New organic matter degradation proxies: Valid in lake systems?

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New organic matter degradation proxies: Valid in lake systems?

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Abstract

We determined concentrations and diagenetic state of organic matter in two cores from Lake Zug, Switzerland. To obtain a general picture of organic matter decay in the lake, we measured bulk parameters such as total organic carbon, total nitrogen, and total hydrolyzable amino acids. In addition, we studied specific compound classes in detail—namely, amino acids and chlorins. From these data we obtained two recently proposed indicators for organic matter degradation state—the amino acid–based degradation index (DI) and the chlorin index (CI). The two indicators complement each other, with the CI being very sensitive during the initial stages of organic matter decay and the DI recording later stages of decay. Further differences are likely caused by nonlinear behavior during degradation. Nonetheless, the two proxies agree in the general picture of the degradation state. Despite higher concentrations of organic matter in the surface sediment at the deeper site, neither of the degradation state indicators showed much difference between the two sites. At depth, the degradation state at the two sites diverges, despite similar concentrations of organic matter. Although we cannot explain all differences between bulk parameters, amino acid composition, and chlorins conclusively, the results indicate a combined effect of different organic matter inputs (e.g., through sediment focusing) and different oxygen availability at the two sites since the onset of eutrophication.

Organic matter degradation is a subject of high complexity, and our understanding of this process is still limited. Because it is one of the major coupling points of various element cycles, knowledge in this field is crucial for understanding geochemical processes on small and global scales. Questions concerning the generation of fossil fuels, the connection of the carbon cycle to climate change, or, on a smaller scale, the problem of eutrophication due to anthropogenic nutrient input have provoked extensive research on organic matter cycling over the last decades. Most of the research on organic matter degradation in sediments so far has been performed in the marine environment. However, lakes, being relatively small and closed systems compared with the ocean, are favorable sites for studying geochemical cycling.

Lake sediments differ from most marine sediments in some important aspects. First, land plants may contribute to a larger extent to the organic matter in lake sediments than they do in the marine system. This terrestrial material contains more refractory organic molecules that are less degradable than planktonic tissue (Capone and Kiene 1988). Second, because of higher primary production and burial, organic carbon accumulation rates are usually higher (Meyers and Ishiwatari 1993). Additionally, the fact that the water column in lakes is shallower than in most marine settings results in a higher proportion of the organic matter produced in the surface water reaching the sediments. Finally, probably the most important difference is the much lower concentration of sulfate in lakes. In the marine system, this is the major electron acceptor for organic matter oxidation under anoxic conditions (Jorgensen 1982; Capone and Kiene 1988). In many lakes, however, the anaerobic oxidation of organic molecules occurs to a larger extent via the process of methanogenesis, which yields less energy.

The detailed behavior of different organic substances during various stages and pathways of decay is still incompletely understood. Organic tissue is composed of a variety of molecules with very different properties and reactivities (Wakeham et al. 1997; Kristensen 2000). Moreover, proba-

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bly not all of the organic matter present in the sediment is subject to remineralization, and the nondegradable fraction increases during degradation. Furthermore, the influence of oxygen availability on the preservation of organic matter is, despite extensive research, still a controversial subject (e.g., Calvert and Pedersen 1992; Hartnett et al. 1998). It is also mostly unknown to which extent the degradation of individual organic compounds is affected by oxygen availability. We have assessed the influence of oxygen availability on organic matter degradation by studying two sites with a different history of oxygen conditions in the bottom water.

Often, information about degradation is obtained by measuring bulk parameters, such as total organic carbon (TOC), total nitrogen (TN), and their ratio (C : N). In this study, in addition to the bulk parameters TOC, TN, and total hydrolyzable amino acids (THAA), two organic compound classes were analyzed in detail: amino acids as a major constituent of organic matter and chlorins, the early decay products of chlorophyll. Both have been proposed to be indicators for the overall state of organic matter degradation (Dauwe and Middelburg 1998; Schubert et al. 2002), and they are compared here for the first time. Furthermore, these proxies have, to our knowledge, not yet been applied to lacustrine systems, although the amino acid-based degradation indicator in particular has proved very useful in the marine environment. The main goals of this study were therefore to (1) apply these proxies to a lake setting and compare the findings to those from marine environments, (2) compare the results of the two degradation indicators, and (3) assess whether the findings can bring new insight into the bulk parameter results.

Materials and Methods

Study site—Sediment samples for this study were obtained from Lake Zug, central Switzerland. Lake Zug consists of two basins (Fig. 1) with water depth increasing continually from north to south. The deepest point of the lake is located in the steep southern basin, at a water depth of 198 m. Because of the steep topography in the southern basin, frequent turbidites disturb the sedimentary sequence there. For this reason, the cores were taken from the northern basin, where the slopes are not >4° (Kelts 1978). The residence time of the water in Lake Zug is comparatively long (14.1 yr; A. Wüest et al. unpubl. data). The lake is meromictic today, with mixing depths in winter rarely having been >100 m since 1950. Together with an increasing rate of primary production due to eutrophication over past decades, this has led to a permanently anoxic deep-water body. The location in the northern basin where this anoxic water body impinges on the slope depends on the extent of oxygen consumption and the degree of mixing and therefore varies seasonally.

A reconstruction of the trophic evolution in Lake Zug on the basis of sedimentary diatoms (F. Elber et al. unpubl. data) showed that the lake experienced several phases of eutrophication. After a first increase in nutrient input and productivity in the middle of the 19th century, the conditions improved toward the beginning of the 20th century, before a second, much more dramatic period of eutrophication set in around 1930. Since the 1960s, hypereutrophic conditions have prevailed in the lake. Continuous measurements of nutrient concentrations in the water column since 1968 (Environmental Agency of Kanton Zug unpubl. data) have shown that both nitrate and phosphate concentrations have decreased since the mid-1980s to present winter concentrations at 5 m depth of ~0.3 g N m^{-3} and 0.1 g P m^{-3}, respectively. Despite this decrease, the lake can still be considered eutrophic.

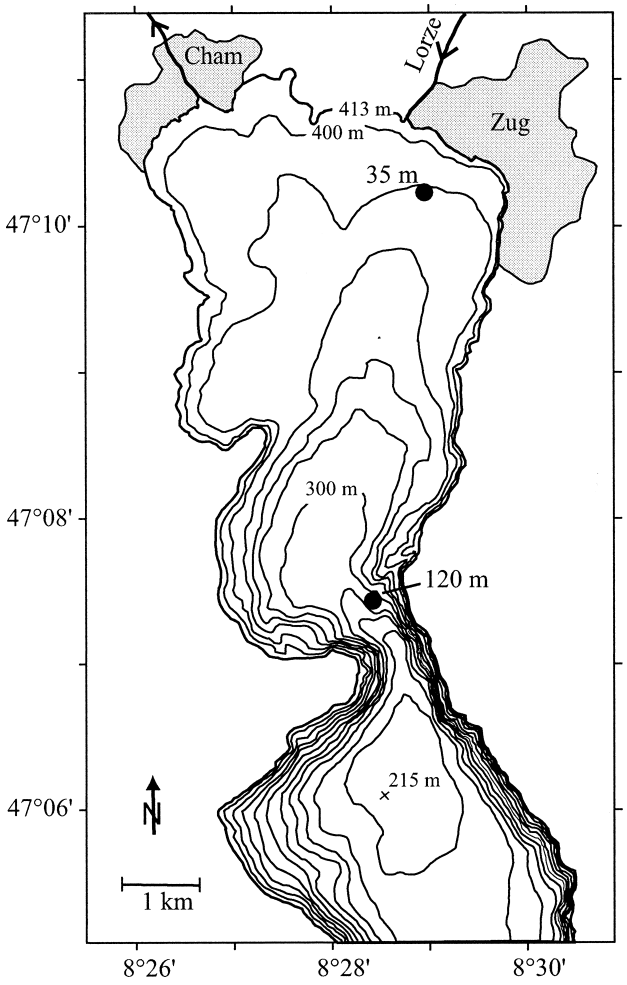

Fig. 1. Map of the northern basin of Lake Zug showing the locations of the two sampling sites at 35 and 120 m water depth. Isobaths are the height above sea level, with a spacing of 20 m. The cross in the southern basin indicates the deepest point, at 198 m water depth.

