; Nijenhuis and de Lange, 2000), in the equatorial Atlantic (Verardo and McIntyre, 1994), and on the northwest Mexican slope (Ganeshram et al., 1999). The $C_{organic}/N_{total}$ increases are most pronounced when total organic carbon (TOC) contents are highest, suggesting that a higher delivery rate of organic matter leads to improved preservation of its carbon.

Because available evidence suggests that both duration of organic matter burial and rate of organic matter delivery are possible factors in altering C/N ratios from their original values, we have measured $C_{organic}/N_{total}$ values in sediments that have been deposited over an 11-My time span under different rates of marine organic matter production and sedimentation at a location under the Benguela Current upwelling system. $C_{organic}/N_{total}$ values are variably elevated over portions of this interval, and our study allows us to reach conclusions about what these higher values signify.

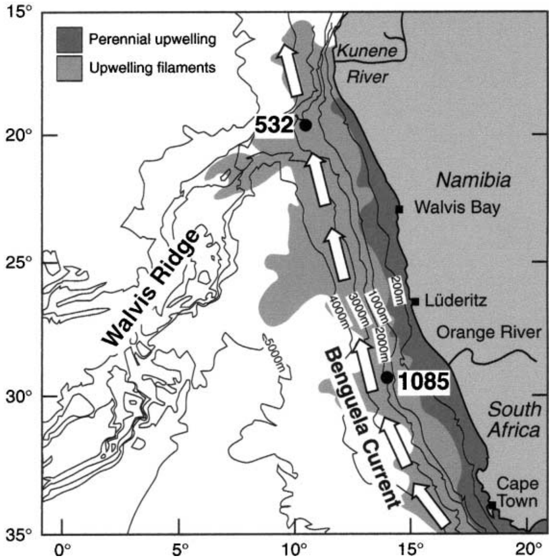

Fig. 1. Locations of ocean drilling program (ODP) Site 1085 and DSDP Site 532 relative to the general axis of the Benguela Current (arrows). Areas of perennial and periodic upwelling as defined by Lutjeharms and Stockton (1987) are shown by shading.

2. Experimental

2.1. Depositional setting

Ocean drilling program (ODP) Site 1085 (29°22′S, 13°59′E) is at a water depth of 1713 m on the continental slope of the Cape Basin of the South Atlantic Ocean. This site is located offshore of the Orange River at the southern end of the Benguela Current upwelling system (Fig. 1). The coastal Namib Desert borders the upwelling zone, and the muds of the Orange River are transported southward and away from Site 1085 by the prevailing bottom currents (Summerhayes et al., 1995). Sediments at Site 1085 consequently consist mainly of greenish-gray, foraminifera-bearing nannofossil oozes (Wefer et al., 1998). Sedimentation rates range from 1.5 cm/ky in the middle Miocene to 7 cm/ky in the early Pliocene. Analyses done onboard D/V JOIDES Resolution during ODP Leg 175 discovered that sediments beneath this region of elevated marine productivity commonly yield unusually high $C_{organic}/N_{total}$ values that range between 14 and 18 (Wefer et al., 1998).

2.2. Sampling and analysis

We obtained 789 samples from ODP Hole 1085A at intervals of 50 cm from Core 15H to Core 64X (135–604 m below seafloor, mbsf). We used 25 samples from Cores 29H and 30H from Hole 1085B to fill a recovery gap between 269 and 279 mbsf in Hole 1085A. The combined sequence provides a continuous hemipelagic sedimentary record from the middle Miocene (14.5 Ma) to the middle Pliocene (3.0 Ma), which encompasses both the late middle Miocene onset and the early Pliocene intensification of the Benguela Current upwelling system and its associated elevated marine productivity (Diester-Haass et al., 2002).

Freeze-dried samples were analyzed for calcium carbonate content by treatment with 3 N HCl using the "Carbonate Bomb" technique. (Müller and Gastner, 1971). The carbonate-free samples were rinsed, dried, and analyzed for organic carbon and residual nitrogen using a Carlo Erba EA1108 CHNS-O analyzer. The TOC content is expressed on a whole-sediment basis after adjusting for the carbonate content removed during the "Carbonate Bomb" procedure. $C_{organic}/N_{total}$ ratios are calculated on an atomic basis.

Organic matter $\delta^{13}C$ values were determined from the carbonate-free samples in the Stable Isotope laboratory at The University of Michigan by combustion at 800 °C in sealed Vycor tubes in the presence of CuO and Cu. The Finnigan Delta S mass spectrometer was calibrated with the NBS-22 (graphite) standard. Data are corrected for ^{17}O and expressed in conventional $\delta^{13}C$ notation (±0.1‰) relative to the PDB standard.

