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Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis

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Abstract—The carbon and nitrogen isotope composition of organic matter has been widely used to trace biogeochemical processes in marine and lacustrine environments. In order to reconstruct past environmental changes from sedimentary organic matter, it is crucial to consider potential alteration of the primary isotopic signal by bacterial degradation in the water column and during early diagenesis in the sediments.

In a series of oxic and anoxic incubation experiments, we examined the fate of organic matter and the alteration of its carbon and nitrogen isotopic composition during microbial degradation. The decomposition rates determined with a double-exponential decay model show that the more reactive fraction of organic matter degrades at similar rates under oxic and anoxic conditions. However, under oxic conditions the proportion of organic matter resistent to degradation is much lower than under anoxic conditions. Within three months of incubation the $\delta^{13}C$ of bulk organic matter decreased by 1.6‰ with respect to the initial value. The depletion can be attributed to the selective preservation of ^{13}C-depleted organic compounds. During anoxic decay, the $\delta^{15}N$ values continuously decreased to about 3‰ below the initial value. The decrease probably results from bacterial growth adding ^{15}N-depleted biomass to the residual material. In the oxic experiment, $\delta^{15}N$ values increased by more then 3‰ before decreasing to a value indistinguishable from the initial isotopic composition. The dissimilarity between oxic and anoxic conditions may be attributed to differences in the type, timing and degree of microbial activity and preferential degradation. In agreement with the anoxic incubation experiments, sediments from eutrophic Lake Lugano are, on average, depleted in ^{13}C (−1.5‰) and ^{15}N (−1.2‰) with respect to sinking particulate organic matter collected during a long-term sediment trap study.

1. INTRODUCTION

The fate of organic matter during early diagenesis is an important concern for many oceanographic and limnological studies (e.g., Meyers and Eadie, 1993; Dean et al., 1994; Bernasconi et al., 1997; Ostrom et al., 1998; Sachs and Repeta, 1999; Hedges et al., 2001). Estimates of organic carbon and nitrogen fluxes to marine and lake sediments are essential for balancing the global carbon budget, as well as for quantifying the importance of organic matter burial as one of the nitrogen removal mechanisms in eutrophic lakes. Marine and lacustrine sediment-trap studies reveal that only 1 to 35% of the organic carbon synthesized in the photic zone reaches the sediment surface (Eadie et al., 1984; Bloesch and Uehlinger, 1990; Bernasconi et al., 1997; Hernes et al., 2001). Further mineralization during early diagenesis leads to burial of only an estimated 0.1% of the global net marine primary production (e.g., Berner, 1989).

Organic matter decomposition is mediated by a variety of aerobic and anaerobic microbial processes, which can progressively modify the bulk composition of the organic substrate because different fractions of organic matter degrade at different rates (Skopintsev, 1981; Henrichs and Doyle, 1986; Hedges et al., 1988; Harvey et al., 1995; Meyers and Eadie, 1993). In addition, a contribution from in situ bacterial biomass may also change the bulk biogeochemical signal. Previous laboratory experiments have shown that 5 to 25% of the degraded algal carbon is converted to bacterial carbon (Harvey et al., 1995), whereby the bacterial matter itself is subsequently modified or destroyed (Meyers and Ishiwatari, 1993). Data compiled by Harvey et al. (1995) indicate that substantial variations of bacterial biomass over the course of the incubations significantly contributed to the observed changes of the relative abundance of carbohydrates, proteins, and lipids in the residual organic matter pool.

In summary, multiple processes acting together result in sedimentary organic matter with a markedly different distribution of biochemical species with respect to the original biogenic material. Hence, it is reasonable to expect that these processes could also affect the primary carbon and nitrogen isotope signals produced in the photic zones of aquatic environments.

The carbon and nitrogen isotope composition of organic matter has been widely used to trace biogeochemical cycling in marine and lacustrine environments (e.g., Bernasconi et al., 1997; Ostrom et al., 1997; Hodell and Schelske, 1998). The $\delta^{13}C_{OM}$ has proven to be a proxy indicator of paleoproductivity and atmospheric pCO_2 levels (e.g., Hollander and McKenzie, 1991; Schelske and Hodell, 1991; Fontugne and Calvert, 1992; Brenner et al., 1999), whereas nitrogen isotopic ratios have been used as a recorder of changes in the degree of nitrate utilization (e.g., Calvert et al., 1992; Francois et al., 1992; Altabet and Francois, 1994; Holmes et al., 1997; Teranes and Bernasconi, 2000), denitrification (e.g., Altabet et al., 1995; Ganeshram et al., 1995; Altabet et al., 1999; Emmer and

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Thunell, 2000; Ganeshram et al., 2000) and N_2-fixation (e.g., Haug et al., 1998). The isotopic composition of sinking or sedimented organic matter may be altered during oxidation in the water column and in the sediments, possibly obscuring the primary signal. While some studies have shown that selective loss of specific fractions of the total organic carbon, which have different composition than the bulk, can create diagenetic shifts in $\delta^{13}C$ (Benner et al., 1987), other studies indicate that the $\delta^{13}C$ of organic matter is resistent to isotopic alteration during water-column or postburial diagenesis (Meyers and Eadie, 1993; Schelske and Hodell, 1995).

In many marine and lacustrine sediment trap studies, microbial degradation of phytoplankton has been associated with an increase in the $\delta^{15}N$ value of the residual organic matter (up to 6‰) as a result of discrimination against ^{15}N during metabolic reactions (Saino and Hattori, 1980; Saino and Hattori, 1987; Altabet, 1988; Fry et al., 1991; Schaefer and Ittekkot, 1993; Altabet and Francois, 1994; Ostrom et al., 1997; Sachs and Repeta, 1999). An increase in sedimentary $\delta^{15}N$ with depth in sediments of the eastern subtropical Atlantic has recently been related to organic matter loss during early diagenesis (Freudenthal et al., 2001). In contrast, only minor changes or depletions in the ^{15}N content of settling particles have been observed in other studies (Saino and Hattori, 1987; Libes and Deuser, 1988; Altabet et al., 1991; Meyers and Eadie, 1993; Altabet et al., 1999). Also, contrasting reports of oxygenation effects on the magnitude and direction of N-isotope shifts have been reported. Sachs and Repeta (1999) suggested that, under anoxic conditions, N-isotopic alteration during organic matter degradation is minimal and the severity of the ^{15}N-enrichment during organic matter decay is proportional to bottom-water oxygen concentrations. Libes and Deuser (1988) reported a ^{15}N-enrichment under oxic and a ^{15}N-depletion under anoxic conditions and attributed this difference to the type and degree of microbial activity.

Experiments conducted to study the changes of the C- and N-isotopic composition of organic matter with microbial degradation have produced contrasting results (Wada et al., 1980; Zieman et al., 1984; Holmes et al., 1999). Therefore, more laboratory studies are necessary to understand the mechanisms that cause isotope effects during organic matter degradation. Here, we report on a series of incubation experiments simulating phytoplankton decay under oxic and anoxic conditions. In addition, we evaluate the impact of microbial degradation on the C- and N-isotope composition of bulk sedimentary organic matter by comparing a long-term sediment trap data set with sediment core isotopic data from the southern basin of Lake Lugano (Switzerland). The southern basin of Lake Lugano is eutrophic, with a mean annual primary productivity (in 1990 to 2000) of $\sim$340 g C m^{-2} yr^{-1}. As a result of thermal stratification and concomitant water-column stagnation, anaerobic conditions prevail in near-bottom waters between May and December/January. Due to the high organic carbon content, oxygen penetration in the sediments during oxic conditions is probably minor as indicated by well-preserved annual laminations.

The purpose of this study is to obtain information on the isotopic alteration of organic matter during early sedimentary diagenesis. A detailed understanding of isotope effects during decomposition will enhance our ability to use organic matter stable isotope abundances from sedimentary records as proxy indicators for past changes of environmental conditions. In addition, it may allow us to use C and N stable isotope ratios as tracers for organic matter transformation processes and, therefore, help to assess the origin of diagenetically altered material.

2. METHODS

2.1. Experimental System and Material

To simulate the microbial degradation of algae during early diagenesis at the water-sediment interface, lacustrine biomass was incubated in 5-L bottles for 111 d in three experiments with different redox conditions/electron acceptor concentrations. Algae, primarily diatom cells, were collected in July 2000 from the photic zone of Lake Lugano, using a 20 μm-plankton net. Three separate aliquots were incubated in bottles on an orbital shaker (60 rpm) in darkness under constant (25°C) temperature. For all experiments, Lake Lugano surface water containing a natural microbial community was used as incubation medium. One of the anoxic experiments was amended with excess Na_2SO_4 (10 mM) to favour sulphate reduction over methanogenesis as the principal microbial degradation process. The natural SO_4^{2-} concentration of Lake Lugano water is generally below 0.2 mM (L.S.A., 1980 to 2000). For the oxic incubation, the vessel was continually aerated (25 mL air/min) to preserve aerobic conditions. For the anoxic experiments, oxygen was initially removed from the water and 200 mL of anoxic lake-bottom water was added as an inoculum to provide a natural anaerobic microbial consortium. Purging with air or N_2 may have removed bio-reactive (e.g., CO_2 NH_3) or bio-inhibiting (e.g., H_2S) gases from the system.