Arrays of two sediment traps (20 m below the surface and 12 m above the lake bottom) were deployed in the center of each basin (at 64 and 197 m depth, respectively) in 1982/1983 (Bloesch and Sturm 1986). Sedimentation rates, as well as particulate organic carbon (POC) concentrations, in the sediment traps were similar in the north and south basin, which suggests a homogenous distribution of productivity in the lake. The yearly sedimentation rate of POC was 85–100 g m^{-2} yr^{-1} in both basins. Vertical differences between the traps were negligible in the yearly mean. However, during single time periods, significantly higher fluxes were ob-

served in the lower trap, which indicates the resuspension of sediment. The sediment of Lake Zug consists mostly of autochthonous material (organic matter and biogenically precipitated calcite), as was shown by scanning electron microscope images of surface sediment and sediment trap material (Kelts 1978; Bloesch and Sturm 1986). The surface sediments in the deeper parts of the lake are varved, with light calcite- and organic-rich material deposited in summer and dark diatom- and detritus-rich winter layers (Thompson and Kelts 1974; Kelts 1978).

The two sampling sites are located at different water depths (35 and 120 m; Fig. 1). At 35 m depth, the water overlying the sediment is permanently oxygenated, whereas the 120 m site lies within reach of the anoxic deep-water body. For example, at the 120 m site, oxygen concentrations of 0.4 mg L^{-1}, and 1.2 mg L^{-1} were observed in the bottom water just above the sediment in December 2001 and June 2002, respectively, whereas concentrations at 35 m were at least 10 times greater (M. Maerki unpubl. data). Recently measured high-resolution electrode pore-water profiles of ammonium and oxygen confirmed that, at the deep site, aerobic remineralization is negligible. In contrast, at the shallow site, a considerable fraction of remineralization at the sediment-water interface follows the aerobic pathway, so that, even there, oxygen is depleted within the first millimeter of the sediment (M. Maerki pers. comm.).

Sampling and processing—At each site, several sediment cores (~40 cm depth) were obtained with a gravity corer in October 2001 so that intact sediment-water interfaces could be recovered. All cores were sampled on the same day; the samples were freeze-dried and homogenized. The sampling intervals were: each centimeter in the top 10 cm, every second centimeter from 10 to 20 cm, every third centimeter from 20 to 30 cm, and every fifth centimeter from 30 to 40 cm.

Core description—At the deep site, the upper 5 cm of the sediment were black and clearly varved, consisting of 2–3-mm-thick black and white couplets. From 5 to 20 cm, laminations became less clear. The black color disappeared, and intervals of variable darkness were observed. Below 20 cm, the sediment color was a very light gray, with still-visible laminations of similar thickness as in the top part. At the shallow site, the upper 4–5 cm were brown in color and were only faintly laminated (2–3 mm per couplet where varves were present). Below 6 cm, light and dark intervals similar to those at the deep site were observed, as well as continued laminations. Although the transition to light-colored sediment was less distinct, it also occurred at ~20 cm depth. At this site, the sediment was homogenous below 20 cm.

Age control—The sediment was dated by Cs-137 measurements in a core from a neighboring site (85 m water depth) at EAWAG, Dübendorf. By this method, the depths of two distinct Cs-137 peaks, which correspond to the Chernobyl accident (1986) and the atmospheric tests of nuclear bombs in 1963, were determined. In addition, the depth of the 1963 peak was determined in the core from the 120-m site, for confirmation. The results from the two cores agreed well, the 1963 peak being located at 10–11 cm depth. Although we had no direct age control in the core from the 35-m site, the lithologies suggested that the sedimentation rate is similar to that at the deeper sites. The age model resulted in a mean sedimentation rate of ~0.3 cm yr^{-1} in the surface sediments, which corresponds well to the observed varve thickness and is on the same order, although somewhat lower, than results from previous studies. From sediment trap flux measurements in 1982–1983, a sedimentation rate of 0.38 cm yr^{-1} was calculated (Moor et al. 1996), which is consistent with results from varve counting and Cs-137 dating in a core from 110 m depth (0.36 cm yr^{-1} between 2 and 6 cm depth and 0.39 cm yr^{-1}, respectively; Moor et al. 1996) and shifts of two black marker layers in cores taken 11 yr apart at the same site in the middle of the northern basin (0.36 cm yr^{-1}; B. Wehrli et al. unpubl data.).

TOC and TN—Total carbon (TC) and TN were determined on an elemental analyzer (Vario EL; Elementar). Inorganic carbon was measured on a coulometer (Coulometrics), and TOC contents were calculated by subtracting inorganic carbon from TC. The SD of the TC measurements was 2% of the mean ($n = 4$), and that of the TN measurement 5% ($n = 4$). For the coulometry, an SD of 1.25% of the mean was obtained for the calcite standards ($n = 22$) and <1.5% for repeated sample measurements. Carbon and nitrogen concentrations were measured on two cores from each site, to assess local heterogeneity. At both sites, the results were almost identical for neighboring cores, which showed that small-scale heterogeneity is not a problem. We therefore only present the results from the cores in which amino acids were also determined.

Amino acids—The concentrations of 18 amino acids were determined according to a method developed by Lindroth and Mopper (1979) and modified by Cowie and Hedges (1992*b*), where it is described in detail. Depending on the organic carbon content, 15–100 mg of 15 freeze-dried samples from each core were used. In short, the amino acids were liberated by hydrolysis with 6 mol L^{-1} HCl at 155°C for 70 min. Before analysis, the amino acids reacted online with orthophthaldialdehyde to form fluorescent derivatives. These were separated by reverse-phase high-performance liquid chromatography (HPLC) with a heated (30°C) C_{18} column and a binary solvent system and then detected by a fluorescence detector. The amino acids proline, tryptophan, and cysteine cannot be determined with this method.

