

- nion and sediments of Lake Kinneret, Israel. *Freshwater Biol.* **33**: 63–72.
- KRABBEHOFT, D. P., C. C. GILMOUR, J. M. BENOIT, C. L. BABIARZ, A. W. ANDREN, AND J. P. HURLEY. 1998. Methyl mercury dynamics in littoral sediments of a temperate seepage lake. *Can. J. Fish. Aquat. Sci.* **55**: 835–844.
- KROM, M. D., AND R. A. BERNER. 1980. The diffusion coefficients of sulfate, ammonium and phosphate in anoxic marine sediments. *Limnol. Oceanogr.* **25**: 327–337.
- , P. DAVISON, H. ZHANG, AND W. DAVISON. 1994. High resolution pore water sampling using a gel sampler. *Limnol. Oceanogr.* **39**: 1967–1972.
- LEE, D. R. 1977. A device for measuring seepage flux in lakes and estuaries. *Limnol. Oceanogr.* **22**: 140–147.
- , AND J. A. CHERRY. 1978. A field exercise on groundwater flow using seepage meters and mini-piezometers. *J. Geol. Educ.* **27**: 610.
- , ———, AND J. F. PICKENS. 1980. Groundwater transport of a salt tracer through a sandy lakebed. *Limnol. Oceanogr.* **25**: 45–61.
- LI, Y.-H., AND S. GREGORY. 1974. Diffusion of ions in seawater and in deep-sea sediments. *Geochim. Cosmochim. Acta* **38**: 703–714.
- MANHEIM, F. T. 1970. The diffusion of ions in unconsolidated sediments. *Earth Planet. Sci. Lett.* **9**: 307–309.
- MANWARING, C. E. 1996. Measurements of salinity gradients in the bottom sediments of Lake Kinneret, using gel and conventional porewater sampling, Israel. M.Sc. thesis, Leeds Univ.
- MORTIMER, R. J. G., M. D. KROM, P. O. J. HALL, S. HULTH, AND H. STÄHL. 1998. Use of gel probes for the determination of high resolution solute distributions in marine and estuarine pore waters. *Mar. Chem.* **63**: 119–129.
- MUNK, W. H. 1966. Abyssal recipes. *Deep Sea Res.* **13**: 707–730.
- NISHRI, A., M. STILLER, A. RIMMER, Y. GEIFMAN, AND M. D. KROM. (1999) Lake Kinneret (The Sea of Galilee): The effects of diversion of external salinity sources and the probable chemical composition of the internal salinity sources. *Chem. Geol.* **158**: 37–52.
- , ———, AND D. RONEN. 1997. Comparison between methods for estimating un-focused seepage from Lake Kinneret bed sediments. IOLR report T14/97.
- SHAW, R. D., AND E. E. PREPAS. 1990. Groundwater–lake interactions: I. Accuracy of seepage meter estimates of lake seepage. *J. Hydrol.* **119**: 105–120.
- SMITH, S. V., S. SERRUYA, Y. GEIFMAN, AND T. BERMAN. 1989. Internal sources and sinks of water, P, N, Ca, and Cl in Lake Kinneret, Israel. *Limnol. Oceanogr.* **34**: 1202–1213.
- STILLER, M. 1994. The chloride content in pore water of Lake Kinneret sediments. *Isr. J. Earth Sci.* **43**: 179–185.

Received: 26 May 1998

Accepted: 14 June 1999

Amended: 30 June 1999

Linking diagenetic alteration of amino acids and bulk organic matter reactivity

Abstract—Examination of amino acids in particulate samples from a variety of marine environments (fresh phytoplankton to deep-sea sediments) revealed systematic compositional changes upon progressive degradation. These consistent trends have been used to derive a quantitative degradation index (DI) that is directly related to the reactivity of the organic material, as indicated by its lability to enzymatic decay and its first-order degradation rate constant. This direct link between molecular composition and degradation rate allows us to quantify the quality of organic matter based solely on its chemical composition.

Decomposition of particulate organic matter (POM) is responsible for oxygen consumption in the ocean and its sediments, for the recycling of essential nutrients, and for most early diagenetic processes. The heterogeneous composition of POM leads to selective preservation of more stable (or less available) molecular compounds and to the loss of labile compounds, resulting in a continuously altered biochemical composition of the material during diagenesis (Tegelaar et al. 1989; Cowie and Hedges 1994; Wakeham et al. 1997). These compositional changes in POM are probably the reason for a decreasing first-order degradation rate (Middelburg 1989) and a reduced nutritional value toward heterotrophic consumers (Tenore et al. 1984) as degradation proceeds. Although intrinsic differences in molecular structure (de Leeuw

and Largeau 1993) and differences in physiochemical association with the sediment matrix (Keil et al. 1994; Mayer 1994) are documented factors acting on early diagenesis of POM, there are few studies that directly link the resulting shifts in biochemical composition to the degradation state (Cowie and Hedges 1994; Wakeham et al. 1997; Dauwe and Middelburg 1998). Moreover, compositional characteristics of organic matter have not yet been linked to its biological availability or its degradation dynamics.