Particulate matter samples were withdrawn from a side port of the bottle for isotope and elemental analysis at distinct intervals. In the anoxic experiments, oxygen-free conditions were ensured by purging the vessel with N_2 gas after each sample collection. Before sampling, the bottle was stirred vigorously to ensure the homogenous suspension of the particles. Thereby, larger aggregates that formed during incubation might have been disrupted, potentially altering particle interaction. Particulate organic carbon (POC) and nitrogen (PON) were quantified by filtration of up to 200 mL sample aliquots through tared, precombusted (400°C for 3h) Whatman GF/F filters and subsequent elemental analysis of a known amount of dried (50°C) material. Particulate matter concentrations determined in the oxic system were corrected for H_2O loss caused by evaporation.

2.2. Field Sampling

2.2.1. Sediment traps

Cylindrical sediment traps (diameter: 10 cm, height: 78 cm) were deployed in 1985, 1986, 1990, and 1993 to 1997 at 20 m, the base of the thermocline, and at 89 m water depths in the southern basin of Lake Lugano. The lower trap was situated 6 m above the sediment to minimize the effect of sediment resuspension. Except for winter, when 3-week deployment times were needed to obtain enough material, sediment traps were emptied biweekly. Between March 1996 and March 1998, an additional trap was deployed at 60 m depth. No preserva-

tives were used in the traps. Particulate matter was weighed after freeze-drying to calculate sediment fluxes (g m^{-2} d^{-1}).

2.2.2. Sediment core

In May 2000, a sediment core was retrieved from the sediment-trap locality at a water depth of 95 m using the method described in Kelts et al. (1986). Varves were identified, and the established varve chronology was confirmed with independent ^{137}Cs dating of annual layers. Details of the ^{137}Cs dating procedure are given in Wan et al. (1987). Annual samples were obtained by carefully sectioning the sediment core into intervals containing a varve couplet. Sediment material was freeze-dried and homogenized for chemical analysis. Core-top sediment accumulation rates of C and N were calculated from a determined average sedimentation rate of 0.7 cm yr^{-1}, a water content of 95%, and an assumed dry sediment density of 2.2 g cm^{-3}.

2.3. Elemental and Isotope Analysis

For organic carbon content determination, particulate matter from the incubation experiment and sediment trap material was decarbonated using 1M HCl, washed with deionized water and combusted in a Carlo Erba CNHS analyzer. The latter was also used to determine the PON content of samples withdrawn from incubation vessels. The nitrogen content of trap material was determined by digestion in mineralization solution containing NaOH (0.35M), $K_2S_2O_8$ (0.2M) and H_3BO_3 (0.5M) at 120°C for 1 h, filtration and subsequent NO_3^- analysis in the filtrate by UV spectrophotometry at 210 nm (American Public Health Association, 1989). The accumulation rate of POC and PON was used to calculate the weighted average isotopic composition of sinking organic matter for the respective years.

For the determination of the carbon and nitrogen isotope composition of organic matter, up to 10 mg of homogenized bulk sample were loaded into tin capsules and measured on a Carlo Erba elemental analyzer interfaced via open-split with a Fisons Optima mass spectrometer with a standard set-up for N_2 and CO_2. The $\delta^{15}N$ was determined on untreated samples. Before carbon isotope analyses, sediment trap samples were acidified (1M HCl) and rinsed with deionized water to remove inorganic carbon. Tests with carbonate-free particulate matter show that this treatment has no effect on the $\delta^{13}C$ value. Nitrogen and carbon isotope ratios are reported in the conventional δ-notation with respect to atmospheric N_2 (AIR) and the V-PDB (Pee Dee Belemnite) carbonate standard, respectively. For both $\delta^{15}N$ and $\delta^{13}C$, reproducibility is ±0.2‰, determined on repeated analyses of samples, as well as on international nitrogen (IAEA-N1, IAEA-N2) and carbon (NBS 22) standards.

3. RESULTS

3.1. Incubation Experiments

3.1.1. Decomposition kinetics

POC and PON concentrations decreased rapidly within the first few days of the experiments (Fig. 1) indicating rapid cell death and onset of degradation. After approximately 20 d of oxic incubation, the POC and PON concentrations were more or less stable at 13±1% of the initial particulate organic matter (POM) concentration. The fraction of POM remaining after 111 d, which degrades either at a very slow rate or is in fact undegradable, was about twice as high in the anoxic as in the oxic incubations (Table 1). In both anoxic experiments, after the initial rapid organic matter loss, the POC and PON concentrations continued to slowly decrease and did not reach a constant value by the end of the experiment. The apparent two-phase organic matter decrease can be described with a double-exponential decay equation (Westrich and Berner, 1984):

$$G_{(t)} = G_{react}\, e^{-k_1 t} + G_{refr}\, e^{-k_2 t} \quad (1)$$

$G_{(t)}$ is the remaining organic constituent at time t, and G_{react} and G_{refr} are the initial pools of the rapidly and slowly degrading organic matter fractions, respectively. Rate constants k_1 for the decay of the reactive fraction of POC and PON range from 60 yr^{-1} to 170 yr^{-1}, and decay constants k_2 for the slowly degrading fraction are generally one to two orders of magnitude lower (Table 1). In agreement with results from other studies (Andersen, 1996; Kristensen and Holmer, 2001), the easily digestible fraction of organic matter is degraded at similar rates under oxic and anoxic conditions. In the anoxic experiment with excess sulphate, the reactive fractions of POC and PON degrade at highest rates. Sulphate-reducing conditions, as indicated by the distinctive smell of H_2S, were maintained only until day 40 of the incubation period. From day 40 on, it is possible that the system became limiting in metabolizable substrate for sulphate-reducing micro-organisms, and the system probably went methanogenic. SO_4^{2-} limitation can be excluded since most sulphate remained in solution.

The decay rates k_1 are not a good measure for the final organic matter loss at the end of the experiment. The degradation potential for organic matter over significant time periods is best characterized by the proportion g_0 of organic matter that has a low susceptibility to microbial degradation. In our experiments, g_0 is about three times larger for anaerobic than for aerobic degradation (Table 1). In general, g_0 as well as k_1 and k_2 are similar for POC and PON.

3.1.2. Carbon and nitrogen isotope ratios in residual organic matter

3.1.2.1. Oxic degradation. The $\delta^{13}C$ and $\delta^{15}N$ values of the fresh algal matter were −24.2±0.15‰ and +4.7±0.2‰ (n=3), respectively. With the onset of degradation, the $\delta^{13}C$ value continuously decreased reaching a minimum of −26.3‰ after 49 d of incubation (Fig. 2a) and remained essentially stable thereafter with values close to −26‰, i.e., 1.8‰ lower than the initial $\delta^{13}C$ value (Table 1). The evolution of $\delta^{15}N$ showed a different pattern (Fig. 2b). During the first week of incubation, the $\delta^{15}N$ value of PON decreased only slightly, indicating that high organic matter loss does not necessarily coincide with large changes in isotopic composition. Over the next 15 d, the $\delta^{15}N$ value increased by more than 4‰ before slowly returning to the initial $\delta^{15}N$ value at the end of the incubation period. Bulk organic matter C/N ratios, ranging between 7.6 and 10.2, are correlated with $\delta^{15}N$ values (r^2 = 0.67, n = 19; compare Fig. 2b and 2c). This correlation indicates that preferential loss of nitrogen with respect to carbon is associated with preferential loss of ^{14}N.