Age control of the upper part of the 11.5 Ma sequence is based on a high resolution benthic $\delta^{18}O$ record that has been tuned to orbital obliquity cycles from 3.0 to 7.1 Ma (Vidal et al., 2002). The tuned isotope record from Site 1085 was then compared to the deep Pacific $\delta^{18}O$ record of Site 846 (Shackleton and Kennett, 1975). The ages of major isotopic events are in agreement for both Sites 1085 and Site 846 (Vidal et al.,

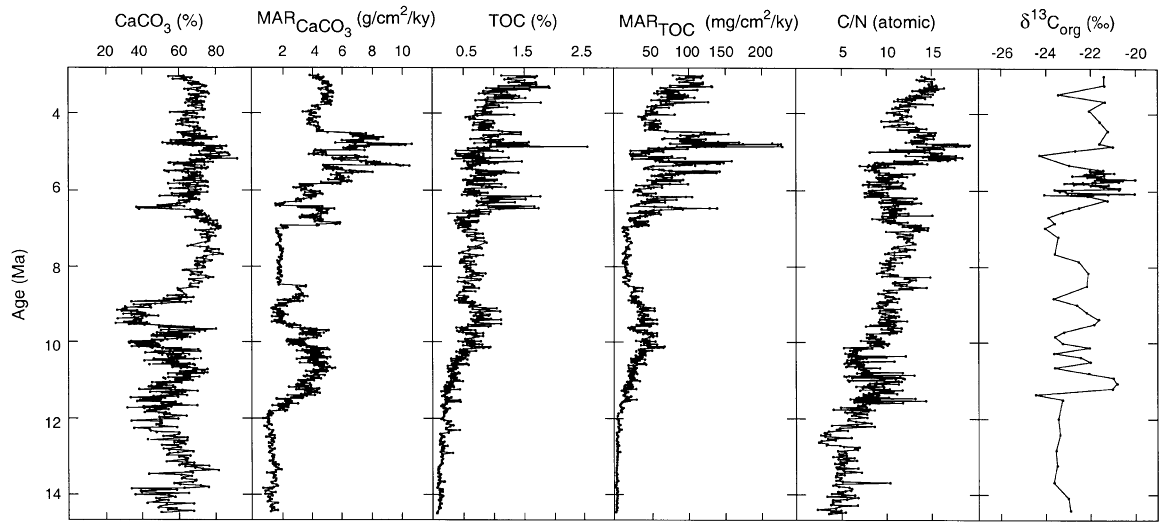

Fig. 2. Contents of calcium carbonate ($CaCO_3$) and total organic carbon (TOC), mass accumulation rates (MAR) of $CaCO_3$ and TOC, atomic $C_{organic}/N_{total}$ values and $\delta^{13}C_{org}$ values (PDB) in sediments from ODP Site 1085 from the middle Miocene through the middle Pliocene.

2002; Diester-Haass et al., 2002). Age control for the lower portion of the sequence (7.1–14.5 Ma) is based on shipboard biostratigraphy (Wefer et al., 1998).

Linear sedimentation rates and mass accumulation rates are derived from the calculated ages of individual samples, their depths below seafloor, and their dry bulk densities as measured onboard the JOIDES Resolution (Wefer et al., 1998). The high resolution chronostratigraphic control points were applied to the sedimentary records to estimate bulk mass accumulation rates (Diester-Haass et al., 2002). Mass accumulation rates (MARs) for $CaCO_3$ (g/cm^2/ky) and TOC (mgC/cm^2/ky) of these two biogenic sediment components were calculated for each sample as:

$$MAR_{component} = (\%\ component/100 \times MAR_{bulk}) \\ (\times\ 1000\ mg/g\ for\ TOC)$$

where MAR_{bulk} is the mass accumulation rate of bulk sediment in g/cm^2/ky.

3. Results and discussion

Results of the carbonate and bulk organic matter analyses of Site 1085 sediments provide information about the record of organic matter production and the degree of its preservation. Contents and MARs of $CaCO_3$ and TOC, and $\delta^{13}C_{org}$ values, were used as proxies to identify changes in marine productivity and delivery of organic matter to the seafloor.

3.1. Calcium carbonate contents and mass accumulation rates

$CaCO_3$ contents throughout the 11.5 My sediment record are generally between 50 and 70% but range as low as 26% at 9.5 Ma and as high as 92% at 5.1 Ma (Fig. 2). These values are similar to those of modern upwelling conditions associated with the Benguela Current in which marine productivity is dominated by coccolithophorids (Summerhayes et al., 1995). Sediments deposited prior to ~9 Ma have somewhat lower $CaCO_3$ contents than subsequent sediments. Variations in carbonate contents appear as relatively short-term increases and decreases related to light–dark cycles in sediment color (Wefer et al., 1998) and as longer term, more systematic increases and decreases (Fig. 2).

