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Accumulation of prokaryotic remains during organic matter diagenesis in surface sediments off Peru

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Abstract

Bacterial biomarkers (D-amino acids and muramic acid) were investigated in surface sediments (0–1 cm) at 22 stations in the Peru margin. Concentrations were used to quantitatively estimate the relative importance of peptidoglycan in the preservation of prokaryotic remains during diagenesis. The bacterial imprint in organic matter was also evident from low molar ratios (average of 1.6) of glucosamine and galactosamine. Estimates of the fraction of biomarkers associated with intact peptidoglycan showed that peptidoglycan became a progressively less important component of prokaryotic remains with ongoing diagenesis, whereas other prokaryotic biomolecules increased in importance. The exact nature of these biomolecules remains unknown, but constant ratios between individual D-amino acids and amino sugars observed in this study provide novel information on their molecular composition. Examination of total hydrolyzable amino acids revealed systematic compositional changes with increasing water depth and age of the sediment, reflecting increased diagenetic alteration of the organic matter. The time scale integrated in the upper 1 cm of the sediment was ca. 2 yr at the shallow sites and up to 20 yr at the deeper stations. The alteration stages of organic matter ranged from coastal and ocean margin sediments at shallow water depth to organic matter as degraded as hemipelagic surface sediments at greater water depths.

Burial of organic matter (OM) in marine sediments represents the major link between the "active" surface pools of carbon in the oceans, in the atmosphere, on land, and in marine sediments, and carbon pools that cycle on much longer, geologic time scales, i.e., carbon in sedimentary rock, coal, and petroleum deposits (Burdige 2007). Hence, understanding the processes that control rates and extent of OM burial in marine sediments is essential for understanding the long-term global carbon cycle.

Prokaryotic organisms (Bacteria and Archaea) play an important role in the degradation and transformation of OM. In marine sediments, they account for most of the OM remineralization (Jørgensen 2000) but they also contribute to the pool of living and nonliving sedimentary OM. Bacteria synthesize a variety of unique organic compounds that can be used to trace bacterial OM, e.g., D-amino acids and muramic acid (Mur), which are building blocks of the cell wall polymer peptidoglycan (Madigan et al. 2009). In earlier sediment studies, D-amino acids have been used as peptidoglycan biomarkers, and relative increases of D- over L-amino acids have been interpreted as a preferential accumulation of bacterial peptidoglycan over proteinaceous material (Pedersen et al. 2001; Grutters et al. 2002; Lomstein et al. 2006). There is increasing evidence that, in addition to peptidoglycan, other bacterial remains contribute to the bacterial fraction of detrital OM (Benner and Kaiser 2003; Niggemann and Schubert 2006; Kaiser and Benner 2008). The macromolecular identity of these bacterial remains is still unknown, but similar amino sugar ratios observed in particulate and dissolved OM from the oceanic water column (Benner and Kaiser 2003) and in marine sediments (Liebezeit 1993; Niggemann and Schubert 2006) indicate a universal prokaryotic signature in detrital OM.

During diagenesis the molecular composition of OM changes (Wakeham et al. 1997). The observation that these changes follow some general pattern led to the definition of diagenetic indicators, and several are based on relative abundance and composition of amino acids (Cowie and Hedges 1994). Proteins are ubiquitous components of living organisms and represent a significant fraction of OM in recent coastal sediments (Keil et al. 2000). Over a wide range of time scales, amino acids are degraded faster than bulk OM (Cowie and Hedges 1992, 1994; Wakeham and Lee 1993). As a consequence, the percentage of total organic carbon (TOC) present as amino acid carbon ($\%T_{AA}C$) and the percentage of total nitrogen (TN) present as amino acid nitrogen ($\%T_{AA}N$) are particularly useful as diagenetic indicators; they are sensitive at different stages of OM alteration and appear uncompromised by source variation (Cowie and Hedges 1994). The relative abundance of non-protein amino acids is also widely used as a diagenetic indicator, e.g., the ratios of protein precursor amino acids (e.g., aspartic acid [Asp] and glutamic acid [Glu]) and their respective non-protein degradation products (β-alanine [β-Ala] and γ-aminobutyric acid [γ-Aba]) decrease during diagenesis (Cowie and Hedges 1992). The molar composition of protein amino acids also changes during diagenesis, and the observation that this follows some general pattern led to the development of the degradation index (DI) by Dauwe and Middelburg (1998). The DI is based on a principal component analysis

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on the total hydrolyzable amino acid (THAA) composition of samples that covered a wide range of diagenetic stages from fresh phytoplankton to highly degraded OM in a turbidite (Dauwe and Middelburg 1998; Dauwe et al. 1999). Applied together, the amino acid–based diagenetic indicators offer congruent information on the relative diagenetic stage and reaction potential of natural OM (Cowie and Hedges 1994; Keil et al. 2000).

In this study, we investigated the accumulation of prokaryotic remains during diagenesis of sedimentary OM. We used a biomarker approach to estimate the contribution of bacterial peptidoglycan subunits to the nonliving OM pool. The degradation stage of sedimentary OM was evaluated by use of amino acid–based and amino sugar–based diagenetic indicators. The abundance and molecular distribution of several biomarkers (D-amino acids and Mur) were determined together with concentrations of total hydrolyzable amino acids and the amino sugars glucosamine (GlcN) and galactosamine (GalN). Our results indicate that other remains of prokaryotes than peptidoglycan became increasingly important in the OM accumulating in more degraded sediments.

Methods

Regional settings and study site—The upwelling off Peru is perennial, wind-driven, and presently most intense in the zones 7–8°S, 11–12°S, and 14–16°S (Zuta and Guillén 1970). The upwelling system is dominated by two currents: the equator-flowing, O_2-rich Peru–Chile Current in the upper 200 m of the water column, and the polar-flowing Peru Undercurrent (Hill et al. 1998). The latter transports oxygen-poor, nutrient-rich water, which is brought to the euphotic zone by upwelling. This results in high primary production, which leads to high sedimentation rates. Mineralization of the large amount of sinking OM results in an oxygen minimum zone (OMZ), which is located at ~50–650 m water depth (Emeis et al. 1991). High primary production, high sedimentation rates, shallow water depth, and oxygen limitation in the water column and sediments favor the accumulation of organic-rich sediments (Thiede and Suess 1983). The sedimentary OM off Peru is predominantly of marine origin, because input from the dry coastal area is limited (Niggemann 2005). The investigated region off Peru reached from 9.5°S to 13.5°S and included both shelf and slope (Fig. 1).

Sampling and sample processing—Sampling was carried out during RV *Sonne* cruise 147 in June 2000. Sediment cores from 22 stations were retrieved by multicorer sampling from water depths of 50–1369 m (Table 1). For analyses, the upper 0–1-cm interval of the sediment cores was transferred to clean glass vials and frozen at −25°C immediately after sampling. The samples were freeze-dried and homogenized by grinding in an agate mortar.