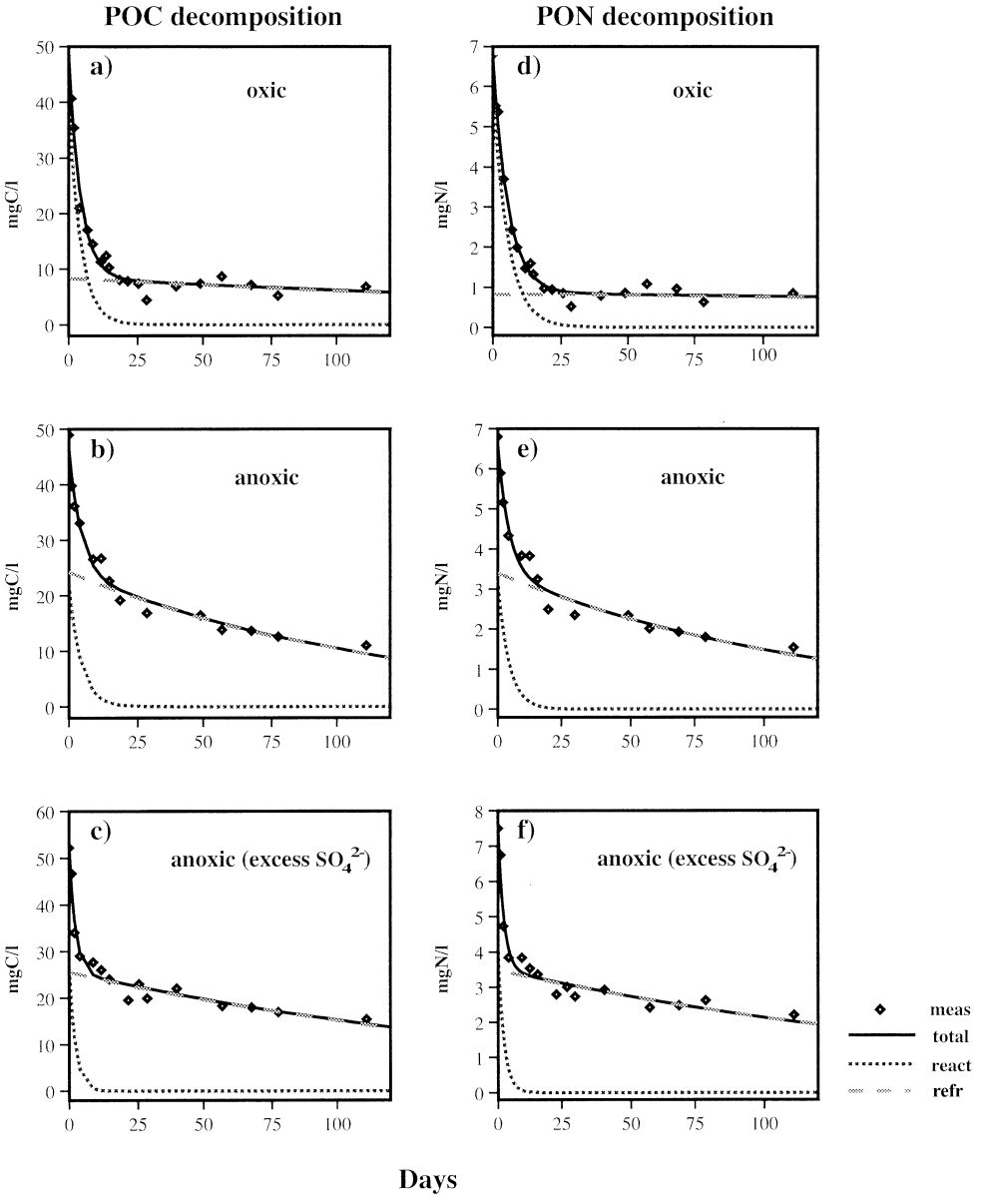

Fig. 1. Time-dependent decomposition of algal particulate organic carbon (a-c) and nitrogen (d-f) with exposure to natural aerobic and anaerobic microbial consortia under aerated and anoxic (with and without excess SO_4^{2-}) conditions. Symbols represent measured POC and PON concentrations during the incubation period. Errors (σ_1) have been determined to be less than 4%. Lines indicate the decomposition of total (full lines), reactive (dotted lines), and slowly-degrading or refractory (dashed lines) POC and PON, according to the best fit to a double-exponential decay model. See text and Table 1 for further information.

3.1.2.2. Anoxic degradation. The $\delta^{13}C$ evolution in the unamended anoxic incubation was similar to the one in the oxic system, albeit with a more rapid and steeper initial decline. After day 49, little change was observed and the final value was 1.6‰ lower than the initial value (Fig. 2d, Table 1). The $\delta^{15}N$ value of PON showed a different pattern compared to the aerobic experiment (Fig. 2e). During the initial 24 h, it increased by 0.6‰, and then decreased by more than 3‰ by day 49 with only a slight increase towards the very end of the experiment. Hence, while the absence of oxygen did not influence the general trend of the $\delta^{13}C$ value, it had a substantial effect on the evolution of the $\delta^{15}N$ value. The impact of anoxic conditions on the direction and magnitude of the isotope alteration is most evident after 3 weeks of incubation, when the difference in $\delta^{15}N$ values between the oxic and anoxic experiments exceeds 5‰. The C/N ratios only showed minor variations throughout the experiment with an average value of 8.30 ± 0.34 (Fig. 2f), in agreement with earlier studies of anoxic algal decay (Harvey et al., 1995).

In the experiment with excess SO_4^{2-}, all parameters showed general trends similar to those in the SO_4^{2-}-poor anoxic system (Fig. 2g-i). C/N ratios remained constant (8.35 ± 0.35) and the ^{15}N depletion was the same, but at the end of the incubation, POM showed a 1‰ lower $\delta^{13}C$ value than for the SO_4^{2-}-poor experi-

Table 1. Experimentally derived decay parameters and isotope shifts.

		f (%)	g_0 (%)	k_1 (yr^{-1})	k_2 (yr^{-1})	$\Delta\delta$ (‰)
Oxic	POC	86.2	16.9 ± 2.2	83.11 ± 6.9	1.13 ± 0.9	−1.81
	PON	87.5	12.7 ± 1.0	64.97 ± 3.6	0	+0.2
Anoxic	POC	77.6	52.1 ± 4.3	83.58 ± 19.3	2.85 ± 0.69	−1.65
	PON	77.5	51.4 ± 4.2	88.33 ± 25.5	3.03 ± 0.37	−2.83
Anoxic (with SO_4^{2-})	POC	70.5	48.2 ± 3.0	162.06 ± 25.5	1.90 ± 0.40	−3.05
	PON	70.5	45.5 ± 2.8	167.90 ± 33.9	1.81 ± 0.47	−2.59

f is the fraction of total POC and PON metabolized after 111 days, g_0 is the model-derived initial fraction of less reactive material, k_1 and k_2 are the first order decay constants for fast and slowly degrading organic matter determined by fitting a double exponential decay model to the time-dependent concentrations of total POC and PON. $\Delta\delta$ ($\sigma_1 = \pm 0.4$‰; n = 3) is the difference between the initial carbon and nitrogen δ-values and the δ-values after 4 months of experimental degradation. Organic matter decay under oxic conditions does not show clear double-exponential behaviour, as indicated by a very low k_2.

ment (Table 1, Fig. 2). In both anoxic incubations, the greatest decline of organic matter $\delta^{13}C$ corresponded with the time of high POC loss.

In all experiments, after three and a half months, microbial decomposition resulted in the residual material being either isotopically depleted in ^{13}C and ^{15}N with respect to the fresh phytoplankton, or not significantly changed as with the $\delta^{15}N$ value under aerobic conditions. However, if organic matter is exposed to oxic degradation only for a few days a marked enrichment of ^{15}N in the residual organic matter is possible.

3.2. Sinking and Sedimentary Organic Matter in Lake Lugano

3.2.1. Upper trap vs. sediment core

The carbon and nitrogen isotope composition of sinking particulate organic matter (SPOM) trapped at 20 m water depth exhibits distinct seasonal patterns, with $\delta^{13}C$ values ranging from −19.9‰ to −41.0‰ and $\delta^{15}N$ values ranging from +18.9‰ to +0.5‰ (Bernasconi et al., 1997; Lehmann et al.,

