Burial and reactivity of sedimentary microalgal lipids in bioturbated Mediterranean coastal sediments

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Abstract

The fate of microalgal lipid biomarkers in marine coastal sediments when acted on by natural bioturbation processes (Carteau Bay, Gulf of Fos, Mediterranean Sea) was studied under laboratory conditions. Both dead phytoplanktonic cells (*Nannochloropsis salina*) and luminophores (inert fluorescent particulate tracers) were deposited at the surface of intact sediment cores which were then incubated for 22, 44 and 63 days. Sediment reworking and concentration profiles of specific lipid components of *N. salina* (*n*-alkenes, alkyl diols, sterols and fatty acids) were determined as a function of time and depth. The results show that, in the sediment investigated, bioturbation occurs essentially as a biodiffusive process and that it has a rapid and significant impact on the qualitative and quantitative record of sedimentary lipids. Whereas most of the biomarkers were detected in the entire reworked layer (0–6 cm) after 22 days, *n*-alkenes were never detected below 3 cm due to their low concentration and their high reactivity. For each individual lipid, the comparison of the amounts obtained from the inventories of biomarkers in the reworked zone, with the amount deposited initially at the sediment surface, allowed the determination of its extent and rate of degradation. These ranged from 72% to 99% and from 0.010 to 0.047 day^{-1}, respectively, depending on the biomarker considered, with polyunsaturated fatty acids (PUFAs) and alkenes being degraded faster than the other components. Comparison with previous work suggests that, in biologically reworked sediments, the apparent reactivity of lipids is: (i) positively correlated with the biological mixing coefficient (D_b) and, (ii) generally much higher than in non-bioturbated (anoxic) sediments. Our results also support the idea that degradation of lipids in reworked sediments involves the combined effects of aerobic and anaerobic degradation processes, but that biological mixing results in diagenetic properties more characteristic of completely oxidized conditions.

Keywords: Lipid biomarkers; Bioturbation; Coastal sediments; Kinetics of degradation; Redox conditions; Mediterranean Sea; Gulf of Fos

1. Introduction

Marine coastal areas are characterised by high primary production and shallow water depths, both allowing a relatively large fraction of the photosynthetically-synthesised organic carbon to reach the sea floor and to be ultimately preserved in anoxic sediments. As a consequence, coastal sediments, which comprise 10% of the ocean floor, store 80% of marine organic carbon (Hedges and Keil, 1995).

In coastal environments where the overlying water is oxygenated, the activity of benthic infauna capable

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of bioturbation is known to influence the decomposition of organic matter (OM) (cf. Aller, 2001; Kristensen and Holmer, 2001). Sediment reworking can, for instance, alter oxic/anoxic boundaries, affect microbial populations directly or indirectly, cause vertical transport of particles, and lead to movement of particles across oxic and anoxic boundaries. The frequency and duration of these processes may significantly influence degradation rates and net preservation of OM (Aller, 1994a). For instance, periodic exposure to oxygen is an important mechanism for achieving low background concentrations of organic carbon (Sun et al., 1993, 2002a; Hulthe et al., 1998).

Lipids are a major organic carbon pool in phytoplankton, making up about 5–20% of total carbon (Sun et al., 1999). The good potential of preservation in marine sediments and the specific structure of some lipids allow them to be widely used as biomarkers in geochemical studies for determining the source, the transformation, and the fate of OM (cf. Summons, 1993 and references therein), and specific palaeoenvironmental conditions (cf. Brassell, 1993). Sedimentary lipids degrade at different rates depending on the redox conditions and are generally mineralized faster in the presence of oxygen (Canuel and Martens, 1996; Harvey and Macko, 1997; Hoefs et al., 2002; Sun et al., 1997, 2002a,b; Sun and Wakeham, 1998, 1999; Teece et al., 1998).

There have been only a few studies on the effects of benthic organisms on the degradation of specific lipids in sediments. Laboratory experiments with individual species of macrofauna (Bianchi et al., 1988; Ingalls et al., 2000), or assemblages of meio- and macrofauna (Webb and Montagna, 1993), have demonstrated the importance of these organisms in the burial and the transformation of sedimentary chloropigments. Recent studies also showed that the activity of the bivalve *Yoldia limatula* can significantly enhance the degradation of algal lipids (Sun et al., 1999) and that the degradation of these compounds is higher in sediment bioturbated by mixtures of specific macrofauna (Polychaeta, Mollusca, Crustacea) than in physically mixed sediment (Sun et al., 2002a,b). To the best of our knowledge, the impact of global bioturbating benthic communities on the diagenesis of sedimentary lipids has been studied only by modeling the steady-state core profiles of planktonic fatty acids and sterols in coastal sediments from Long Island Sound (USA) (Sun et al., 1997; Sun and Wakeham, 1999), or more recently, by following the fate of chlorophyll-*a* in intact bioturbated sediment box-cores enriched with ^{14}C-labelled phytodetritus (Josefson et al., 2002).