Total hydrolyzable amino acids and amino sugars—Freeze-dried sediment samples (~0.5 g) were hydrolyzed with 10 mL of 6 mol L^{-1} HCl at 105°C for 24 h under N_2, after which the samples were placed in an ice bath to stop

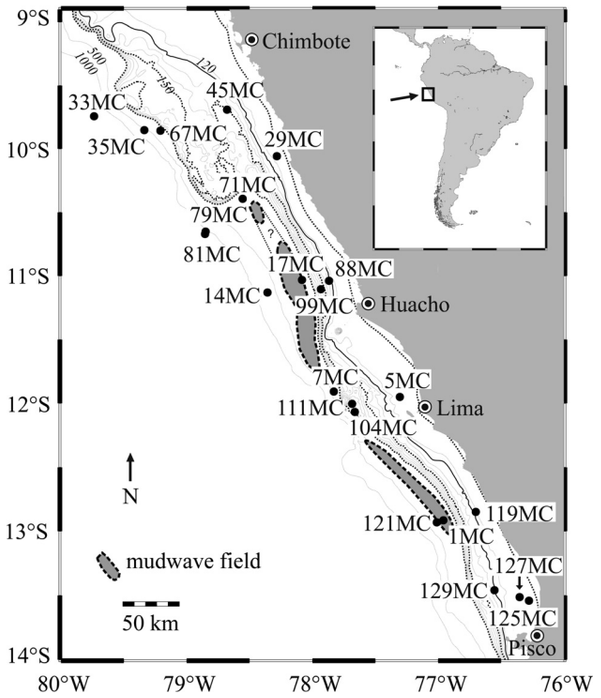

Fig. 1. Chart of investigated area with bathymetry and sampling sites plotted (modified from Reinhardt et al. 2002).

the hydrolysis. Subsamples of hydrolyzate (100 μL) were transferred to new glass vials, dried under vacuum at 50°C, redissolved in Milli-Q water, and dried again following the procedure described in Lomstein et al. (2006). The dried samples were then dissolved in 4 mL Milli-Q water, and subsamples (~3 mL) were filtered (0.2-μm filter; Satorius) into pico vials. The concentration of THAA in the dissolved hydrolyzate was analyzed by reverse-phase high-performance liquid chromatography (HPLC) of fluorescent *o*-phthaldialdehyde–derived products according to the method of Lindroth and Mopper (1979). The concentrations of the individual amino acids were calculated from individual standard curves, produced from a mixture of the amino acid standard solution AA-S-18 (Sigma-Aldrich) to which were added β-Ala, γ-Aba, taurine (Tau) and ornithine (Orn). L-aminobutyric acid (L-Aba) was used as an internal standard, because L-Aba was not present in the samples. Estimates of $\%T_{AA}C$ and $\%T_{AA}N$ were based on the 18 identified amino acids and TOC and TN concentrations obtained from Niggemann (2005). The concentration of the two amino sugars GlcN and GalN in the dissolved hydrolyzate was calculated from individual standard curves, produced from a mixture of GlcN and GalN standards (Sigma G4875 and G0500, respectively) to which was added L-Aba as internal standard. Concentrations were corrected for losses during hydrolysis, which were 25.5% and 21.6% for GlcN and GalN, respectively.

Mur was measured in a separate chromatographic HPLC analysis following the procedure described previously for THAA analysis, with the exception that freeze-dried sediment samples (~100 mg) were hydrolyzed with

Table 1. Sampling sites with positions of stations, water depth, sediment location relative to water column oxygen minimum zone (OMZ), surface sediment (0–1 cm) total organic carbon (TOC) in percentage of sediment dry weight, and the C : N ratio given as the molar ratio between TOC and total nitrogen.

Station	Latitude	Longitude	Water depth (m)	Location relative to OMZ*	TOC† (% dry wt)	C : N†
1MC	12°55.21′S	76°58.25′W	321	Within	20.2	10.4
5MC	11°56.95′S	77°18.04′W	96	Upper edge	3.7	8.7
7MC	11°54.36′S	77°49.73′W	282	Within	12.9	10.3
14MC	11°08.00′S	78°21.33′W	654	Below	6.1	8.6
17MC	11°01.63′S	78°04.72′W	252	Within	12.2	9.1
29MC	10°03.28′S	78°17.10′W	102	Upper edge	4.9	8.2
33MC	9°44.56′S	79°44.22′W	1369	Below	5.7	10.0
35MC	9°51.15′S	79°20.32′W	598	Below	6.4	7.7
45MC	9°41.47′S	78°40.99′W	153	Within	14.1	9.1
67MC	9°51.52′S	79°12.74′W	270	Within	5.6	7.9
71MC	10°23.42′S	78°33.51′W	238	Within	14.3	10.1
79MC	10°39.17′S	78°51.17′W	1174	Below	3.7	9.1
81MC	10°40.04′S	78°51.15′W	1278	Below	3.3	9.1
88MC	11°01.56′S	77°52.35′W	127	Within	7.8	7.8
99MC	11°06.53′S	77°58.41′W	219	Within	13.1	7.9
104MC	12°03.68′S	77°39.84′W	185	Within	5.2	7.9
111MC	12°00.55′S	77°40.70′W	179	Within	13.8	8.5
119MC	12°50.79′S	76°42.05′W	115	Within	7.3	9.6
121MC	12°55.54′S	77°00.12′W	360	Within	16.4	10.3
125MC	13°32.19′S	76°16.97′W	50	Upper edge	1.9	7.9
127MC	13°30.87′S	76°21.03′W	86	Upper edge	4.7	10.7
129MC	13°28.05′S	76°33.13′W	123	Upper edge	11.1	9.8

* After Böning et al. (2004).
† After Niggeman (2005).

2 mL of 3 mol L^{-1} HCl at 95°C for 4 h under N_2. L-Aba was used as internal standard. The concentration of total hydrolyzable amino sugars (THAS) was the sum of GlcN, GalN, and Mur.

Blanks were prepared in the same way as samples, except that sediment was omitted. The blanks showed negligible concentrations of amino acids and amino sugars from handling and reagents.

During strong acid hydrolysis, acetyl groups are removed from amino sugars, but in this study we do not know whether the amino sugars were acetylated prior to hydrolysis. Calculations of amino sugar carbon contents in the samples were based on six carbon atoms per amino sugar, as done by Benner and Kaiser (2003).

DI—The DI was calculated for each station to test whether the inter-site trend observed in the molar composition of THAA could be used to rank the stations in terms of OM quality, as suggested by Dauwe and Middelburg (1998). The factor coefficients, averages, and standard deviations from Dauwe et al. (1999) were used to calculate the DI.

The DI was estimated according to the formula

$$\mathrm{DI} = \sum_i [(\mathrm{var}_i - \mathrm{AVGvar}_i)/\mathrm{STDvar}_i] \times \mathrm{fac.coef}_i \quad (1)$$

where var_i is the nonstandardized mole percentage of amino acid i, AVGvar_i and STDvar_i are the mean and standard deviation in the dataset, and $\mathrm{fac.coef}_i$ is the factor coefficient for amino acid i (Dauwe and Middelburg 1998).

Stereochemical composition of selected amino acids—D- and L-isomers of Glu, serine (Ser), and alanine (Ala) were measured in THAA according to the HPLC method given in Mopper and Furton (1991), with the modifications described in Guldberg et al. (2002). The only modification to Guldberg et al. (2002) was that the internal standard β-amino glutaric acid was replaced with L-glutamine. An attempt was also made to quantify D-aspartic acid, but because of low concentrations of this amino acid, which eluted as a shoulder on a much higher L-aspartic acid (L-Asp), it was not possible to quantify it. The concentrations of the D- and L-isomers of Glu, Ser, and Ala were calculated from individual three- to five-point calibration curves of the respective amino acids. Blanks were prepared as described previously and showed negligible amino acid concentrations compared to samples.

D- and L-concentrations of the respective amino acids were corrected for racemization during the liquid-phase acid hydrolysis according to Kaiser and Benner (2005). They found that the average percentages of D-enantiomers ($\%\mathrm{D} = 100 \times [\mathrm{D}/(\mathrm{D} + \mathrm{L})]$) produced during acid hydrolysis of L-enantiomers were 2.0%, 0.3%, and 1.2% for Glu, Ser, and Ala, respectively.