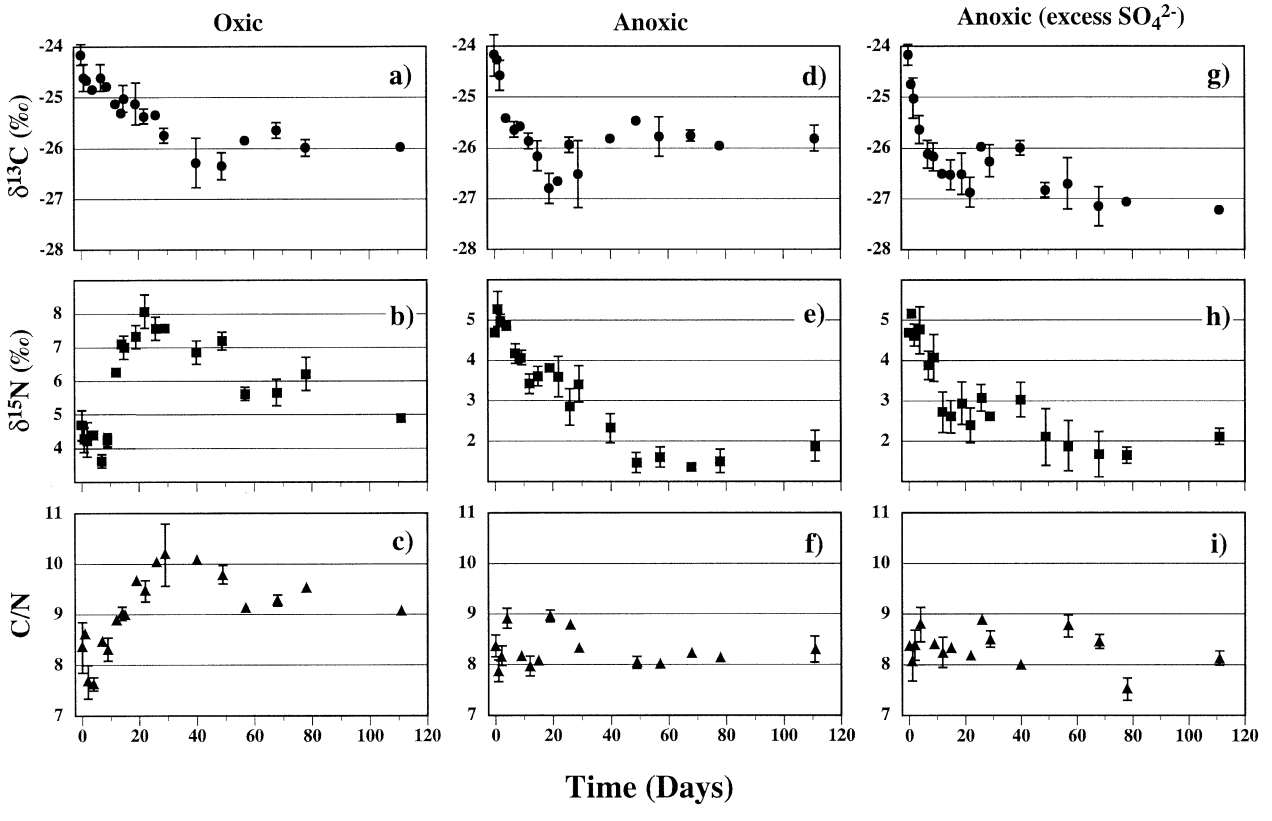

Fig. 2. Variation of $\delta^{13}C$ (circles), $\delta^{15}N$ (squares) and C/N ratios (triangles) of particulate organic matter during experimental oxic (a-c) and anoxic (d-i) microbial decomposition of plankton. Errors have been determined from replicate measurements. Note different scales for $\delta^{15}N$. Lake Lugano surface water was used as the incubation medium. For the anoxic experiments, oxygen-deficient lake bottom water was added to provide a natural anaerobic microbial consortium. In one of the anoxic experiments, 10 mM Na_2SO_4 was added to promote sulphate-reduction (g-i). Total incubation time was 111 d. See text for discussion.

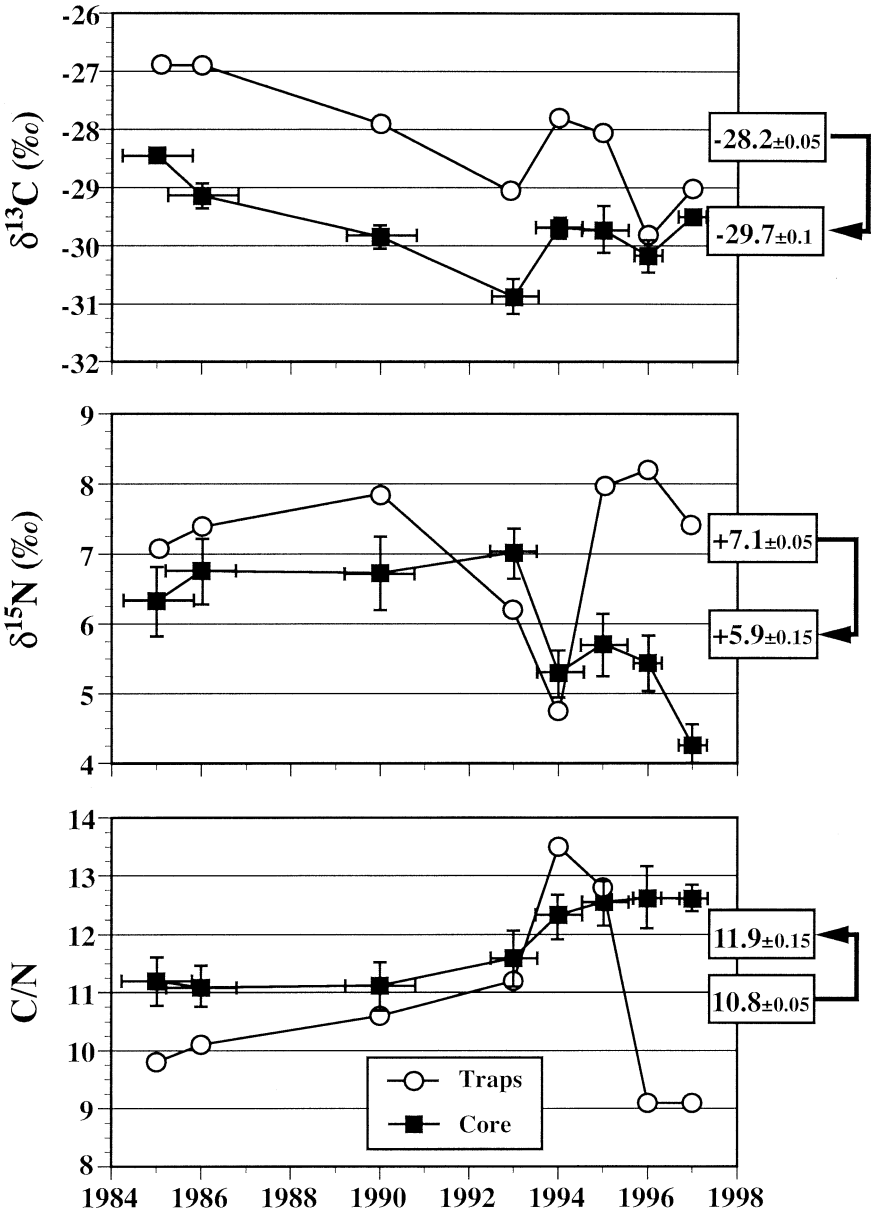

Fig. 3. Carbon and nitrogen isotope composition and C/N ratios for sinking organic material from 20-m sediment traps (circles) and organic matter from corresponding varves in a sediment core (squares). The trap data represent annual values that were obtained by integrating analyses of sediment trap samples collected bi- or triweekly in 1985, 1986 and 1990 and between 1993 and 1997. Errors for sediment-trap isotope values and C/N ratios are smaller than ±0.1‰ and 0.1, respectively. The numbers in boxes are average values for the entire sampling period. The arrows point to the mean values for sedimentary organic matter and, hence, are indicative of the direction of apparent isotope and C/N ratio shifts associated with early diagenetic processes.

2002). The POC and PON accumulation rates in the different years vary between 87 and 116 g C m^{-2} yr^{-1} and 8.8 and 12.8 g N m^{-2} yr^{-1}, respectively (Lehmann et al., 2002). Details on the annual and interannual variability of the carbon and nitrogen isotope composition and particulate organic matter fluxes are given elsewhere (Lehmann et al., 2002). The average $\delta^{13}C$ values of organic matter, when weighted by mass, vary between −26.9‰ and −29.9‰ (Fig. 3), the $\delta^{15}N$ values range from +7.0‰ to +4.7‰. These isotope data were obtained by integrating organic matter fluxes and isotope analyses of up to 25 sediment trap samples per year. Therefore, confidence intervals are below ±0.1‰ for both weighted $\delta^{13}C$ and $\delta^{15}N$. Weight-averaged isotopic compositions and C/N ratios (9.1 to 13.5±0.08) of the trap material are indicative of lacustrine organic matter of dominantly autochthonous algal origin (Meyers and Ishiwatari, 1993).

The $\delta^{13}C_{core}$ values for organic matter from sediment layers that are time-equivalent to the sediment traps range from −28.9‰ to −30.9‰, the $\delta^{15}N_{core}$ values vary between +6.3‰ and +4.3‰ (Fig. 3). The comparison of C_{org} accumulation

Table 2. Mean nitrogen fluxes (g N m^{-2} yr^{-1}) and weight-averaged N isotope compositions of settling particulate matter collected between March 1996 and March 1998. The number of measurements being integrated in the two-year means is n = 45.

	PON Flux	$\delta^{15}N$ (‰)
Upper Trap (20 m)	11.23	7.82 ± 0.05
Intermediate Trap (60 m)	11.26	8.16 ± 0.05
Near-bottom trap (89 m)	13.08	8.38 ± 0.05

rates in the upper part of the sediment core (62.4 g C m^{-2} yr^{-1}) with those in the 20-m sediment traps (on average 98.7 g C m^{-2} yr^{-1}) indicate that 60 to 70% of the organic matter leaving the epilimnion is deposited in surface sediments.

