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Amino acid biogeo- and stereochemistry in coastal Chilean sediments

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Abstract

The spatial distribution of total hydrolysable amino acids (THAA) and amino acid enantiomers (D- and L-forms) was investigated in sediments underlying two contrasting Chilean upwelling regions: at ~23 °S off Antofagasta and at ~36 °S off Concepción. The contribution of amino acids to total organic carbon (%T_{AA}C: 7–14%) and total nitrogen (%T_{AA}N: 23–38%) in surface sediments decreased with increasing water depth (from 126 to 1350 m) indicating that organic matter becomes increasingly decomposed in surface sediments at greater water depth. Changes in the ratio between the protein amino acid aspartate and its non-protein degradation product β-alanine confirmed this observation. Furthermore, estimates of THAA mineralization showed that sedimentary amino acid reactivity decreased with both increasing water depth as well as progressive degradation status of the organic matter that was incorporated into the sediment. Reactivity of organic matter in the sediment was also assessed using the Degradation Index (DI) developed by [Dauwe, B., Middelburg, J.J., 1998. Amino acids and hexosamines as indicators of organic matter degradation state in North Sea sediments. *Limnol. Oceanogr.* **43,** pp. 782–798]. Off Concepción, DI was successfully applied to examine the degradation status of sedimentary organic matter at different water depths. However, unexpected results were obtained at the Antofagasta stations as DI increased with sediment depth, suggesting more degraded organic matter at the surface than deeper in the cores. The contribution of peptidoglycan amino acids to THAA was estimated from the concentrations of D-aspartate, D-glutamic acid, D-serine, and D-alanine. Peptidoglycan amino acids accounted for >18% of THAA in all investigated samples. In surface sediments peptidoglycan amino acids accounted for a progressively larger fraction of THAA at increasing water depths (up to >26%). Further, the contribution of peptidoglycan amino acids to THAA increased with increased sediment depth and age (up to 288-year-old) reaching up to 59%. Independent estimates based on D-amino acid concentrations in selected laboratory strains, bacterial counts and the sedimentary concentrations of D-amino acids indicate that a large fraction of the measured D-amino acids (>47 to >97%) originated from cell wall residues rather than from enumerated cells.

1. Introduction

More than 99% of the organic matter from global primary production is ultimately oxidized to CO_2, a highly efficient process that leaves only a small residue preserved, primarily in marine sediments (Cowie and Hedges, 1994). Most organic matter in the ocean is therefore at some intermediate stage of degradation. The process of organic decay influences not only the quantity and quality of organic matter ultimately preserved but also the extent of remineralization (e.g., Hedges and Keil, 1995; Hartnett et al., 1998; Keil et al., 2000). The diagenetic history of organic matter is important from both biological and geological perspectives, since carbon burial together with pyrite burial controls the concentration of atmospheric oxygen. Hence, the diagenetic status of organic matter and the development of diagenetic indicators are central to understanding carbon preservation.

Proteins are ubiquitous components of living organisms and represent a significant fraction of organic matter present in recent coastal marine sediments (e.g., Keil et al., 2000 and references therein). Over a wide range of time scales, amino acids are degraded faster than bulk organic

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matter (e.g., Cowie and Hedges, 1992; Wakeham and Lee, 1993; Cowie and Hedges, 1994). As a consequence the percentage of total organic carbon present as amino acid carbon ($\%T_{AA}C$) and the percentage of total nitrogen present as amino acid nitrogen ($\%T_{AA}N$) are particularly useful as diagenetic indicators; they are sensitive to different stages of alteration and appear to be uncompromised by source variations (Cowie and Hedges, 1994). Further information on the degradation state of organic matter is provided by the relative abundance of non-protein amino acids, which generally increases during diagenesis. The result is a decrease in the ratio between the protein precursor (e.g., aspartate) and the non-protein degradation product (e.g., β-alanine; Cowie and Hedges, 1992; Cowie and Hedges, 1994). Applied together, $\%T_{AA}C$, $\%T_{AA}N$, and the ratio between source protein amino acid and its non-protein degradation product offer congruent information on the relative diagenetic stage and reaction potential of natural organic material (Cowie and Hedges, 1994; Keil et al., 2000).

In a detailed investigation on the relationship between amino acid composition and diagenesis, Dauwe and Middelburg (1998) demonstrated that amino acid composition provides a powerful measure of quality and degradation history of sedimentary organic matter. They applied a Principal Component Analysis (PCA), based on the mole percent contribution of amino acids, which showed systematic changes in amino acid composition as a consequence of organic matter degradation. Based on the results of this PCA, Dauwe and Middelburg (1998) defined a Degradation Index (DI), which ranked changes in individual amino acids according to a general scheme in which the amino acids glycine, serine and threonine, bound in diatom cell wall structures such as glycocoating proteins (Ingalls et al., 2003) were enriched upon progressive degradation. In contrast, other amino acids such as phenylalanine, glutamic acid, tyrosine, leucine, and isoleucine become depleted with increasing degradation state. The DI values reported by Dauwe and Middelburg (1998) ranged from 1.5 for fresh phytoplankton to −2.2 in strongly degraded sediment.

Recently, Keil et al. (2000) applied the Dauwe and Middelburg (1998) algorithm on compiled literature data. They observed that peptidoglycan from bacterial cell walls can also have a relatively low DI because of its enrichment in glycine. Hence, the authors concluded that DI seems to incorporate the enhanced preservation of bacterial cell walls in its quantification of diagenetic state. This addresses the important question, whether specific bacterial components are recalcitrant and make a significant contribution to the organic matter that is ultimately buried in marine sediments. Bacteria uniquely produce D-amino acids as a component of their cell wall biopolymer peptidoglycan (e.g., Schleifer and Kandler, 1972). In surface sediments off California, USA, Pollock and Kvenvolden (1978) found that D-alanine, D-aspartate, and D-glutamic acid constituted ~8, 7, and 2%, respectively, of the total amount of hydrolyzed D + L alanine, aspartate and glutamic acid. The contribution of bacteria as a source of organic matter to sediments and the in situ bacterial production of recalcitrant organic matter has been uncertain until recently. However, Pedersen et al. (2001) and Grutters et al. (2002) used the presence of D-amino acids in sediments to estimate the contribution of peptidoglycan amino acids to total hydrolyzable amino acids (THAA). Both groups observed that peptidoglycan seems to be retained for a longer period of time in particulate form compared to other proteinaceous material.

In the present study, we examined (1) the organic matter degradation state and (2) the contribution of amino acids from bacterial cell walls to THAA in sediments underlying two contrasting upwelling cells off the coast of Chile. The degradation state was examined from three compositional characteristics: $\%T_{AA}C$, $\%T_{AA}N$, and the ratio between aspartate and its degradation product β-alanine. Further, diagenetic alteration of sedimentary amino acids was assessed using the Degradation Index developed by Dauwe and Middelburg (1998). The contribution of amino acids from bacterial cell walls to THAA was inferred from the concentrations of D-aspartate, D-glutamic acid, D-serine, and D-alanine. Our goal was to investigate whether the preservation of organic carbon, in the form of bacterial cell walls, was related to the general degradation status of the sediments.

2. Methods

2.1. Study site

Observations of sea surface temperature (Fonseca and Farías, 1987) and pigment concentrations based on coastal zone color scanning (Thomas, 1999) identified areas of especially pronounced upwelling along the Chilean coast near 20°S, 23°S, 30°S, 33°S, and 37°S. For this study we concentrated on sediments underlying the upwelling cells off Antofagasta (~23°S) in the North and off Concepción (~36°S) in the central region (Fig. 1). Upwelling off central Chile occurs seasonally during austral summer months (Brandhorst, 1971; Ahumada et al., 1983), whereas at more northerly latitudes, attenuated upwelling also occurs during winter (Morales et al., 1996; Blanco et al., 2001).

Near Antofagasta the sediments receive only small amounts of terrestrial material due to extremely low precipitation and prevailing alongshore winds that limit river discharge and aeolian input (Lamy et al., 1998). Strong bottom currents scour the narrow shelf and the steep slope off northern Chile and allow significant accumulation of sediments only in protected areas, e.g., local depressions or basins. In general, sediment accumulation rates along the Chilean coast increase from North to South reflecting increasing annual precipitation in the adjacent coastal areas that lead to enhanced river runoff and higher input of terrestrial material to the sediments (Hebbeln et al., 2000). However, sediment accumulation rates obtained

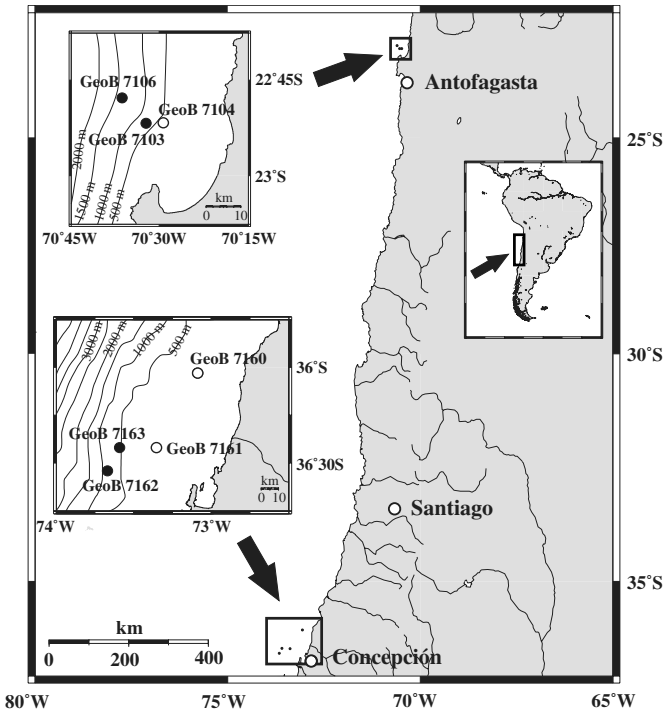

Fig. 1. Study area and location of sampling sites off Antofagasta and Concepción. Note the different scales.

from ^{210}Pb analysis at the investigated sites were similar in both regions (Table 1).

2.2. Sampling and sample processing

Sampling was carried out during RV Sonne cruise SO-156 in April 2001. Sediments were retrieved with multicorers from water depths of 307–1350 m near Antofagasta and 126–798 m near Concepción (Table 1). The shallowest sites sampled GeoB 7104, GeoB 7160, and GeoB 7161 were located within the actual oxygen minimum zone (OMZ, <0.5 ml O_2 L^{-1}) of the water column (Table 1). For geochemical analyses the sediment cores were sliced in 1 cm intervals in the upper 6 cm and in 2 cm intervals below 6 cm. The samples were transferred into clean glass vials and frozen at −25 °C immediately after sampling. The sediment samples were later freeze-dried and particulate material larger than 0.5 cm in size (fish bones etc.) was removed from the sediment before grinding. Numerous tests of benthic foraminifera were found in all sediments from the Antofagasta region and were especially abundant at GeoB 7104. Dominant species were of the family *Nonionidae* (T. Cedhagen, personal communication), which are particularly adapted to oxygen limited conditions (Bernhard et al., 1997). The high abundances of calcerous foraminifera tests were reflected in generally higher inorganic carbon concentrations in the sediments near Antofagasta (up to 2.2% dw) compared to those near Concepción (<0.4% dw; Niggemann, unpubl. results).