A series of molecular diagenetic maturity indicators have been used to estimate the relative degradation state of the organic matter (Cowie and Hedges 1994; Wakeham et al. 1997), varying from short-term (e.g., chlorophyll) to longer term (e.g., nonprotein amino acids) indicators. Broadly applicable degradation state indicators should be based on major components that are widely distributed geographically and that are omnipresent in organisms so that variability in sources of organic matter is minimized. Moreover, they should ideally be sensitive to all stages of alteration. Proteins are ubiquitous components of all source organisms and degradation mixtures (Cowie and Hedges 1992). Although there is some dissimilarity in amino acid composition of the ultimate source organisms (e.g., diatoms, coccolithophorids, and bacteria) (Cowie and Hedges 1992), these differences are minor compared to the alteration of the spectra upon degradation (Dauwe and Middelburg 1998).

Table 1. Data matrix of the protein amino acid-based DI. (1–6) Source materials (Source): 1 microalgae (Brown 1991), 2 phytoplankton (Cowie and Hedges 1992), 3 bacteria (Cowie and Hedges 1992), 4 zooplankton (Cowie and Hedges 1992), and 5 and 6 sediment trap (T) material from Saanich Inlet (Saan) and Dabob Bay (Dab) (Cowie and Hedges 1992; Cowie et al. 1992). (7–17) Coastal sediments (Coastal): 7–13 North Sea (Dauwe and Middelburg 1998): SK, Skagerrak; GB1, GB2 = German Bight 1 and 2; FF, Frisian Front; BF, Broad Fourteens; BG-A, BG-B, Brouwershavense-gat A and B; 14, 15 surface sediment (S1); and 16, 17 subsurface sediment (S2) of Saanich Inlet (Cowie et al. 1992) and Dabob Bay (Cowie and Hedges 1992). (18–20) Eastern Mediterranean samples (34°52'30"N, 21°07'08"W, 2,539-m water depth): 18, 19 hemipelagic sediments (Med-1 and Med-2), and 20 sapropel (Sap), (21–28) Turbidite samples. Depth profile of the MAP f-turbidite in core 86P25 (30°44'22"N, 25°22'45"W, 5,400-m water depth) (de Lange et al. 1994): 21–24: Tur-ox, oxidized section, and 25–28; Tur-red, reduced section. The DI for samples outside our data set can be calculated on the basis of their protein amino acid spectra, and the factor coefficients based on the first axis of the PCA, listed according to the formula

$$DI = \sum_i \left[\frac{\text{var}_i - \text{AVG var}_i}{\text{STD var}_i} \right] \cdot \text{fac.coef}_i$$

where var_i is the original (nonstandardized) mole percentage of amino acid i , AVG var_i and STD var_i are its mean and standard deviation in our data set, and fac.coef_i the factor coefficient for amino acid i .

No.	Sample	Depth interval (cm)	DI	Amino acid	Factor coefficient (first axis)	AVG	STD	Factor coefficient (second axis)	Factor coefficient (third axis)
Source									
1	Phy-B	—	1.10	THR	−0.129	7.1	1.5	0.060	0.028
2	Phy-C	—	1.48	ARG	−0.115	6.1	2.3	−0.206	0.059
3	Bac	—	1.27	ASP	−0.102	13.4	2.7	−0.046	−0.247
4	Zoo	—	1.01	GLY	−0.099	17.6	3.8	0.195	0.187
5	Saan-T	—	1.25	VAL	−0.044	7.6	1.1	−0.219	0.250
6	Dab-T	—	1.01	ALA	−0.043	11.8	0.8	−0.148	−0.110
Coast									
7	SK	0–15	−0.35	SER	0.015	7.2	1.9	0.260	0.145
8	FF	0–15	0.32	GLU	0.065	10.0	2.3	−0.077	−0.444
9	GB-2	1–15	−0.11	MET	0.134	1.2	1.0	0.104	−0.076
10	BG-A	0–15	0.40	PHE	0.134	3.7	1.2	−0.115	0.242
11	GB-1	0–1	0.13	ILE	0.139	4.5	0.8	−0.129	0.197
12	BV	0–15	0.38	HIS	0.158	1.0	0.8	0.077	−0.103
13	BG-B	0–15	1.01	LEU	0.169	6.6	1.5	−0.121	0.016
14	Saan-S1	0–1	0.20	TYR	0.178	2.1	1.2	0.065	0.003
15	Dab-S1	0–1	0.09						
16	Saan-S2	74–80	0.22						
17	Dab-S2	48–50	0.06						
Med									
18	Med-1	0–0.5	−0.92						
19	Med-2	9–11	−2.02						
20	SAP	24.5–25	0.67						
Tur-ox									
21	Ox-1	756–766	−2.17						
22	Ox-2	767–777	−1.41						
23	Ox-3	780–789	−1.47						
24	Ox-4	795–802	−1.53						
25	Red-1	807–817	−0.30						
Tur-red									
26	Red-2	855–868	−0.02						
27	Red-3	905–916	0.01						
28	Red-4	927–940	−0.31						