The relative variations in sediment trap $\delta^{13}C$ are recorded reasonably well by the sediments (Fig. 3), but all core samples are on average depleted in ^{13}C by approximately −1.5‰. Except for two samples, the $\delta^{15}N$ value of the sediments is lower than that of the corresponding sediment trap, but the difference is not constant. Particularly in the uppermost part of the sediment core, the $\delta^{15}N$ values do not, however, parallel the interannual trends, as recorded by sediment trap material (Fig. 3). The $\Delta\delta^{15}N_{core\text{-}trap}$ varies quite strongly, and, for two years (1993 and 1994), it appears to be indicative of a diagenetic N-isotope shift towards heavier $\delta^{15}N$ values.

Sediment C/N ratios (11.1 to 12.6) lie in a narrower range than the C/N ratios of SPOM. In particular, the lower C/N ratios in the youngest trap sample are not reflected by the C/N ratios determined in the uppermost core. On the whole, C/N ratios are higher in the sediment than in trap samples, suggesting that nitrogen is preferentially lost during early sedimentary diagenesis and/or that the sediment contains a higher amount of organic detritus from terrestrial sources.

3.2.2. Upper trap vs. lower traps

Over the 12-yr collection period, the mean primary production of organic carbon in Lake Lugano (365.8 g C m^{-2} yr^{-1}) is about four times higher than the mean carbon flux at 20 m water depth (Lehmann et al., 2002). Hence, approximately 75% of the primary production is recycled in the epilimnion. The average organic matter flux in the near-bottom sediment trap (113 g C m^{-2} yr^{-1}) exceeds the mean flux leaving the photic zone by ~15%. Bernasconi et al. (1997) suggested that lateral sediment transport is responsible for excess sediment in the lower trap. During summer, when productivity is high, the organic matter flux at 89-m water depth barely falls below the flux in the upper trap by more then 10%. This suggests that mineralization in the water column below the photic zone is of minor importance, or, if it is not minor, it is compensated by lateral sediment transport. The residence time of the principle part of sinking particles (>10μm particle size) in the water column can be estimated to be less than 1 d (Bloesch and Burns, 1980).

Only two years of $\delta^{15}N$ data of SPOM are available for a comparison among different collection depths. The weight-averaged $\delta^{15}N$ values slightly increase with depth (Table 2) with a total change of 0.6‰ between the 20-m trap and the near-bottom trap. This change also coincides with a flux increase of 16%. Unfortunately, no comparative $\delta^{13}C$ data are available for the same period. Bernasconi et al. (1997) observed a change in $\delta^{13}C$ from −28.3‰ at 20 m depth to −30.2‰ at 89 m depth at the same location in 1994. They concluded that lateral organic matter transport and contribution from terrestrial organic matter rather than isotope alteration in the water column caused the difference in the C-isotope composition.

4. DISCUSSION

4.1. Organic Matter Decomposition

4.1.1. Decomposition kinetics

The decay constants for reactive organic matter degradation found in this study are high compared to most degradation rates for phytoplankton reported in earlier studies (Foree and McCarty, 1970; Jewell and McCarty, 1971; Emerson and Hedges, 1988; Harvey et al., 1995; Kristensen and Holmer, 2001). The large variability of reported decay rates, ranging over three orders of magnitude, is partially due to the differing algal material and incubation temperatures used. In addition, the use of double- vs. single-exponential decay models to determine the decay rates also contributes significantly to the variability because the rate at which the entire organic matter pool is degraded, underestimates the rate for the reactive organic matter fraction. Kristensen and Holmer (2001), using a double-exponential decay model, derived similar or even higher decay constants for reactive organic matter from diatom incubations. Reevaluation of the data of Harvey et al. (1995) with a double-exponential model yields a decay rate of 28.8±11.7 yr^{-1} for fast-degrading diatomaceous organic matter under anoxic conditions. This is several times higher than the k value originally reported using a single-exponential decay model (2.9 yr^{-1}), but it is still much lower than the rates determined in our anoxic experiments, possibly reflecting the lower incubation temperatures (19°C) in the experiments of Harvey et al. (1995). The refractory fraction of organic matter, g_0, is critical for the quantification and interpretation of the actual decay constants (Kristensen and Holmer, 2001). It is possible that g_0 depends on the incubation system employed (through-flow vs. static). A static system like our closed incubation may become limiting in either the diversity of the microbial consortia or an individual oxidant (Harvey et al., 1995) and, therefore, generally yields higher values for g_0. The significant amount of refractory components in all of our experiments may be attributed to limiting conditions. However, the system employed probably mimics best organic matter degradation in stagnant (anoxic) water bodies, where the supply of electron acceptors is limited and products of microbial activity are not carried away except by diffusion. A closed incubation might be less adequate to simulate degradation under un-stratified (oxic) conditions.

The rapid decline of POC and PON concentrations during the first days can be attributed to the break-down of carbohydrates, lipids and proteins by leaching and enzymatic hydrolysis into soluble organic matter compounds available for subsequent mineralization (Harvey et al., 1995; Tyson, 1995). There are contrasting reports on whether the reactive fraction from fresh organic substrate is more rapidly degraded under oxic than under anoxic conditions (compilation in Kristensen and Holmer, 2001). Again, this is partly a consequence of the

differing experimental set-ups and decay models applied. Harvey et al. (1995) stated that oxygen has a substantial effect on overall rates of organic carbon decomposition. However, if we reconsider their data applying the double-exponential decay model, we find similar rates for oxic (25.5 ± 10.9 yr^{-1}) and anoxic degradation (28.8 ± 11.7 yr^{-1}) of the more reactive organic matter fraction. Also, in our experiments, except those with SO_4^{2-} added, the decay rates for the fast-degrading fraction are similar in oxic and anoxic experiments. The highest decay rates in the experiment with excess SO_4^{2-} coincide with high values for g_0. The lowest g_0 was observed in the oxic incubation. This means that bulk algal organic matter has a chemical composition less susceptible to anaerobic than to aerobic decay. A relatively small fraction of algal organic matter, however, is most susceptible to microbial degradation under predominantly sulphate reducing conditions.

It is likely that bacterial matter, synthetized during the incubation, significantly contributes to the total POC and PON pools. Therefore, since k values are derived from bulk particulate organic matter concentrations and the decay model applied ignores bacterial growth, decomposition rates may generally be underestimated.

4.1.2. Carbon and nitrogen isotope alteration

The observed decline in $\delta^{13}C$ value with time can either be explained by the preferential removal of an organic matter fraction enriched in ^{13}C or the gain of components depleted in ^{13}C. Carbohydrates and proteins are generally enriched, and lipids are depleted in ^{13}C compared to total plant tissue (Degens, 1969; Deines, 1980). Selective loss of carbohydrates and proteins, which are particularly susceptible to microbial degradation (Hedges et al., 1988; Harvey et al., 1995), would lead to a decrease in the $\delta^{13}C$ value of residual organic matter. The limited amount of algal matter incubated did not allow us to determine concentrations of individual biochemical fractions. However, the evolution of major biochemical concentrations from other similar incubation experiments, which indicate relative enrichment of lipids in residual particulate matter with ongoing decay (Harvey et al., 1995), may well be adopted here.

Harvey et al. (1995) reported highly variable bacterial abundances over the course of phytoplankton incubations with, in general, greatest activity during periods of high organic matter loss. Macko and Estep (1984) have shown that bacterial cells are generally enriched in ^{13}C relative to the substrate compounds. Therefore, although bacterial growth is likely to have contributed to the particulate organic matter in our experiments, it probably did not contribute to the observed decrease in $\delta^{13}C$. In addition, it has been shown that hydrolysis of reactive compounds is associated with ^{13}C enrichment in the residual material (Bada et al., 1989; Silfer et al., 1992). Consequently, we conclude that the effect of selective preservation of compounds with more negative $\delta^{13}C$ values outweighs possible carbon isotope fractionations during enzymatic hydrolysis and bacterial carbon incorporation. The variability of bacterial abundances due to growth and decay of the decomposers themselves, however, may be responsible for minor changes of the $\delta^{13}C$ value observed in the second half of the experimental period. All experiments show a decrease in the $\delta^{13}C$ value, yet, the degree of isotopic depletion and the rates of the change varied quite significantly in detail. This could be due to differences in relative decay rates and g_0 values for specific biochemical fractions for the different microbial communities. It is very unlikely that anaerobic microbial methane oxidation potentially producing strongly ^{13}C-depleted biomass contributed to the negative isotope shift since the isotope effect observed in the SO_4^{2-}-poor anoxic experiment (where CH_4 is most likely to occur) is not larger than in the oxic set-up.