2.3. Total hydrolysable amino acids

Sediment samples (~0.5 g) for analysis of total hydrolysable amino acids (THAA) and D- and L-isomers of THAA were hydrolyzed with 10 ml of 6 N HCl at 105 °C for 24 h under N_2. Subsamples of hydrolysate (100 µl) were transferred to new glass vials, dried under vacuum at 50 °C, redissolved in Milli-Q water, and dried again. The dried samples were finally dissolved in 4 ml Milli-Q water. The concentration of THAA in the dissolved hydrolysate was analyzed as dissolved free amino acids by high-performance liquid chromatography (HPLC, Waters Chromatographic Systems) of fluorescent *o*-phthaldialdehyde (OPA)-derived products according to the method of Lindroth and Mopper (1979). Fig. 2A shows an example of the chromatographic traces of a sample hydrolyzate. The concentrations of identified amino acids were calculated from individual three- to five-point calibration curves from a mixture of the amino acid standard solution AA-S-18 (Sigma–Aldrich) to which were added β-alanine (β-Ala), taurine and ornithine. δ-amino valeric acid (δ-Ava) was used as internal standard, as δ-Ava was not present in the samples. The concentration of unidentified OPA-reactive

Table 1
Sampling sites with positions of stations, water depth, bottom water [O_2], sediment location relative to water column OMZ, bottom water temperature, depth of sediment mixing zone and sediment accumulation rate

Station	Latitude	Longitude	Water depth (m)	Bottom water O_2 (ml L^{-1})[a]	Location relative to position of OMZ	Bottom water temperature (°C)	Depth of mixed zone[b] (cm)	Sediment accumulation rate (cm yr^{-1})[c]
GeoB 7103	22°51.99 S	70°32.54 W	891	1.00	below	4.6	None	0.15
GeoB 7104	22°52.00 S	70°29.42 W	307	0.15	within	11.6	n.d.	n.d.
GeoB 7106	22°48.00 S	70°36.70 W	1350	1.18	below	3.2	None	0.11 0.26[d]
GeoB 7160	36°02.33 S	73°04.39 W	367	0.16	within	8.8	10	0.19
GeoB 7161	36°25.51 S	73°23.32 W	126	0.01	within	11.1	8	0.10
GeoB 7162	36°32.52 S	73°40.02 W	798	2.36	below	4.5	10	0.17
GeoB 7163	36°25.55 S	73°35.71 W	536	2.30	below	6.2	5	0.15

[a] Data from CTD-profiling (Hebbeln et al., 2001).
[b] Almost constant ^{210}Pb activity in the upper sediment layer indicated effective sediment mixing (Niggemann, 2005).
[c] Sediment accumulation rates were calculated from the down-core decrease of ^{210}Pb activity (Niggemann, 2005).
[d] Higher rates were observed in the deeper part of the sediment (8–20 cm).

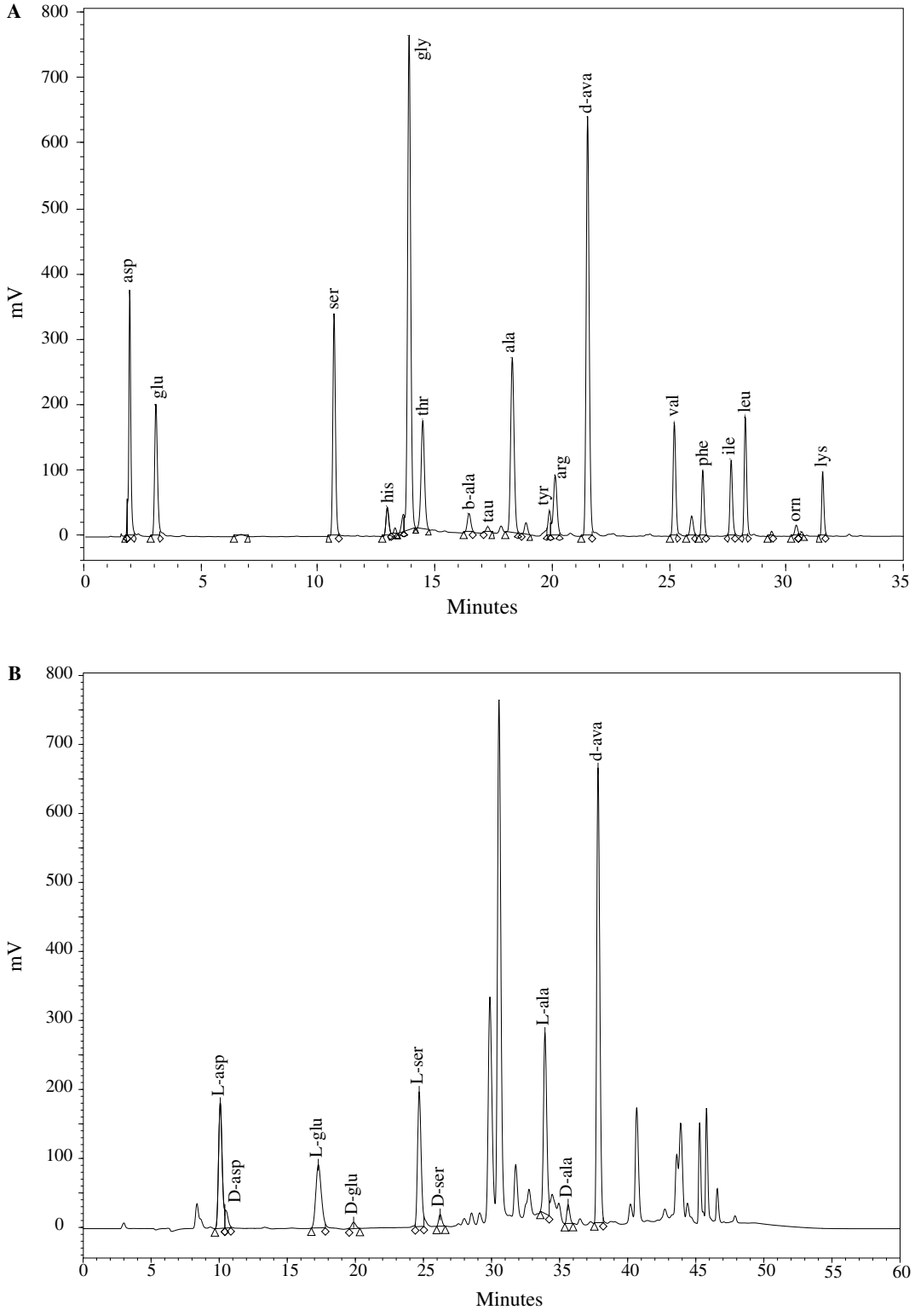

Fig. 2. Chromatograms of the amino acid composition in a hydrolyzate from 18 to 20 cm depth at GeoB 7162 after derivatization with OPA (A) and chromatographic traces of selected D- and L- amino acids in a hydrolyzate from the same depth and site after derivatization with OPA and the chiral thiol *N*-isobutyryl-L-cysteine (B). (A) the retention times of the unidentified OPA-reactive compounds (named others in Table 3) were the following: 1.85, 6.68, 13.26, 13.62, 18.85, 25.93, 29.35, and 30.63 min.

compounds (named others) was calculated by use of the average calibration curve of the standards. NH_4^+ was not included in this estimate.

Blanks were prepared as samples, with the exception that sediment was omitted. Blanks showed negligible concentrations of amino acids from handling and reagents

compared to the sample concentrations reported in this paper.

2.4. Stereochemical composition of selected amino acids

D- and L-isomers of aspartate (Asp), glutamic acid (Glu), serine (Ser), and alanine (Ala) were measured in THAA according to the method of Mopper and Furton (1991), with the modifications described in Guldberg et al. (2002). Fig. 2B shows an example of the chromatographic traces of a sample hydrolyzate. The concentrations of the D- and L-isomers of Asp, Glu, Ser, and Ala were calculated from individual three to five-point calibration curves of the respective amino acids. δ-Ava was used as internal standard. Blanks were prepared as described above and showed negligible amino acid concentrations compared to samples.

D- and L-concentrations of the respective D-amino acids were corrected for racemization during the liquid-phase acid hydrolysis according to Kaiser and Benner (2005). Their approach for racemization correction of amino acid enantiomer measurements in natural samples was to establish a maximal range of hydrolysis-induced racemization with free amino acids and proteins (lysozyme and bovine serum albumin) and then use the average of the two extremes to correct measured enantiomer concentrations. They argued that most environmental samples (marine DOM and POM and soil) very likely display racemization characteristics somewhere between intact proteins and free amino acids. The average percentages of D-enantiomers ($\%D = 100 \times D/(D + L)$) produced during acid hydrolysis of L-enantiomers were the following for Asp, Glu, Ser, and Ala: 4.4%, 2.0%, 0.3%, and 1.2%, respectively (Kaiser and Benner, 2005). In addition, we tested racemization during acid hydrolysis of D-Ala-D-Ala-D-Ala (Sigma no. A 7777). A standard of this peptide (1 ml of 10 μM) was added to 1 ml 12 N HCl and hydrolyzed at 105 °C for 24 h under N_2. The concentrations of D- and L-Ala were analyzed as described earlier and were compared to standards of dissolved free amino acids. Blanks were prepared as described previously and showed negligible amino acid concentrations compared to samples. The percentage of L-Ala enantiomer produced during hydrolysis ($\%L = 100 \times L/(D + L)$) was 0.9% and thus comparable to the average %D-Ala (1.2%) used for correction.

2.5. D-Amino acid content of selected pure cultures

The 6 Gram-negative pure cultures that were analyzed for their contents of D-Asp, D-Glu, D-Ser, and D-Ala are given in Table 2. Cultures were harvested at the end of the exponential growth phase or in the transition between the exponential and the stationary growth phase. Cultures grown in complex growth media were washed prior to acid hydrolysis to remove amino acids from the growth medium. Cultures (1 ml) were added to 1 ml 12 N HCl and hydrolyzed at 105 °C for 24 h under N_2. The concentrations of the respective D-amino acids were analyzed as described earlier. The D-amino acid concentrations were corrected for racemization during the liquid-phase acid hydrolysis as previously described. The cell number in the different cultures was determined by epifluorescence microscopy using Acridine Orange staining.

2.6. Statistical methods

A Principal Component Analysis (PCA) was used to test whether the inter-site and down-core trends observed in the molar composition of THAA could be used to rank the stations in terms of organic matter quality as suggested by Dauwe and Middelburg (1998).

The statistical package SPSS 10 was applied for the analysis. As suggested by Dauwe and Middelburg (1998) we only used the first axis and estimated the position of a given sample on this axis (i.e., the site score), which provided the best projection of its position in multidimensional space onto this axis. For a detailed description of the mathematic and interpretations of PCA see Meglen (1992). The site scores were calculated from the values of the original variables with the aid of the factor coefficients. The Degradation Index (DI), which is equivalent to the site score, was estimated according to the formula:

Table 2
Cell-specific concentrations of D-Asp, D-Glu, D-Ser, and D-Ala in selected pure cultures. Values are corrected for racemization during hydrolysis

Strain	Gram reaction	Type of metabolism	Growth medium	D-Asp amol cell^{-1}	D-Glu amol cell^{-1}	D-Ser amol cell^{-1}	D-Ala amol cell^{-1}
Salmonella mountmagnet	Negative	Fermentative	NB[1]	3.7	11.7	n.d.	10.7
Paracoccus pantotrophus	Negative	Denitrifying	NB[1] + 2 g KNO_3/L	3.1	23.7	12.6	17.1
Desulfofaba hansenii[a]	Negative	Sulfate reducing	See Abildgaard et al. (2004)	14.9	20.8	1.1	21.9
Desulfovibrio aerotolerans[b]	Negative	Sulfate reducing	See Mogensen et al. (2005)	3.4	55.0	0.4	39.6
But 6.1[c]	Negative	Sulfate reducing	TDB[2]	n.d.	n.d.	10.0	11.6
But 6.2[c]	Negative	Sulfate reducing	TDB[2]	n.d.	6.0	5.6	7.6
Average				4.2	29.5	4.9	18.1

NB is nutrient broth medium and TDB is tryptone dextrose broth. [1,2]NB and TDB, made up according to the formulation of the American Public Health Association (Downes and Ito, 2001), were obtained from Becton–Dickinson (Becton–Dickinson Company, New Jersey, USA).