Mass accumulation rates reveal dramatic changes in delivery of $CaCO_3$ to the seafloor at Site 1085 since 12 Ma (Fig. 2). The MAR_{CaCO_3} remains ~1.5 g/cm^2/ky from 14.5 to 12 Ma, when it increases to reach 5 g/cm^2/ky at 10.8 Ma before decreasing to ~2 g/cm^2/ky at 9.6 Ma. MAR_{CaCO_3} values again increase beginning 7 Ma and exceed 8 g/cm^2/ky between 5.4 and 4.8 Ma. This peak in carbonate accumulation is followed by lower, but still enhanced, values of 4–5 g/cm^2/ky from 4.5 to 3 Ma. Because the coccolithophorids that Summerhayes et al. (1995) found to be dominant today have probably dominated algal productivity in the Benguela Current region of the South Atlantic over this entire time span (Wefer et al., 1998), the MAR_{CaCO_3} values can be interpreted as proxies for marine paleoproductivity rates.

Their general increase since 12 Ma, therefore, indicates important growth in marine productivity over time, especially since 7 Ma (Diester-Haass et al., 2002). However, dissolution of $CaCO_3$ at the seafloor can weaken the validity of this proxy. In particular, the low MAR_{CaCO_3} from 9.6 to 7 Ma corresponds to periods of globally enhanced carbonate dissolution (Diester-Haass et al., 2001; Lyle et al., 1995). We consequently employed a second proxy, MAR_{TOC}, to examine changes in the history of marine productivity over Site 1085.

3.2. Total organic carbon contents and mass accumulation rates

TOC contents in Site 1085 sediments increase progressively from the middle Miocene to the Pliocene. The order of magnitude increase, from 0.1% in sediment deposited around 14 Ma to $\sim$1.5% at 3 Ma, is notably different from the relatively small increase in $CaCO_3$ contents over the 11-My time span (Fig. 2). Another important difference between the contents of TOC and those of $CaCO_3$ is that higher TOC contents correspond to darker sediment in the light–dark color cycles that are well-developed in this sequence and especially in sediment deposited since 6.4 Ma (Wefer et al., 1998). The cycles have been postulated to represent glacial–interglacial variations in the marine productivity associated with the Benguela Current upwelling system (Diester-Haass et al., 1990).

A similar increase in sediment TOC content since the Miocene has been documented at DSDP Sites 362 and 532 on the Walvis Ridge (Siesser, 1980; Meyers et al., 1983). However, this trend is not as well developed at Site 1085 as at the more northerly locations, where TOC contents reach 5–10% in Pliocene and Pleistocene sediments. Nonetheless, the contents found in the Pliocene sediments at Site 1085 are higher than in Pliocene–Pleistocene deep-sea sediments from the South Atlantic (ca. 0.3%: Keswani et al., 1984), and they represent burial of significant amounts of organic matter along the southwest Africa margin.

TOC mass accumulation rates increase since the middle Miocene, and they reveal details in organic matter burial not evident from the contents (Fig. 2). The MAR_{TOC} gradually increases from $\sim$2 to $\sim$5 mgC/cm^2/ky from 14.5 to 12 Ma, when it grows to remain around 45 mgC/cm^2/ky from 10.2 to 9.1 Ma before dropping to $\sim$15 mgC/cm^2/ky at 8.3 Ma. MAR_{TOC} values increase again at 7 Ma to peak at 225 mgC/cm^2/ky at 4.8 Ma. This peak in organic carbon accumulation is followed by a drop to $\sim$50 mgC/cm^2/ky from 4.4 to 3.8 Ma and then grows again to reach $\sim$100 mgC/cm^2/ky at 3 Ma. Nearly all of these MAR_{TOC} values are significantly higher than those under open-ocean gyres (0.3 mgC/cm^2/ky: Suess and Müller, 1980), and many are greater than those under the zone of Atlantic equatorial upwelling (10–80 mgC/cm^2/ky: Verardo and McIntyre, 1994). Furthermore, they are virtually equivalent to MAR_{TOC} values (60–150 mgC/cm^2/ky: Giraudeau et al., 2002) at Site 532 on the Walvis Ridge where TOC contents are not as diluted by calcium carbonate and are consequently much higher (5–10%).

The general concordance in increases of the two paleoproductivity proxies—MAR_{CaCO_3} and MAR_{TOC}—starting at 12 M and peaking around 5 Ma is strong evidence that marine productivity increased and then subsequently waned in the region of Site 1085. However, the decreases in productivity at 9.6–7 Ma and 6.4 Ma suggested by the MAR_{CaCO_3} record do not appear in the MAR_{TOC} values, which suggests that these events represent periods of heightened carbonate dissolution and not diminished paleoproductivity. Moreover, the MAR_{TOC} record indicates that paleoproductivity increased from 3.8 to 3 Ma and did not decrease as suggested by the MAR_{CaCO_3} values (Fig. 2). However, contributions of land-derived organic matter have the potential to bias the MAR_{TOC} record and to create a falsely magnified record of marine productivity. Even though Site 1085 is offshore a coastal desert having little vegetation, we explored the possibility of continental contributions of organic matter to sediments at this location.