Recently, the molecular composition of protein amino acids was used to derive a quantitative DI (Dauwe and Middelburg 1998). Here, we significantly extend this approach to a wider range of diagenetic conditions and present a more balanced data set, including older and calcareous sediments. The revised DI will be linked to the fraction of chemically hydrolyzable amino acids that is enzymatically available within 6 h and the first-order rate constant for mineralization of bulk organic carbon.

Materials—We have examined the protein amino acid composition (based on the 14 most common protein amino acids; Table 1) of marine particulate matter samples across a wide range of degradation states. The samples were comprised of unaltered source organisms (phytoplankton, bacteria, and zooplankton); partly degraded sediment-trap material from Dabob Bay (Cowie and Hedges 1992) and Saanich Inlet (Cowie et al. 1992); progressively degraded coastal sedimentary organic matter from the North Sea (Dau-

we and Middelburg 1998), Dabob Bay (Cowie and Hedges 1992), and Saanich Inlet (Cowie et al. 1992); and extensively degraded organic matter from hemipelagic and sapropelic sediments in the Eastern Mediterranean (de Lange et al. 1994). Eastern Mediterranean deep-sea sediments consist of interbedded organic carbon-poor and organic carbon-rich deposits. Sapropels, layers with >2 wt % of organic carbon, are formed during periods of enhanced carbon fluxes to the seafloor and/or increased preservation due to bottom-water oxygen depletion (Rossignol-Strick et al. 1982). We have also included a depth profile through the oxidized and reduced sections of an abyssal turbidite from the Madeira Abyssal Plain (MAP), eastern Atlantic (Prahl et al. 1989; de Lange et al. 1994). Turbidites are deposits originating from catastrophic deposition events that transport large masses of sediments from the continental slopes down to deep abyssal plains. A remarkable feature of the distal MAP turbidites is their homogeneity upon emplacement (Prahl et al. 1989). Postdepositional exposure to oxygen (and nitrate) under pelagic conditions for about 10–20 kyr caused carbon removal in the uppermost section due to a downward-progressing oxidation front (Wilson et al. 1986). The lowermost section of the initially homogeneous sediments has survived postoxic conditions without significant degradation for about 140 kyr (Weaver and Kuijpers 1983; Cowie et al. 1995; Prahl et al. 1997).

Analytical methods—Amino acid and hexosamine concentrations were determined on freeze-dried sediment after hydrolysis by reverse-phase high-pressure liquid chromatography (HPLC), as described by Dauwe and Middelburg (1998) or as taken from the literature. Literature data are also based on reverse-phase HPLC and precolumn derivatization with *o*-phthalaldehyde (OPA) (Lindroth and Mopper 1979), and mole percentage values have been recalculated to a common set of amino acids.

Enzymatically hydrolyzable amino acids (EHAA) and total hydrolyzable amino acids (THAA) were determined following the method introduced by Mayer et al. (1995), which has been described in detail by Dauwe et al. (1999). Briefly, sediment-buffer slurries with added bacterial inhibitor (0.1 M sodium arsenate and 0.1 mM pentachlorophenol in a pH 8 sodium phosphate buffer) and a nonspecific proteolytic enzyme (“Proteinase-k” by Sigma No. P8044) were incubated for 6 h. Trichloroacetic acid was added to stop the reaction and to precipitate the low-molecular-weight (LMW) bioavailable fraction. The LMW fraction and freeze-dried sediment were hydrolyzed, and the amino acid concentration was determined by fluorimetry following derivatization with OPA. The fraction EHAA:THAA will be used as a measure of bioavailability of the peptide pool. The reactivity of the organic material was calculated as a first-order decomposition rate constant ($k \text{ yr}^{-1}$) (Hargrave and Phillips 1981) as $k = -(1/t_1) \cdot \ln(C_1/C_0)$ where k the first-order degradation constant, t_1 is the incubation period, C_0 is the organic carbon concentration at the beginning of the time course, and C_1 is the organic carbon concentration at time t_1 ($C_0 - \Sigma \text{CO}_2$). The production of inorganic carbon was measured using sediment–water slurries during 3-week (North Sea samples) and

11-week (Eastern Mediterranean samples) incubations in the dark as described by Dauwe (1999).