[a] Strains described in Abildgaard et al. (2004).

[b] Strains described in Mogensen et al. (2005).

[c] But 6.1 and But 6.2 are two strains, which were grown with butyrate as electron donor.

$$DI = \sum_i [(var_i - AVGvar_i)/STDvar_i] \times fac \cdot coef_i \quad (1)$$

where var_i is the non-standardized mole percentage of amino acid i, $AVGvar_i$, and $STDvar_i$ are the average and standard deviation of the non-standardized mole percentage of amino acid i in all samples, respectively, and the $fac \cdot coef_i$ is the factor coefficient for amino acid i.

3. Results

3.1. THAA concentration

Off Antofagasta the highest surface THAA concentration was detected at the shallowest station (GeoB 7104) at 307 m water depth (Figs. 3A and C), whereas lower concentrations of THAA were observed at GeoB 7103 (891 m) and GeoB 7106 (1350 m). At GeoB 7104 there was a subsurface maximum in the concentration of THAA at 10 cm depth in addition to the surface maximum. At GeoB 7103 and GeoB 7106 the THAA concentration decreased slightly with sediment depth.

Off Concepción the highest surface concentration of THAA was also found at the shallowest station (GeoB 7161 at 126 m; Figs. 3B and C). At the deeper stations, GeoB 7160, GeoB 7162, and GeoB 7163, the surface THAA concentration was reduced to approximately half of the concentration at GeoB 7161. At GeoB 7161 the THAA concentration decreased gradually downcore (Fig. 3B), whereas there were only minor decreases in the THAA concentration with sediment depth at the other stations off Concepción (Fig. 3B).

The highest surface percentages of organic carbon identifiable as amino acid carbon ($\%T_{AA}C$) were found at the shallowest stations off Antofagasta (GeoB 7104) and off Concepción (GeoB 7161) (Figs. 4A and B). These stations also showed the highest surface percentage of total sedimentary nitrogen measurable as amino acid nitrogen ($\%T_{AA}N$; Figs. 4C and D). In both regions, there was a clear relation between surface $\%T_{AA}C$ or $\%T_{AA}N$ and water depth (Figs. 4E and F), the percentages decreasing with increasing water depth.

With the exception of the shallow sites off Antofagasta (GeoB 7104) and off Concepción (GeoB 7161), there was little variation in $\%T_{AA}C$ and $\%T_{AA}N$ with sediment depth. At GeoB 7104 there was a gradual but somewhat variable decrease in $\%T_{AA}C$ and $\%T_{AA}N$ in the upper 10 cm of the sediment below which depth the $\%T_{AA}C$ and $\%T_{AA}N$ remained relatively constant (Figs. 4A and C). At GeoB 7161 there was a subsurface maximum in $\%T_{AA}C$ and $\%T_{AA}N$ at 3–4 cm depth (Figs. 4B and D).

The unidentified OPA-reactive compounds given in Fig. 2 were incorporated in the calculations of $\%T_{AA}C$ and $\%T_{AA}N$. It was assumed that the carbon and nitrogen contents of the unidentified OPA-reactive compounds were equivalent to the average carbon and nitrogen contents of the identified amino acids (4.94 mol C and 1.44 mol N per molecule, respectively). As shown in Table 3 these other amino acids comprised ~5% or less of the THAA concentrations and they showed little depth trend.

3.2. THAA composition

At all stations glycine dominated the THAA pool followed by aspartate, glutamic acid, serine and alanine (Table 3, Fig. 5). With the exception of station GeoB 7104 there were only minor down-core changes in the amino acid composition (Table 3, Figs. 5A–H). At GeoB 7104, glycine decreased from 31 mole-% in the upper 0–1 cm to 22 mole-% at 4–6 cm depth. Below this depth the mole-% of glycine remained within the range of 14–24 mole-% (Fig. 5A). In contrast, the mole-% of leucine and isoleucine remained relatively constant within the upper 6 cm of the sediment, below which depth it increased (Figs. 5C and E). Other amino acids such as phenylanaline showed a similar depth distribution (Table 3). The contribution of aspartate was variable with depth at most stations (Figs. 5G and H). At GeoB 7104 the contribution of aspartate peaked within the upper 6 cm.

The non-protein amino acids β-alanine, ornithine, and taurine occurred in minor concentrations at all investigated stations (Table 3). With the exception of the shallow sites off Antofagasta (GeoB 7104) and off

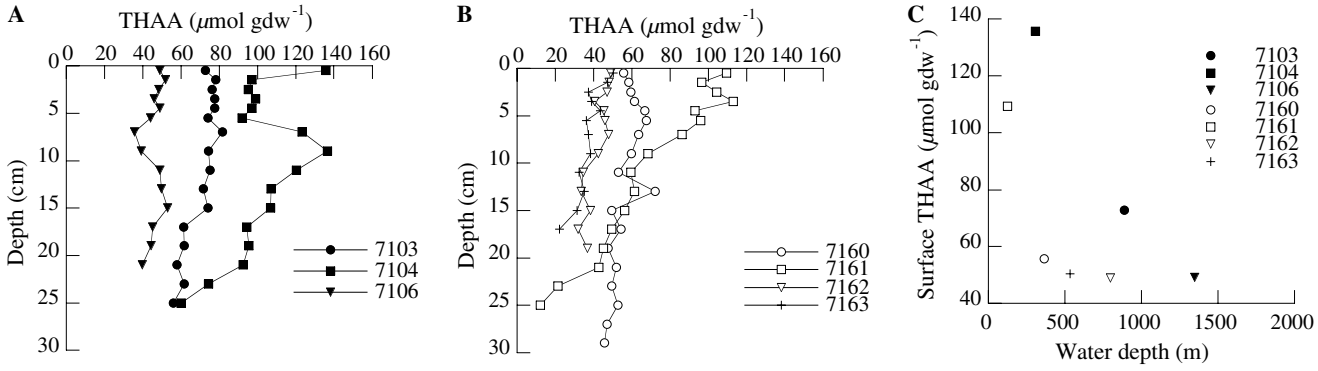

Fig. 3. THAA concentration profiles for stations off Antofagasta (A) and off Concepción (B). Surface (0–1 cm) concentrations of THAA versus water depth (C).

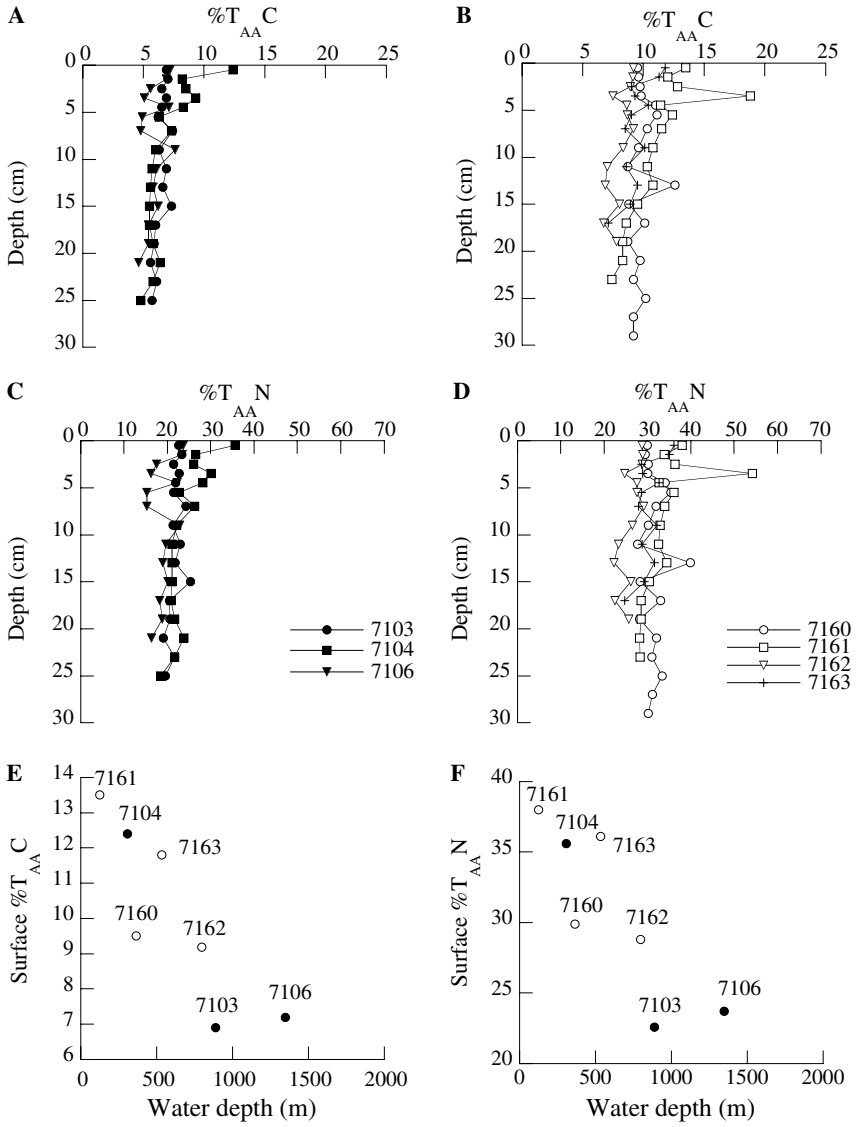

Fig. 4. Fraction of THAA-C relative to total organic carbon (%T_{AA}C) off Antofagasta (A) and off Concepción (B). Fraction of THAA-N to total nitrogen (%T_{AA}N) off Antofagasta (C) and off Concepción (D). Surface %T_{AA}C versus water depth (E) and surface %T_{AA}N versus water depth (F). Closed symbols represents sites off Antofagasta and open symbols sites Concepción.

Concepción (GeoB 7161), the molar aspartate: β-alanine (asp: β-ala) ratio did not show any consistent trend with depth in the sediment (Figs. 6A and B). At GeoB 7104 the molar asp: β-ala ratio decreased slightly with depth of the sediment (Fig. 6A). At GeoB 7161 there was a substantial decrease in the asp: β-ala ratio from the surface to the end of the core (Fig. 6B). In general, there was a decrease in surface asp: β-ala ratios with increasing water depth (Fig. 6C).

3.3. Occurrence of D- and L-enantiomers

With the exception of GeoB 7104 and GeoB 7161, the concentration of the four identified D-amino acids (aspartate, glutamic acid, serine, and alanine) remained relatively constant with depth in the sediment (Figs. 7A–H). At GeoB 7104 there was a subsurface maximum at 8–10 cm depth in D-Asp, D-Glu, D-Ser, and D-Ala of 2.5, 0.6, 0.8, and 0.9 μmol gdw^{-1}, respectively. At GeoB 7161 there was a subsurface maximum at 1–2 cm depth in the respective D-amino acids of 1.1, 0.7, 0.4, and 1.0 μmol gdw^{-1}, respectively.