Charge-matched internal recovery standards added after hydrolysis allowed us to account for adsorption or other loss of the liberated amino acids. A standard amino acid mixture (Sigma) with the internal standards added was run after every fourth sample, to calculate response factors of the individual amino acids relative to the internal standard of their charge group. The SD of 10 standard measurements ranged from 1.2% (leucine) to 7.3% (tyrosine) of the mean. Parallel hydrolyses and HPLC analyses of replicate subsamples of one sample ($n = 5$) resulted in SDs of <1–2% of the mean for most amino acids. Exceptions were tyrosine (2.3%), β-alanine (BALA; 2.4%), arginine (4.3%), histidine (6.1%), and ornithine (12.2%). THAAs are the sum of the individual

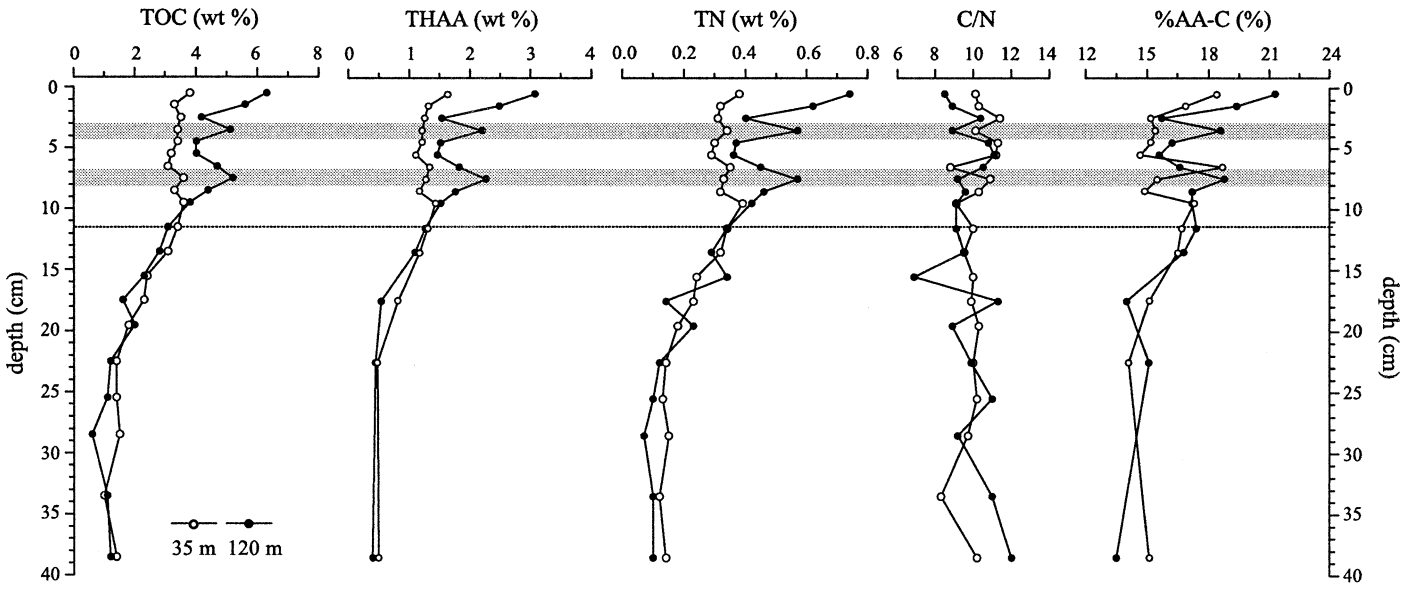

Fig. 2. Sediment profiles of TOC, TN, THAA (in wt%) and the derived parameters C : N and %AA-C from the two cores. Shaded bars indicate the position of two dark layers in the core from 120 m, and the dashed line the approximate depth corresponding to the onset of major eutrophication in Lake Zug.

amino acid concentrations; the percentage of TOC contained in amino acids (%AA-C) was inferred from the amount of each amino acid and the number of carbon atoms it contains.

Chlorins—For the analysis of chlorins, material was taken from different cores obtained at the two sites. Chlorins were extracted by threefold sonication of the freeze-dried samples in acetone (Schubert et al. 2000). After each extraction, vials were centrifuged and the supernatant transferred to a new vial. During the procedure, the samples were cooled under low light conditions, to prevent decomposition of the chlorins. Sediment extracts were brought to equal volume and measured fluorimetrically (Hitachi F-2000 fluorimeter) immediately after extraction with an excitation wavelength of 428 nm and an emission wavelength of 671 nm. Chlorophyll *a* (Sigma) that was transformed to the chlorin phaeophytin by acidification with a few drops (~100 μl) of 25% hydrochloric acid was used as a standard. The precision of the method tested on ten samples with the same weight was better than 5%. However, it is important to use similar sample weight : acetone ratios. Sun et al. (1991) proposed that part of the Chl *a* pool might be attached to intact cell material or other sediment matrix components, inhibiting their release during sonication of the samples and imposing a potential error on chlorin concentrations.

To obtain the chlorin index (CI), the extract was remeasured after acidification with hydrochloric acid (Schubert et al. 2002). This treatment chemically transforms labile pigments, changing their optical properties and leading to a lower fluorescence yield. An extract of fresh phytoplankton will therefore change its optical properties more dramatically than an extract of old sediments, where pigments have already been transformed by degradation. The CI is defined as the ratio of the fluorescence value of the acidified sample to that of the original sample.

Results and discussion

Bulk parameters—When the two sites were compared, the bulk parameter profiles showed clear differences in the upper part of the sediment (Fig. 2). The deep site (120 m) exhibited much higher surface concentrations of TOC, TN, and THAA—6.3, 0.74, and 3.1 wt%, respectively. Therefore, the decrease in concentrations within the core was much more pronounced at this site. Furthermore, the profiles from the deep site show marked peaks at 3–4 and 7–8 cm depth, corresponding to darker layers in this core. In contrast, at the shallow site (35 m), the surface values were much lower (3.8, 0.38, and 1.6 wt%, respectively), and the slight decreasing trends were rather constant with depth. However, these differences were only found in the surface sediments. Below ~12 cm, concentrations became similar at the two sites, with slight decreases of TOC, TN, and THAA contents to values of ~1.2, 0.12, and 0.5 wt%, respectively.

In contrast to the concentration of organic matter, the C : N ratio was similar at the two sites. Only in the uppermost 5 cm was the C : N ratio slightly lower at the deeper site. A small increase of C : N with sediment depth was observed at the deep site, with values of 8–9 at the surface and 11–12 at depth, whereas, at the shallow site, the values were ~10 throughout the core. As for C : N ratios, the %AA-C was more similar at the two sites than was the organic matter concentration. However, differences in %AA-C were observed at the sediment surface and in the organic-rich layers, with higher values at the deep site. After a clear decrease directly below the surface at both sites, the %AA-C varied between 15 and 18 in the upper part of the cores; a slight but consistent decrease with depth was observed below 12 cm.

The decrease in organic matter concentration with depth at both sites is probably in part caused by postburial remin-

eralization. The slight gradient seen in the lower part of the sediment particularly resembled a first-order decay profile. However, eutrophication, which has led to an increase in the recent accumulation of organic matter in the sediment, most likely also contributed to the observed gradient in the upper part of the sediment. The differences in organic matter concentrations between the two sites will be discussed below in context of the results from the degradation state indicators.

%AA-C is a measure of the relative contribution of proteinaceous material to organic matter. In addition, C : N ratios are strongly influenced by the abundance of amino acids, because these are major N-containing constituents of organic matter (Parsons et al. 1977; Lee and Cronin 1982). The relative contribution of proteins can be affected by variations in the initial composition of the organic material. Land plants, which are one potential source of organic matter, have fewer proteins and, therefore, higher C : N ratios and lower %AA-C values than plankton. The slight increase of %AA-C toward the surface at both sites could therefore be partly related to an increasing contribution of planktonic material due to eutrophication. A different contribution of terrestrial organic matter at the two sites seems unlikely, because differences in C : N and %AA-C in the two cores were only observed at the sediment surface and the upper organic-rich layer.