3.3. Origins of sediment organic matter

Pollen contents of sediments from Site 532 on the Walvis Ridge (Fig. 1) indicate that the Namib Desert has existed since the late Miocene (van Zinderen Bakker, 1984). Delivery of much land-derived organic matter is therefore unlikely since the onset of coastal upwelling $\sim$12 Ma. We nonetheless employed two independent organic geochemical parameters—stable carbon isotopic compositions and Rock-Eval pyrolysis results—as proxies to test for the presence of continental organic matter in Site 1085 sediments.

Organic matter $\delta^{13}C$ values were determined for a subset of 49 samples that survey the entire 814-sample sequence and another subset of 70 samples clustered between 301 and 340 mbsf (5.5–6.2 Ma). The $\delta^{13}C_{org}$ values range between -20 and -24‰ (Fig. 2). The larger $\delta^{13}C_{org}$ values expected of marine algal organic matter (-20 to -22‰) generally coincide with higher MAR_{TOC} values (Fig. 3). Inasmuch as typical $\delta^{13}C_{org}$ values of organic matter produced by C_3 land plants are about -27‰ (Smith and Epstein, 1971; Jasper and Gagosian, 1990; Meyers, 1994), the absence of such low $\delta^{13}C_{org}$ values in sediments from Site 1085 indicates that contributions of land-derived organic matter are minor to lacking. However, it is possible that C_4 plants, which have $\delta^{13}C_{org}$ values that average about -14‰ (O'Leary, 1988; Meyers, 1994), may have contributed some organic matter to these sediments, although this possibility

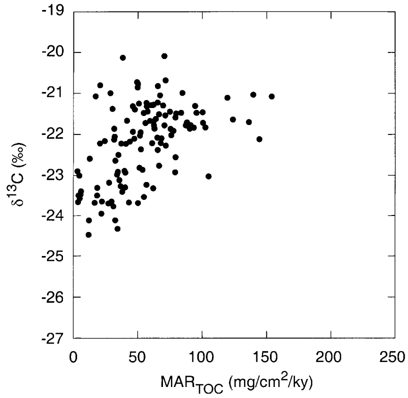

Fig. 3. Comparison of $\delta^{13}C_{org}$ values and MAR_{TOC} values in Site 1085 sediment samples. Correspondence between less negative $\delta^{13}C_{org}$ values and larger MAR_{TOC} values indicates that marine-derived material dominates the organic matter composition of these sediments.

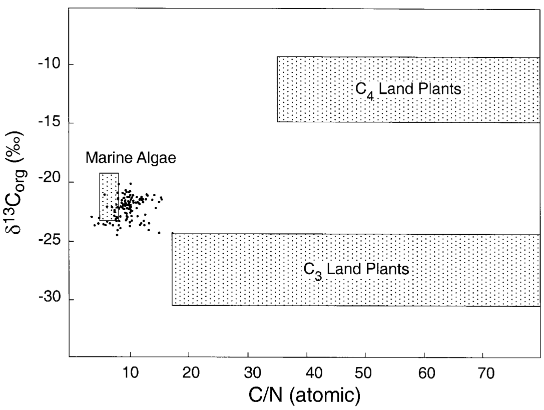

Fig. 4. Comparison of $\delta^{13}C_{org}$ values and atomic $C_{organic}/N_{total}$ values in Site 1085 sediment samples (dots) to elemental and isotopic identifiers of bulk organic matter produced by marine algae, C_3 land plants, and C_4 land plants (regular patterns). Organic matter in these samples is predominantly marine in origin. Adapted from Meyers (1994).

is made remote by comparison of both $\delta^{13}C_{org}$ values and $C_{organic}/N_{total}$ ratios of sediments with those of typical land plants (Fig. 4). None of the sediment samples have combinations of $\delta^{13}C_{org}$ values and $C_{organic}/N_{total}$ ratios that can be obtained by mixing organic matter from C_4 land plants with algal organic matter, although many of the Site 1085 samples have $C_{organic}/N_{total}$ values that are higher than typical algal organic matter.

Results of the Rock-Eval analyses of organic-carbon-rich Site 1085 sediments carried out during ODP Leg 175 indirectly support the algal origin of the organic matter, as inferred from $\delta^{13}C_{org}$ values. The organic matter appears to consist of varying mixtures of Type II algal material and Type III land–plant material (Wefer et al., 1998; Meyers, 2001). However, the possibility of large proportions of land–derived organic matter conflicts with $C_{organic}/N_{total}$ ratios in these sediments that are too low (<20) for land-plant organic matter. The inconsistency between the Rock-Eval source characterization and the elemental source characterization suggests that the sediments contain marine organic matter that has been partially oxidized to resemble Type III material (Espitalié et al., 1977; Peters, 1986).