There was a decrease in total surface sediment D-amino acid concentration (D-Asp + D-Glu + D-Ser + D-Ala) with water column depth at both the northern and the southern stations (Fig. 8).

In general the molar D to L ratio of Asp exceeded that of Glu, Ser, and Ala (Figs. 9A–H). D/L-Asp increased with sediment depth, there were only minor changes in D/L-Glu with sediment depth and D/L-Ser and D/L-Ala showed a slight increase with sediment depth (Figs. 9A–H).

Table 3
Mole-% composition and concentrations of THAA amino acids in sediments off Antofagasta and off Concepción used in the PCA analysis. Others are unidentified OPA-reactive compounds excl. ammonium

Station/depth (cm)	Asp	Glu	Ser	His	Gly	Thr	β-Ala	Tau	Ala	Arg	Tyr	Val	Phe	Ileu	Leu	Orn	Lys	Others	[THAA] μmol gdw^{-1}
GeoB 7103																			
0.5	8.9	6.8	7.8	1.5	22.4	6.4	0.9	0.5	10.0	4.9	2.1	6.0	3.1	3.2	4.9	0.8	5.7	4.3	72.8
1.5	9.0	7.0	7.8	1.5	22.8	6.3	0.9	0.4	9.9	4.9	2.2	6.0	2.8	3.1	4.7	0.7	5.7	4.4	78.3
2.5	8.0	6.6	7.8	1.4	23.1	6.3	0.8	0.5	10.1	5.0	2.2	6.0	3.2	3.2	4.9	0.7	5.9	4.3	76.3
3.5	8.8	6.6	7.8	1.5	22.8	6.3	0.9	0.5	10.0	4.9	2.2	5.9	3.2	3.2	4.8	0.7	5.8	4.0	77.6
4.5	8.8	6.6	7.9	1.5	21.9	6.3	0.9	0.5	10.0	5.0	2.2	5.9	3.4	3.4	4.9	0.7	5.8	4.4	77.7
5.5	9.1	6.6	7.6	1.5	21.9	6.4	0.9	0.5	10.1	5.0	2.3	6.1	3.2	3.3	4.8	0.7	5.7	4.4	74.2
7	9.3	6.8	7.6	1.4	20.8	6.3	0.9	0.5	10.2	4.8	2.3	6.2	3.3	3.2	4.8	0.7	5.8	5.0	81.6
9	9.7	6.9	7.4	1.5	21.6	6.2	0.8	0.5	9.9	4.7	2.2	5.9	3.2	3.3	4.7	0.7	5.8	4.9	74.5
11	8.8	6.4	7.5	1.5	22.1	6.3	0.8	0.5	10.2	4.8	2.3	6.0	3.3	3.4	4.9	0.7	5.7	4.7	75.1
13	9.3	6.8	7.4	1.4	21.8	6.3	0.8	0.5	9.9	4.7	2.2	5.9	3.2	3.3	4.8	0.8	5.8	5.0	71.6
15	9.4	6.9	7.1	1.5	20.9	6.3	0.8	0.5	9.9	5.4	2.0	6.2	3.3	3.4	4.9	0.7	5.8	4.9	74.1
17	8.7	6.4	6.8	1.4	22.9	6.0	0.8	0.5	10.1	4.9	2.2	6.0	3.4	3.4	5.0	0.8	6.0	4.7	61.3
19	7.7	6.4	6.8	1.4	22.7	6.0	0.9	0.5	10.4	5.0	2.3	6.0	3.4	3.5	5.1	0.8	6.3	4.7	61.7
21	8.8	6.3	6.5	1.4	21.6	5.7	0.8	0.5	10.4	5.0	2.4	6.1	3.6	3.6	5.3	0.8	6.3	4.8	57.9
23	8.6	6.7	6.4	1.4	20.4	5.9	0.8	0.5	10.6	5.1	2.5	6.4	3.6	3.7	5.5	0.8	6.4	4.7	61.7
25	8.7	6.4	6.1	1.4	21.5	5.7	0.8	0.5	10.4	5.0	2.5	6.2	3.6	3.7	5.5	0.8	6.3	4.7	56.0
GeoB 7104																			
0.5	10.2	9.3	6.0	1.1	31.3	4.8	0.5	0.2	11.2	4.3	1.5	4.4	2.6	2.4	4.1	0.5	4.4	1.2	135.7
1.5	12.3	8.3	6.3	1.2	26.9	5.2	0.7	0.4	10.5	4.0	1.9	5.1	2.9	2.9	4.4	0.6	5.0	1.6	97.2
2.5	12.4	9.5	6.1	1.2	25.5	5.3	0.7	0.4	10.4	4.1	2.0	5.2	2.9	2.8	4.4	0.6	5.2	1.4	95.1
3.5	11.3	9.6	5.9	0.8	27.3	5.0	0.7	0.3	11.0	4.3	1.8	4.8	2.8	2.7	4.3	0.6	4.8	1.9	99.1
4.5	12.6	9.7	5.7	0.9	25.6	5.1	0.7	0.3	10.4	4.2	1.8	5.1	2.9	2.8	4.3	0.6	4.9	2.3	97.0
5.5	12.9	9.4	5.6	0.9	22.3	5.1	0.7	0.4	10.5	4.7	2.1	5.5	3.3	3.2	4.9	0.7	5.6	2.4	91.9
7	12.2	7.8	5.7	0.9	14.1	5.3	0.8	0.5	10.4	5.4	2.8	6.8	4.7	4.5	6.9	0.8	7.6	2.9	123.4
9	11.2	7.9	5.3	1.0	17.3	5.1	0.7	0.5	10.0	5.1	2.5	6.6	4.6	4.4	6.9	0.8	7.5	2.6	136.7
11	10.9	7.5	5.5	1.0	18.2	4.9	0.7	0.5	10.3	5.3	2.5	6.5	4.6	4.4	6.9	0.8	7.3	2.4	120.5
13	10.8	7.4	5.6	1.0	16.4	5.2	0.7	0.5	10.4	5.6	2.7	6.7	4.7	4.4	7.1	0.8	7.6	2.5	107.1
15	10.8	7.1	5.5	1.0	16.7	5.2	0.7	0.6	10.5	5.5	2.7	6.6	4.8	4.4	7.0	0.8	7.5	2.7	106.8
17	9.4	6.9	5.6	1.0	18.1	5.3	0.7	0.6	10.7	5.9	2.2	6.6	4.7	4.3	7.0	0.9	7.9	2.3	94.4
19	10.5	7.2	5.3	0.9	18.2	5.1	0.7	0.5	10.4	5.6	2.5	6.4	4.5	4.1	6.7	0.8	7.5	2.8	95.6
21	11.5	7.8	5.4	1.0	18.2	5.2	0.7	0.6	10.4	5.4	2.6	6.1	4.5	4.1	6.4	0.8	6.8	2.5	92.4
23	9.5	6.6	5.4	1.0	19.7	5.3	0.7	0.6	10.7	5.2	2.6	6.5	4.7	4.3	6.6	0.9	6.9	2.8	74.5
25	9.9	8.3	5.4	1.0	24.0	4.8	0.5	0.5	11.4	5.3	2.2	5.5	3.9	3.5	5.8	1.0	5.9	1.2	60.2
GeoB 7106																			
0.5	10.8	7.6	7.7	1.2	21.6	6.1	1.2	0.4	9.7	4.5	1.3	5.3	2.9	3.0	4.5	1.2	5.5	5.5	49.1
1.5	10.9	7.5	7.7	1.2	21.5	6.1	1.1	0.4	9.7	4.5	1.4	5.3	2.9	3.0	4.4	1.1	5.5	5.6	52.0
2.5	10.8	7.6	7.7	1.3	22.0	6.1	1.1	0.4	9.8	4.5	1.3	5.2	2.9	3.0	4.5	1.1	5.5	5.2	48.5
3.5	10.1	7.4	7.7	1.3	22.6	5.9	1.2	0.4	9.9	4.5	1.3	5.2	2.9	3.0	4.6	1.2	5.8	5.0	46.0
4.5	11.3	7.7	7.4	1.2	21.6	6.0	1.1	0.4	9.7	4.5	1.3	5.3	2.9	3.1	4.5	1.2	5.4	5.2	49.1
5.5	11.6	7.7	7.4	1.2	21.2	6.0	1.1	0.4	9.6	4.5	1.3	5.3	2.9	3.1	4.5	1.2	5.4	5.5	44.0
7	11.4	7.8	7.4	1.3	21.3	5.7	1.2	0.4	9.6	4.6	1.2	5.3	2.9	3.1	4.5	1.4	5.5	5.4	35.8
9	10.7	7.6	7.3	1.3	20.5	5.9	1.1	0.4	9.8	4.7	1.8	5.4	3.0	3.2	4.6	1.5	5.5	5.7	39.4
11	10.2	7.2	7.0	1.2	21.5	5.9	1.1	0.4	10.0	5.0	1.6	5.3	3.1	3.2	4.8	1.2	6.2	5.0	49.1
13	9.9	6.9	6.7	1.2	21.1	5.9	1.1	0.4	10.2	4.9	1.9	5.5	3.3	3.3	5.0	1.2	6.4	5.0	49.9
15	10.1	6.9	6.7	1.3	20.5	6.0	1.1	0.4	10.0	5.1	2.0	5.7	3.4	3.4	5.0	1.1	6.4	5.0	53.1
17	9.6	6.6	6.5	1.3	20.5	5.9	1.1	0.4	10.4	5.2	2.0	5.7	3.5	3.4	5.1	1.3	6.6	5.1	45.2
19	10.0	6.7	6.2	1.2	20.4	5.8	1.1	0.4	10.3	5.2	2.0	5.7	3.5	3.5	5.2	1.3	6.7	4.8	44.3
21	10.1	6.7	5.7	1.2	19.1	5.6	1.1	0.5	10.4	5.4	2.3	5.8	3.6	3.5	5.3	1.3	6.9	5.3	39.8
GeoB 7160																			
0.5	9.6	7.9	9.4	1.6	21.3	6.7	1.1	0.4	9.8	3.6	1.6	5.0	2.9	3.0	4.8	1.1	5.2	5.4	55.8
1.5	9.3	7.9	8.8	1.4	21.5	6.7	1.1	0.4	10.0	3.7	1.7	5.0	2.9	3.0	4.9	1.0	5.5	5.3	58.5
2.5	9.3	7.2	9.6	1.4	21.2	6.6	1.1	0.4	9.8	3.7	1.8	5.0	2.9	3.0	4.8	1.2	5.3	5.6	59.7
3.5	9.3	8.2	9.4	1.4	21.2	6.5	1.1	0.4	9.9	3.7	1.8	4.9	2.9	3.0	4.8	1.0	5.4	5.4	61.4
4.5	10.6	8.4	9.3	1.4	20.5	6.7	1.0	0.4	9.7	3.6	1.6	5.2	2.9	3.0	4.6	1.0	4.9	5.2	66.8
5.5	9.4	8.1	8.6	1.4	22.5	6.6	1.0	0.4	10.4	3.8	1.6	5.1	2.9	2.7	4.4	1.0	4.9	5.2	67.8
7	10.1	8.2	9.1	1.4	20.6	6.6	1.0	0.3	9.7	3.6	1.7	5.2	2.9	3.1	4.7	1.1	5.0	5.7	63.7
9	9.3	7.6	9.4	1.3	21.6	6.6	1.1	0.4	10.0	3.6	1.6	5.1	2.9	3.0	4.8	1.1	5.3	5.3	59.9
11	8.8	7.7	9.5	1.3	21.8	6.4	1.2	0.4	10.1	3.5	1.6	4.9	3.0	3.0	4.8	1.4	5.4	5.3	53.1
13	9.3	7.5	9.0	1.5	19.7	6.3	0.9	0.5	10.4	3.7	2.1	5.1	3.2	3.0	5.5	1.2	5.3	5.8	72.3