In the present work, bioturbated sediment cores were collected in a coastal marine area (Gulf of Fos, Mediterranean Sea), and microalgal cakes supplemented with inert particulate tracers (luminophores) were deposited on top of the cores to simulate a natural pulse of material that settles after a water column bloom. The concentrations of specific microalgal lipids (*n*-alkenes, long-chain alkyl diols, sterols and fatty acids) were then determined as a function of incubation time and sediment depth to monitor the qualitative and quantitative short-term fates (burial, extents and rates of degradation) of these biomarkers within the reworked layer of the sediment defined by the luminophore distribution.

2. Experimental

2.1. Materials

The seawater and the sediment cores were collected in Carteau Bay (Gulf of Fos, Mediterranean Sea) at 43°23′ N–4°53′ E in March 1999. At this station, the bottom water and the surface sediments (0–5 mm) are oxygenated throughout the year. Sediment cores (9.5 × 30 cm) were sampled by scuba divers in a 1 m^2 area. Following sampling, the water and the sealed cores were immediately stored at the same temperature as that encountered in situ (12 °C).

Bioturbation processes in Carteau Bay sediments have been extensively studied (Pérès, 1982; Gerino, 1992; Gerino et al., 1994; Gilbert et al., 1996, 1998; Grossi et al., 2002). The sediment is classified as muddy sand sediment and is occupied by a macrofauna assemblage characteristic of muddy sand in sheltered areas. Organisms larger than 250 μm have a density of 6000 ± 2000 individuals/m^2, and more than 90% are located in the first 10 cm of sediment. Polychaetes are the most representative class of macrofauna (40–60% of total macrofauna), essentially represented by the Cirratulideae *Tharyx heterochaeta* and the Spionideae *Paradoneis lyra*.

The marine microalga *Nannochloropsis salina* (Eustigmatophyceae) was grown at 12 °C in a 20-l batch culture (Grossi et al., 2001). Cells were harvested by centrifugation and kept frozen until the beginning of the experiment. This phytoplankton was chosen because of its high lipid content (Volkman et al., 1993), and because some of its lipid constituents are absent (e.g. long-chain alkenes) or only present in small amounts (e.g. alkyl diols) in the sediment from Carteau Bay (Table 1). This helped to distinguish between deposited material and material already present in the sediment.

2.2. Microcosm set-up and sampling

The height of sediment in the cores was adjusted to 13 cm by cutting off the bottom of the sediment. The bottom of the cores was then sealed and the overlying seawater was carefully replaced by fresh filtered seawater. The cores were placed into large polycarbonate reservoirs, each containing enough seawater to equal the water height in the cores. This kept the temperature constant during the experiment and prevented leakage from the base of the cores.

Three series of cores were considered (Fig. 1). A first set of six cores (cores A) was enriched at the sediment surface with concentrated microalgal cells. Accordingly, the concentrated cells were thoroughly mixed with sieved (1 mm) sediment, which increased the organic content of the sediment by 0.5%. The mixed sediment was made into 5-mm-thick cakes with diameters the same as the cores. The frozen cakes were then deposited at the seawater surface of each core and allowed to reach the sediment–water interface. A second set of six cores (cores B) was enriched with the same cakes supplemented with luminophores (size 80–250 μm). These are inert fluorescent particles used as conservative tracers of the sediment's solid phase rearrangement (Gerino et al., 1998). The third set of six cores (cores C) received only sieved sediment cakes where neither phytoplankton nor luminophores were added. The overlying seawater in all cores was continuously purged with air to keep it oxygenated. Incubations were carried out at 12 °C with a 12 h dim light/12 h dark regime.

At different sampling times (22, 44 and 63 days), duplicate cores were collected within each set, and oxygen profiles were determined in these cores using minielectrodes (Grossi et al., 2002). Almost all of the overlying water in the remaining cores was carefully replaced to prevent any variation in salinity due to evaporation, whereas the water from the collected cores was removed. For each core, any suspended particles present in the overlying water were collected by filtration on pre-combusted GF/F paper. Sediment was extruded from each sampled core and sliced as follows: 0–1 cm in 0.5 cm intervals, 1–6 cm in 1 cm intervals and 6–10 cm in 2 cm intervals; the final 10–13 cm section was left as such.

Table 1
Amounts and percentages of enrichment of lipid biomarkers deposited on top of the sediment cores (as a mixture of *N. salina* cells and sieved sediment) and considered for this study

Compounds	Amount deposited (μg)[a]	Enrichment (%)[a,b]
n-Alkenes		
Σ $C_{27:1}$ + $C_{27:2}$ + $C_{29:2}$ + $C_{27:3}$[c] + $C_{29:3}$	100	100
Alcohols		
$C_{29}\Delta^5$-ethyl sterol[d]	160	40
$C_{29}\Delta^{5,24(28)}$-ethyl sterol[d]	25	50
n-C_{30} diols[c]	40	60
n-C_{32} diol	90	85
n-$C_{32:1}$ diol	40	100
Fatty acids		
$C_{14:0}$	620	35
$C_{16:0}$	2100	30
$C_{16:1}\omega7$	2500	60
$C_{18:1}\omega9$	960	45
$C_{18:3}\omega6$	40	50
$C_{20:5}\omega3$	1600	65

[a] Average of duplicate ± 10%.
[b] Amount deposited/(amount deposited + amount present between 0 and 6 cm depth before deposition).
[c] Present as two isomers.
[d] $C_{29}\Delta^5$-ethyl = 24-ethylcholesta-5-en-3β-ol; $C_{29}\Delta^{5,24(28)}$-ethyl = 24-ethylcholesta-5,24(28)E-dien-3β-ol.