3.4. High $C_{organic}/N_{total}$ ratios and their significance in marine sedimentary sequences

Atomic $C_{organic}/N_{total}$ values range between 2.4 and 19.1 in the Site 1085 sequence (Fig. 2). Most of the values in sediments from 14.5 to 11.6 Ma are similar to those of unaltered algal organic matter (5–8: Emerson and Hedges, 1988; Meyers, 1994). Values generally increase in the younger parts of the sequence, although with systematic variations, to reach ~ 15 between 5.2 and 5 Ma and again at about 3.3 Ma (Fig. 2). Despite their variability, higher C/N values correlate significantly ($r^2=0.36$; $n=814$) with higher MAR_{TOC} values. Many of the variations in C/N values roughly mimic variations in MAR_{TOC}. For example, the period of modestly elevated MAR_{TOC} values (~ 15 mgC/cm^2/ky) from 8.3 to 7 Ma is accompanied by $C_{organic}/N_{total}$ values that are elevated (10–13) relative to algal values (Fig. 2). Most importantly, the initial increase in $C_{organic}/N_{total}$ values at 11.6 Ma fairly closely follows 12 Ma, when increases in MAR_{CaCO_3}, MAR_{TOC}, and benthic foraminiferal accumulation rates (Diester-Haass et al., 2001) indicate that paleoproductivity first began to increase at Site 1085.

If increased rates of organic matter accumulation result in increased sediment $C_{organic}/N_{total}$ values, then some threshold might exist at which elevated MAR_{TOC} values are first accompanied by $C_{organic}/N_{total}$ ratios that are amplified above their initial algal values. The minimum MAR_{TOC} associated with high C/N values is ~ 10 mgC/cm^2/ky in Site 1085 sediments (Fig. 5). This threshold value is approximately the same as that noted in Verardo and MacIntyre (1994) in which $C_{organic}/N_{total}$ values are larger than initial algal values in late Pleistocene sediment from the equatorial Atlantic Ocean. However, it is clear from the range of MAR_{TOC} values that accompany any given $C_{organic}/N_{total}$ ratio in Fig. 5 that the relation between these two parameters is not simple. Moreover, the increases and decreases in $C_{organic}/N_{total}$ values evident at different times in this sedimentary sequence (Fig. 2) indicate that factors in addition to the MAR_{TOC} impact the elemental ratio.

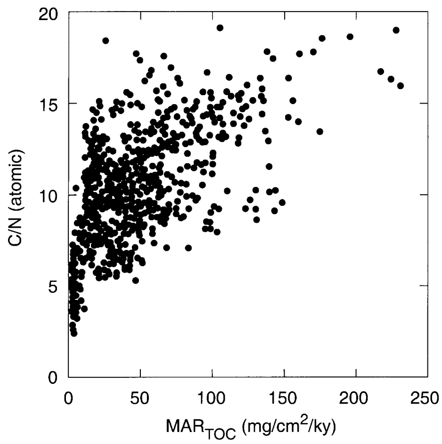

Fig. 5. Comparison of atomic $C_{organic}/N_{total}$ values and MAR_{TOC} values in Site 1085 sediment samples. C/N values increase as MAR_{TOC} values increase above a threshold of ~ 10 mgC/cm^2/ky, but the range of C/N values indicates that factors in addition to the MAR_{TOC} impact the elemental ratio.

The original C/N ratio of the organic matter that eventually was incorporated into the Site 1085 sediment samples probably approximated the algal average of 106/16 (6.6; Redfield, 1942) at the sea surface. Therefore, the higher values (>10) that typify organic matter in sediments deposited since 11.6 Ma (Fig. 2) must arise from alterations during sinking and perhaps after deposition on the seafloor. Verardo and MacIntyre (1994) postulated that the high $C_{organic}/N_{total}$ values they found in sediments under areas of elevated algal productivity in the equatorial Atlantic Ocean reflect more rapid loss of nitrogen than carbon from organic matter during settling from the photic zone. They reasoned that nitrogen-containing proteinaceous matter is more readily utilized by microbes than carbohydrate components. They found no evidence of post-depositional alteration of C/N values over the 300-ky record of their sediment cores. Similarly, little alteration of $C_{organic}/N_{total}$ values after sedimentation is implied by the preservation of algal C/N values in a subtropical North Atlantic Ocean sediment core in which microbial activity halved TOC contents over the top 10 cm (Freudenthal et al., 2001). Variations in the $C_{organic}/N_{total}$ values in the Site 1085 sediments may therefore record variations in water-column processes that affected the elemental composition of the organic matter that reached the seafloor at different periods of time.

A sediment trap study in the oxygen-deficient zone of the eastern tropical North Pacific Ocean shows how organic matter C/N values may increase during sinking. Van Mooy et al. (2002) conclude that the modes of organic matter degradation under oxic and suboxic conditions differ. Suboxic microbial degradation via denitrification preferentially utilizes nitrogen-rich amino acids and consequently leaves a greater proportion of carbon-rich organic matter components intact. This change necessarily leads to higher C/N values in the surviving organic matter. Oxygen-deficient zones commonly develop under areas of high productivity because the large downward fluxes of organic matter draw down the dissolved oxygen content of seawater. A connection between high surface productivity, high TOC mass accumulation rates in the seafloor, and high $C_{organic}/N_{total}$ values would follow.