Organic carbon was determined on freeze-dried samples that had been finely powdered and homogenized. A 20–50-mg split was combusted at 1,010°C in a Carlo Erba Elemental Analyzer NA-1500 after removal of carbonate by in situ acidification with 25% HCl within silver sample cups (Nieuwenhuize et al. 1994). The 0–15-cm depth-integrated values reported in Table 1 were derived from the analysis of multiple depth intervals within the sediment as described by Dauwe (1999) for the determination of the first-order degradation rate constant, by Dauwe et al. (1999) for the determination of %EHAA:THAA, and by Dauwe and Middelburg (1998) for the amino acid concentrations. The other samples have been analyzed only at the depth intervals indicated in Table 1.

Results and discussion—The protein amino acid spectra of these 28 samples were used in a variance-oriented method (Principal Component Analysis = PCA) to derive the principal components, which have the property that the maximum variance is found along the first axis, the maximum of the remainder along the second axis, etc. Factor coefficients (also known as unrotated loadings) give the relation between the PCA axis and the original variables (mole percentage of protein amino acids), while factor scores quantify relative positions of samples along the PCA axis.

The first axis of the PCA explains 36% of the total variation and has positive coefficients for tyrosine, leucine, histidine, isoleucine, phenylalanine, and methionine and negative coefficients for threonine, arginine, aspartic acid, and glycine (Table 1). The second axis of the PCA explains another 24% of the total variation and has positive coefficients for glycine and serine and negative coefficients for valine, arginine, alanine, isoleucine, leucine, and phenylalanine (Table 1). The third axis explains another 14% of the total variation, has positive loadings for valine, phenylalanine, isoleucine, glycine, and serine, and has negative loadings for glutamic acid, aspartic acid, alanine, and histidine (Table 1).

The behavior of most amino acids found in this comprehensive analysis agrees well with results of a PCA on a more limited data set, dominated by coastal sediments (Dauwe and Middelburg 1998). Because the first axis is interpreted to reflect organic matter degradation, scores on this axis can be considered as degradation state indicators (Fig. 1). The amino acids leucine, isoleucine, and phenylalanine decrease over the entire range of the DI (Fig. 1A–C), while the amino acids tyrosine, histidine, and methionine decrease rapidly during the initial stages of alteration (Fig. 1D–F).

The preferential accumulation of glycine and threonine is probably due to their concentration in cell walls (Hecky et al. 1973) that are preserved during sinking and decomposition (Siezen and Mague 1978; Lee and Cronin 1984; Müller et al. 1986), whereas amino acids that are concentrated in cell plasma (tyrosine, phenylalanine, and glutamic acid) (Hecky et al. 1973) tend to be depleted during degradation. Sediment-trap studies sampling POM at increasing depth in the water column confirm these compositional changes of amino acids during decay (Lee and Cronin 1984; Cowie and Hedges 1992; Cowie et al. 1992).