Potential mechanisms leading to changes in the $\delta^{15}N$ value of residual organic matter involve preferential loss of isotopically distinct fractions, kinetic isotopic fractionation during hydrolysis and bacterial growth. Previously reported increases in $\delta^{15}N$ for suspended particles with depth in the water column (Saino and Hattori, 1980; Saino and Hattori, 1987; Altabet, 1988; Fry et al., 1991; Schaefer and Ittekkot, 1993; Altabet and Francois, 1994; Ostrom et al., 1997; Sachs and Repeta, 1999) are generally thought to result from the release of ^{15}N-depleted dissolved nitrogen during decomposition. The exact mechanisms are unknown, but kinetic isotope fractionation during protein hydrolysis (Bada et al., 1989; Silfer et al., 1992) is likely to contribute to the ^{15}N-enrichment. The decrease in $\delta^{15}N$ observed in our anoxic experiments can be explained either by the preferential loss of a nitrogen fraction enriched in ^{15}N or the gain of a fraction depleted in ^{15}N. In some phytoplankton and bacterial cultures, the total protein within a cell has been found to be enriched in ^{15}N ($\sim$3‰) relative to bulk nitrogen (Macko et al., 1987). The decrease of $\delta^{15}N$ values with degradation could partly reflect the selective removal of proteins. It is unlikely, however, that this relatively small isotope effect exceeds the opposite isotope effect associated with the hydrolysis of organic matter, which preferentially releases ^{14}N. Experimentally derived enrichment factors $\varepsilon_{s\text{-}p}$ for peptide bond breakage range between 2.5‰ and 4‰ and are expected to be even higher at room temperature (Silfer et al., 1992). Hence, we conclude that the addition of ^{15}N-depleted organic matter from bacterial growth using soluble nitrogenous compounds is likely to have led to the observed decline in $\delta^{15}N$. A similar decrease in $\delta^{15}N$ during the incubation of marine diatom cells and zooplankton (Wada et al., 1980) and in sinking bulk organic matter in the Peru Upwelling Area (Libes and Deuser, 1988) was attributed to bacterial biosynthesis. The isotopic depletion in bacterial nitrogen is thought to be associated with the loss of ^{15}N during biosynthesis, possibly by preferential excretion of ^{15}N-ammonia (Macko and Estep, 1984). Harvey et al. (1995) showed that, during microbial peak-time growth in their incubations, bacteria contribute more then 20% to the total biomass and that the evolution of bacterial abundances differed significantly between individual experiments, depending on redox conditions and the nature of the incubated material. It is, therefore, not surprising that in our experiments the nitrogen isotope evolution, which reflects the complex interplay of organic matter break-down, bacterial growth and decay, is also variable with differing conditions.

The strong increase in $\delta^{15}N$ values under oxic conditions corresponds with a preferential removal of nitrogen over carbon, as indicated by the increasing C/N ratios. The subsequent decrease in $\delta^{15}N$ is associated with decreasing C/N ratios. In situ bacterial growth is expected to result in lower C/N ratios since the C/N of bacterial biomass generally ranges between 4 and 5 (Müller, 1977). Therefore, the N-isotope and C/N ratio

data imply that between days 7 and 21, the liberation of ^{15}N-depleted organic matter with low C/N is predominating, whereas, thereafter, the contribution from ^{15}N-depleted bacterial biomass becomes progressively important. During the initial week of the experiment, when the δ^{15}N values remained steady, the effects of the two processes seem to cancel each other out. Very similar trends of δ^{15}N values during organic matter decomposition under suboxic conditions have been reported by Holmes et al. (1999),who also attributed the variability in δ^{15}N values to the counteracting processes of substrate degradation and bacterial biosynthesis.

We cannot be certain about the exact reasons for the variations of C/N ratios, and we are not able to clarify why the aerobic versus anaerobic microbial activities have such a dissimilar impact on the variability of C/N ratios. The completely different evolution of the C/N ratios in the oxic relative to the anoxic experiment might be indicative of different bacterial metabolisms and activities. Generally, if remineralization were the sole process acting on organic particles, we would rather expect an increase of the C/N ratios because of preferential degradation of high-N compounds (Fenchel et al., 1998). The unchanged C/N ratios determined for anoxically incubated material suggest that bacterial growth, producing biomass with low C/N, efficiently (and more steadily than in the oxic experiment) counteracts the effect of remineralization.

4.2. Early Sedimentary Diagenesis in Lake Lugano—Constraints on Isotope Signal Preservation

In agreement with other reports (Eadie et al., 1984; compilation in Bloesch and Uehlinger, 1990), the total export carbon flux determined at 20 m water depth in Lake Lugano represents about one fourth of the mean annual primary productivity. In contrast to sediment trap studies from Lake Michigan, indicating 67% organic matter loss in the hypolimnion (Eadie et al., 1984; Meyers and Ishiwatari, 1993), our flux data suggest that organic matter loss below the photic zone is small. The discrepancy might be attributed to differences in the trophic state of the two lakes. Whereas Lake Michigan is oligotrophic, the south basin of Lake Lugano is eutrophic with high C_{org} fluxes and partial water-column anoxia during summer. Yet, the δ^{15}N values for sinking PON tend to increase with increasing depth (Table 2), indicating a slight but significant isotope shift during water column settling. PON collected from the sediment surface and from bacterial biomass in the nepheloid layer shows a lower δ^{15}N than trap material (Lehmann et al., 2002). Therefore, the small δ^{15}N increase in the near-bottom trap cannot be explained by the addition of resuspended sediment or biomass synthesized in the deep hypolimnion. The enrichment in ^{15}N in sinking PON with increasing depth is consistent with the increased δ^{15}N values found after the first week of experimental aerobic decomposition.

The difference in accumulation rates between sediment and traps demonstrates that organic matter loss during early sedimentary diagenesis (0 to 3 yr) is significant (30 to 40%) but less pronounced compared to other (more oxic) environments (Meyers and Ishiwatari, 1993). Similar diagenetic losses of organic matter ranging between 25 and 28% for organic carbon and between 41 and 50% for organic nitrogen have been reported from other highly productive Swiss lakes (Höhener, 1990; Teranes and Bernasconi, 2000). This degree of early sedimentary mineralization seems to be characteristic for eutrophic or hypertrophic lakes, where high organic matter fluxes lead to oxygen-deficiency in the sediment, potentially enhancing organic matter preservation (Dean et al., 1994). Although near-bottom waters in Lake Lugano are only seasonally anoxic, anaerobic conditions in the sediment persist throughout the year. The comparatively low loss of organic matter at the anoxic water-sediment interface in Lake Lugano is in agreement with the enhanced preservation in the anaerobic incubations as indicated by higher g_0.

The comparison of the weighted δ^{13}C and δ^{15}N values of trap material and sediment reveals that the sediments do not always reliably reflect the isotopic composition of the primary organic matter. This is not neccessarily due to the substantial loss of organic matter during early diagenesis, as studies from Lake Ontario (Hodell and Schelske, 1998) and Lake Baldegg (Teranes and Bernasconi, 2000) suggest that, despite significant diagenetic organic matter loss, the δ^{13}C and δ^{15}N values of sedimentary organic matter do record a primary signal. δ^{13}C and δ^{15}N data from Lake Lugano clearly indicate an overall isotopic depletion during early sedimentary diagenesis supporting the validity of our results from the anoxic experiments for field studies. The isotopic shift in δ^{13}C can be attributed to the preferential degradation of ^{13}C enriched organic compounds. In addition, methylotrophic bacteria consuming strongly ^{13}C-depleted CH_4 from methanogenic reactions may also have contributed to the observed negative isotope effect as bacterial biomass with δ^{13}C values as low as -61‰ was observed at the hypolimnetic redoxcline of Lake Lugano (Lehmann et al., 2002).

The generally lower δ^{15}N of the sediments compared to the sediment traps in Lake Lugano is additional evidence that microbial degradation can cause N-isotopic depletions in residual organic matter, as reported in a few other studies (e.g., Libes and Deuser, 1988; Altabet et al., 1991). Organic matter degradation is generally considered to lead to ^{15}N-enrichment in the bulk sediment. For example, Freudenthal et al. (2001) recently suggested that the increase of δ^{15}N in eastern subtropical Atlantic sediments is due to the progressive liberation of ^{15}N-depleted dissolved nitrogen, related to bacterial metabolism. In contrast, we relate the lower δ^{15}N values in the Lake Lugano sediment to a strong influence of bacterial growth adding ^{15}N-depleted biomass to the bulk sedimentary matter. This is supported by δ^{15}N values of -5‰ found for bacterial biomass at the oxic-anoxic interface (Lehmann et al., 2002). The bacteria probably grow on dissolved organic nitrogen and NH_4^+ derived from organic matter degradation.

When using sedimentary C and N-isotope ratios to reconstruct past changes in environmental conditions, it is generally assumed that potential isotope shifts are constant or their variations are small compared to fluctuations of the primary isotope signal. In support of this assumption, the δ^{13}C values from Lake Lugano sediments buried for more than four years reflect well the trends determined for sinking organic matter. Here, the isotope shift is constant and relative variations of the original δ^{13}C value are not diagenetically masked. However, the carbon isotope shift determined from the two most recent sample pairs is much lower and could indicate a lesser degree of diagenetic alteration for the youngest sediment layers.