The conclusion that modifications to the C/N values probably occurred during sinking of marine material from the sea surface appears at first to conflict with evidence for the non-selective preservation of organic matter in sinking particles at sites in the equatorial Pacific Ocean and the Arabian Sea (Hedges et al., 2001), but agreement may actually exist. Only 1% of the particulate organic matter present in the photic zone reaches sediment traps ~ 3 km below the surface at these sites. Organic matter C/N values at the moderately productive and therefore oxic Pacific Ocean site change little from 7.0 to 8.1 over this depth. However, the values increase from 7.4 to 9.7 at the highly productive and suboxic Arabian Sea location, and most of this increase occurs in the upper 500 m of the water column. Because the majority of organic matter remineralizaton occurs in the upper part of the water column (e.g. Hedges et al., 2001), we speculate that selective degradation is most important during initial sinking from the photic zone, and that amplification of $C_{organic}/N_{total}$ ratios occurs during this phase.

Consequences of this early diagenetic process are evident in other types of organic-carbon-rich sedimentary sequences. $C_{organic}/N_{total}$ values in Mediterranean sapropels are commonly in the range of 15–18 (Bouloubassi et al., 1999; Meyers and Doose, 1999; Nijenhuis and de Lange, 2000), and range between 20 and 45 in Cenomanian–Turonian black shales (summarized by Meyers, 1997). These two types of accumulations are believed to contain marine-derived organic matter in which carbon-rich components have been preserved better than nitrogen-rich components. In contrast to marine settings, $C_{organic}/N_{total}$ values in organic matter in lacustrine deposits do not appear to experience similar selective diagenetic modification, and instead faithfully record changes in proportions of lake-derived and land-derived organic matter (Meyers and Lallier-Vergès, 1999). The difference may reflect important differences in delivery of organic matter, sinking times, and burial rates between the deep sea and lakes. Primary among the possible differences is the relative availability of dissolved nitrate, which is seldom a limiting nutrient to primary producers in lake waters but is commonly limited in marine systems.

4. Conclusions

We have compared $C_{organic}/N_{total}$ values, MAR_{CaCO_3} values, MAR_{TOC} values, and $\delta^{13}C_{org}$ values in sediments from ODP Site 1085 that were deposited over an 11-Ma period during which the high productivity associated with the Benguela Current upwelling system evolved. $C_{organic}/N_{total}$ values increase from ~ 5 to reach as high as ~ 15 as the biogenic component mass accumulation rates increase. Organic matter is predominantly marine in origin throughout this period. Selective diagenesis of organic matter has apparently increased algal C/N values from their original values between 5 and 8. Because of its relation to the growth in productivity, much of this change probably records a shift in relative rates of preservation of the carbon-rich and nitrogen-rich components as the flux of organic matter to the seafloor increased. We postulate that the relative rate of degradation of carbon-rich components of organic matter has remained the same or possibly decreased while that of nitrogen-rich components has increased. $C_{organic}/N_{total}$ values consequently increased.

We further postulate that most of the increase in $C_{organic}/N_{total}$ values occurs early in the sinking process. Once deposited on the seafloor, C/N values of organic-carbon-rich sediments appear to experience little further change. This inference implies that elevated $C_{organic}/N_{total}$ values in other marine sedimentary sequences may be useful as indicators of former times of elevated paleoproductivity. However, the lack of a straightforward relationship between $C_{organic}/N_{total}$ values and TOC mass accumulation rates in the Site 1085 sedimentary record indicates that additional and still unknown factors affect the $C_{organic}/N_{total}$ ratios. This complexity is underscored by the absence of similar diagenetic increases in $C_{organic}/N_{total}$ values of lacustrine sediments during times of elevated productivity.

Acknowledgements

M. Lyle and J. Rullkötter provided detailed and very helpful reviews of this manuscript. We thank R.S. Robinson for her technical direction during this study and H.-L. Lin for her helpful comments on an early version of this contribution. P.A.M. is grateful to the Deep Sea Drilling Project and the Ocean Drilling Program, both funded by the National Science Foundation and IPOD countries, for the unparalleled opportunity to study the evolution of the Benguela Current upwelling system during Legs 75 and 175. This study was supported by funds from the Deutsche Forschungsgemeinschaft and JOI-USSSP.

Associate Editors—**S. Wakeham and J. Curiale**

References

Bouloubassi, I., Rullkötter, J., Meyers, P.A., 1999. Origin and transformation of organic matter in Pliocene–Pleistocene Mediterranean sapropels: organic geochemical evidence. Marine Geology 153, 177–197.