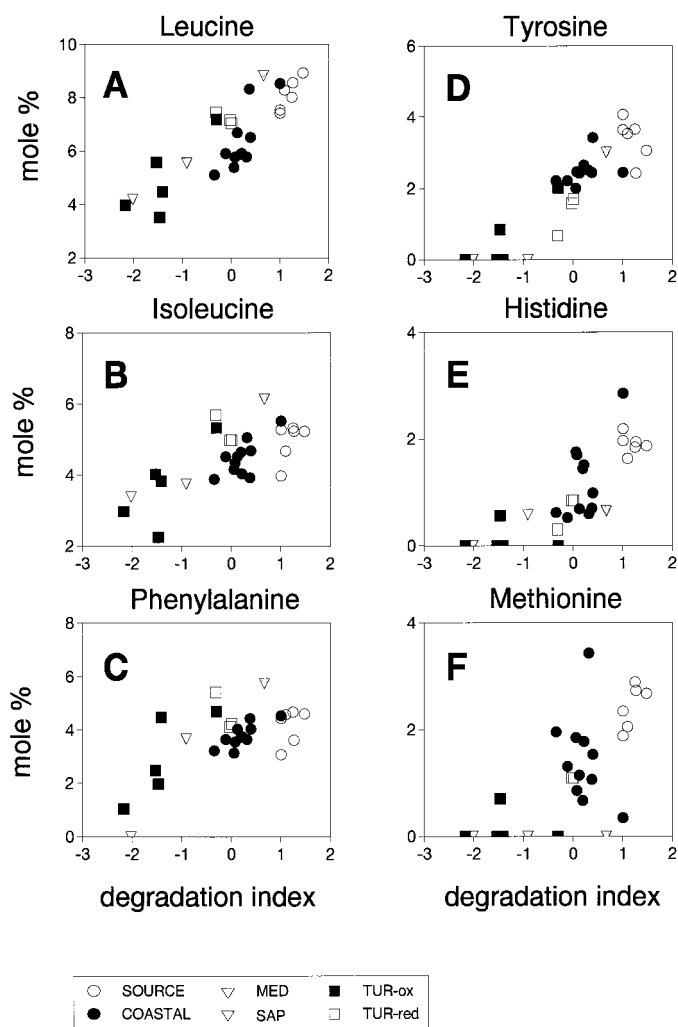


Fig. 1. Mole percentage of selected individual amino acids vs. the DI. Legend abbreviations are in Table 1.

The amino acid-based DI varies from -2.2 to 1.5 (Fig. 1), with sources such as phytoplankton, bacteria, and sediment-trap matter having DIs between 1 and 1.5 , which are higher than those of POM in coastal and ocean margin sediments (-0.3 to 1) and of refractory POM from pelagic deep-sea sediments (< -1). Moreover, subsurface layers are generally more degraded than surface samples (Table 1), except for the Eastern Mediterranean sapropel that appears less degraded, perhaps due to bottom-water oxygen depletion (Rossignol-Strick et al. 1982). Coastal sediments are important sites of POM burial and degradation (Middelburg et al. 1997). The North Sea samples vary from labile ($+1$) to rather refractory (-0.3) due to extensive predepositional degradation during repetitive deposition-erosion cycles (Dauwe and Middelburg 1998).

The DI also tracks the extent of degradation of the MAP turbidite as a result of postdepositional exposure to bottom-water oxygen and nitrate (Fig. 2). The upper oxidized layer is depleted in organic carbon (0.2 – 0.4 wt % total organic carbon [TOC]) and has a lower DI (-2.2 to -1.4) than the reduced layer (1.1 wt % TOC with a DI = 0 to -0.3). The

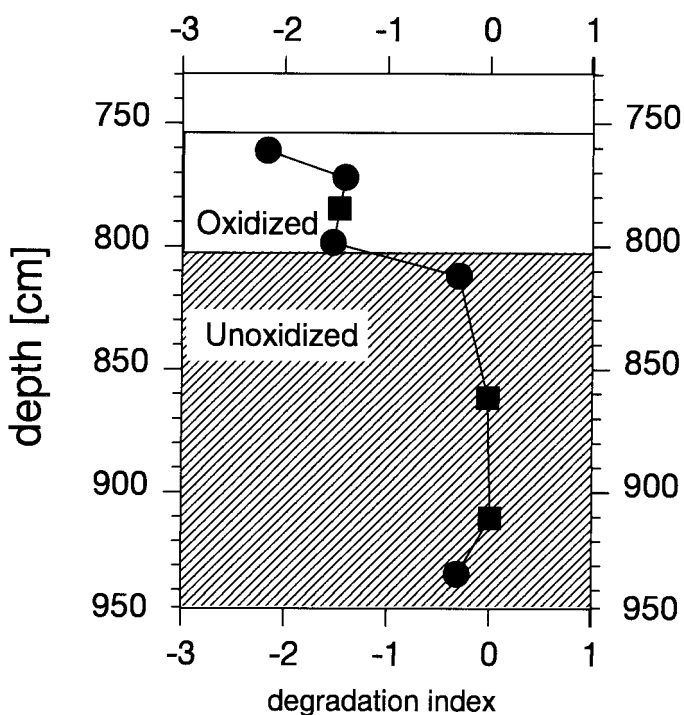


Fig. 2. Changes in the DI between the oxidized upper (light shading) and unoxidized lower (dark shading) core section of MAP turbidite f in core 86P25 (Prahl et al. 1989; de Lange et al. 1994; Cowie et al. 1995; Prahl et al. 1997). The oxidized section (0.2 wt % TOC in the surface samples 21–22; 0.4 wt % sample 24) is depleted in organic carbon relative to the reduced section (1.1 wt % TOC) due to postdepositional exposure to bottom-water oxygen and nitrate. Solid dots and squares are based on methods of Dauwe and Middelburg (1998) and de Lange et al. (1994), respectively. The uppermost sample has been affected by bioturbation.

extent of degradation of the unoxidized layer is comparable to that of refractory North Sea sediments (-0.1 to -0.3), confirming the often-made assumption that this section has not been altered significantly since its export from the continental margin (Cowie et al. 1995; Prahl et al. 1997). Oxidation of the upper section has occurred in the absence of benthic animals, except for the top sample, which has the lowest index (-2.2), possibly due to mixing with more refractory pelagic material or stimulation of degradation by the activity of fauna (Kristensen and Blackburn 1987).