The primary $\delta^{15}N$ signal is poorly recorded by the sediment archive and isotope shifts are highly variable. Contrary to expectations, the offset is highest in the youngest sediment samples. Bacterial growth producing ^{15}N-depleted biomass cannot solely explain the shift to relatively lower $\delta^{15}N$ values in the sediment. Higher C/N ratios in the upper part of the core indicate a contribution of terrestrial organic matter debris. Turbidites with high amounts of terrestrial plant debris showed $\delta^{15}N$ values of 1 to 2‰, $\delta^{13}C$ values around –27‰, and C/N ratios above 17. If we assume a 35% contribution of terrestrial organic matter, with a $\delta^{15}N$ of 1.5‰, a $\delta^{13}C$ of -27‰ and a C/N ratio of 17, the resulting shifts of all measured parameters are similar to those observed for older sediments, and, consequently, the primary trends are better reflected by the sediment.

5. CONCLUSION

The carbon and nitrogen isotope ratio of organic matter in sediments results from several complex processes including biosynthesis in the photic zone, organic matter degradation and bacterial growth in the water column and in the sediment, and the input from allochthonous sources. Oxygenation conditions have a direct effect on the preservation of the organic matter, with enhanced preservation under anoxic conditions. The isotopic composition of bulk organic matter undergoes significant alteration during microbial decomposition. The main processes acting together and partially outweighing each other are isotope fractionation during the initial break-down of complex organic compounds, selective preservation of isotopically distinct fractions of organic matter and bacterial biosynthesis. The continuous decrease in $\delta^{13}C$ values observed in all incubation experiments can be attributed to the selective preservation of less reactive compounds depleted in ^{13}C. The depletion of ^{15}N observed for anaerobic incubations indicates the loss of ^{15}N-enriched nitrogen from the PON pool and possibly a contribution to PON from ^{15}N-depleted bacterial biomass. Not only the preservation of organic matter but also the magnitude and direction of diagenetic isotope shifts during organic matter decomposition is affected by redox conditions. The different impact of oxic versus anoxic conditions on the $\delta^{15}N$ value of residual material may be due to metabolic pathways different for aerobic and anaerobic bacteria.

Our results do not claim general validity. We cannot ensure that steady state was reached at the end of the experimental period. In addition, significant processes and conditions (e.g., the effect of benthos activity under oxic conditions, of turbulent diffusion, or of bottom-water hydrodynamics) cannot be reproduced in the laboratory. Our experimental and lake data, however, indicate that microbial activity during early diagenesis under anoxic conditions can cause nitrogen isotope depletions in the residual organic matter. In Lake Lugano, the correlation between sedimentary and primary isotope values is reasonably good in sediments where the effect of variable input from external sources can be excluded. This suggests that the diagenetic isotope alteration in Lake Lugano has stopped after less than two years and surface water signals are reasonably well recorded in the sediment. Yet, varying degrees of organic matter preservation associated with variable environmental conditions, in particular oxygenation conditions, can affect the magnitude and direction of the isotope alteration. Therefore, relative changes of photic zone isotope signals may be obscured and not be conserved in the sediment if preservation conditions at the sediment-water interface changed over time.

Our data set is directly applicable to early degradation in a lake on a time span of weeks to years and, thus, may not be as directly pertinent to deep-sea sediment records. However, our data indicate that variations of sedimentary $\delta^{15}N$ values, which have formerly been interpreted to reflect changes in paeleoproductivity or nitrate utilization, e.g., in the Holocene and upper Pleistocene sediments of the eastern Mediterranean (Calvert et al., 1992), may be signals indicating past changes of oxygenation and, hence, preservation conditions. To better quantify the possible effects of diagenetic alteration on the carbon and nitrogen isotope ratios of bulk organic matter and, thus, to enhance the use of stable isotopes for paleoceanography and paleolimnology, more experimental work and field observations are needed.

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REFERENCES

Altabet M. A. (1998) Variations in nitrogen isotopic composition between sinking and suspended particles: implications for nitrogen cycling and particle transformation in the open ocean. *Deep-Sea Res. Part A.* **35**(4), 535–554.

Altabet M. A. and Francois R. (1994) Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. *Global Biogeochem. Cycles* **8**(1), 103–116.

Altabet M. A., Deuser W. G., Honjo S., and Stienen C. (1991) Seasonal and depth-related changes in the source of sinking particles in the North Atlantic. *Nature* **354,** 136–139.

Altabet M. A., Francois R., Murray D. W., and Prell W. L. (1995) Climate-related variations in denitrification in the Arabian Sea from sediment $^{15}N/^{14}N$ ratios. *Nature* **373,** 506–509.

Altabet M. A., Pilskaln C., Thunell R., Pride C., Sigman D., Chavez F., and Francois R. (1999) The nitrogen isotope biogeochemistry of sinking particles from the margin of the eastern North Pacific. *Deep-Sea Res. Part I* **46**(4), 655–679.

American Public Health Association (A.P.H.A.). (1989) Standard methods for the examination of water and wastewater. Washington.

Andersen F. Ø. (1996) Fate of organic carbon added as diatom cells to oxic and anoxic marine sediment microcosms. *Mar. Ecol. Prog. Ser.* **134**(1–3), 225–233.

Bada J. L., Schoeninger M. J., and Schimmelmann A. (1989) Isotopic fractionation during peptide bond hydrolysis. *Geochim. Cosmochim. Acta* **53**(12), 3337–3341.

Benner R., Fogel M. L., Sprague E. K., and Hodson R. E. (1987) Depletion of ^{13}C in lignin and its implications for stable isotope studies. *Nature* **329,** 708–710.

Bernasconi S. M., Barbieri A., and Simona M. (1997) Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. *Limnol. Oceanogr.* **42**(8), 1755–1765.

Berner R. A. (1989) Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over Phanerozoic time. In *The long term stability of the Earth system* (ed. E. J. Barron), Vol. 1, pp. 97–122. Elsevier.

Bloesch J. and Burns N. M. (1980) A critical review on sedimentation trap technique. *Schweiz. Z. Hydrol.* **42,** 15–55.

Bloesch J. and Uehlinger U. (1990) Epilimnetic carbon flux and turnover of particle size classes in oligo-mesotrophic Lake Lucerne, Switzerland. *Arch. Hydrobiol.* **118**(4), 403–419.

Brenner M., Whitmore T. J., Curtis J. H., Hodell D. A., and Schelske C. L. (1999) Stable isotope $\delta^{13}C$ and $\delta^{15}N$ signatures of sedimented organic matter as indicators of historic lake trophic state. *J. Paleolimn.* **22**(2), 205–221.

Calvert S. E., Nielsen B., and Fontugne M. R. (1992) Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels. *Nature* **359,** 223–225.

Dean W. E., Gardner J. V., and Anderson R. Y. (1994) Geochemical evidence for enhanced preservation of organic matter in the oxygen minimum zone of the continental margin of Northern California during the late Pleistocene. *Paleoceanography* **9**(1), 47–61.

Degens E. T. (1969) Biogeochemistry of stable carbon isotopes. In *Organic geochemistry: Methods and results* (eds. G. Eglinton and M. T. J. Murphy). Springer.

Deines P. (1980) The isotopic composition of reduced organic carbon. In *Handbook of environmental isotope geochemistry* Vol. 1, The terrestrial environment, A. pp. 329–406 Elsevier.

Eadie B. J., Chambers R. L., Gardner W. S., and Bell G. L. (1984) Sediment trap studies in Lake Michigan: resuspension and chemical fluxes in the southern basin. *J. Great Lakes Res.* **10**(3), 307–321.

Emerson S. and Hedges J. I. (1988) Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography* **3**(5), 621–634.

Emmer E. and Thunell R. C. (2000) Nitrogen isotope variations in Santa Barbara Basin sediments: Implications for denitrification in the eastern tropical North Pacific during the last 50,000 years. *Paleoceanography* **15**(4), 377–387.

Fenchel T., King G. M., and Blackburn T. H. (1998) Bacterial biogeochemistry: The ecophysiology of mineral cycling. Academic Press.

Fontugne M. R. and Calvert S. E. (1992) Late Pleistocene variability of the carbon isotopic composition of organic matter in the eastern Mediterranean: monitor of changes in carbon sources and atmospheric CO_2 concentrations. *Paleoceanography* **7**(1), 1–20.

Foree E. G. and McCarty P. L. (1970) Anaerobic decomposition of algae. *Env. Sci. Tech.* **4**(10), 842–849.

Francois R., Altabet M. A., and Burckle L. H. (1992) Glacial to interglacial changes in surface nitrate utilization in the Indian sector of the Southern Ocean as recorded by sediment $\delta^{15}N$. *Paleoceanography* **7**(5), 589–606.

Freudenthal T., Wagner T., Wenzhöfer F., Zabel M., and Wefer G. (2001) Early diagenesis of organic matter from sediments of the eastern subtropical Atlantic: Evidence from stable nitrogen and carbon isotopes. *Geochim. Cosmochim. Acta* **65**(11), 1795–1808.