Results

Concentrations of THAA and amino sugars—Surface (0–1 cm) concentration of THAA varied between 601 μmol g dry wt^{-1} (Sta. 1MC, 321 m) and 50 μmol g dry wt^{-1} (Sta. 81MC, 1278 m). The highest concentrations of THAA were

Table 2. Mole percentage composition for each hydrolyzable amino acid and concentration of total hydrolyzable amino acids (THAA) in surface sediments off Peru.*

Station	Water depth (m)	Mole %																		[THAA] (μmol g dry wt^{-1})
		Asp	Glu	Ser	His	Gly	Thr	Arg	β-Ala	Tau	Ala	γ-Aba	Tyr	Val	Phe	Ileu	Leu	Orn	Lys	
1 MC	321	12.7	9.4	9.1	1.7	17.9	8.0	3.8	0.9	0.3	10.2	0.7	2.6	4.9	2.9	3.1	4.9	0.3	6.5	589.7
5 MC	96	9.0	7.9	9.2	1.2	18.8	7.9	3.4	0.6	0.1	11.5	0.7	2.8	6.5	3.9	4.1	7.0	0.2	5.1	118.1
7 MC	282	12.8	9.4	8.5	1.8	16.4	8.1	4.4	0.9	0.2	9.7	0.7	2.9	5.6	3.6	3.9	5.4	0.4	5.3	301.4
14 MC	654	13.3	8.8	8.4	1.7	19.3	7.0	3.8	1.3	0.3	10.1	0.7	2.2	5.7	2.9	3.3	5.0	0.2	6.0	101.7
17 MC	252	10.1	8.4	9.5	1.7	19.8	7.2	3.5	0.8	0.1	10.9	0.7	2.7	5.6	3.5	3.7	5.8	0.4	5.8	300.9
29 MC	102	11.1	9.6	9.3	1.3	16.5	8.6	3.4	0.6	0.0	11.3	0.6	2.8	5.7	3.7	4.0	6.5	0.1	4.7	147.8
33 MC	1369	11.7	7.4	7.6	1.7	23.7	6.4	3.9	1.4	0.3	10.2	0.7	1.8	6.3	2.9	3.3	4.8	0.7	5.2	84.9
35 MC	598	12.4	9.5	8.3	1.8	21.0	6.4	4.1	1.3	0.1	10.4	0.7	2.4	5.2	3.0	3.0	4.7	0.3	5.3	107.6
45 MC	153	11.8	9.3	8.7	1.6	17.4	6.6	3.9	0.9	0.1	10.8	0.8	2.8	5.7	3.6	3.8	6.1	0.3	5.6	352.9
67 MC	270	13.2	10.4	7.5	1.5	19.4	6.6	3.5	0.8	0.2	9.8	0.5	2.9	6.0	3.3	3.7	5.3	0.4	4.8	128.0
71 MC	238	12.4	9.3	8.5	1.7	17.7	7.0	3.9	1.0	0.1	10.3	0.7	2.7	5.6	3.3	3.6	5.5	0.4	6.1	343.7
79 MC	1174	13.0	8.5	7.6	1.7	22.3	6.2	4.0	1.6	0.4	9.6	0.9	1.0	5.7	2.8	3.1	4.9	0.5	6.3	59.9
81 MC	1278	13.3	9.0	7.9	1.6	21.8	6.6	4.1	1.8	0.2	10.6	0.7	0.8	5.2	2.7	2.9	4.3	0.9	5.8	48.3
88 MC	127	10.0	9.4	8.7	1.6	14.4	7.4	3.4	0.6	0.1	10.9	0.7	3.3	6.6	4.4	4.7	7.8	0.3	5.9	298.9
99 MC	219	10.5	8.6	9.0	1.5	18.7	7.4	3.6	0.7	0.2	10.8	0.7	2.9	5.7	3.8	3.9	6.3	0.3	5.5	341.1
104 MC	185	13.2	10.1	8.2	1.6	14.2	8.0	4.1	0.4	0.1	10.0	0.6	3.4	6.2	4.3	4.5	6.4	0.3	4.4	150.2
111 MC	179	11.5	9.5	8.3	1.8	15.9	7.1	3.6	0.7	0.2	9.8	0.8	3.2	6.5	4.0	4.4	6.6	0.2	5.8	375.2
119 MC	115	10.0	8.7	9.1	1.4	17.1	8.2	3.7	0.8	0.2	11.2	0.8	2.6	6.3	3.6	3.8	6.8	0.1	5.8	201.0
121 MC	360	13.3	10.0	8.9	1.8	17.7	7.9	3.8	0.9	0.3	10.0	0.7	2.1	4.9	2.9	3.2	4.8	0.2	6.7	511.0
125 MC	50	8.5	7.8	9.1	1.4	16.4	8.3	3.4	0.7	0.1	11.6	1.2	2.0	6.7	4.6	4.8	7.3	0.5	5.6	67.7
127 MC	86	9.9	7.8	9.3	1.4	19.0	7.7	3.4	1.1	0.3	11.0	1.0	2.3	5.9	3.5	3.7	6.4	0.2	6.1	107.8
129 MC	123	12.4	9.3	8.2	1.5	17.1	7.7	4.2	0.7	0.2	10.0	0.8	2.7	6.0	3.7	3.9	5.9	0.4	5.2	284.4

* Asp, aspartic acid; Glu, glutamic acid; Ser, serine; His, histidine; Gly, glycine; Thr, threonine; Arg, arginine; β-Ala, β-alanine, Tau, taurine; Ala, alanine; γ-Aba, γ-aminobutyric acid; Tyr, tyrosine; Val, valine; Phe, phenylalanine; Ileu, isoleucine; Leu, leucine; Orn, ornithine; Lys, lysine.

found at stations located in a mud wave in the southern region (Stas. 1MC, 321 m, and 121MC, 360 m; Table 2). The shallow Stas. 5MC, 29MC, 125MC, and 127MC (<102 m water depth) were low in THAA (<149 μmol g dry wt^{-1}), whereas there was a general decrease in the THAA concentration with increasing water depth at the remaining stations (Fig. 2A). Surface concentrations of THAS showed a similar spatial distribution as the THAA concentration with high concentrations (up to 70 μmol g dry wt^{-1}; Table 3) in the southern mud-wave stations and low concentrations at the shallow stations <102 m water depth (<15 μmol g dry wt^{-1}). At the remaining stations there was a decrease in the concentration of THAS with increasing water depth (Fig. 2B). The lower concentrations of THAA and THAS at the shallower sites near the coast might be explained by dilution of sedimentary OM with clastic terrigenous material delivered by small rivers or aeolian dust (Scheidegger and Krissek 1982). The elevated concentrations of THAA and THAS at the two mud-wave stations might be explained by accumulation of organic rich material in fine-grained mud-wave sediments. Concentrations of THAA were in the same range as concentrations found in other surface sediments from upwelling areas: 62–470 μmol g dry wt^{-1} in the Peru upwelling region near 15°S (Henrichs et al. 1984) and ~30 to <1000 μmol g dry wt^{-1} in Chilean coastal sediments (Pantoja and Lee 2003; Lomstein et al. 2006). There are only a limited number of studies on the distribution of amino sugars in marine sediments, and we are aware of only one other study of sediments from upwelling areas. Niggemann and Schubert (2006) studied the sources and fate of amino sugars at three of the stations included in the present study (Stas. 29MC, 71MC, and 81MC). Our results agree well with their data. In the few other studies available on the distribution of amino sugars in surface sediments lower concentrations were observed: <~7 μmol g dry wt^{-1} in North Sea sediments at 3–270-m water depth (Dauwe and Middelburg 1998), ~1 μmol g dry wt^{-1} in Antarctic Ocean sediments at 1951–2983-m water depth (Liebezeit 1993), <~2 μmol g dry wt^{-1} in the Bay of Bengal at 1956–2983-m water depth (Gupta et al. 1997), and an average of ~3 μmol g dry wt^{-1} in Brazil margin sediments at 940–1280-m water depth (Jennerjahn and Ittekkot 1999). These low amino sugar concentrations may be explained by low TOC concentrations compared to the TOC concentrations in the present study.