2.3. Luminophores counting

Each section of the cores from set B was sieved through a 250-μm mesh to remove the biggest particles and the macrofauna. The total number of luminophores was counted in three replicate samples (0.25 g) of the sieved sediment as described by Gerino et al. (1998).

Fig. 1. Schematic experimental set-up.

2.4. Extraction and analysis of lipids

Each entire sediment section was saponified with 1N KOH in MeOH/H_2O (3:2; reflux 4 h). For the section 0–0.5 cm, the filters containing particles present in the overlying water were saponified together with the sediment. Following filtration through a Buchner funnel (pre-rinsed Whatman qualitative paper), total neutral lipids were extracted from the basic filtrate (*n*-hexane, 4 × 30 ml), whereas total acidic lipids were extracted following addition of HCl (pH = 2, *n*-hexane, 4 × 30 ml). Extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The neutral lipids were separated by column chromatography (silica gel; 3% H_2O) into a hydrocarbon fraction and a fraction containing more polar compounds (e.g. phytol, sterols, alkyl diols) with hexane and dichloromethane/methanol (DCM/MeOH; 1:1 v/v) as eluents, respectively. The hydrocarbon fraction was further separated on silica gel impregnated with $AgNO_3$ (5% $AgNO_3$, activated at 120 °C) using solvents of increasing polarity from hexane through 20% ethyl acetate–hexane. The latter fraction containing *n*-alkenes was collected.

For quantification of individual components, internal standards (9-tricosene, squalane and nonadecanoic acid for hydrocarbons, polar and acidic compounds, respectively) were added. Alkenes were quantified by GC-MS using a HP 5890 series II plus gas chromatograph coupled with a HP 5972 mass spectrometer (Grossi et al., 2001). Alcohols and acids were silylated with a mixture of pyridine/BSTFA (1:1 v/v, 20 min at 60 °C) before GC and GC-MS analyses. These compounds were identified by GC-MS and quantified by GC-FID using a HP 4890 gas chromatograph (Grossi et al., 2002). Separations were performed with a HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) for alkenes and acidic compounds, and with a BPX50 bonded phase capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) for alcohols. The oven temperatures were programmed from 60 to 130 °C at 20 °C/min and then at 4 °C/min to 300 °C at which they were held for 10 min.

3. Results and discussion

3.1. Biological particles reworking

Our experimental set-up and the inert character of luminophores implied that the amount of these particles that was initially deposited remained constant during the experiment. Fig. 2 shows the depth distribution of luminophores after 22 and 63 days of incubation. The shape of the profiles indicates a dominance of biodiffusive processes within the sedimentary column. Most of the particulate tracers (i.e.

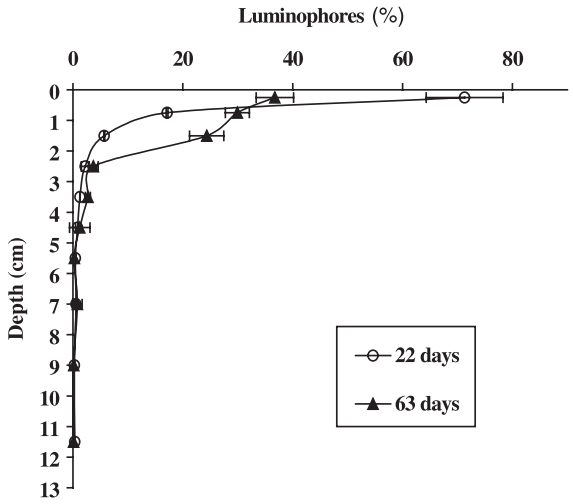

Fig. 2. Depth profiles of luminophores in microalga-enriched (*N. salina*) sediment cores after 22 and 63 days of incubation (each data point represents the average of duplicate cores ± standard deviation; the distribution after 44 days is not shown due to lack of clarity).

99% of the amount deposited) remained in the upper part of the cores (0–6 cm) throughout the experiment. This subsurface layer was defined as the reworked layer, and corresponds well with the maxima of in situ reworking activity and of macrofauna density (Gerino et al., 1994). Within this layer, the depth profiles of luminophores changed with time and clearly showed a transport of particles downward (Fig. 2). The percentage of luminophores recovered below 1 cm increased from 9% after 22 days of incubation to 22% and 31% after 44 and 63 days, respectively.

To quantify the sediment reworking, the down-core profiles of luminophores were modeled according to the following equation (Cochran, 1985), which expresses the development of a conservative tracer distribution (C) as a function of time (t) and depth (x) for a biodiffusive system: $\frac{\partial C}{\partial t} = D_b \frac{\partial^2 C}{\partial x^2}$ where D_b = biological mixing coefficient.

D_b, calculated from our microcosms, was equal to 0.006 ± 0.001 cm^2 day^{-1} ($n = 6$), which is consistent with the mean sediment reworking coefficient determined during field work in Carteau Bay (0.007 ± 0.003 cm^2 day^{-1}, $n = 9$; Gerino, 1992). This clearly indicated that bioturbation processes occurring in the microcosms incubated under laboratory conditions for 63 days were comparable with the natural conditions of bioturbation.