During degradation, amino acids have generally been observed to be comparatively labile organic matter components (e.g., Lee and Cronin 1982; Keil et al. 2000). If proteins are degraded preferentially, lower TOC contents should correspond to higher C : N ratios and lower %AA-C values. However, literature findings have been equivocal. Colombo et al. (1998) reported decreasing %AA-C values with sediment depth but no trend in the water column. In decay experiments with phytoplankton biomass, Lehmann et al. (2002) reported increasing C : N ratios under oxic, but not anoxic, conditions. In contrast, several other laboratory studies have found no trends in C : N or %AA-C during degradation under either oxic or anoxic conditions (e.g., Harvey et al. 1995; Nguyen and Harvey 1997). In the sediment of Lake Zug, the decrease in %AA-C in the first centimeters at both sites indicates the preferential removal of amino acids. However, the overall small gradient with depth suggests that preferential removal mainly affects the initial stages of degradation and that any subsequent alteration is nonselective. To draw further conclusions about the preferential degradation of proteins in Lake Zug, it would be necessary to study changes at a millimeter scale.

Molecular-level evidence and degradation indicators—Amino acid composition. The amino acid compositions observed in the surface sediments of Lake Zug were very similar at the two sites (Fig. 3), in contrast to the differences seen in TOC, TN, THAA, and, to a lesser extent, %AA-C and C : N. The most abundant amino acids were glycine, alanine, aspartic acid, threonine, and glutamic acid. Only some of the amino acids showed significant down-core trends. Decreasing values were observed in both cores for aspartic acid, glutamic acid, lysine, and tyrosine. A clear increase with sediment depth was found in the contributions of glycine, as well as the nonprotein amino acids BALA and ornithine. For many amino acids, the trends were more obvious or were even exclusively visible in the core from the deep site. This was especially the case for the decreases in valine, leucine, isoleucine, and phenylalanine, as well as the increase in γ-aminobutyric acid (GABA).

The amino acid composition in Lake Zug sediments was very similar to that of surface sediments from the North Sea (Dauwe and Middelburg 1998), consistent with studies that found no differences in the amino acid composition of a broad range of potential organic matter sources (Cowie and Hedges 1992*a;* Colombo et al. 1998). Furthermore, the observed down-core changes in the amino acid composition were similar to observations in the marine environment (e.g., Burdige and Martens 1988; Cowie and Hedges 1992*a;* Dauwe and Middelburg 1998). These changes indicate that individual amino acids are degraded preferentially. However, the reasons are not yet fully understood, because various processes potentially affect amino acids during degradation. Matrix protection could lead to different liberation rates of the individual amino acids during the initial hydrolysis (Cowie and Hedges 1992*a*). The depletion of tyrosine, glutamic acid, and phenylalanine, which are mainly contained in diatom cell plasma, and the accumulation of glycine, which is associated with diatom cell walls, could be explained this way. The nonprotein amino acids BALA, GABA, and possibly ornithine are produced from protein amino acids during bacterial remineralization (e.g., Mueller and Suess 1977; Lee and Cronin 1982). Hence, the increasing concentrations, especially of BALA, observed in our study indicate ongoing organic matter degradation in the sediments. In contrast to the bulk parameters, the concentration gradients were continuous throughout the cores or were even larger at depth. Notably, synthesis of proteins in situ by bacteria and protection from decay by adsorption onto mineral surfaces or reaction with other compounds may also have contributed to changes in observed amino acid spectra (e.g., Henrichs and Sugai 1993; Keil et al. 1994; Keil 1999).

Amino acid degradation index (DI)—Many studies have shown that variations in amino acid composition are generally connected to organic matter decay. Hence, they can be used as degradation indicator, which has been done repeatedly and successfully in the marine system. One proposed proxy is the sum of nonprotein amino acids (Whelan 1977; Cowie and Hedges 1994). However, the low yields of these amino acids that we measured (0.6–3.0% for the sum of GABA and BALA) are consistent with the earliest stages of organic matter decay, during which this parameter is comparatively insensitive (Cowie and Hedges 1994; Keil et al. 2000).

To take the variations of the contributions of all individual amino acids into account, a new proxy for degradation was proposed by Dauwe and Middelburg (1998) and revised later (Dauwe et al. 1999). Their DI was based on principal components analysis (PCA) of the protein amino acid composition in sediment samples. The data set was composed of a suite of samples of very different degradation states, ranging from organic matter sources (different plankton species and bacteria) and coastal surface sediments in various settings to very degraded deep-sea sediments. Therefore, the authors

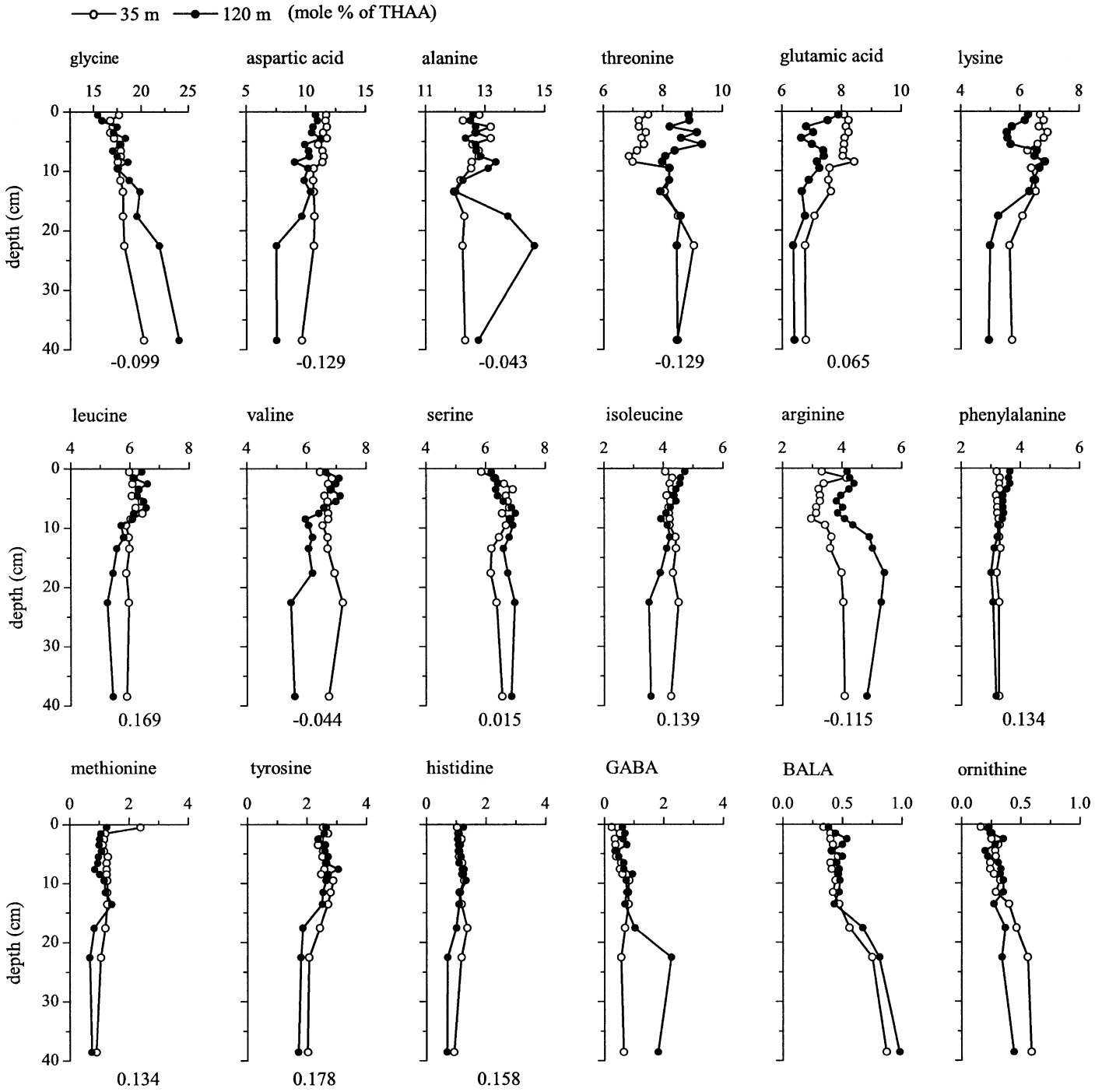

Fig. 3. Contributions of the 18 measured amino acids to THAA in the two cores. Note the different scales for glycine, aspartic acid, BALA, and ornithine. Numbers underneath the graphs are the respective factor coefficients for calculating the DI, given by Dauwe et al. (1999). Higher absolute numbers imply greater importance of the respective amino acid contribution for the DI value. Lysine and the nonprotein amino acids are not used for the DI.