Fry B., Jannasch H. W., Molyneaux S. J., Wirsen C. O., Muramoto J. A., and King S. (1991) Stable isotope studies of the carbon, nitrogen and sulfur cycles in the Black Sea and the Cariaco Trench. *Deep-Sea Res. Part A.* **38**(Suppl 2A), S1003–S1019.

Ganeshram R. S., Pedersen T. F., Calvert S. E., and Murray J. W. (1995) Large changes in oceanic nutrient inventories from glacial to interglacial periods. *Nature* **376,** 755–758.

Ganeshram R. S., Pedersen T. F., Calvert S. E., McNeill G. W., and Fontugne M. R. (2000) Glacial-interglacial variability in denitrification in the world's oceans: Causes and consequences. *Paleoceanography* **15**(4), 361–376.

Harvey H. R., Tuttle J. H., and Bell J. T. (1995) Kinetics of phytoplankton decay during simulated sedimentation: Changes in biochemical composition and microbial activity under oxic and anoxic conditions. *Geochim. Cosmochim. Acta* **59**(16), 3367–3377.

Haug G. H., Pedersen T. F., Sigman D. M., Calvert S. E., Nielsen B., and Peterson L. (1998) Glacial/interglacial variation in nitrogen fixation in the Cariaco Basin during the last 580 kyr. *Paleoceanography* **13**(5), 427–432.

Hedges J. I., Clark W. A., and Cowie G. L. (1988) Fluxes and reactivities of organic matter in a coastal marine bay. *Limnol. Oceanogr.* **33**(5), 1137–1152.

Hedges J. I., Baldock J. A., Yves G., Lee C., Peterson M., and Wakeham S. G. (2001) Evidence for non-selective preservation of organic matter in sinking marine particles. *Nature* **409,** 801–803.

Henrichs S. M. and Doyle A. P. (1986) Decomposition of ^{14}C-labeled organic substances in marine sediments. *Limnol. Oceanogr.* **319**(4), 765–778.

Hernes P. J., Peterson M. L., Murray J. W., Wakeham S. G., Lee C., and Hedges J. I. (2001) Particulate carbon and nitrogen fluxes and compositions in the central equatorial Pacific. *Deep-Sea Res. Part I* **48,** 1999–2023.

Hodell D. A. and Schelske C. L. (1998) Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. *Limnol. Oceanogr.* **439**(2), 200–214.

Höhener P. (1990) Der Stickstoffhaushalt von Seen, illustriert am Beispiel des Sempachersees. Ph. D. thesis, ETH Zürich.

Hollander D. J. and McKenzie J. A. (1991) CO_2 control on carbon-isotope fractionation during aqueous photosynthesis: A paleo-pCO_2 barometer. *Geology* **19**(9), 929–932.

Holmes M. E., Schneider R. R., Muller P. J., Segl M., and Wefer G. (1997) Reconstruction of past nutrient utilization in the eastern Angola Basin based on sedimentary $^{15}N/^{14}N$ ratios. *Paleoceanography* **12**(4), 604–614.

Holmes M. E., Eichner C., Struck U., and Wefer G. (1999) Reconstruction of surface ocean nitrate utilization using stable nitrogen isotopes in sinking particles and sediments. In *Use of proxies in paleoceanography: examples from the South Atlantic* (eds. G. Fischer and G. Wefer), pp. 447–468. Springer.

Jewell W. J. and L. M. P. (1971) Aerobic Decomposition of Algae. *Env. Sci. Tech.* **5**(10), 1023–1031.

Kelts K., Briegel U., Ghilardi K., and Hsü K. (1986) The Limnogeology—ETH coring system. *Schweiz. Z. Hydrol.* **48**(1), 104–115.

Kristensen E. and Holmer M. (2001) Decomposition of plant materials in marine sediment exposed to different electron acceptors (O_2, NO_3^-, and SO_4^{2-}), with emphasis on substrate origin, degradation kinetics, and role of bioturbation. *Geochim. Cosmochim. Acta* **65**(3), 419–433.

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

S. A. Laboratorio Studi Ambientali (1980 to 2000). Ricerche sull' evoluzione del Lago di Lugano, aspetti limnologici. Ann. reports. Commissione Internazionale per la Protezione delle Acque Italo-Swizzere. Milano.

Lehmann M. F. (2002) Dynamics of the stable carbon and nitrogen isotope geochemistry in eutrophic Lake Lugano (Switzerland/Italy). Ph. D. thesis, ETH Zurich.

Macko S. A. and Estep M. L. F. (1984) Microbial alteration of stable nitrogen and carbon isotopic compositions of organic matter. *Org. Geochem.* **6,** 787–790.

Macko S. A., Fogel M. L., Hare P. E., and Hoering T. C. (1987) Isotopic fractionation of nitrogen and carbon in the synthesis of amino acids by microorganisms. *Chem. Geol.: Iso. Geo. Sect.* **65**(1), 79–92.

Meyers P. A. and Eadie B. J. (1993) Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. *Org. Geochem.* **20**(1), 47–56.

Meyers P. A. and Ishiwatari R. (1993) Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenisis in lake sediments. *Org. Geochem.* **20**(7), 867–900.

Müller P. J. (1977) C/N ratios in Pacific deep-sea sediments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta* **41,** 549–553.

Ostrom N. E., Macko S. A., Deibel D., and Thompson R. J. (1997) Seasonal variation in the stable carbon and nitrogen isotope biogeochemistry of a coastal cold ocean environment. *Geochim. Cosmochim. Acta* **61**(14), 2929–2942.

Ostrom N. E., Long D. T., Bell E. M., and Beals T. (1998) The origin and cycling of particulate and sedimentary organic matter and nitrate in Lake Superior. *Chem. Geol.* **152**(1–2), 13–28.

Sachs J. P. and Repeta D. J. (1999) Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events. *Science* **286,** 2485–2488.

Saino T. and Hattori A. (1980) 15N natural abundance in oceanic suspended particulate matter. *Nature* **283,** 752–754.

Saino T. and Hattori A. (1987) Geographical variation of the water column distribution of suspended particulate organic nitrogen and its ^{15}N natural abundance in the Pacific and its marginal seas. *Deep-Sea Res. Part A* **34**(5/6), 807–827.

Schaefer P. and Ittekkot V. (1993) Seasonal variability of $\delta^{15}N$ in settling particles in the Arabian Sea and its palaeogeochemical significance. *Nature* **80**(11), 511–513.

Schelske C. L. and Hodell D. A. (1991) Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. *Limnol. Oceanogr.* **36**(5), 961–975.

Schelske C. L. and Hodell D. A. (1995) Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnol. Oceanogr.* **40**(5), 918–929.

Silfer J. A., Engel M. H., and Macko S. A. (1992) Kinetic fractionation of stable carbon and nitrogen isotopes during peptide bond hydrolysis: experimental evidence and geochemical implications. In *Isotope fractionations in organic matter: biosynthetic and diagenetic processes* (eds. S. A. Macko and M. H. Engel) Vol. 101, pp. 211–221. Elsevier.

Skopintsev B. A. (1981) Decomposition of organic matter of plankton, humification and hydrolysis. In *Marine organic chemistry: evolution, composition, interactions and chemistry of organic matter in seawater* (eds. E. K. Duursma and R. Dawson) pp. 125–177. Elsevier.

Teranes J. L. and Bernasconi S. M. (2000) The record of nitrate utilization and productivity limitation provided by $\delta^{15}N$ values in lake organic matter—A study of sediment trap and core sediments from Baldeggersee, Switzerland. *Limnol. Oceanogr.* **45**(4), 801–813.

Tyson R. V. (1995) Sedimentary organic matter: Organic facies and palynofacies. Chapman & Hall.

Wada E., Goldberg E. D., Horibe Y., and Saruhashi K. (1980) Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments. In *Isotope marine chemistry* (eds. E. D. Goldberg, Y. Horibe, and K. Saruhashi). pp. 375–398. Uchida Rokakuho Publ.

Wan G. J., Santschi P. H., Sturm M., Farrenkothen K., Lueck A., Werth E., and Schuler C. (1987) Natural (^{210}Pb,^{7}Be) and fallout (^{137}Cs,$^{239,\ 240}Pu$,^{90}Sr) radionuclides as geochemical tracers of sedimentation in Greifensee, Switzerland. *Chem. Geol.* **63(3–4),** 181–196.

Westrich J. T. and Berner R. A. (1984) The role of sedimentary organic matter in bacterial sulfate reduction: The G model tested. *Limnol. Oceanogr.* **29**(2), 236–249.

Zieman J. C., Macko S. A., and Mills A. L. (1984) Role of seagrasses and mangroves in estuarine food webs: temporal and spatial changes in stable isotope composition and amino acid content during decomposition. *Bull. Mar. Sci.* **35**(3), 380–392.