3.2. Fate of microalgal lipids

The lipid composition of *N. salina* consists mainly of fatty acids, sterols, phytol, long-chain alkyl diols, alkenes and alkenols (Volkman et al., 1992; Gelin et al., 1997; Grossi et al., 2001). Although *N. salina* has never been observed in the Carteau Bay (B. Berland, personal communication), some of its lipids, common to many species of plankton, are also present in the sediment from this site (phytol, sterols, fatty acids and some diols). For this reason, in this study, only the compounds for which the contribution from the deposited *N. salina* cells was high enough were considered. Reliable (Bravais–Pearson, $n = 6$, $\alpha = 0.05$) kinetics of degradation (see below) were obtained for compounds whose enrichment was $\geq 30\%$ (Table 1). *N*-alkenols could not be satisfactorily quantified due to co-elution and thus were not considered.

We draw attention to the fact that the analytical procedure used for the extraction of lipids yielded a mixture of extractable (free + esterified) and non-extractable (ester-bound) neutral or acidic compounds. This allowed us to consider the fate of some alkyl diols, which occur in *Nannochloropsis* partly esterified to non-extractable polar lipids (Volkman et al., 1992; Gelin et al., 1997). However, since a correction from background lipids was considered using control cores, the diagenetic parameters described below mostly reflect the fate of the reactive lipids of *N. salina*.

3.2.1. Burial and distribution of lipids

Like luminophores, the lipid profiles were characteristic of biodiffusive processes. Apart from *n*-alkenes, which were never observed below 3 cm, all the deposited lipids were detected down to a 6-cm depth after 22 days of incubation (Fig. 3). For compounds that were present in both *N. salina* cells and the original sediment (e.g. sterols and fatty acids; see Table 1), the concentration always reached the background concentration below 6 cm, indicating that deeper sediments were not significantly influenced, in terms of lipid concentration, by the addition of microalgal cells at the water–sediment interface. This was supported by the absence of detectable *n*-$C_{32:1}$ diol (a compound not present in the original sediment) beneath 6 cm and corresponded to the zone of biological reworking defined by the luminophore distribution (Fig. 2).