interpreted the first component of the PCA (PC1), which explained 36% of the variance in the data, to reflect organic matter degradation. The DI of a sample is defined as its value of PC1, which is the sum of the contributions of each amino acid (in mole%), standardized within the reference data set and weighted by the respective factor coefficient (Fig. 3). Thereby, lower DI values correspond to more degraded material. Averages and SDs for the standardization, as well as factor coefficients, are given by Dauwe et al. (1999). The DI is a purely statistical parameter, and the interpretation of PC1 to reflect degradation is subjective. However, this parameter has by now been applied to marine samples from various settings (e.g., Keil et al. 2000; Amon et al. 2001; Van Mooy et al. 2002), and the findings confirmed this in-

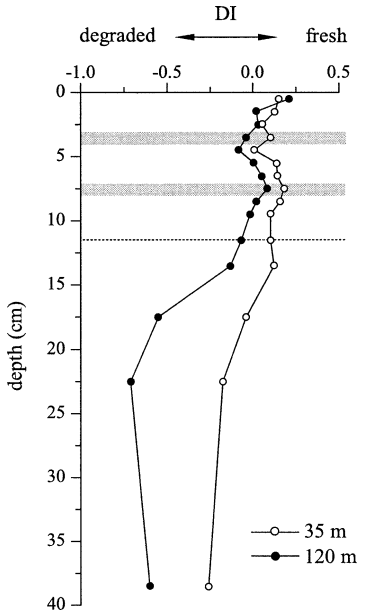

Fig. 4. Profiles of the DI in the two cores. The DI is based on the amino acid composition and is calculated according to the method of Dauwe et al. (1999). Shaded bars and dashed line as in Fig. 2.

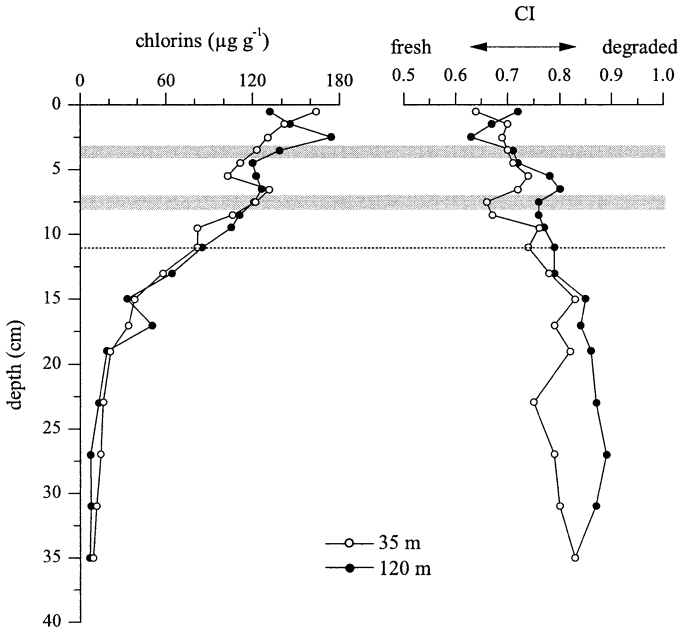

Fig. 5. Concentrations of chlorins in the two cores and the obtained CI, according to the method of Schubert et al. (2002). The shaded bars and dashed line are as in Fig. 2.

terpretation. An advantage of the DI is that it is a very robust parameter because it is based on a large number of individual measurements.

The values that we obtained for the DI (Fig. 4) varied between −0.7 and 0.2, and the precision (determined by repeat measurements of one sample; $n = 5$) was 8% of the mean. The DI values were very similar in the two cores in the upper part of the sediment, in accordance with the similar amino acid composition measured there but in contrast to the different organic matter concentrations. The distinct peaks observed in the upper section of the bulk concentration profiles from the deep site were much less evident in the DI profile. In the deeper part of the sediment, the DI profiles from the two cores diverged, with the core from the deep site exhibiting consistently lower values than the other core.

Both the constant and similar values of DI in the surface sediment and the divergence at depth were based on the same trends in many individual amino acid contributions (Fig. 3). In the surface sediment, hardly any amino acid exhibited significant trends (the exceptions were glycine, isoleucine, and, to some extent, serine), and differences between the sites were only observed for threonine, glutamic acid, and arginine. The divergence of DI values at depth was mostly due to changes in glycine, alanine, leucine, isoleucine, tyrosine, and histidine, most of which have been attributed high (positive or negative) factor coefficients. The contributions of aspartic acid, valine, and serine showed inconsistent effects, but the small factor coefficients of the latter two reduce their influence on DI values. An exceptional behavior was seen in the contributions of threonine, which were different at the two sites in the surface sediments and converged at depth. However, overall, the similarity of the DI results with most amino acid profiles showed that the DI results represented real changes that are consistent with organic matter decay.

The DI values in Lake Zug lie well in the range observed by Dauwe et al. (1999). These authors reported DI values of −2.2 (pelagic deep sea sediment) to 1.5 (source material). DI values >1 were found in source (plankton and bacteria) and sediment trap material. Values ~0 were found mostly in coastal sediments (Saanich Inlet, Dabob Bay, and the North Sea). The signs of the factor coefficients found by Dauwe et al. (1999) correspond well to the observed trends of the amino acid contributions with depth (Fig. 3), with negative signs for accumulating amino acids and positive signs for those that are depleted during degradation. The only exceptions were aspartic acid, valine, and serine. This good agreement with the literature findings shows that the degradation effects on amino acids are similar in lacustrine and marine environments, despite the potential differences in the degradation process in these two systems.

Chlorins—The concentration of chlorins was similar at the two sites and decreased strongly with depth in a uniform manner (Fig. 5). The similar chlorin concentrations at the two sites was surprising, given the large differences in the concentrations of TOC and THAA observed in the upper part of the cores. However, it is possible that our sampling resolution did not allow the potential differences in the initial sedimentary degradation of these rapidly degrading substances to be observed. The chlorin concentrations that we measured were higher than those usually found in marine sediments (Schubert et al. 2000), but most of the chlorins disappeared by 20 cm depth.

The degradation state of the chlorins is indicated by the CI, which reflects the refractory component of total chlorins

as represented by a decrease in fluorescence on acid treatment (Schubert et al. 2002). This parameter showed a comparable picture to the chlorin concentration. Values were generally similar at both sites, although slightly higher CI values were observed for the 120 m site in most samples and especially at depth. At both sites, an increasing trend down-core was found mainly in the upper 15 cm. CI values of 0.6–0.9 were at the higher end of the range measured to date in marine sediments (0.4–0.9; Schubert et al. 2002). The high CI values at depth (0.8–0.9) indicated that the small remaining total chlorin concentrations were almost entirely due to decay products that are essentially refractory even to acid treatment.