Table 3 (*continued*)

Station/depth (cm)	Asp	Glu	Ser	His	Gly	Thr	β-Ala	Tau	Ala	Arg	Tyr	Val	Phe	Ileu	Leu	Orn	Lys	Others	[THAA] μmol gdw^{-1}
15	10.3	7.9	8.4	1.3	21.7	6.3	1.1	0.6	9.9	3.5	1.6	5.0	2.9	3.1	4.5	1.3	5.1	5.7	49.5
17	9.1	7.7	8.7	1.4	22.1	6.4	1.1	0.5	9.7	3.7	1.6	5.0	2.9	3.1	4.6	1.3	5.4	5.8	54.4
19	9.0	7.8	8.6	1.4	21.8	6.4	1.2	0.4	9.7	3.7	1.6	5.1	2.9	3.1	4.7	1.3	5.3	6.0	47.6
21	10.1	7.7	8.7	1.4	21.7	5.9	1.1	0.4	9.6	3.7	1.6	5.2	2.9	3.0	4.6	1.3	5.1	5.9	52.1
23	9.7	7.5	8.6	1.4	21.8	6.3	1.2	0.4	9.7	3.7	1.6	5.1	2.9	3.1	4.6	1.4	5.2	5.8	49.6
25	9.6	7.4	8.2	1.4	21.8	6.4	1.1	0.4	9.7	3.8	1.7	5.2	3.0	3.1	4.7	1.4	5.3	5.9	52.9
27	8.2	7.3	8.5	1.6	22.5	6.3	1.2	0.4	9.8	3.7	1.6	5.1	3.0	3.1	4.7	1.3	5.5	6.2	47.2
29	11.0	7.8	8.3	1.3	20.1	6.4	1.1	0.3	9.6	4.0	1.7	5.3	3.0	3.2	4.5	1.3	5.1	6.0	45.8
GeoB 7161																			
0.5	10.5	9.1	8.6	1.4	18.6	6.9	0.8	0.4	10.2	3.4	2.1	6.2	3.3	3.7	5.6	0.7	4.7	3.7	109.4
1.5	9.8	8.9	8.6	1.4	19.9	6.8	0.8	0.5	10.5	3.4	2.1	5.9	3.3	3.5	5.7	0.8	4.9	3.2	96.7
2.5	10.2	8.9	8.5	1.4	19.5	6.9	0.8	0.5	10.3	3.4	2.1	6.1	3.3	3.5	5.5	0.8	4.7	3.7	104.6
3.5	10.4	9.0	8.6	1.4	19.3	6.8	0.8	0.4	10.3	3.3	2.1	6.1	3.3	3.6	5.5	0.7	4.5	3.8	113.2
4.5	9.9	8.6	8.7	1.4	20.0	6.9	0.9	0.4	10.4	3.3	2.1	6.1	3.3	3.5	5.6	0.8	4.7	3.6	93.2
5.5	10.5	8.7	8.5	1.4	19.7	6.9	0.8	0.4	10.3	3.4	2.0	6.0	3.2	3.5	5.4	0.8	4.5	3.9	96.0
7	10.1	8.6	8.4	1.4	19.9	6.8	0.9	0.4	10.3	3.4	2.1	5.9	3.2	3.5	5.5	0.9	4.7	3.9	86.4
9	10.4	8.1	8.1	1.5	20.5	6.7	1.0	0.5	10.2	3.4	2.1	5.9	3.2	3.4	5.2	1.1	4.7	4.0	68.4
11	10.0	7.6	8.1	1.5	21.2	6.7	1.1	0.5	10.3	3.4	2.1	5.7	3.2	3.3	5.1	1.2	4.8	4.3	59.7
13	9.8	7.5	8.0	1.5	21.6	6.6	1.1	0.5	10.3	3.4	2.1	5.7	3.2	3.3	5.2	1.1	4.9	4.0	61.3
15	9.6	7.4	7.8	1.6	21.6	6.6	1.1	0.6	10.4	3.6	2.1	5.7	3.2	3.4	5.3	1.1	5.0	4.1	56.1
17	9.5	7.2	7.5	1.6	21.0	6.6	1.2	0.6	10.2	3.7	2.3	5.8	3.3	3.4	5.2	1.3	5.1	4.6	49.6
19	8.9	7.2	7.7	1.6	22.4	6.4	1.0	0.4	10.5	3.9	2.1	5.8	3.3	3.3	5.3	1.0	5.3	3.9	45.3
21	9.1	6.9	7.6	1.6	22.1	6.6	1.0	0.4	10.4	3.9	2.1	5.9	3.3	3.5	5.3	1.1	5.2	4.1	42.8
23	8.1	6.6	7.3	1.7	21.7	6.6	1.3	0.7	10.6	4.0	1.4	5.8	3.4	3.5	5.6	1.6	5.7	4.2	21.4
25	8.0	6.3	6.7	1.9	19.6	7.0	1.7	1.0	10.8	3.9	1.1	6.3	3.4	3.8	5.9	2.3	6.0	4.3	12.2
GeoB 7162																			
0.5	9.7	7.8	10.3	1.6	21.8	6.8	1.2	0.3	9.9	3.5	1.4	5.1	2.8	3.0	4.8	0.8	5.4	3.6	49.0
1.5	10.5	7.8	10.4	1.5	21.2	7.0	1.2	0.3	9.8	3.8	1.1	5.2	2.8	2.9	4.6	0.9	5.2	3.7	48.3
2.5	10.3	7.9	10.4	1.5	21.5	7.0	1.2	0.3	9.8	3.7	1.1	5.1	2.8	2.9	4.5	0.9	5.2	3.9	47.0
3.5	8.1	7.1	10.5	1.4	24.8	6.4	1.4	0.4	9.9	3.8	0.7	4.6	2.6	2.7	4.7	1.0	6.0	3.8	40.7
4.5	10.2	7.7	10.5	1.5	21.9	7.0	1.2	0.3	9.8	3.9	0.7	5.2	2.8	2.9	4.5	0.9	5.1	3.9	45.5
5.5	10.3	7.7	10.4	1.5	22.3	6.9	1.3	0.3	9.8	3.9	0.6	5.1	2.7	2.8	4.5	0.9	5.2	3.9	45.9
7	11.1	8.0	10.2	1.5	21.0	7.2	1.1	0.3	9.6	3.9	0.7	5.3	2.8	3.0	4.4	0.9	4.9	4.0	48.0
9	10.0	7.6	10.2	1.4	22.4	7.1	1.3	0.3	9.8	3.8	0.8	5.3	2.8	2.9	4.5	0.9	5.2	3.8	42.6
11	8.7	6.9	9.6	1.4	25.2	6.5	1.4	0.3	9.9	3.8	0.5	4.9	2.7	2.7	4.6	1.1	5.9	3.9	34.7
13	9.0	6.8	9.6	1.4	25.0	6.6	1.3	0.3	10.0	3.9	0.5	5.1	2.8	2.8	4.7	1.1	5.6	3.6	33.7
15	10.6	7.5	9.3	1.5	22.3	7.1	1.2	0.3	9.7	4.0	0.7	5.5	2.9	3.0	4.6	1.0	5.1	3.7	38.4
17	8.8	7.0	9.3	1.5	24.7	6.7	1.3	0.3	9.9	3.9	0.5	5.0	2.8	2.9	4.7	1.1	5.9	3.8	32.0
19	10.6	7.3	8.8	1.4	22.2	7.0	1.1	0.3	9.7	4.0	0.7	5.6	3.0	3.2	4.7	1.1	5.3	4.0	36.7
GeoB 7163																			
0.5	11.2	9.0	9.8	1.5	20.1	7.8	0.8	0.5	9.6	3.5	1.3	5.8	2.9	3.2	4.7	0.4	4.6	3.2	50.4
1.5	11.1	9.1	9.8	1.5	20.7	7.8	1.1	0.5	9.6	3.3	1.2	5.7	2.9	3.1	4.7	0.5	4.7	2.8	47.2
2.5	9.1	7.8	10.0	1.5	23.5	7.4	1.3	0.5	10.0	3.3	1.0	5.3	2.7	2.8	4.8	0.6	5.5	2.9	37.5
3.5	10.1	8.2	9.7	1.5	23.3	7.4	1.2	0.5	9.8	3.3	1.0	5.3	2.6	2.8	4.6	0.6	5.2	3.0	39.0
4.5	11.0	8.7	9.9	1.5	21.4	7.7	1.1	0.4	9.7	3.4	1.1	5.6	2.7	2.9	4.5	0.6	4.8	2.8	43.6
5.5	9.9	7.9	9.7	1.4	23.7	7.4	1.2	0.5	9.9	3.3	0.9	5.1	2.6	2.8	4.6	0.6	5.3	3.0	36.2
7	9.6	7.9	9.8	1.5	23.9	7.4	1.3	0.5	10.0	3.2	1.0	5.2	0.8	2.8	4.7	0.6	5.5	4.5	37.5
9	12.0	8.6	9.3	1.6	21.5	7.6	1.1	0.5	9.7	3.3	1.0	5.6	2.7	3.1	4.4	0.7	4.7	2.7	38.5
11	10.9	8.3	9.1	1.6	23.3	7.4	1.3	0.5	10.0	3.2	0.9	5.2	0.7	2.7	4.6	0.7	5.4	4.4	32.5
13	12.6	8.6	8.9	1.5	21.3	7.8	1.1	0.5	9.7	3.4	1.0	5.8	0.9	3.0	4.4	0.5	4.7	4.4	35.3
15	11.6	8.2	8.8	1.5	22.5	7.5	1.2	0.5	9.9	3.4	0.9	5.5	2.7	2.9	4.5	0.7	4.9	2.6	31.3
17	10.3	7.4	7.7	1.4	24.9	7.1	1.4	0.6	10.3	3.6	0.6	5.2	2.6	2.7	4.8	0.7	5.9	2.8	22.3

3.4. Cell specific concentrations of D-amino acids in selected pure cultures

In order to relate the occurrence of D-amino acids in the sediment to the D-amino acid concentrations of bacterial cells, D-amino acids in whole-cell hydrolyzates were analyzed (Table 2). Only half of the cultures contained all four investigated D-amino acids, and the relative proportion of the different D-amino acids varied widely between cultures (Table 2). However, D-Ala accounted for one third to half of the total cell specific D-amino acid concentration in the different strains. Similarly, D-Glu made up a large fraction of the D-amino acid concentration in five of the six strains analyzed.