The highest $\%T_{AA}C$ and $\%T_{AA}N$ were found at the shallowest stations (up to 22% and 46%, respectively, at Sta. 88MC) and there was a general decrease in both parameters with increasing water depth (Fig. 3A,B). Because $\%T_{AA}C$ and $\%T_{AA}N$ are measures for the degradation state of OM, the observed trends indicate that the "freshness" of OM was influenced by the time of settling through the water column and the time period integrated in the upper 1 cm of the sediment (covering ages of ca. 2 yr at shallow stations to 20 yr at the deeper

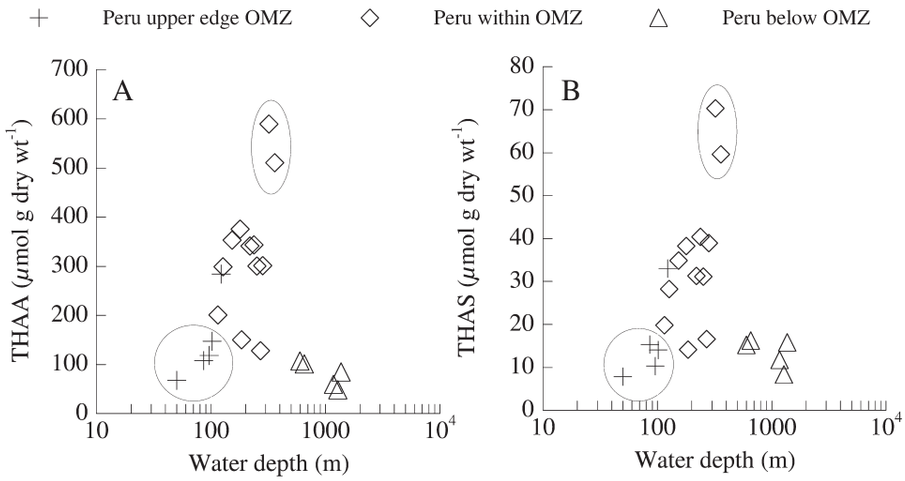

Fig. 2. Surface sediment (0–1 cm) concentrations of (A) total hydrolyzable amino acids (THAA) and (B) total hydrolyzable amino sugars (THAS) vs. water depth. Circles indicate mud-wave stations and stations diluted with clastic material.

stations, according to sedimentation rates compiled by Niggemann 2005). The behavior of $\%T_{AA}C$ and $\%T_{AA}N$ found in the present study agrees well with results from a more limited number of stations from the Chilean upwelling region (Lomstein et al. 2006). According to the changes in $\%T_{AA}C$ and $\%T_{AA}N$, the surface sediments investigated in the present study represented OM alteration stages similar to sinking particles and shallow sediments including sediments underlying oxygen deficient waters (Keil et al. 2000). The data compilation made by Keil et al. (2000) covered a wide range of marine sediments, source materials, and depositional settings.

The percentages of TOC and TN identifiable as amino sugar carbon or nitrogen ($\%T_{AS}C$ and $\%T_{AS}N$, respectively) did not show any consistent trend with water depth (data not shown). The average $\%T_{AS}C$ and $\%T_{AS}N$ were

Table 3. Mole percentage composition for each hydrolyzable amino sugar and concentration of total hydrolyzable amino sugars (THAS) in surface sediments off Peru.*

		Mole %			
Station	Water depth (m)	GlcN	GalN	Mur	[THAS] (μmol g dry wt^{-1})
1MC	321	60.4	39.2	0.4	70.3
5MC	96	59.9	38.6	1.5	10.3
7MC	282	61.5	38.0	0.5	39.0
14MC	654	60.6	38.6	0.8	16.3
17MC	252	62.3	36.9	0.9	31.2
29MC	102	59.6	39.2	1.2	14.1
33MC	1369	61.5	37.9	0.6	15.9
35MC	598	60.9	38.4	0.7	15.2
45MC	153	60.2	39.4	0.3	34.9
67MC	270	62.5	36.1	1.4	16.6
71MC	238	61.5	37.9	0.6	40.4
79MC	1174	60.0	39.7	0.3	11.8
81MC	1278	63.5	35.9	0.6	8.4
88 MC	127	60.7	37.9	1.3	28.3
99MC	219	59.1	40.0	0.9	31.4
104MC	185	63.3	35.5	1.1	14.2
111MC	179	62.4	36.5	1.1	38.3
119MC	115	59.6	38.9	1.5	19.9
121MC	360	38.1	38.1	0.3	59.7
125MC	50	61.3	36.9	1.9	7.9
127MC	86	56.1	42.9	1.1	15.3
129MC	123	61.5	37.8	0.7	33.0

* GlcN, glucosamine; GalN, galactosamine; Mur, muramic acid.

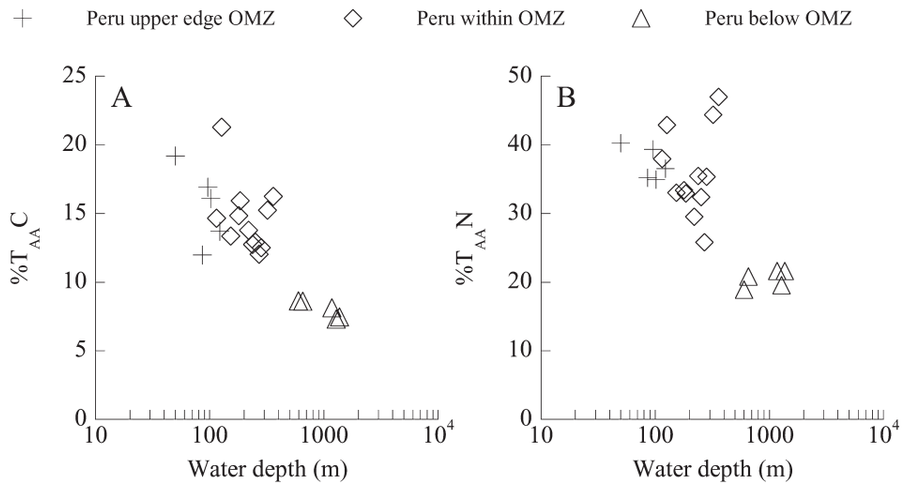

Fig. 3. (A) The percentage of total organic carbon present as amino acid carbon ($\%T_{AA}C$) and (B) the percentage of total nitrogen present as amino acid nitrogen ($\%T_{AA}N$) in surface sediment vs. water depth.

2% and 3%, respectively, and fall within the range of values previously reported from sediments from different oceanic regions, and various water and sediment depths (*see* data compilation in Niggemann and Schubert 2006). In total, between 9% and 24% of the TOC and between 21% and 52% of the TN were identified as carbon or nitrogen derived from THAA and THAS.

THAA and THAS composition—In all the investigated stations, the dominant amino acid was glycine (14–23 mole %) followed by Asp, Ala, Glu, and Ser (Table 2).