Several studies have used the chlorin concentration as a proxy for productivity (Harris et al. 1996; Schubert et al. 1998). Hence, the high concentrations of chlorins that we measured probably reflect the relatively high primary production in this lake setting, as well as a possible effect of the shallow water depth. Despite this, the comparatively high CI values from the surface samples suggest that considerable degradation has already occurred. This is in agreement with the findings of Lee et al. (2000), who reported rapid losses of pigments in the surface water. The depletion of chlorins within the sediments, combined with measurable increases in CI values down-core, suggests that chlorin decay continues within the sediments at both sites. However, the recent increase in primary production in the lake due to eutrophication has also undoubtedly contributed to increased chlorin concentrations and perhaps also to their degradation state.

Comparison of DI and CI—When comparing the two degradation state indicators applied here, DI and CI, one has to keep in mind the different nature of these proxies. While the DI is based on a molecular-level analysis of the amino acid pool, the CI relies on a compound-level assessment of the degradability of chlorins. The exact types of chlorins involved remain unknown. Furthermore, the DI is calculated using multivariate statistics, thus providing a composite from a suite of individual measurements, whereas the CI is a ratio of the results of two measurements. Therefore, DI values in particular cannot be expected to change linearly when degradation progresses, and trends in DI are unlikely to be matched in absolute terms by trends in CI. Finally, amino acids and chlorins are very different organic compounds and could be degraded at different rates. The chlorin and THAA profiles suggest that chlorins are degraded more strongly in Lake Zug sediments.

Indeed, the correlation of DI and CI within the cores was rather poor (r^2 = 0.55 and 0.17 at 35 and 120 m, respectively; data not shown). Nevertheless, the two degradation indicators were in general agreement—despite the different organic matter concentrations, both suggest a roughly similar degradation state at the two sites in the surface sediments. Both the DI and CI correlated negatively with the total concentrations of amino acids and chlorins, respectively (Fig. 6A,B). The CI varied linearly over the full chlorin concentration range, whereas the most pronounced changes in DI appeared to occur predominantly during later stages of amino acid decomposition (as inferred from low THAA concentrations at depth in the cores). Hence, the CI seems to have better represented early stages in sedimentary organic matter decay than the amino acids. It is interesting to note in this context that even measurements of the amino acids that are supposed to be most easily degraded (e.g., histidine and methionine; Dauwe et al. 1999) did not show trends in the surface sediment.

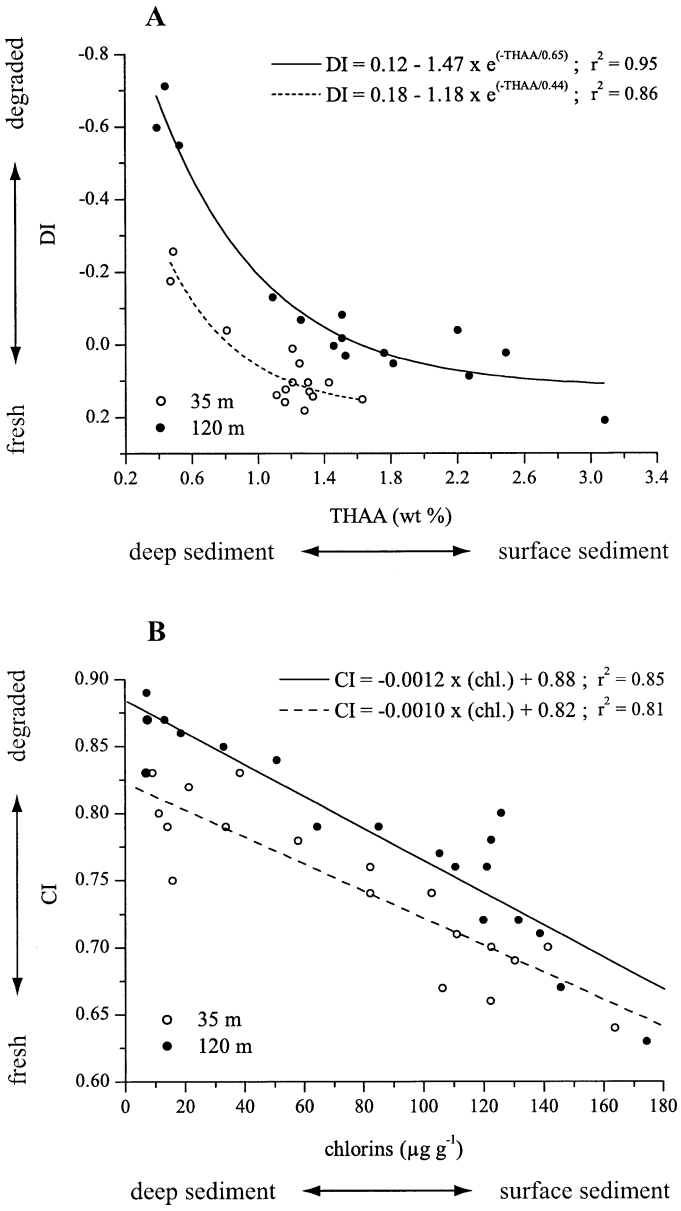

Fig. 6. (A) Correlation between DI values and THAA in the two cores. (B) Correlation of CI and chlorin concentration in the two cores. Equations of the regression lines are given together with the respective correlation coefficients.

CI and DI values were also consistent in that both showed generally higher values at the deep site for a given chlorin or THAA concentration. The regression lines in Fig. 6 indicate that this is a general phenomenon throughout the cores, although the differences were most pronounced at depth. The divergence in degradation state in the two cores at depth was more obvious in DI values than in the CI. This

could be the consequence of the nonlinear behavior of the DI reacting strongly to changes in some amino acids. Another possible explanation is the small amount of chlorins remaining at these depths and their already very degraded nature, which might not allow clear observations of further degradation.

Possible causes for observed organic matter concentration and degradation state profiles—In the absence of sediment trap deployments or other means for assessing organic matter input, it is not possible to determine the efficiency of organic matter burial at the two sites. Therefore, we cannot be entirely conclusive concerning the primary causes for observed differences in sedimentary organic matter concentrations or the apparent discrepancies between bulk parameters and degradation indicators. At face value, the similar organic matter degradation states in the surface sediments at the two sites suggest that the different organic matter concentrations may be caused by differences in organic matter dilution or delivery. The shallow site is closer to the inflow of the Lorze River, which could contribute more inorganic material at this site. However, the sediment load of the river is usually very low, because another lake is located upstream of Lake Zug, and the small delta at the river mouth, which was described in a seismic survey (Kelts 1978), is far away from our sampling site. Hence, dilution is unlikely to be of major significance.