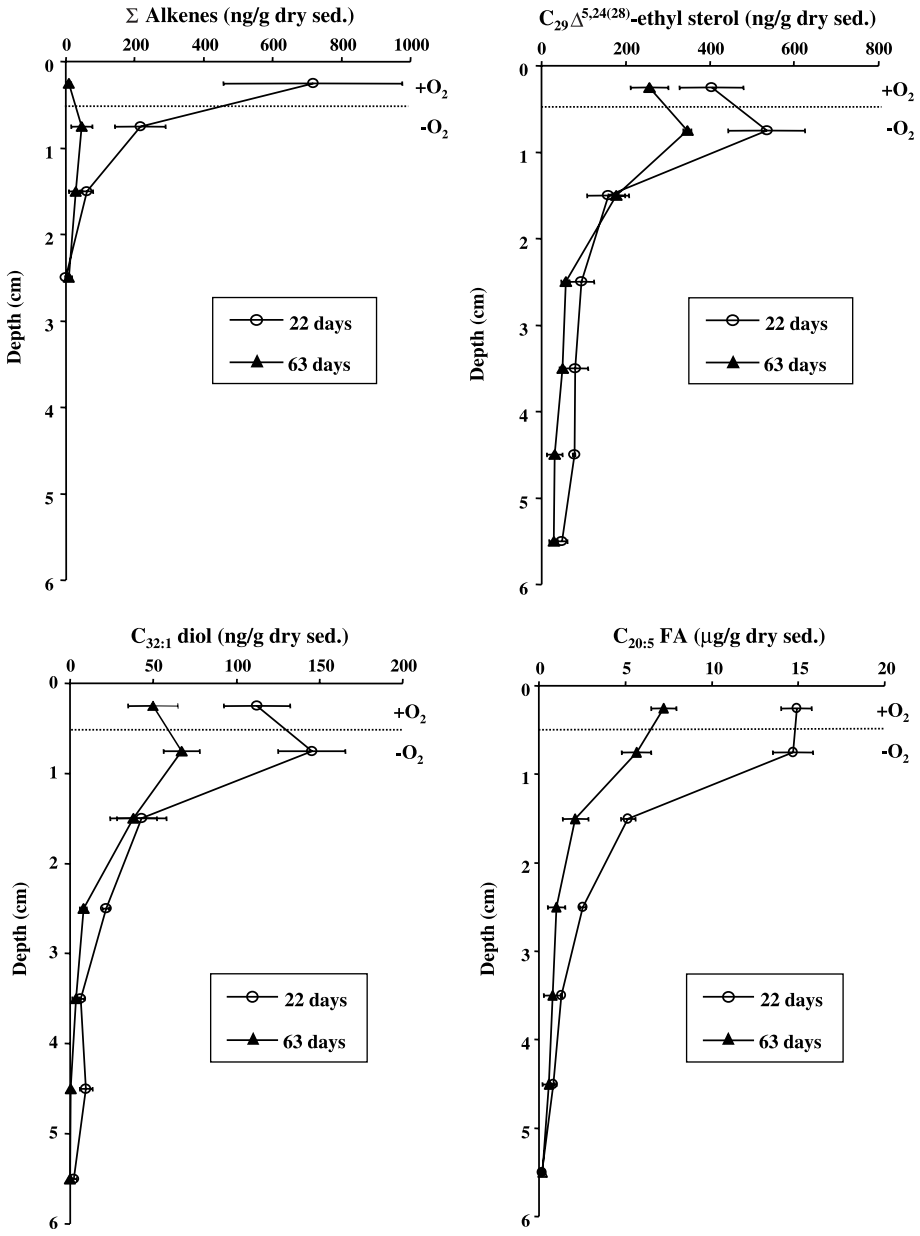

Fig. 3. Depth profiles of some lipid biomarkers in microalga-enriched (*N. salina*) sediment cores after 22 and 63 days of incubation (each data point represents the average of duplicate cores ± standard deviation; the distribution after 44 days is not shown due to lack of clarity). The dotted lines show the limit of the permanently oxygenated sediment layer (0–0.5 cm).

Rapid transport of sedimentary material to depth had already been observed during laboratory (Sun et al., 1999, 2002a,b; Ingalls et al., 2000) and in situ (Blair et al., 1996; Middelburg et al., 2000) ^{13}C-labeling studies. This transport is generally explained by a feeding-associated activity, although other causes (e.g. migration of benthic algae, physical mixing) may be involved in certain cases. Deposit-feeding animals can transport fresh phytodetritus at vertical velocities >1 cm day^{-1} in some environments (Graf, 1989). In the

present study, it is likely that the first step of the burial of lipids was essentially due to the activity of meiofauna, as previously suggested by Webb and Montagna (1993) for organically-enriched habitats. However, since meiofauna are known to be mostly active in the first centimeter of the sedimentary column (Giere, 1993), the transport of material to deeper sediment might have involved deposit-feeding macrofauna (Webb and Montagna, 1993; Josefson et al., 2002).

The evolution of the lipid depth profiles throughout the experiment showed a decrease of the overall concentrations with time. This was especially characterised by an attenuation of the slopes of the profiles in the first centimeters of the cores (Fig. 3). The use of minielectrodes showed that the upper 5 mm of sediment were constantly oxygenated, suggesting that lipids which were buried deeper were, at least once, submitted to contrasting redox conditions throughout the incubation. It is also likely that the activity of macrobenthic organisms induced intermittent oxygen penetration into the anoxic part of the sediment. For this latter reason, we cannot rule out the possibility that reworked lipids were degraded exclusively in the presence of oxygen. Nevertheless, the evolution of the lipid depth profiles (Fig. 3) rather suggests that the biomarkers were reworked and degraded simultaneously and were thus subjected to both aerobic and anaerobic degradation processes. These latter may include NO_3^- reduction, Mn and Fe reduction and SO_4^{2-} reduction, depending on the availability of these different electron acceptors at varying depths (Aller, 1994b).

Finally, throughout the experiment, the concentration of some lipids was lower in the uppermost sediment layer constantly oxygenated (0–0.5 cm) than just below this zone (Fig. 3). This can be interpreted either as a more efficient degradation of the compounds under oxic conditions (see discussion below) or as a non-local transport of material downwards (Boudreau, 1986; Middelburg et al., 2000).

3.2.2. Extent and kinetics of degradation

The extent of degradation and degradation rate constants calculated in this study represent net losses of compounds, including transformation and remineralization. It is possible that, for some compounds (i.e. saturated and monounsaturated fatty acids), the data also include a microbial production within the sediment column and/or a contribution from benthic animals (Sun et al., 1997; Sun and Wakeham, 1999). Nonetheless, the correction with the control cores minimized the latter source of compounds (see below).

Diagenetic processes that affect lipid distribution in Carteau Bay sediments include particle reworking due to bioturbation and lipid degradation due to digestion of organic matter by benthic fauna, microbial decomposition and abiotic reactions. Net losses for individual lipid biomarkers (ΔQ) were evaluated by calculating the difference between their amount (μg) in the microalgal cakes (Q_0; see Table 1), and the amounts recovered in the section 0–6 cm of incubated cores (Q_{t0-6}) after correction obtained from the control cores (Q_{tc0-6}; background lipids): $\Delta Q = Q_0 - (Q_{t0-6} - Q_{tc0-6})$. The extents of degradation were then obtained by the ratio $\Delta Q/Q_0$.