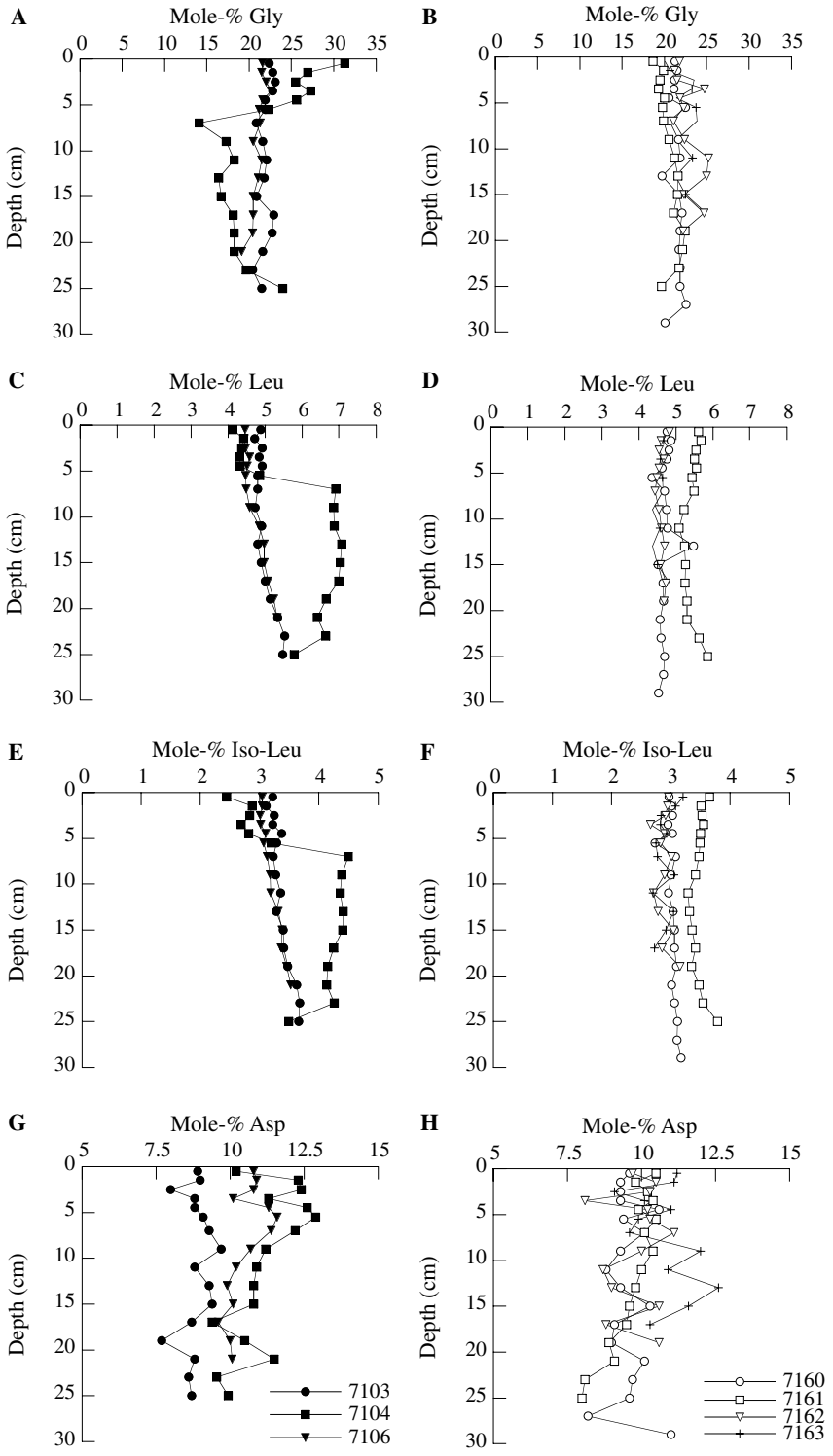

Fig. 5. Profiles of the mole-% of THAA of Glycine (Gly), Aspartate (Asp), Leucine (Leu), and Iso-Leucine (Iso-Leu) off Antofagasta (left-hand panels) and off Concepción (right-hand panels).

4. Discussion

4.1. Amino acid concentrations and reactivity

Organic matter in marine sediments is depleted in amino acids by a factor of 2 or more compared to either plankton sources or sinking particles. In open-ocean sediments amino acid are depleted by several orders of magnitude (Whelan, 1977; Keil et al., 2000). THAA concentrations from both transects followed this general trend with higher sediment surface THAA concentrations at the shallow stations. In general, the surface THAA concentrations were higher off Antofagasta compared to Concepción (Fig. 3C). This difference can partly be explained by lower

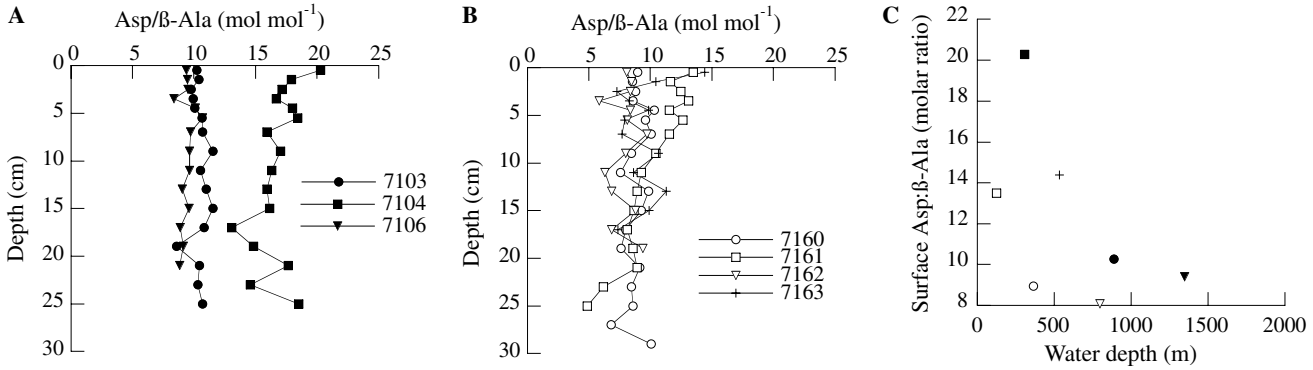

Fig. 6. Profiles of the aspartate to β-alanine ratio (Asp: β-Ala) off Antofagasta (A) and Concepción (B). Surface (0–1 cm) Asp: β-Ala ratios versus water depth (C).

TOC concentrations off Concepción compared to the Antofagasta sites (Niggemann, 2005).

Concentrations of THAA at the shallowest Concepción station GeoB 7161 were slightly lower but comparable to those recorded by Pantoja and Lee (2003) at their Station 26, which was located near GeoB 7161. Similarly, the THAA concentrations furthest off-shore (stations GeoB 7103, 7106, and 7162) at water depth ~800–1350 m were in the same range as those reported at 1050 m water depth in sediments off Central Chile by Pantoja and Lee (2003).

Data obtained in this study show that changes in sediment THAA concentrations were influenced by distance off shore, and hence water depth of the sampling station. In contrast, changes in THAA concentrations with sediment depth were small except for the shallow stations GeoB 7104 off Antofagasta and GeoB 7161 off Concepción. Vertical decreases in THAA concentrations are generally thought to be due to decomposition by benthic macro- and microorganisms. The relatively small decrease in THAA concentration with sediment depth at the deeper stations can be explained by THAA reaching the sediment being less reactive here than at the shallower stations. Off Concepción all stations were strongly bioturbated with mixing depths down to 10 cm (Table 1), which may also help to explain the observed homogenous distribution of THAA with depth. Similar lack of changes in THAA concentrations with sediment depth have been reported by Pantoja and Lee (2003) for their stations 18 and 40 off the coast of central Chile, whilst Dauwe and Middelburg (1998) observed a rather homogenous amino acid distribution with depth in the bioturbated zones of North Sea sediments.

Sedimentary THAA concentration profiles followed the trends of the TOC and TN concentration profiles at the deeper stations (GeoB 7106, GeoB 7162, and GeoB 7163) with a resultant homogenous distribution of $\%T_{AA}N$ and $\%T_{AA}C$ with depth (Figs. 4A–D). This may indicate that there was no preferential degradation of THAA relative to bulk TOC and TN and that the organic matter was already substantially degraded prior to incorporation into the sediment as previously suggested. Grutters et al. (2001) reached a similar conclusion in sediments across the Northeastern Atlantic continental slope. At the shallowest stations off Antofagasta and off Copcepción (GeoB 7104 and GeoB 7161, respectively) $\%T_{AA}N$ and $\%T_{AA}C$ decreased with depth in the sediment, suggesting a preferential degradation of THAA relative to bulk organic matter and thus incorporation of more recent and less mineralized organic matter into the sediment. It is worth noting that average values of $\%T_{AA}C$ and $\%T_{AA}N$ in the northern and southern transects were slightly different (~6 and 10% for C, respectively, and 22 and 31% for N, respectively). However, $\%T_{AA}C$ and $\%T_{AA}N$ values were within the range typical for continental margin systems of $12 \pm 10\%$ carbon and $30 \pm 12\%$ nitrogen in the amino acid form (Keil et al., 2000). Further indications on the "freshness" of the organic matter incorporated into the sediment were provided by decreases in both surface $\%T_{AA}N$ and surface $\%T_{AA}C$ with increased water depth (Figs. 4E and F). Previous studies have shown that $\%T_{AA}N$ decreases as diagenesis progresses (e.g., Cowie and Hedges, 1994 and references in there; Keil et al., 2000). In contrast, mole percentages of the non-protein amino acids, β-alanine and γ-amino-butyric acid, typically increase relative to their more abundant protein amino acid counterparts upon progressive diagenesis (e.g., Cowie and Hedges, 1994; Keil et al., 2000). The asp: β-ala ratio decreased with sediment depth at the shallowest stations (GeoB 7104 and GeoB 7161). In contrast, the asp: β-ala ratio remained relatively constant with depth at the deeper stations (Figs. 6A and B). In addition, there was a gradual, but somewhat variable, decrease in the surface asp: β-ala ratio with increasing water depth (Fig. 6C).

Estimates of THAA-N mineralization, as a measure of THAA reactivity, was obtained from the following formulation:

$$\text{THAA} - \text{N mineralization} = (\%T_{AA}C \times 2 \times \text{SRR})/(100 \times \text{C} : \text{N}_{\text{THAA}}) \quad (2)$$