Different input of organic matter at the two sites could be due to different productivity or to preferential transport of fine, organic matter–rich material to the deep site by bottom currents or sediment focusing. As was mentioned above, productivity in the lake seems more or less homogenous (Bloesch and Sturm 1986). Bottom current transport could be stimulated by internal waves (seiches) observed both in the north and the south basin, but current speeds (in a north-south direction) are usually low. In 1993, these rarely reached 5 cm s^{-1} at 2 m above bottom (Wüest and Gloor 1998). Grain size analyses in the upper 2.5 cm of the sediment indicated only a slight gradient along the basin, with somewhat smaller median grain sizes at the deeper sites (Maerki et al. 2004). Hence, bottom current transport might play a role but is probably not crucial for the different organic matter concentrations. Nonetheless, focusing of organic material mobilized at the lake margin could occur at the deep site. This process does not depend on bottom currents but can be driven by wave action or stronger currents in shallow waters and is common both in lakes and coastal embayments (e.g., Blais and Kalff 1995; Smoak et al. 2000). The higher flux in the deeper sediment traps at times during their deployment in 1982–1983 could be explained by sediment focusing. Thereby, low-density, organic matter–rich debris can be preferentially removed from the margins and transported to deep sites. With overall increased organic matter fluxes due to eutrophication, the difference in delivery between the sites could have become more pronounced.

However, the difference in the degradation state at the two sites at depth, despite the similar organic matter concentrations, cannot be readily explained by this process alone. Because the depositional conditions were likely to have been more similar at the two sites before the onset of eutrophication and hypoxia, a different extent of degradation within the sediment is not probable. Very different sediment accumulation rates at the two sites during this time cannot be excluded, but this also seems unlikely on the basis of the lithologies. A plausible explanation for the contrasting degradation indicator values before the onset of eutrophication (at ~11–12-cm depth) is that organic matter accumulating at the deep site was generally more degraded. A possible reason for this is a longer residence time in the water column, due to some combination of the effects of a longer water column and sediment focusing. Since eutrophication, some factor must have counteracted this difference, resulting in the similar degradation state observed in the surface sediment. The responsible factor could be the reduction of oxygen exposure time due to the extension of suboxic bottom water. This would have affected degradation in the water column as well as at the sediment-water interface at the deep site.

The effect of oxygen availability and exposure time on sedimentary organic matter distributions and preservation is still controversial (Calvert and Pedersen 1992; Kristensen 2000 and references therein), and the impact on amino acid and chlorin degradation is even less clear to date. For example, Van Mooy et al. (2002) did not observe a difference in DI after the incubation of sediment trap material under oxic and suboxic conditions for 5 d. For chlorin concentrations, Shankle et al. (2002) found a relation to oxygen availability and water depth across the oxygen minimum zone in the Arabian Sea.

In lakes, low oxygen concentration could have a different impact because of the fact that anaerobic degradation occurs mainly via methanogenesis instead of sulfate reduction. The effect of the different pathways on anaerobic organic matter degradation rates is not clear. Although sulfate reduction is the more energy-efficient process (e.g., Capone and Kiene 1988), Teece et al. (1998) found similar or even higher degradation rates under methanogenic conditions during long (>1 yr) incubations. Nonetheless, in Lake Zug, the observed bulk concentration profiles correspond well to the oxygenation history of the lake. The onset of hypertrophic conditions in the lake in the early 1960s corresponded to a sediment depth of 11–12 cm, above which the organic matter concentration in the two cores diverged. Furthermore, within the dating uncertainties, the depths of the two organic matter peaks in the core from the deep site (Fig. 2) corresponded to two periods with especially low oxygen concentrations in the lake—namely, the mid-1970s and early 1990s (Environmental Agency of Kanton Zug, unpubl. data). These periods of low bottom water oxygenation were probably caused by decreased mixing due to warmer winters (A. Wüest et al. unpubl. data).

If the degradation indicators indeed respond to oxygen availability, it is not clear why the DI profile at the deep site was almost constant in the upper part of the sediment, despite the apparent correspondence between low oxygen concentration and peaks in TOC and THAA. There was also no correlation between CI values and periods of pronounced oxygen depletion. Hence, there is no conclusive explanation for the differences between the degradation state and the bulk concentrations. Nonetheless, it seems likely that differ-

ent oxygen availability at the two sites has a superimposed or even dominant effect on both the organic matter concentration and degradation state in Lake Zug, in addition to factors such as differing organic matter delivery through sediment focusing.

In conclusion, the results of this study show that both the amino acid–based DI and the chlorin-based CI are applicable to lakes. Both add important insights into the degradation process in the sediment. The trends in DI and in the concentration of non–protein amino acids below 15-cm sediment depth show that organic matter decay continued within the sediments and that the down-core gradient in organic matter concentration is not simply due to eutrophication. Differences observed between down-core trends in DI and CI values could be due to the nonlinear response of either parameter as decay progresses or to different reactivity of amino acids and chlorins. Ultimately, the CI seems to be most useful during the earliest stages in organic matter decay, whereas the DI appears to better represent later stages. To better interpret the statistical parameter DI, the mechanisms that cause the underlying compositional changes of amino acids need to be further explored. The two degradation indicators agree in the general picture of the degradation state at the two sites. Despite higher TOC and amino acid concentrations in the surface sediment at the deep site, both DI and CI values indicated a similar or even higher degradation state at this site. Although the reasons remain unclear, the most likely factors are sediment focusing and oxygen exposure time. The results illustrate that bulk parameters alone do not yield enough information to assess organic matter degradation. High-resolution studies on a compound-class level are necessary to improve our understanding of the initial stages of the sedimentary degradation process.

References

AMON, R. M. W., H. P. FITZNAR, AND R. BENNER. 2001. Linkages among the bioreactivity, chemical composition, and diagenetic state of marine dissolved organic matter. Limnol. Oceanogr. **46:** 287–297.

BLAIS, J. M., AND J. KALFF. 1995. The influence of lake morphometry on sediment focusing. Limnol. Oceanogr. **40:** 582–588.

BLOESCH, J., AND M. STURM. 1986. Settling flux and sinking velocities of particulate phosphorus (PP) and particulate organic carbon (POC) in Lake Zug, Switzerland, p. 481–490. *In* P. E. Sly [ed.], Sediment and water interactions. Springer.

BURDIGE, D. J., AND C. S. MARTENS. 1988. Biogeochemical cycling in an organic-rich coastal marine basin 10: The role of amino acids in sedimentary carbon and nitrogen cycling. Geochim. Cosmochim. Acta **52:** 1571–1584.

CALVERT, S. E., AND T. F. PEDERSEN. 1992. Organic carbon accumulation and preservation in marine sediments: How important is anoxia?, p. 231–263. *In* J. K. Whelan and J. W. Farrington [eds.], Organic matter: Productivity, accumulation and preservation in recent and ancient sediments Columbia Univ. Press.

CAPONE, D. G., AND R. P. KIENE. 1988. Comparison of microbial dynamics in marine and freshwater sediments: Contrasts in anaerobic carbon catabolism. Limnol. Oceanogr. **33:** 725–749.

COLOMBO, J. C., N. SILVERBERG, AND J. N. GEARING. 1998. Amino acid biogeochemistry in the Laurentian Trough: Vertical fluxes and individual reactivity during early diagenesis. Org. Geochem. **29:** 933–945.

COWIE, G. L., AND J. I. HEDGES. 1992*a*. Sources and reactivities of amino acids in a coastal Maine environment. Limnol. Oceanogr. **37:** 703–724.

———, AND ———. 1992*b*. Improved amino acid quantification in environmental samples: Charge-matched recovery standards and reduced analysis time. Mar. Chem. **37:** 223–238.

———, AND ———. 1994. Biochemical indicators of diagenetic alteration in natural organic matter mixtures. Nature **369:** 304–307.

DAUWE, B., AND J. J. MIDDELBURG. 1998. Amino acids and hexosamines as indicators of organic matter degradation state in North Sea sediments. Limnol. Oceanogr. **43:** 782–798.