The correlation of the DI with the mole percentage of the nonprotein amino acids, γ -aminobutyric acid (GABA) and β -alanine (BALA) (Fig. 3A), and the hexosamines, glucosamine and galactosamine (Fig. 3B), demonstrates the consistency of the DI with well-established indicators of diagenetic alteration. The microbial production of GABA and BALA from their protein precursors and their subsequent preservation in sedimentary deposits has been proposed as a degradation state indicator of marine sediments (Lee and Cronin 1984; Cowie and Hedges 1994). Similarly, hexosamines are generally incorporated into structural biopolymer matrices such as bacterial cell walls and chitinous material (de Leeuw and Largeau 1993) and are enriched in more refractory materials (Dauwe and Middelburg 1998). These

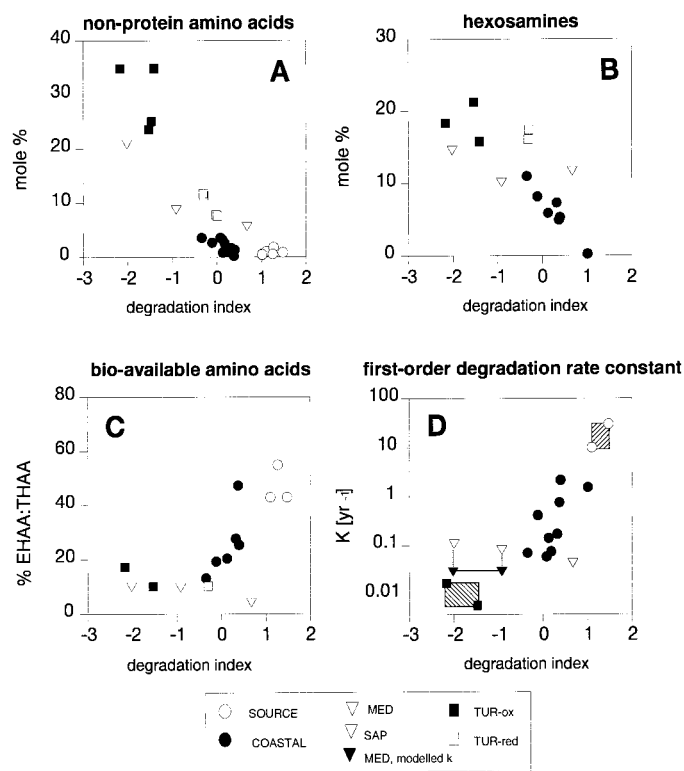


Fig. 3. Changes in the biochemical composition and degradation kinetics of organic matter vs. the protein amino acid-derived DI. (A) Mole percentage of nonprotein amino acids (γ -aminobutyric acid + β -alanine). (B) Mole percentage of hexosamines (glucosamine + galactosamine). No data are available for samples 1–6, 14–17, 23, 26, and 27. (C) Fraction of enzymatically hydrolyzable amino acids with respect to the pool of total acid hydrolyzable amino acids (%EHAA:THAA) that is released after incubation with a proteolytic enzyme. No data are available for samples 4–6, 13–17, 22, 23, and 26–28. Samples 1–3 (phytoplankton and bacteria) are based on laboratory cultures (Dauwe et al. 1999). (D) First-order rate constant (k) of organic matter degradation. K -values of samples 7–13 (North Sea) and 18–20 (Eastern Mediterranean) are based on the ratio of the amount of CO_2 generated during sediment–water slurry incubations and organic carbon contents. Other k -values are based on modeling degradation experiments (phytoplankton) (Middelburg 1989) and solid-phase organic carbon profiles; MAP turbidites (Wilson et al. 1986), Saanich inlet sediments (Cowie et al. 1992), Dabob Bay sediments (Cowie and Hedges 1992), and Eastern Mediterranean sediments (Jung et al. 1997). No data are available for samples 3–6 and 25–28.

nonprotein amino acids and hexosamines are sensitive indicators for intermediate to extensively degraded materials ($\text{DI} < 0.5$).

The results presented here confirm that the protein amino acid-based DI covers a very wide range of alteration stages, is uncompromised by source variations, and is robust with regard to differences in analytical methods (Fig. 2). It provides a solid frame to determine the relative reactivity, and hence applicability, of different biomarkers under various natural conditions, which is a prerequisite for reliable reconstruction of paleoenvironmental processes and environments. The DI can also be used to quantitatively link amino acid

compositional characteristics of organic matter with dynamics of organic matter degradation and biological availability of organic matter.