A major part of the biomarkers considered disappeared during the experiment, but differences were observed between component classes (Table 2). Whereas alkenes and polyunsaturated fatty acids (PUFAs) were almost entirely removed from our analytical window,

Table 2
Apparent first-order decay constants (k, day^{-1}), determination coefficients (r^2, $n=6$) and extent of degradation after 63 days of specific lipid biomarkers during the incubation of the sediment cores

Compounds	k	r^2	Degraded (%)
n-Alkenes			
$C_{27:1}$	0.042	0.813	94
$C_{27:2}$	0.039	0.666	88
$C_{29:2}$	0.037	0.979	96
$C_{27:3}$[a]	0.043	0.803	99
$C_{29:3}$	0.036	0.543	99
Alcohols			
$C_{29}\Delta^5$-ethyl sterol[b]	0.025	0.973	85
$C_{29}\Delta^{5,24(28)}$-ethyl sterol[b]	0.017	0.862	85
n-C_{30} diols[a]	0.018	0.754	85
n-C_{32} diol	0.010	0.997	79
n-$C_{32:1}$ diol	0.016	0.970	82
Fatty acids			
$C_{14:0}$	0.018	0.792	75
$C_{16:0}$	0.017	0.983	72
$C_{16:1}$	0.013	0.879	79
$C_{18:1}$	0.028	0.993	82
$C_{18:3}$	0.043	0.903	99
$C_{20:5}$	0.047	0.985	97

[a] Present as two isomers.
[b] $C_{29}\Delta^5$-ethyl = 24-ethylcholesta-5-en-3β-ol; $C_{29}\Delta^{5,24(28)}$-ethyl = 24-ethylcholesta-5,24(28)E-dien-3β-ol.

sterols, alkyl diols and saturated and monounsaturated fatty acids were still present in significant amounts (15–30% of the deposited amount) at the end of the experiment. For these latter compounds, a longer incubation time might have resulted in further degradation, although a part could have been preserved within the sediment.

The decrease of individual lipid quantities was fitted using least square regressions of lipid inventories in the reworked zone (corrected from background) vs. time to yield average rate constants (k) using the simple first-order model: $\frac{\partial C_i}{\partial t} = -kC_i$ where C_i = inventory of lipid compound i. This decomposition kinetic model that assumes a logarithmic decrease of lipid concentration with time has been widely used to examine bulk and individual biochemical fractions during diagenesis (Aller et al., 2001; Grossi et al., 2001 and references therein). As already mentioned, experimental curves fit the data well only for the compounds that were deposited in sufficient amounts above the background concentrations (i.e. enrichment $\geq 30\%$; Table 1). The apparent first-order degradation constants of the individual components ranged from 0.010 day^{-1} for C_{32} diol to 0.047 day^{-1} for $C_{20:5}$ fatty acid (Table 2). Alkenes and PUFAs were the most labile lipids and were degraded 1.5 to 5 times faster than the other compounds. The low amount of alkenes in *N. salina* (Table 1) and their high reactivity most likely explain why these compounds were never detected beneath a 3-cm depth, contrary to the other biomarkers (Fig. 3). Although the high reactivity of PUFAs was in agreement with the general view that unsaturation is an important parameter in regulating the lability of lipids, this was not true for alkenes, whose reactivity seemed independent of their degree of unsaturation (Table 2). Also, monounsaturated fatty acids were not systematically more reactive than their saturated homologues, and the diunsaturated C_{29} sterol ($\Delta^{5,22}$) was degraded slower than the chain-saturated C_{29} sterol (Δ^{5}). Alkenes are generally easily degraded under both oxic and anoxic conditions (Harvey and Macko, 1997; Grossi et al., 1998, 2000), and therefore, they rarely enter the sedimentary record. Differences in the potential of preservation of several linear alkenes were noted, however, during a field study in the Black Sea (Wakeham et al., 1991) and during the anaerobic biodegradation of the lipids of the microalga *N. salina* under laboratory conditions (Grossi et al., 2001). These differences were attributed to differences in the chemical structure (e.g. the position and the geometry of the double bonds) of the compounds. The relative homogeneity of the degradation rates of individual alkenes observed in the present work suggests that differences in reactivity of these compounds appear essentially when anaerobic conditions prevail. It has been suggested that a comparable feature occurs for fatty acids, which seem to be degraded at similar rates independently of their degree of unsaturation in the presence of oxygen, whereas unsaturated acids are preferentially degraded under anoxic conditions (Haddad et al., 1992; Harvey and Macko, 1997; Sun et al., 1997). In the present case, it is likely that contrasting redox conditions due to sediment reworking were responsible for the sequence of reactivity observed within each compound class, including sterols and alkyl diols.

There have been few reports on the reactivity of alkyl diols in marine sediments. At first sight, it seems that these compounds are not highly reactive in spite of the presence of hydroxyl groups and unsaturation and that their reactivity is not directly related to their chain-length nor to their degree of unsaturation (Sun and Wakeham, 1994; Grossi et al., 2001; Hoefs et al., 2002; Sinninghe Damsté et al., 2002). In the present study, alkyl diols were significantly degraded in 63 days of incubation and C_{30} diols appeared to degrade faster than the C_{32} diols (Table 2). It should be noted that alkyl diols are building blocks of biomacromolecules (termed algaenans) present in *N. salina*, where they occur essentially bound to extractable and non-extractable polar lipids through different linkages (Volkman et al., 1992; Gelin et al., 1997). It is possible that exchanges between different pools of diols (e.g. free, esterified, bound) have occurred during the incubation and have influenced the overall degradation rate constants of these compounds, as it has been observed previously during anaerobic incubations (Grossi et al., 2001). On the other hand, the degradation rates of alkyl diols were sometimes comparable to those of C_{29} sterols (Table 2), contrary to previous observations, which showed either a better potential of preservation of alkyl diols compared to sterols or the reverse depending on the redox conditions (Sun and Wakeham, 1994; Grossi et al., 2001; Hoefs et al., 2002; Sinninghe Damsté et al., 2002). Finally, significant differences between oxic and

anoxic degradation are generally observed for planktonic sterols, which are much less reactive in the absence of oxygen (Harvey and Macko, 1997; Sun and Wakeham, 1998). Among individual sterols, selective preservation is generally considered important, especially in strictly anoxic sediments (Sun and Wakeham, 1994, 1998; Grossi et al., 2001).