Non-protein amino acids occurred in minor concentrations, with β-Ala being the most abundant (up to 1.8 mole %) followed by γ-Aba (<1.2 mole %), Orn (<0.7 mole %), and Tau (<0.4 mole %). These compounds generally increased in relative abundance with increasing water depth (Table 2). Moreover the Asp : β-Ala ratio decreased with increasing water depth (Fig. 4A) and thereby proved to be a sensitive diagenetic indicator over the full range of OM alteration included in the present data set. Numerous previous studies have shown similar trends in Asp : β-Ala ratios in sediments of different OM quality or in surface sediments at contrasting water depths (Lee and Cronin 1982; Dauwe and Middelburg 1998; Lomstein et al. 2006). The Glu : γ-Aba ratio did not show any consistent trend with water depth (Fig. 4B).

Application of the protein amino acid–based DI (Dauwe et al. 1999) resulted in DI values ranging from 1.03 at 127-m water depth (Sta. 88MC) to −0.62 at 1174 m (Sta. 81MC), and there was a clear and consistent decrease in DI values with increasing water depth (Fig. 4C). The range of DI values covered alteration stages of OM from coastal and ocean margin sediments (−0.3 to 1.0; Dauwe et al. 1999) at shallow water depth to OM almost as degraded as

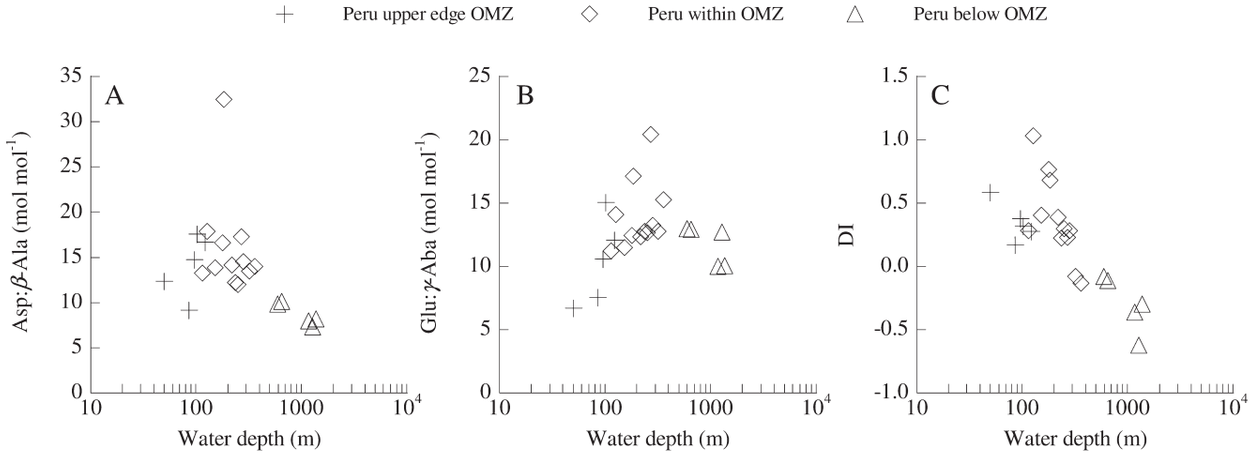

Fig. 4. Surface sediment molar ratios between (A) aspartic acid and β-alanine (Asp : β-Ala), (B) glutamic acid and γ-aminobutyric acid (Glu : γ-Aba), and (C) the degradation index (DI) vs. water depth.

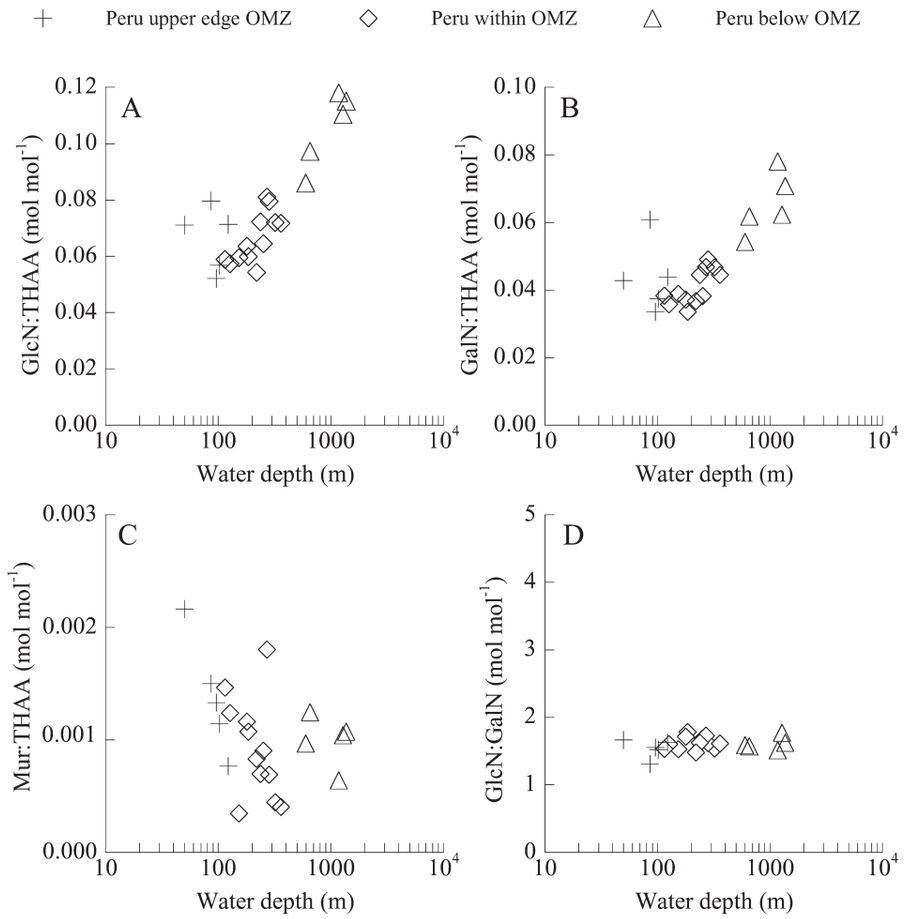

Fig. 5. Surface sediment ratios between (A) glucosamine and total hydrolyzable amino acids (GlcN : THAA), (B) galactosamine and total hydrolyzable amino acids (GalN : THAA), and (C) muramic acid and total hydrolyzable amino acids (Mur : THAA), and (D) the molar ratio between glucosamine and galactosamine (GlcN : GalN), vs. water depth.

OM in hemipelagic surface sediments at greater water depth. Opposed to Vandewiele et al. (in press) there was no effect of the OMZ on the DI (or any of the other applied diagenetic indicators). They observed that the sediments in the upper OMZ transition zone and below the OMZ were more degraded (with lower DI values) than inside the OMZ in sediments from the Pakistan margin.

The dominant amino sugar was GlcN (56–64 mole %) followed by GalN (36–43 mole %; Table 3). At all stations Mur contributed <2 mole % to THAS. The mole percentage of GlcN and GalN did not show any consistent trend with water depth, whereas the mole percentage of Mur decreased with increasing water depth (Table 3).