———, ———, P. M. J. HERMAN, AND C. H. R. HEIP. 1999. Linking diagenetic alteration of amino acids and bulk organic matter reactivity. Limnol. Oceanogr. **44:** 1809–1814.

HARRIS, P. G., M. ZHAO, A. ROSELL-MELÉ, R. TIEDEMANN, M. SARNTHEIN, AND J. R. MAXWELL. 1996. Chlorin accumulation rate as a proxy for Quaternary marine primary productivity. Nature **383:** 63–65.

HARTNETT, H. E., R. G. KEIL, J. I. HEDGES, AND A. H. DEVOL. 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature **391:** 572–574.

HARVEY, H. R., J. H. TUTTLE, AND J. T. BELL. 1995. Kinetics of phytoplankton decay during simulated sedimentation—changes in biochemical-composition and microbial activity under oxic and anoxic conditions. Geochim. Cosmochim. Acta **59:** 3367–3377.

HENRICHS, S. M., AND S. F. SUGAI. 1993. Adsorption of amino acids and glucose by sediments of Resurrection Bay, Alaska, USA: Functional group effects. Geochim. Cosmochim. Acta **57:** 823–835..

JORGENSEN, B. B. 1982. Mineralization of organic matter in the sea bed—the role of sulfate reduction. Nature **296:** 643–645.

KEIL, R. G. 1999. Early diagenesis of amino acids in high organic content marine sediments, p. 259–262. *In* H. Armannsson [ed.], Geochemistry of the Earth's surface. Balkema.

———, D. B. MONTLUCON, F. G. PRAHL, AND J. I. HEDGES. 1994. Sorptive preservation of labile organic matter in marine sediments. Nature **370:** 549–552.

———, E. TSAMAKIS, AND J. I. HEDGES. 2000. Early diagenesis of particulate amino acids in marine systems, p. 69–82. *In* G. A. Goodfriend, M. J. Collins, M. L. Fogel, S. A. Macko, and J. F. Wehmiller [eds.], Perspectives in amino acid and protein chemistry. Oxford Univ. Press.

KELTS, K. 1978. Geological and sedimentary evolution of Lakes Zurich and Zug, Switzerland. Ph.D. thesis, ETH Zürich.

KRISTENSEN, E. 2000. Organic matter diagenesis at the oxic/anoxic interface in coastal marine sediments, with emphasis on the role of burrowing animals. Hydrobiologia **426:** 1–24.

LEE, C., AND C. CRONIN. 1982. The vertical flux of particulate organic nitrogen in the sea: Decomposition of amino acids in the Peru upwelling area and the equatorial Atlantic. J. Mar. Res. **40:** 227–251.

———, S. G. WAKEHAM, AND J. I. HEDGES. 2000. Composition and flux of particulate amino acids and chloropigments in equatorial Pacific seawater and sediments. Deep-Sea Res. I **47:** 1535–1568.

LEHMANN, M. F., S. M. BERNASCONI, A. BARBIERI, AND J. A. MCKENZIE. 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochim. Cosmochim. Acta **66:** 3573–3584.

LINDROTH, P., AND K. MOPPER. 1979. High performance liquid chromatographic determination of subpicomole amounts of

amino acids by precolumn fluorescence derivatization with *o*-phthaldialdehyde. Anal. Chem. **51:** 1667–1674.

MAERKI, M., B. WEHRLI, C. DINKEL, AND B. MÜLLER. 2004. The influence of tortuosity on molecular diffusion in freshwater sediments of high porosity. Geochim. Cosmochim. Acta **68:** 1519–1528.

MEYERS, P. A., AND R. ISHIWATARI. 1993. Lacustrine organic geochemistry: An overview of indicators of organic matter sources and diagenesis in lake sediments. Org. Geochem. **20:** 867–900.

MOOR, H. C., T. SCHALLER, AND M. STURM. 1996. Recent changes in stable lead isotope ratios in sediments of Lake Zug, Switzerland. Environ. Sci. Technol. **30:** 2928–2933.

MUELLER, P. J., AND E. SUESS. 1977. Interaction of organic compounds with calcium carbonate: III. Amino acid composition of sorbed layers. Geochim. Cosmochim. Acta **41:** 941–949.

NGUYEN, R. T., AND H. R. HARVEY. 1997. Protein and amino acid cycling during phytoplankton decomposition in oxic and anoxic waters. Org. Geochem. **27:** 115–128.

PARSONS, T. R., M. TAKAHASHI, AND B. HARGRAVE. 1977. Biological oceanographic processes, 2nd ed. Pergamon.

SCHUBERT, C. J., T. G. FERDELMAN, AND B. STROTMANN. 2000. Organic matter composition and sulfate reduction rates in sediments off Chile. Org. Geochem. **31:** 351–361.

———, G. KLOCKGETHER, J. NIGGEMANN, T. G. FERDELMAN, AND B. B. JORGENSEN. 2002. The chlorine index: A new parameter for organic matter freshness in sediments. Geochim. Cosmochim. Acta **66:** A689–A689.

———, AND OTHERS. 1998. Stable phytoplankton community structure in the Arabian Sea over the past 200,000 years. Nature **394:** 563–566.

SHANKLE, A. M., R. GOERICKE, P. J. S. FRANKS, AND L. A. LEVIN. 2002. Chlorin distribution and degradation in sediments within and below the Arabian Sea oxygen minimum zone. Deep-Sea Res. I **49:** 953–969.

SMOAK, J. M., W. S. MOORE, AND R. C. THUNELL. 2000. Influence of boundary scavenging and sediment focusing on Th-234, Th-228 and Pb-210 fluxes in the Santa Barbara Basin. Estuar. Coast. Shelf Sci. **51:** 373–384.

SUN, M. Y., R. C. ALLER, AND C. LEE. 1991. Early diagenesis of chlorophyll-a in Long-Island Sound sediments—a measure of carbon flux and particle reworking. J. Mar. Res. **49:** 379–401.

TEECE, M. A., J. M. GETLIFF, J. W. LEFTLEY, R. J. PARKES, AND J. R. MAXWELL. 1998. Microbial degradation of the marine prymnesiophyte *Emiliania huxleyi* under oxic and anoxic conditions as a model for early diagenesis: Long chain alkadienes, alkenones, and alkyl alkenoates. Org. Geochem. **29:** 863–880.

THOMPSON, R., AND K. KELTS. 1974. Holocene sediments and magnetic stratigraphy from Lakes Zug and Zurich, Switzerland. Sedimentology **21:** 577–596.

VAN MOOY, B. A. S., R. G. KEIL, AND A. H. DEVOL. 2002. Impact of suboxia on sinking particulate organic carbon: Enhanced carbon flux and preferential degradation of amino acids via denitrification. Geochim. Cosmochim. Acta **66:** 457–465.

WAKEHAM, S. G., C. LEE, J. I. HEDGES, P. J. HERNES, AND M. L. PETERSON. 1997. Molecular indicators of diagenetic status in marine organic matter. Geochim. Cosmochim. Acta **61:** 5363–5369.

WHELAN, J. K. 1977. Amino acids in a surface sediment core of the Atlantic abyssal plain. Geochim. Cosmochim. Acta **41:** 803–810.

WÜEST, A., AND M. GLOOR. 1998. Bottom boundary mixing: The role of near-sediment density stratification, p. 485–502. *In* J. Imberger [ed.], Physical processes in lakes and oceans. Coastal and Estuarine Studies 54. American Geophysical Union.

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