4. General discussion

4.1. Reactivity of lipids in bioturbated sediments

The reactivity of lipids in bioturbated sediment depends on a variety of factors such as the quality (i.e. decomposition stage), the origin (i.e. marine vs. terrigenous) and the chemical structure of the components, the density of bioturbating organisms, their type of activity (biodiffusion, burrow construction, etc.) and their impact on the microbial assemblages/activities, and the temperature (Aller et al., 2001). Direct relationships between these different factors and the degradation of lipids have, however, rarely been reported. Recently, laboratory experiments provided quantitative estimates of the enhanced degradation of algal lipids caused by an increasing abundance of the sub-surface deposit-feeding bivalve *Y. limatula* (Sun et al., 1999; Ingalls et al., 2000). Net degradation rate constants of lipids such as fatty acids and phytol were shown to be linearly correlated with abundance of *Yoldia* (Sun et al., 1999), whereas chlorophyll-*a* was demonstrated to have a continuum of degradation rate constants related to redox conditions, transport and *Yoldia* abundance as a function of depth (Ingalls et al., 2000). This latter study further showed that the biological mixing coefficient (D_b) and the reactivity of chlorophyll-*a* are positively correlated. Although one would expect that this is also the case (i) in the natural environment and (ii) for other organic components, studies showing a relationship between the reactivity of sedimentary lipids and D_b are still lacking.

During a study on the diagenesis of lipids in sediments from Long Island Sound (LIS; New York, USA), Sun and Wakeham (1999) observed that, in early spring, the reactivity of planktonic fatty acids and sterols can be 5 to 700 times higher at a station permanently oxygenated throughout the year (station P), compared to a station where hypoxia occurs in bottom waters and in underlying sediment during summer (station A), although the two sites showed similar bioturbation rates ($D_b = 0.03$ cm^2 day^{-1}). The authors explained these differences of reactivity by spatial and temporal variations in carbon flux and oxygen content, which regulate the composition and activity of benthic communities.

Additional information on the apparent reactivity of sedimentary lipids in biologically mixed sediments could be obtained by comparing the turnover times (defined as the reciprocal of the degradation rate constants) of some compounds considered in the present study, with those reported by Sun and Wakeham (1999) for the above defined station P of LIS, both comparable in terms of oxygenation (Table 3). The reactivity of individual fatty acids and, to a lesser extent of individual sterols, appears higher in LIS sediments, which exhibit a mixing coefficient five times greater than the sediments from Carteau Bay. This reinforces the idea that, in oxygenated sediments, the biological mixing coefficient (D_b) and the reactivity of planktonic lipids are positively correlated. It should be emphasized, however, that the diffusive mixing coefficient reported by Sun and Wakeham (1999) was based on ^{234}Th data, whereas the present D_b was calculated using luminophores, and that mixing coefficients calculated with different tracers may lead to different (albeit of the same order of magnitude) estimates of overall particle transport (Gerino et al., 1998).

In a recent laboratory study examining the influence of different mixing processes on algal lipid degradation in surficial sediments, Sun et al. (2002b) observed that the degradation rates of lipid subjected to specific bioturbation were close to those in unmixed cores where aerobic conditions dominate at the surface. To further clarify these findings, we compared the turnover times of lipids deduced from the data of Sun et al. (2002b), and those from the above defined bioturbated sediments (Carteau Bay and LIS station P), with those observed during kinetics of degradation of phytoplanktonic lipids under stable conditions of oxygenation (Table 4). Clearly, the values obtained in reworked sediments are generally comprised within the intervals of values defined for similar classes of components under aerobic and strictly anaerobic conditions, appearing generally closer to aerobic conditions. This supports the assumption that diagenetic parameters calculated

Table 3
Comparison of turnover times of lipid biomarkers determined in bioturbated and non-bioturbated marine sediments

	Location	Reference	Bottom water	Sediment interface	D_b (cm^2/day)	τ (days)	Method of calculation
Bioturbated sediments							
	Carteau Bay	this study	oxic	oxic	0.006[a]	*n*-alkenes: 23–28 *n*-alkyl diols: 55–100 sterols: 40–59 acids: 21–76	kinetic of lipid inventory
	Long Island Sound (station P)	Sun and Wakeham, 1999	oxic	oxic	0.03[b]	sterols: 24–50 acids: 11–17	core profile modeling[c]
		Sun et al., 1997				acids: 8–50	core profile modeling[c]
Non-bioturbated sediments							
	Cape Lookout Bight	Canuel and Martens, 1996	oxic	dysoxic/ anoxic	–	sterols: 11–170 acids: 17–250	kinetic of lipid concentration[d]
		Haddad et al., 1992				acids: 250–2500	core profile modeling[c]
	Peru upwelling	Mc Caffrey, 1990	dysoxic	dysoxic/ anoxic	–	br-alkene: 2300 *n*-alkanols: 2100–6100 sterols: 680–2400	core profile modeling[c]
	Black Sea	Sun and Wakeham, 1994	anoxic	anoxic	–	br-alkene: 8900 *n*-alkyl diols: 26000–33000 sterols: 16000–26000 acids: 6500–14000	core profile modeling[c,e]