The molar ratio between GlcN and THAA (GlcN : THAA) and GalN and THAA (GalN : THAA) increased with increasing water depth (Fig. 5A,B), showing that these amino sugars became enriched relative to THAA during decomposition in the water column and early diagenesis in surface sediments. Contrary to this, the molar ratio between Mur and THAA (Mur : THAA) decreased with increasing water depth (Fig. 5C), showing that Mur became depleted relative to THAA during decomposition in the water column and early diagenesis in surface sediments. Generally, amino sugars are considered relatively resistant to decomposition because of their incorporation in structural polymer matrices, such as bacterial cell walls (Mur and GlcN) and chitinaceous material (GlcN). This is consistent with an increase in GlcN and GalN relative to THAA during decomposition, as was observed by Dauwe and Middelburg (1998) in North Sea sediments. Further, Kawasaki and Benner (2006) experimentally showed that GlcN and GalN had significantly lower decay coefficients than Mur and D-amino acids, indicating the relative resistance of GlcN and GalN to decomposition.

GlcN and GalN were found in similar relative proportions in all samples (Fig. 5D), and a surprisingly narrow range of GlcN : GalN values (1.6 ± 0.1 mol mol^{-1}) was observed. This suggests that these amino sugars were closely associated and had similar reactivities (Benner and Kaiser 2003). Benner and Kaiser (2003) obtained GlcN : GalN ratios of $\sim$1.9 in particulate OM and $\sim$1.5

Table 4. Concentration of D- and L-isomers of glutamic acid (Glu), serine (Ser), and alanine (Ala), the sums of L- and D-amino acids (ΣL-AA and ΣD-AA), and the percentage of D-amino acids in the total D+L-amino acids (%D/[D+L]) in surface sediments off Peru.

Station	Water depth (m)	μmol g dry wt^{-1}								
		L-Glu	D-Glu	L-Ser	D-Ser	L-Ala	D-Ala	ΣL-AA	ΣD-AA	D/(D+L) (%)
1MC	321	49.8	1.2	53.3	0.6	61.4	1.7	164.6	3.6	2.2
5MC	96	7.9	0.2	10.7	0.1	13.3	0.3	31.9	0.7	2.0
7MC	282	26.1	0.6	28.5	0.4	33.2	0.9	87.8	1.9	2.2
14MC	654	8.2	0.3	8.3	0.3	10.1	0.4	26.6	1.0	3.7
17MC	252	22.1	0.7	26.4	0.3	30.8	1.2	79.3	2.1	2.6
29MC	102	12.0	0.5	12.8	0.2	16.2	0.4	41.0	1.1	2.6
33MC	1369	5.7	0.1	6.6	0.2	8.1	0.5	20.4	0.8	4.0
35MC	598	9.4	0.4	9.2	0.3	11.8	0.6	30.5	1.4	4.3
45MC	153	34.1	1.0	34.8	0.6	42.4	1.4	111.3	3.0	2.6
67MC	270	10.6	0.3	9.0	0.3	10.9	0.4	30.4	1.0	3.2
71MC	238	32.3	0.8	33.6	0.5	39.3	1.3	105.2	2.7	2.5
79MC	1174	4.7	0.2	4.9	0.2	5.8	0.2	15.5	0.6	3.6
81MC	1278	3.9	0.2	4.0	0.2	5.3	0.2	13.2	0.5	3.9
88MC	127	24.0	1.3	23.7	0.2	28.7	1.0	76.4	2.4	3.1
99MC	219	25.0	0.9	29.4	0.4	35.7	1.2	90.0	2.4	2.6
104MC	185	14.0	0.2	13.6	0.2	17.0	0.3	44.6	0.7	1.6
111MC	179	29.5	1.0	30.0	0.3	36.3	1.2	95.9	2.5	2.5
119MC	115	15.1	0.4	16.9	0.4	21.5	0.6	53.4	1.4	2.5
121MC	360	44.3	1.0	44.6	0.5	50.6	1.6	139.6	3.1	2.1
125MC	50	5.5	0.1	5.4	0.1	7.2	0.2	18.1	0.5	2.5
127MC	86	8.1	0.4	9.6	0.3	11.6	0.3	29.3	1.0	3.3
129MC	123	22.9	0.6	24.9	0.4	32.2	1.0	80.0	2.0	2.4

in ultrafiltered dissolved OM in diverse geographic regions (the Pacific, Atlantic, and Arctic Oceans). A low and constant GlcN : GalN ratio (typically <3) has previously been suggested to indicate a major prokaryotic source of marine OM (Benner and Kaiser 2003; Liebezeit 1993; Niggemann and Schubert 2006) compared to much higher ratios obtained in copepods (14–17; Benner and Kaiser 2003).

Occurrence of D- and L-amino acid enantiomers—The most abundant D-amino acid identified was D-Ala (up to 1.7 μmol g dry wt^{-1}) followed by D-Glu and D-Ser (Table 4). Total surface (0–1 cm) concentration of the three D-amino acids varied between 3.6 μmol g dry wt^{-1} (Sta. 1MC, 321 m) and 0.5 μmol g dry wt^{-1} at one of the deepest stations (Sta. 81MC, 1278 m). In general, the distribution of total D-amino acids followed that of THAA, with highest concentrations at stations located in the mud wave (Stas. 1MC, 321 m, and 121MC, 360 m; Fig. 6A), and low concentrations at the shallow Stas. 5MC, 29MC, 125MC, and 127MC (<102 m water depth; <1.1 μmol g dry wt^{-1}). At the remaining stations there was a general

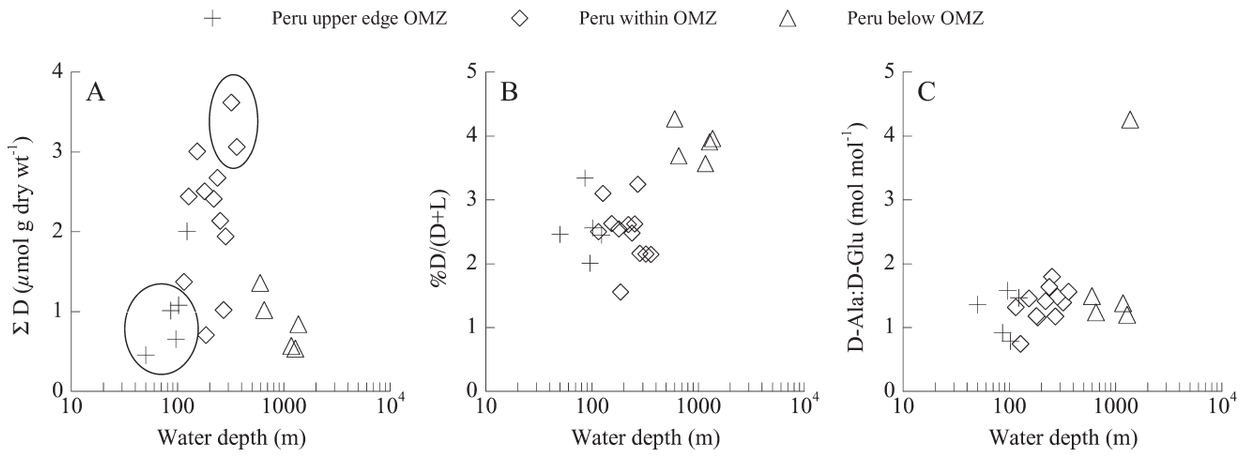

Fig. 6. Surface sediment (A) total concentrations of quantified D-amino acids, (B) percentage of quantified D-amino acids to the respective total D + L-amino acids (%D/[D + L]), and (C) the molar ratio between D-alanine and D-glutamic acid (D-Ala : D-Glu) vs. water depth. Circles indicate mud-wave stations and stations diluted with clastic material.