Diester-Haass, L., Meyers, P.A., Rothe, P., 1990. The Benguela Current: glacial/interglacial fluctuations during its Miocene northward migration across the Walvis Ridge. Paleoceanography 5, 685–707.

Diester-Haass, L., Meyers, P.A., Vidal, L., 2002. The late Miocene onset of high productivity in the Benguela Current upwelling system as part of a global pattern. Marine Geology 180, 87–103.

Diester-Haass, L., Meyers, P.A., Vidal, L., Wefer, G., 2001. Late Miocene changes in paleoproductivity and carbonate dissolution in the Benguela Current upwelling system: local or global control. EOS Transactions AGU 80 (46), F589. (abstract).

Emerson, S., Hedges, J.I., 1988. Processes controlling the organic carbon content of open ocean sediments. Paleoceanography 3, 621–634.

Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. Revue Institut de l'Francais du Pétrole 32, 23–42.

Freudenthal, T., Wagner, T., Wenzhöfer, F., Zabel, M., Wefer, G., 2001. Early diagenesis of organic matter from sediments of the eastern subtropical Atlantic: evidence from stable nitrogen and carbon isotopes. Geochimica et Cosmochimica Acta 65, 1795–1808.

Ganeshram, R.S., Calvert, S.E., Pedersen, T.F., Cowie, G.L., 1999. Factors controlling the burial of organic carbon in laminated and bioturbated sediments off NW Mexico: implications for hydrocarbon preservation. Geochimica et Cosmochimica Acta 63, 1723–1734.

Giraudeau, J., Meyers, P.A., Christensen, B.A., 2002. Accumulation of organic and inorganic carbon in Pliocene–Pleistocene sediments along the southwestern African margin. Marine Geology 180, 49–69.

Hedges, J.I., Baldock, J.A., Gelinas, Y., Lee, C., Peterson, M., Wakeham, S.G., 2001. Evidence for non-selective preservation of organic matter in sinking marine particles. Nature 409, 801–804.

Ishiwatari, R., Uzaki, M., 1987. Diagenetic changes of lignin compounds in a more than 0. 6 million-year old latchstring sediment (Lake Biwa, Japan). Geochimica et Cosmochimica Acta 51, 321–328.

Jasper, J.P., Gagosian, R.B., 1990. The sources and deposition of organic matter in the Late Quaternary Pygmy Basin, Gulf of Mexico. Geochimica et Cosmochimica Acta 54, 117–1132.

Keswani, S.R., Dunham, K.W., Meyers, P.A., 1984. Organic geochemistry of late Cenozoic sediments from the subtropical South Atlantic Ocean. Marine Geology 61, 25–42.

Lutjeharms, J.R., Stockton, P.L., 1987. Kinematics of the upwelling of southern Africa. South African Journal of Marine Science 5, 35–49.

Lyle, M., Dadey, K.A. Farrell, J.W., 1995. The late Miocene (11–8 Ma) eastern Pacific carbonate crash: evidence for reorganisation of deep-water circulation by the closure of the Panama gateway. In: Pisias, N. Mayer, L.A., Janacek, T.R., et al. (Eds.), Proceedings of the Ocean Drilling Program,