br = branched; *n* = linear.
[a] Calculated from luminophore data.
[b] Calculated from ^{234}Th.
[c] Steady-state models.
[d] Concentration changes over deposition time.
[e] Using the 1-C model based on weight units.

for lipids in reworked sediment reflect an array of aerobic and anaerobic degradation processes due to oscillating redox conditions induced by bioturbating organisms. This also highlights, at the level of specific organic molecules, that biological mixing results in diagenetic properties more characteristic of completely oxidized conditions, in spite of the fact that dissolved oxygen may penetrate into the sediment only a few millimeters (Aller, 1994a). This may be explained by the involvement of metal oxides, such as MnO_2, in suboxic diagenetic reactions (Hulth et al., 1999).

4.2. Comparison with non-bioturbated sediments

As bioturbating organisms require oxygen to live, biologically reworked sediments are characterised by oxygenated water columns and water–sediment interfaces. Variations in oxygen content of bottom water have been shown to regulate the composition and the activity of benthic communities (Sun and Wakeham, 1999), and generally, non-bioturbated sediments are associated with anoxic bottom waters. In special cases, such as the coastal sediments from Cape Lookout Bight (CLB; North Carolina, USA), perma-

Table 4
Turnover times of phytoplanktonic lipids determined in bioturbated sediments (contrasted redox conditions) and during kinetics of degradation under oxic ($+O_2$) or strictly anoxic ($-O_2$) conditions

Compounds	τ (days)			Reference
	$+O_2$	Contrasted	$-O_2$	
n-Alkenes		23–28		this study
			110–1300	Grossi et al., 2001
	23		159–2500	Teece et al., 1998
	9–15		57–349	Harvey and Macko, 1997
Sterols		40–59		this study
			1300–2000	Grossi et al., 2001
		24–50[a]		Sun and Wakeham, 1999
			71–500	Sun and Wakeham, 1998
	11		142	Harvey and Macko, 1997
n-Alkyl diols		55–100		this study
			220–1400	Grossi et al., 2001
Fatty acids		21–77		this study
	15–21	18–26[a]		Sun et al., 2002a,b
			42–520	Grossi et al., 2001
		11–17[b]		Sun and Wakeham, 1999
	5–25	8–50[b]	5–25	Sun et al., 1997
	12–16		41–87	Harvey and Macko, 1997

[a] Laboratory experiment with sieved sediment and selected macrofauna.
[b] Long Island Sound (station P).

nently oxygenated waters overlay sediments where dysoxic to anoxic conditions prevail, therefore limiting bioturbation processes from occurring (Haddad et al., 1992; Canuel and Martens, 1993, 1996). In the particular case of CLB, this is due to the flushing action of tidal currents and to a very high sedimentation rate (10 cm/year) in a shallow (10 m water column) area (E.A. Canuel, personal communication).

Table 3 gives the turnover times of different lipid classes determined for bioturbated and non-bioturbated marine sediments. Values of sterols and fatty acids' apparent reactivity reported for CLB sediments by Canuel and Martens (1996) are in the same order of magnitude as those related to permanently bioturbated sediments (Carteau Bay and station P of LIS). The range of turnover times of individual classes of components appears, however, larger in CLB compared to the reworked sediments. This may suggest that bioturbation processes tend to homogenise lipid reactivity though differences in lipid sources and molecular structures may also have influenced the degradation rates. In contrast, the reactivity of lipids in sediments overlain by dysoxic to anoxic water columns appears two to three orders of magnitude lower than that in reworked sediments, as shown for the Peru upwelling area and the Black Sea (Table 3). The oxygen content in the water column and the surface sediments appear as one major factor controlling the lipid degradation in sediments, although different environmental factors such as the primary production, the water column depth, and the sedimentation rate may be responsible for the substantial range of apparent reactivity reported (see Sun and Wakeham, 1994 and Canuel and Martens, 1996 for a general discussion). This likely supports, at the molecular level, the assumption made by Hartnett et al. (1998) that, in continental margin sediments, longer oxygen exposure times of OM result in lower organic carbon preservation. In bioturbated sediments, the activity of benthic macrofauna creates a continuous reworking between oxic and anoxic zones, which may enhance the exposure time of organic compounds in the oxygenated zone and thus increase the degradation rates of oxygen-sensitive components.

Finally, it should be noted that the degradation rate constants determined by modeling down-core lipid profiles are generally underestimated compared to

those obtained using kinetics of lipid inventories, as shown for fatty acids in CLB sediments (Table 3). This bias is due to difficulties in determining the concentration of compounds at the time that they were deposited, and to short-term variations in delivery (Canuel and Martens, 1996).

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