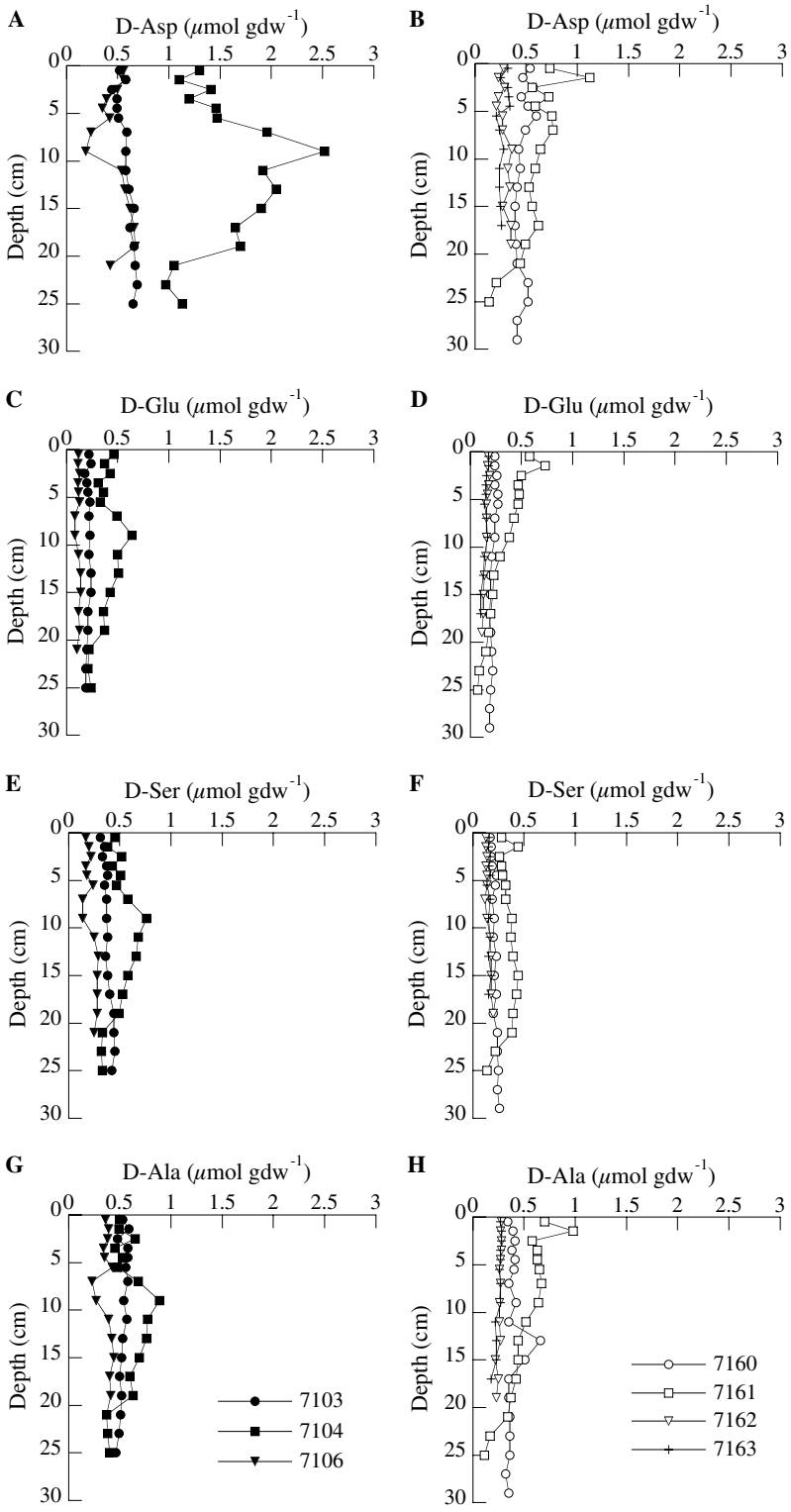

Fig. 7. Concentration profiles of D-aspartate (D-Asp), D-glutamic acid (D-Glu), D-serine (D-Ser), and D-alanine (D-Ala) off Antofagasta (left-hand panels) and Concepción (right-hand panels).

THAA-N mineralization was considered as a minimum estimate as it was only based on the fraction of carbon oxidation that was due to sulfate reduction ($2 \times SRR$). $C{:}N_{THAA}$ was the molar C:N ratio in THAA. $C{:}N_{THAA}$ was estimated at each depth of each station as the ratio between summed μmol-C gdw^{-1} and summed μmol-N gdw^{-1} from individual amino acids in THAA. $C{:}N_{THAA}$ fell in the range of 3.0–3.4. Sulfate reduction rates were obtained from Niggemann (2005). According to Pantoja and Lee (2003) we assumed that all THAA are associated with

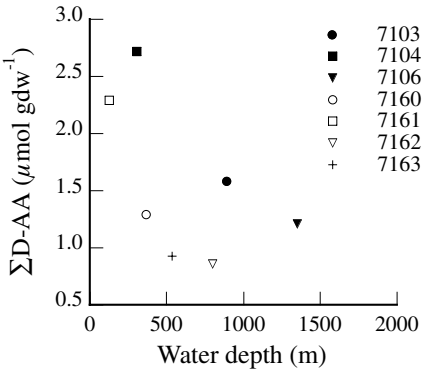

Fig. 8. Total surface concentrations of the sum of the four D-amino acids versus water depth.

the solid phase since the contribution from pore water amino acids to the total amino acid pool in sediments usually is small. THAA-N mineralization rates ranged from 10.4 μmol-N m^{-2} d^{-1} at GeoB 7106 to 84.7 μmol-N m^{-2} d^{-1} at GeoB 7161 (Table 4) and there was a general decrease in THAA-N mineralization, and thus THAA reactivity, with increasing water depth. Hence, the changes in THAA-N mineralization with distance off shore, in both regions, support the indications on "freshness" of the organic matter judged from changes in $\%T_{AA}C$, $\%T_{AA}N$, and the asp: β-ala ratio (Figs. 4E and F and 6C, respectively). Grutters et al. (2001) estimated first-order degradation rate constants for individual amino acids at different water depths in sediments from the Northeastern Atlantic continental slope. They found that THAA degradation rate constants decreased with increasing water depth confirming the data obtained in this study. However, the estimated THAA-N mineralization rates were low compared to the THAA-N mineralization estimated by Pantoja and Lee (2003) in Chilean coastal sediments. At their station 26, the THAA-N mineralization rate was ~15 times greater than our estimated THAA-N mineralization rate at the nearby GeoB 7161. In contrast to our study Pantoja and Lee (2003) used the $\sum CO_2$ production rate (Thamdrup and Canfield, 1996) and not the SRR to estimate the THAA-N mineralization rate. However, the difference in the estimated THAA-N mineralization rate between our study and that of Pantoja and Lee (2003) cannot be explained by the fact that we underestimated carbon oxidation by using twice the sulfate reduction rate as a minimum estimate of carbon oxidation. Thamdrup and Canfield (1996) and Ferdelman et al. (1997) reported sulfate reduction rates at station 26, which were ~25 times greater than the rate recorded by Niggemann (2005) for station GeoB 7161. We consider that the major difference in sulfate reduction rates obtained in these two studies and that of Niggemann (2005) was related to seasonal variations in the supply of organic matter to the shelf sediments. Sampling by Niggemann (2005) was carried out towards the end of the upwelling season, in the second half of April, whereas the former two studies were carried out in March.

4.2. Bacterially derived amino acids

The uniform concentrations of the four D-amino acids, D-Asp, D-Glu, D-Ser, and D-Ala, with sediment depth at the deeper stations (GeoB 7103, 7106, 7160, 7161, 7162, and 7163) demonstrate that there was no net production of D-amino acids in the sediment. This supports previously discussed indications of a lower reactivity of the organic matter incorporated into the sediment at the deeper stations. However, at stations GeoB 7104 and GeoB 7161 there were subsurface maxima at 8–10 cm and 1–2 cm depth, respectively, which might be indicative of in situ net production of bacterially derived D-amino acids in the form of bacterial cells and/or peptidoglycan in cell wall remains.

Bacteria have previously been suggested to be the source for D-Asp, D-Ala and probably also D-Glu in marine surface sediments (Pollock and Kvenvolden, 1978) as well as in the water column (Lee and Bada, 1977; McCarthy et al., 1998). However, recent studies in marine sediments have demonstrated that D-Ser is also a common D-amino acid (Pedersen et al., 2001; Grutters et al., 2002). Further, Schleifer and Kandler (1972) showed that D-ornithine, D-diaminobutyric acid, and D-diaminopimelic acid could be present in peptidoglycan in addition to the four D-amino acids quantified in the present study.

Very little is known as to whether D-amino acids in sediments reflect intact bacteria, empty cell sacs, or peptidoglycan (Pedersen et al., 2001). Further, it is arguable as to whether bacterial biomass is a major component of sedimentary organic matter (Keil et al., 2000 and references therein) and there is little information about the relative contribution of peptidoglycan to THAA in marine sediments (Pedersen et al., 2001; Grutters et al., 2002). In order to address this question we have estimated the expected D-amino acid content of the enumerated bacterial cells and compared this to the measured concentrations of the respective D-amino acids. Bacterial abundance was determined by epifluorescence microscopy using DAPI staining in the upper 5 cm of the sediment, at all stations, with the exception of GeoB 7160 (W. Serrano, pers. comm.). The D-amino acid contribution from bacterial cells was estimated from the number of bacteria times the respective average cell specific concentrations of D-Asp, D-Glu, D-Ser, and D-Ala in the cultures presented in Table 2. Off Antofagasta enumerated bacteria contributed <3%, <47%, <7%, and <12% of the measured concentration of D-Asp, D-Glu, D-Ser, and D-Ala, respectively. Off Concepción the respective contributions of enumerated bacteria were <9%, <53%, <16%, and <31%, respectively. Because of the inherent variability among known peptidoglycan structures (Schleifer and Kandler, 1972) and the poorly defined species composition of marine bacterial communities, contributions of D-amino acids from enumerated bacteria to the measured sediment D-amino acids cannot be calculated accurately. However, the estimated contributions of enumerated bacteria to the D-amino acid concentrations might be considered as maximum estimates, because the cell

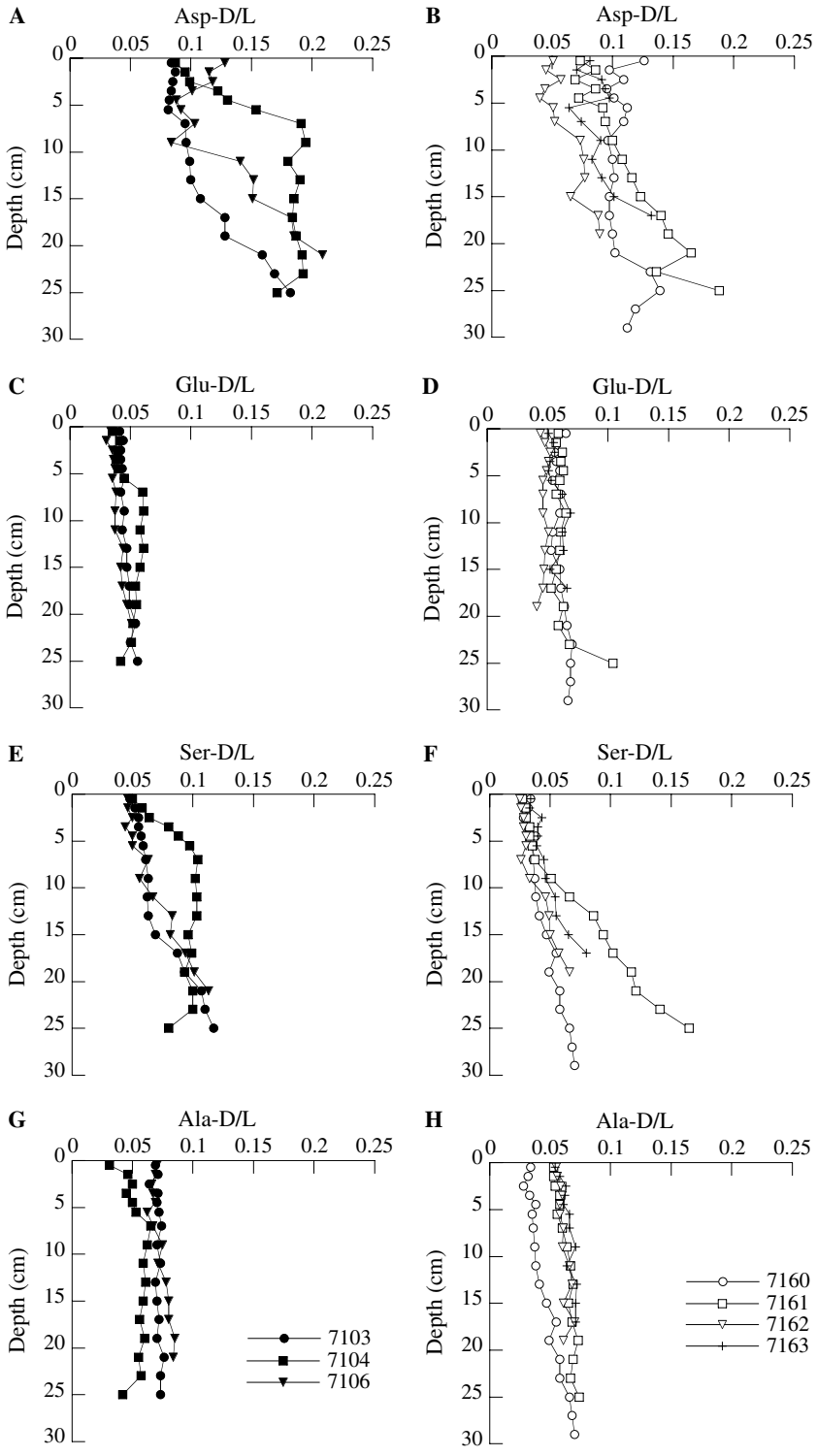

Fig. 9. Profiles of the D/L ratio of Asp, Glu, Ser, and Ala off Antofagasta (left-hand panels) and Concepción (right-hand panels).