Scientific Results, 138, Ocean Drilling Program, College Station (TX), College Station, pp. 821–838.
Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. Chemical Geology 144, 289–302.
Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Organic Geochemistry 27, 213–250.
Meyers, P.A., 2001. Miocene–Pleistocene sedimentary record of carbon burial under the Benguela Current upwelling system, southwestern margin of Africa. In: Wefer, G., Berger, W., Richter, C. et al. (Eds.), Proceedings of the Ocean Drilling Program, Scientific Results, 175. pp. 1–19, Ocean Drilling Program, College Station, TX (Available from: http://www-odp.tamu.edu/publications/175_SR/VOLUME/CHAPTERS/SR175_06.PDF).
Meyers, P.A., Doose, H., 1999. Sources, preservation, and thermal maturity of organic matter in Pliocene–Pleistocene organic-carbon rich sediments of the western Mediterranean Sea. In: Zahn, R., Comas, M.C., Klaus, A. (Eds.), Proceedings of the Ocean Drilling Program, Scientific Results, 161. Ocean Drilling Program, College Station, TX, pp. 383–390.
Meyers, P.A., Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. Journal of Paleolimnology 21, 345–372.
Meyers, P.A., Huc, A.Y., Brassell, S.C., 1983. Organic matter patterns in South Atlantic sediments deposited since the late Miocene beneath the Benguela upwelling system. In: Bjorøy, M., Albrecht, P., Cornford, C., de Groot, K., et al. (Eds.), Advances in Organic Geochemistry 1981. Wiley, Chichester, pp. 465–470.
Meyers, P.A., Silliman, J.E., Shaw, T.J., 1996. Effects of turbidity flows on organic matter accumulation, sulfate reduction, and methane generation in deep-sea sediments on the Iberia Abyssal Plain. Organic Geochemistry 25, 69–78.
Müller, P.J., 1977. C/N ratios in Pacific deep-sea sediments: effects of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochimica et Cosmochimica Acta 41, 765–776.
Müller, G., Gastner, M., 1971. The "Karbonat-Bombe", a simple device for the determination of the carbonate content in sediments, soils, and other materials. Neues Jahrbuch für Mineralogie 10, 466–469.
Nijenhuis, I.A., de Lange, G.J., 2000. Geochemical constraints on Pliocene sapropel formation in the eastern Mediterranean. Marine Geology 163, 41–63.
O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. Bioscience 38, 328–336.
Peters, K.E., 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. AAPG Bulletin 70, 318–329.
Prahl, F.G., Bennett, J.T., Carpenter, R., 1980. The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. Geochimica et Cosmochimica Acta 44, 1967–1976.
Prahl, F.G., Ertel, J.R., Goñi, M.A., Sparrow, M.A., Eversmeyer, B., 1994. Terrestrial organic carbon contributions to sediments on the Washington margin. Geochimica et Cosmochimica Acta 58, 3048–3055.
Premuzic, E.T., Benkovitz, C.M., Gaffney, J.S., Walsh, J.J., 1982. The nature and distribution of organic matter in the surface sediments of world oceans and seas. Organic Geochemistry 4, 63–77.
Redfield, A.C., 1942. The processes determining the concentrations of oxygen, phosphate and other organic derivatives within the depths of the Atlantic Ocean. Papers on Physical Oceanography and Meteorology 9.
Shackleton, N.J., Kennett, J.P., 1975. Paleotemperature history of the Cenozoic and initiation of Antarctic glaciations (Initial Reports of the Deep Sea Drilling Project, 29) United States Government Printing Office, Washington, DC.
Siesser, W.G., 1980. Late Miocene origin of the Benguela upwelling system off northern Namibia. Science 208, 283–285.
Silliman, J.E., Meyers, P.A., Bourbonniere, R.A., 1996. Record of postglacial organic matter delivery and burial in sediments of Lake Ontario. Organic Geochemistry 24, 463–472.
Smith, B.N., Epstein, S., 1971. Two categories of $^{13}C/^{12}$ ratios for higher plants. Plant Physiology 47, 380–384.
St-Onge, G., Hillaire-Marcel, C., 2001. Isotopic constraints of sedimentary inputs and organic carbon burial rates in the Saguenay Fjord, Quebec. Marine Geology 176, 1–22.
Suess, E., Müller, P.J., 1980. Productivity, sedimentation rate and sedimentary organic matter in the oceans II.—Elemental fractionation. Biogeochimie de la matire organique a l'interface eau-sèdiment marin, CNRS Colloques Internationaux 293, 17–26.
Summerhayes, C.P., Kroon, D., Rosell, M.A., Jordan, R.W., Schrader, H.J., Hearn, R., Villanueva, J., Grimalt, J.O., Eglinton, G., 1995. Variability in the Benguela Current upwelling system. Progress in Oceanography 35, 207–251.
Ujiie, H., Hatakeyama, Y., Gu, X.X., Yamamoto, S., Ishiwatari, R., Maeda, L., 2001. Upward decrease of organic C/N ratios in the Okinawa Trough cores: proxy for tracing the post-glacial retreat of the continental shore line. Palaeogeography, Palaeoclimatology, Palaeoecology 165, 129–140.
van Mooy, B.A.S., Keil, R.G., Devol, A.H., 2002. Impact of suboxia on sinking particulate organic carbon: enhanced carbon flux and preferential degradation of amino acids via denitrification. Geochimica et Cosmochimica Acta 66, 457–465.
van Zinderen Bakker, E.M., 1984. Palynological evidence for late Cenozoic arid conditions along the Namibia coast from Holes 532 and 530A, Leg 75, Deep Sea Drilling Project. In: Hay, W.W., Sibuet, J.-C., Barron, E.J., Brassell, S.C., et al. (Eds.), Initial Reports of the Deep Sea Drilling Project, 75. United States Government Printing Office, Washington, DC, pp. 763–767.
Verardo, D.J., McIntyre, A., 1994. Production and preservation: control of biogenous sedimentation in the tropical Atlantic 0–300,000 years B.P. Paleoceanography 9, 63–86.
Vidal, L., Bickert, T., Wefer, G., Röhl, U., 2002. Late Miocene stable isotope stratigraphy of Site 1085: relation to Messinian events. Marine Geology 180, 71–85.
Waples, D.W., Sloan, J.R., 1980. Carbon and nitrogen diagenesis in deep sea sediments. Geochimica et Cosmochimica Acta 44, 1463–1470.
Wefer, G., Berger, W., Richter, C., et al., 1998. Proceedings of the Ocean Drilling Program (Initial Reports, 175). Ocean Drilling Program, College Station, TX.