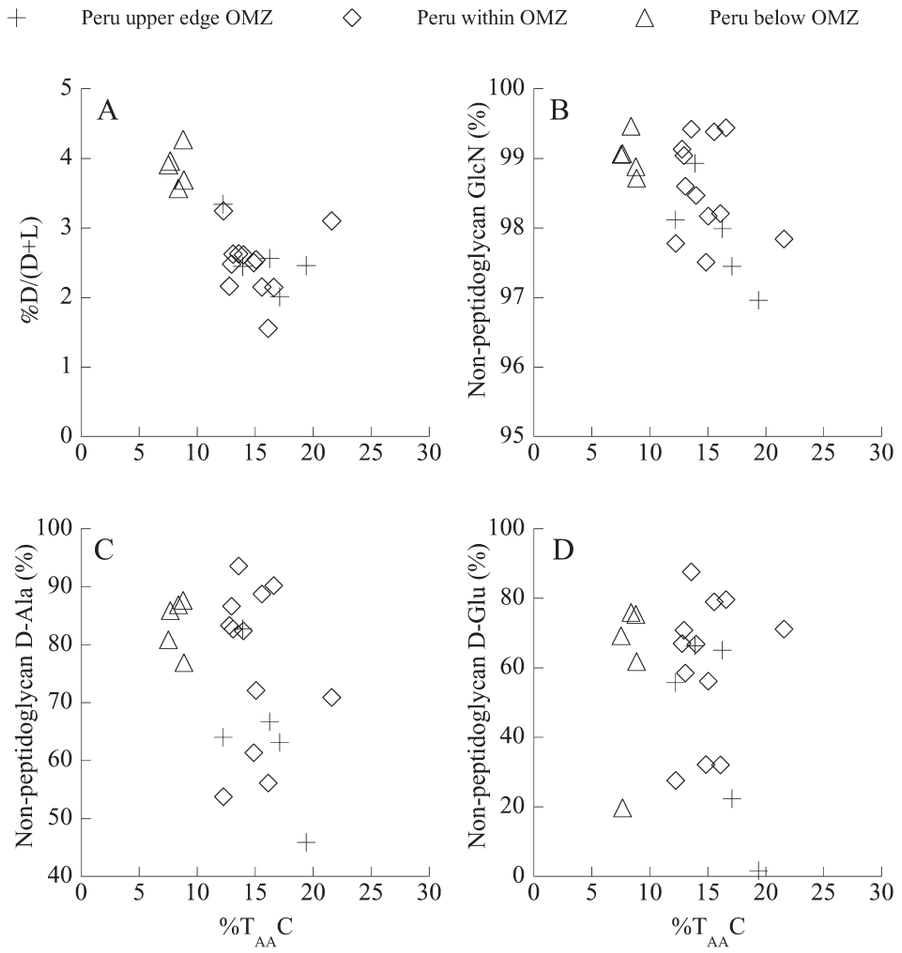

Fig. 7. Plots of (A) the percentage of quantified D-amino acids to the respective total D- + L-amino acids (%D/[D + L]), (B) the percentage of glucosamine not associated with intact peptidoglycan, (C) the percentage of D-alanine not associated with intact peptidoglycan, and (D) the percentage of D-glutamic acid not associated with intact peptidoglycan vs. the percentage of total organic carbon present as amino acid carbon ($\%T_{AA}C$).

decrease in the concentration of D-amino acids with increasing water depth (Fig. 6A). The percent of D-amino acids of the total D + L concentrations of the three identified enantiomers (%D/[D + L]) increased with increasing water depth (Fig. 6B), suggesting that bacterial remains (D-amino acid–containing cell wall complexes) became an increasingly abundant and important component of OM as diagenesis proceeded. These results support and confirm the data of Lomstein et al. (2006) and add to the growing list of studies that indicate that prokaryotic OM that escapes mineralization contributes to the large pool of slowly cycling OM in the ocean (McCarthy et al. 1998; Pedersen et al. 2001; Grutters et al. 2002).

D-Ala and D-Glu were found in similar relative proportions in all samples (Fig. 6C), and a surprisingly narrow range of D-Ala : D-Glu values (1.3 ± 0.3 mol mol^{-1}) was observed. This suggests that these D-amino acids were closely associated and had similar reactivity. The only exception to this was at Sta. 33MC, where D-Ala : D-Glu was 4.3 mol mol^{-1}.

Discussion

Contribution of D-amino acids and Mur from intact cells—D-amino acids and Mur have previously been applied as bacterial biomarkers (Kaiser and Benner 2008), and it has been shown that a substantial fraction of these compounds is associated with nonliving OM. The contribution of D-amino acids from intact prokaryotic cells to the measured concentration of D-amino acids was estimated from an assumed number of bacteria of 2.5×10^9 cells g dry wt^{-1} multiplied with the average D-amino acid concentrations in six gram-negative (G^-) cultures quantified by Lomstein et al. (2006). Because there were no cell counts available in the present study, we used the average cell number in surface sediments (0–1 cm) from the upwelling region off Chile given in Lomstein et al. (2006). The cultures analyzed by Lomstein et al. (2006) were harvested at the end of the exponential growth phase or in the transition between the exponential and the stationary growth phase, which ensured that the cells were in a good physiological

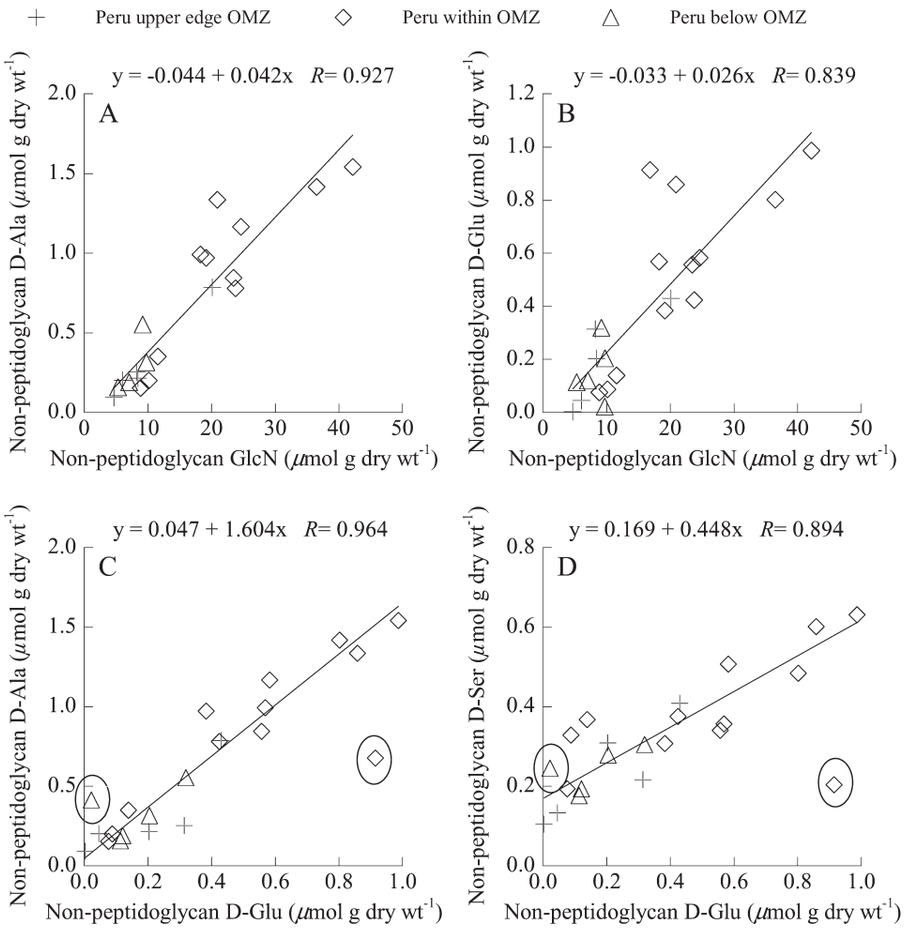

Fig. 8. Plots of the concentration of (A) D-alanine unrelated to peptidoglycan (non-peptidoglycan D-Ala) and (B) D-glutamic acid unrelated to peptidoglycan vs. the concentration of glucosamine unrelated to peptidoglycan. Plots of the concentration of (C) D-alanine unrelated to peptidoglycan and (D) D-serine unrelated to peptidoglycan vs. the concentration of D-glutamic acid unrelated to peptidoglycan. Circles indicate data points omitted from the linear regression.