The DI is correlated with the fraction of hydrolyzable amino acids (%EHAA:THAA) that is released after incubation with a proteolytic enzyme for 6 h (Fig. 3C). This biomimetic, kinetics-based approach (Mayer et al. 1995) is most sensitive during the initial to intermediate stages of alterations ($\text{DI} > -0.5$), similar to histidine, methionine and tyrosine (Fig. 1D–F). About 10% of the amino acids is always available from the pore waters or through desorption and does not require proteolytic enzymes (Dauwe et al. 1999). This relationship between amino acid composition characteristics and biological availability indicates that alteration results in compositional changes that lower the availability of amino acids to enzymes and hence, the nutritional value of the associated organic matter to organisms.

This applicability to a wide range of degradation states allows us to link the DI to the first-order rate constant (k) for POM degradation (Middelburg 1989). The logarithm of measured and model-based literature-derived first-order degradation rate constants for TOC is linearly correlated ($r^2 = 0.47$, $n = 15$, $P < 0.005$) with the DI based on protein amino acids (Fig. 3D). This is the first direct relationship between organic matter degradation state, amino acid compositional characteristics, and bulk organic carbon degradation kinetics. It appears that though they contribute only about 10–30% to the total carbon pool in sediments (i.e., Dauwe and Middelburg 1998), amino acids provide representative information on the bulk organic matter degradation state. Moreover, the logarithm of the first-order degradation rate constant is correlated linearly with the logarithm of degradation time (Middelburg 1989). Hence, through coupling of the DI– k relation and the power model (Middelburg 1989) time– k relation (Fig. 3D), there is in principle a coupling of degradation time with amino acid composition and amino acid compositional changes. Application of these relations to other sediments should make it possible to determine the lability, degradation history, and preservation potential of the associated organic matter. This tool will improve our capabilities of predicting the effect of diagenesis on carbon preservation and the formation of fossil fuel sources.

Birgit Dauwe
Jack J. Middelburg¹
Peter M. J. Herman
Carlo H. R. Heip

Netherlands Institute of Ecology
Centre for Estuarine and Coastal Ecology
P.O. Box 140
4400 AC Yerseke, The Netherlands

¹ Corresponding author.

Acknowledgments

We thank Leon Moodley, Ralf Haese, and Gert de Lange for providing samples; Eric Boschker, Rick Keil, John Hedges, and an anonymous reviewer for constructive comments; and Jan Sinke, Joop Nieuwenhuize, and Pieter van Rijswijk for analytical support. This work was supported by the Netherlands Organization for the Advancement of Science, project VvA, under grant 770-18-235, and the MAST and ENVIRONMENT programs of the European Commission. Publication 2541 of the Netherlands Institute of Ecology.