condition. The contribution of D-amino acids from intact cells to the measured concentration of D-amino acids was 9% ± 7% for D-Ala, 22% ± 17% for D-Glu, and 5% ± 2% for D-Ser. This suggests that a large fraction of the measured D-amino acids (>78% to <95%) originated from cell remains (including cell wall matrices) rather than from intact cells that can be viewed in the microscope after DNA staining. This finding supports previous studies by Pedersen et al. (2001), Lomstein et al. (2006), and Kaiser and Benner (2008), which suggested that bacteria are an important source of the nonliving OM in the ocean. We did not consider a potential contribution of D-amino acids from gram-positive (G^+) bacteria in the estimate because G^+ bacteria do not seem to be important in marine sediments. Among the limited number of studies we have been able to find in a thorough ISI Web of Knowledge℠ survey of literature, we only came across one study by Ravenschlag et al. (2001) in which the environmental conditions (temperature, lack of fresh water influence, sediment depth and depth of the overlying water column) were similar to those of the present study. Ravenschlag et al. (2001) reported that G^+ bacteria were near the detection limit when using ribosomal ribonucleic acid (rRNA) slot blot hybridization.

Lomstein et al. (2006) did not quantify Mur in the pure cultures they investigated. However, the contribution of Mur from cells to the sedimentary Mur concentration could be estimated based on the Mur : D-Ala and Mur : D-Glu ratios in cultures screened by Kaiser and Benner (2008) and the cell-specific concentrations of D-Ala and D-Glu obtained by Lomstein et al. (2006). We assume that variation in average Mur : D-Ala and Mur : D-Glu ratios are mainly because of inter-species variation rather than the size of bacteria. The estimated cell-specific Mur concentrations for the Lomstein et al. (2006) cultures were 13 ± 8 amol cell^{-1} and 18 ± 15 amol cell^{-1} based on an average Mur : D-Ala ratio of 0.7 and an average Mur : D-Glu ratio of 0.8, respectively (Kaiser and Benner 2008). The contribution of Mur from intact cells to the measured concentration of Mur in the sediments was 23% ± 18% and 33% ± 26%

based on the Mur : D-Ala ratio and the Mur : D-Glu ratio, respectively. Thus, when compared to the contribution estimated for D-amino acids, a larger fraction of the sedimentary Mur could be attributed to intact cells, which indicates that the relative reactivity of Mur exceeded that of D-amino acids. This finding is in accordance with previous studies that have shown that Mur seems to be a marker of living bacteria (Moriarty 1977) and of relatively fresh bacterial necromass (Benner and Kaiser 2003; Tremblay and Benner 2006, Niggemann and Schubert 2006).

Accumulation of prokaryotic remains during OM diagenesis—There was a continuous accumulation of prokaryotic remains during OM diagenesis, which was illustrated by a clear and consistent increase in %D/(D + L) with decreasing values of $\%T_{AA}C$ (Fig. 7A). In the following discussion we will use $\%T_{AA}C$ as indicator for the diagenetic stage of the sedimentary OM, because it is a well-established diagenetic indicator (Keil et al. 2000) and it has proved to provide information on the reaction potential of natural organic mixtures under both oxic and anoxic depositional conditions (Cowie and Hedges 1994).

The accumulation of D- over L-amino acids during diagenesis has previously been related to a preferential preservation of bacterial peptidoglycan (Pedersen et al. 2001; Grutters et al. 2002; Lomstein et al. 2006). However, differences in reactivity of Mur and D-amino acids (Kawasaki and Benner 2006) indicate that there are additional prokaryotic biomolecules preserved. Macromolecular sources of GlcN and D-amino acids were characterized by comparing the distributions of Mur, GlcN, D-Ala, and D-Glu in the sediments with their characteristic distributions in peptidoglycan. It was assumed (1) that the measured sedimentary concentrations of Mur represented intact bacteria or fragments of peptidoglycan remaining in the sediments after cell death, (2) that the measured concentrations of GlcN were of prokaryotic origin, and (3) that the bacterial community was dominated by G^- bacteria, as was discussed in the previous section. Ratios of GlcN : Mur, D-Ala : Mur, and D-Glu : Mur in peptidoglycan from G^- bacteria are 1, 0.75, and 1, respectively (Schleifer and Kandler 1972). Thus, concentrations of GlcN, D-Ala, and D-Glu that exceed the respective concentrations that could be attributed to an association with Mur in intact peptidoglycan units indicate the occurrence of GlcN, D-Ala, and D-Glu in other macromolecules (Kaiser and Benner 2008). Most of the GlcN was present in other macromolecules than peptidoglycan (average 99% ± 1%) and there was a gradual increase in the contribution of GlcN from other macromolecules with increased diagenetic state of the sediments (decreasing $\%T_{AA}C$ values; Fig. 7B). The contribution of D-Ala and D-Glu from other macromolecules than peptidoglycan were 46% and <2%, respectively, at the shallowest station (Sta. 127MC at 50 m water depth) and >80% and >69%, respectively, at the deeper stations. There was a gradual accumulation of D-Ala and D-Glu in other macromolecules than peptidoglycan with ongoing degradation (Fig. 7C,D), although it was less clear for D-Glu than for GlcN and D-Ala (Fig. 7B–D). Overall these data indicate that intact peptidoglycan subunits became progressively less important with increased degradation stage of the OM, whereas the fractions of GlcN, D-Ala, and D-Glu associated with other biomolecules increased in importance. This is in accordance with the results obtained by Kawasaki and Benner (2006) in a study of the bacterial release of dissolved OM during cell growth and decline. Hence, the macromolecular composition of prokaryotic remains that are preserved on a longer time scale and are imprinted in more degraded OM is still not known.

Apart from the constant ratio between GlcN and GalN reported earlier, our study provides new information on the macromolecular nature of the prokaryotic remains that are preserved during OM diagenesis. We observed constant molar ratios between D-Ala and GlcN (0.042), D-Glu and GlcN (0.026), D-Ala and D-Glu (1.6), and D-Ser and D-Glu (0.448) in OM that is not intact peptidoglycan (Fig. 8). These consistent ratios reflect similar reactivities indicating that the D-amino acids, GlcN, and GalN are associated in common molecules. The only possible source of D-amino acids and low molar ratios of GlcN and GalN is prokaryotes. Kaiser and Benner (2008) stated that Archaea are not a likely source of particulate D-amino acids in the oceanic water column. However, it cannot be excluded that Archaea contribute to the pool of prokaryotic necromass in sediments. Vetriani et al. (1999) found that Archaea contribute between 2.5% and 8% of the total prokaryotic rRNA in deep-sea sediments, whereas a recent study by Lipp et al. (2008) found that Archaea contributed up to 75% of total microbial intact polar lipids in Black Sea surface sediments.

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