References

- BROWN, M. R. 1991. The amino-acid and sugar composition of 16 species of microalgae used in mariculture. *J. Exp. Mar. Biol. Ecol.* **145**: 79–99.
- COWIE, G. L., AND J. I. HEDGES. 1992. Sources and reactivities of amino acids in a coastal marine environment. *Limnol. Oceanogr.* **37**: 703–724.
- , AND ———. 1994. Biochemical indicators of diagenetic alteration in natural organic matter mixtures. *Nature* **369**: 304–307.
- , ———, AND S. E. CALVERT. 1992. Sources and relative activities of amino acids, neutral sugars, and lignin in an intermittently anoxic marine environment. *Geochim. Cosmochim. Acta* **56**: 1963–1978.
- , ———, F. G. PRAHL, AND G. J. DE LANGE. 1995. Elemental and major biochemical changes across an oxidation front in a relict turbidite: An oxygen effect. *Geochim. Cosmochim. Acta* **59**: 33–46.
- DAUWE, B. 1999. Organic matter quality in North Sea sediments. Ph.D. thesis, Univ. of Groningen.
- , 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. VAN RIJSWIJK, J. SINKE, P.M.J. HERMAN, AND C.H.R. HEIP. 1999. Enzymatically hydrolyzable amino acids in North Sea sediments and their possible implication for sediment nutritional values. *J. Mar. Res.* **57**: 109–134.
- DE LANGE, G. J., AND OTHERS. 1994. Possible early diagenetic alteration of Paleo proxies, p. 225–228. *In* R. Zahn [ed.], Carbon cycling in the glacial ocean. NATO ASI series edition, v. 1/17. Springer.
- DE LEEUW, J. W., AND C. LARGEAU. 1993. A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal, and petroleum formation, p. 23–63. *In* M. H. Engel and S. A. Macko [eds.], Organic geochemistry: Principles and applications. New York: Plenum.
- HARGRAVE, B. T., AND G. A. PHILLIPS. 1981. Annual *in situ* carbon dioxide and oxygen flux across a subtidal marine sediment. *Estuarine Coastal Shelf Sci.* **12**: 725–737.
- HECKY, R. E., K. MOPPER, P. KILHAM, AND E. T. DEGENS. 1973. The amino acid and sugar composition of diatom cell-walls. *Mar. Biol.* **19**: 323–331.
- JUNG, M., J. ILMBERGER, A. MANGINI, AND K. C. EMEIS. 1997. Why some Mediterranean sapropels survived burn-down (and others did not). *Mar. Geol.* **141**: 51–60.
- KEIL, R. G., D. B. MONTLUÇON, F. G. PRAHL, AND J. I. HEDGES. 1994. Sorptive preservation of labile organic matter in marine sediments. *Nature* **370**: 549–552.
- KRISTENSEN, E., AND T. H. BLACKBURN. 1987. The fate of organic carbon and nitrogen in experimental marine sediment systems: Influence of bioturbation and anoxia. *J. Mar. Res.* **45**: 231–257.
- LEE, C., AND C. CRONIN. 1984. Particulate amino acids in the sea: Effects on primary productivity and biological decomposition. *J. Mar. Res.* **42**: 1075–1097.
- 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.
- MAYER, L. M. 1994. Surface area control of organic carbon accumulation in continental shelf sediments. *Geochim. Cosmochim. Acta* **58**: 1271–1284.
- , L. L. SCHICK, T. SAWYER, C. J. PLANTE, P. A. JUMARS, AND R.F.L. SELF. 1995. Bioavailable amino acids in sediments: A biomimetic, kinetics-based approach. *Limnol. Oceanogr.* **40**: 511–520.
- MIDDELBURG, J. J. 1989. A simple rate model for organic matter decomposition in marine sediments. *Geochim. Cosmochim. Acta* **53**: 1577–1581.
- , K. SOETAERT, AND P.M.J. HERMAN. 1997. Empirical relationships for use in global diagenetic models. *Deep-Sea Res. Part I. Oceanogr. Res. Pap.* **44**: 327–344.
- MÜLLER, P. J., E. SUESS, AND C. A. UNGERER. 1986. Amino acids and amino sugars of surface particulate and sediment trap material from waters of the Scotia Sea. *Deep-Sea Res. Part I. Oceanogr. Res. Pap.* **33**: 819–838.
- NIEUWENHUIZE, J., Y.E.M. MAAS, AND J. J. MIDDELBURG. 1994. Rapid analysis of organic carbon in particulate materials. *Mar. Chem.* **45**: 217–224.
- PRAHL, F. G., G. J. DE LANGE, M. LYLE, AND M. A. SPARROW. 1989. Post-depositional stability of long-chain alkenones under contrasting redox conditions. *Nature* **341**: 434–437.
- , ———, S. SCHOLTEN, AND G. L. COWIE. 1997. A case of post-depositional degradation of terrestrial organic matter in turbidite deposits from Madeira Abyssal Plain. *Org. Geochem.* **27**: 141–152.
- ROSSIGNOL-STRICK, M., W. NESTEROFF, P. OLIVE, AND C. VERGNAUD-GRAZZINI. 1982. After the deluge: Mediterranean stagnation and sapropel formation. *Nature* **295**: 105–110.
- SIEZEN, R. J., AND T. H. MAGUE. 1978. Amino acids in suspended particulate matter from oceanic and coastal waters of the Pacific. *Mar. Chem.* **6**: 215–231.
- TEGELAAR, E. W., S. DERENNE, C. LARGEAU, AND J. W. DE LEEUW. 1989. A reappraisal of kerogen formation. *Geochim. Cosmochim. Acta* **53**: 3103–3107.
- TENORE, K. R., R. B. HANSON, J. MCCLAIN, A. E. MACCUBBIN, AND R. E. HODSON. 1984. Changes in composition and nutritional value to a benthic deposit feeder of decomposing detritus pools. *Bull. Mar. Sci.* **35**: 299–311.
- 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.
- WEAVER, P.P.E., AND A. KUIJPERS. 1983. Climatic control of turbidite deposition on the Madeira Abyssal Plain. *Nature* **306**: 360–363.
- WILSON, T.R.S., J. THOMSON, D. J. HYDES, S. COLLEY, F. CULKIN, AND J. SØRENSEN. 1986. Oxidation fronts in pelagic sediments: Diagenetic formation of metal-rich layers. *Science* **232**: 972–975.

Received: 15 September 1998

Accepted: 25 May 1999

Amended: 8 June 1999