specific bacterial D-Ala concentrations used here were high relative to previously reported values for both Gram-positive and Gram-negative bacteria (Pedersen et al., 2001). It should be noted that the cell specific D-Ala concentrations in Pedersen et al. (2001) were not corrected for racemization during acid hydrolysis. Thus, it is likely that a large fraction of the measured sediment D-amino acids were from empty cell sacs and cell wall fragments, including peptidoglycan, which persisted in the sediment after cell death. Pedersen et al. (2001) reached a similar conclusion by a slightly different approach in a study on bacterial influence on amino acid enantiomerization in a coastal marine sediment.

The contribution of bacterial amino acid nitrogen to THAA-N was estimated from the bacterial cell number, a dry weight of bacterial cells of 2.8 10^{-13} g, a protein dry

Table 4
Estimated THAA-N mineralization rates

Station	Water depth (m)	μmol THAA-N m^{-2} d^{-1}
GeoB 7103	891	23.4
GeoB 7104	307	33.0
GeoB 7106	1350	10.4
GeoB 7160	367	44.6
GeoB 7161	126	84.7
GeoB 7162	798	40.8
GeoB 7163	536	n.d.

weight content of 55% (Brock and Madigan, 1991) and the traditional nitrogen to protein conversion factor of 6.25 (Jones, 1931). Off Antofagasta and off Concepción, bacteria contributed <7% and <14%, respectively, to the measured concentration of THAA-N. The lowest contribution of bacterial amino acid nitrogen to THAA-N (<2%) was at GeoB 7104.

The relative contribution of peptidoglycan amino acids to THAA ($THAA_{pep}$/THAA) was estimated from the measured D-amino acids and the average L/D ratio of peptidoglycan from the Gram-positive *Staphylococcus aureus* given in Pedersen et al. (2001). The estimated $THAA_{pep}$/THAA in the upper 1 cm of the sediment of 18–25% (Figs. 10A and B) is somewhat lower than previously obtained maximum $THAA_{pep}$/THAA contributions of ~40% in coastal surface sediments (Pedersen et al., 2001) and 46% in sediment from the mixed layer in the Northeastern Atlantic Ocean (Grutters et al., 2002). However, the estimated surface $THAA_{pep}$/THAA is in agreement with model estimates of the contribution of peptidoglycan to the amino acid pool in average marine sediment of 22% and 25% in "high-organic-content" sediments (Keil et al., 2000). The increase in surface $THAA_{pep}$/THAA with increasing water depth (except at GeoB 7162; Fig. 10C) might reflect that bacteria and cell wall remains in source material were degraded at a slower rate than other proteinaceous material during their transfer through the water column. Thus, even though surface sediments in shallow waters have a higher concentration of D-amino acids compared to surface sediments at greater water depth (Fig. 8) our data suggest that peptidoglycan-amino acids account for a larger fraction of THAA in particulate organic material that reaches the sediments in deeper water. This hypothesis is consistent with water column studies on the role of bacterial contribution to marine dissolved organic nitrogen (McCarthy et al., 1998), the production of refractory dissolved organic matter by bacteria (Ogawa et al., 2001), the role of microbial processes in the alteration of dissolved organic matter (Benner and Kaiser, 2003) and indications of peptidogly-

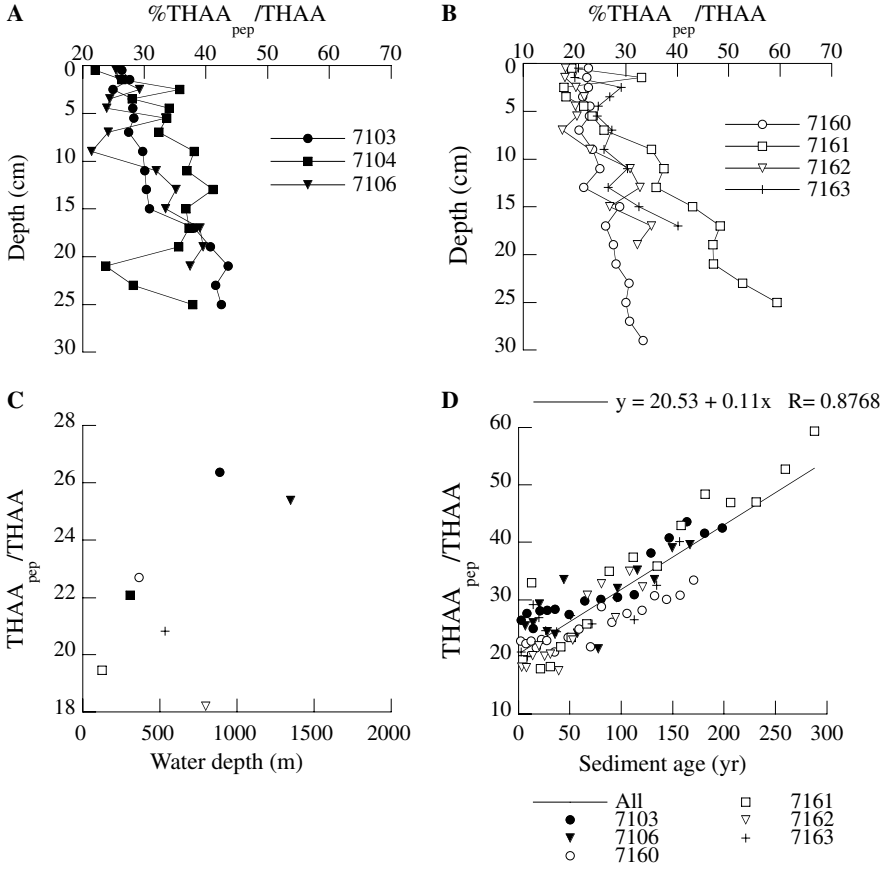

Fig. 10. Profiles of the estimated contribution of peptidoglycan amino acids to THAA ($THAA_{pep}$/THAA) off Antofagasta (A) and Concepción (B). Surface $THAA_{pep}$/THAA versus water depth (C) and $THAA_{pep}$/THAA versus age of the sediment at the respective depth and stations investigated (D).

can in Gram-negative bacteria being more resistant to degradation than that of Gram-positive bacteria (Jørgensen et al., 2003). Further, Nagata et al. (2003) found that first-order rate constant of peptidoglycan mineralization was 2–21 times lower than those of total proteins in surface waters.

In accordance with the increase in the estimated surface $THAA_{pep}$/THAA with increased water depth, there was an increase in $THAA_{pep}$/THAA with increased depth and age of the sediments. The *y*-intercept of 21% in Fig. 10D gives the average $THAA_{pep}$/THAA ratio of organic matter arriving to the sediment surface off Chile. This value is in line with the model estimates given by Keil et al. (2000) that were discussed earlier. The age of the sediment at a given depth at the different stations was estimated from the sediment accumulation rates given in Table 1. The implications of the increase in $THAA_{pep}$/THAA with increased age of the sediments are that THAA becomes progressively enriched with bacterial peptidoglycan as degradation proceeds. Hence, our results are in accordance with Pedersen et al. (2001) who hypothesized that THAA is composed of at least two different pools with different reactivity: (1) structural biopolymers including D- and L-amino acids of bacterial cell walls and peptidoglycan and (2) cellular proteinaceous material that is largely composed of L-amino acids. With time, the proteinaceous material is degraded by microorganisms to a larger degree than is peptidoglycan, leading to the observed enrichment of THAA with D-amino acids.

4.3. Racemization

The increasing proportion of D-isomers of THAA with depth and age of the sediment can, in addition to a bacterial origin, be the result of chemical racemization (e.g., Bada, 1982). In order to examine whether racemization could have been an important process in the formation of the quantified D-amino acids, we estimated the apparent racemization rate constants for Asp at the different depth in the sediment and compared them with the estimated Asp racemization rate constants (k) at each site. The apparent racemization rate constants were calculated from the observed increases in D/L values (after correction for racemization during hydrolysis), at the different depth in the sediment at each station, using the ^{210}Pb ages estimated from the sediment accumulation rates given in Table 1. The estimated racemization rate constants at each site were based on the Goodfriend (1997) formulation:

$$\ln k = 42.64 - 14,620(1/T) \quad (3)$$

where T is the temperature in degrees Kelvin. The bottom water temperatures given in Table 1 were used (D. Gerdes, pers. comm.). The Goodfriend (1997) formulation was obtained from the results of a heating experiment of a specimen of the colonial anemone *Gerardia*. The estimated racemization rate constants accounted for 2 to <10% of the apparent racemization constants except at GeoB 7161, where it accounted for 18% (Table 5). These results clearly indicate that biological processes dominated the production of D-amino acids at the investigated sites, and that the increase of D-amino acids with sediment depth was not simply a function of in situ chemical racemization. Lee and Bada (1977); Pollock and Kvenvolden (1978); Pedersen et al. (2001); and Grutters et al. (2002) reached similar conclusions in studies from contrasting marine environments.

Table 5
Calculated apparent and actual racemization rate constants at the different sites off the coast of Chile

Station	Average $k_{apparent}$ (yr^{-1})	$k_{estimated}$ (yr^{-1})	$k_{estimated}$ as % of $k_{apparent}$
GeoB 7103	6.1×10^{-4} ($n=11$)	4.5×10^{-5}	7.4
GeoB 7106	1.0×10^{-3} ($n=7$)	3.5×10^{-5}	3.3
GeoB 7160	1.0×10^{-3} ($n=9$)	10.0×10^{-5}	9.6
GeoB 7161	8.4×10^{-4} ($n=12$)	1.5×10^{-4}	18.1
GeoB 7162	9.5×10^{-4} ($n=8$)	4.5×10^{-5}	4.7
GeoB 7163	1.1×10^{-3} ($n=8$)	6.2×10^{-5}	5.7

The apparent racemizaton rate constant ($k_{apparent}$) is given as the average $k_{apparent}$ from the different depth in the sediment at each station, since there were no trends in $k_{apparent}$ with depth. Negative $k_{apparent}$'s, caused by variation in the D/L profiles, were not included in the average $k_{apparent}$. The number of $k_{apparent}$ (n) included in the average is given in brackets.

4.4. THAA compositional changes

Dauwe et al. (1999) argued that 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). By use of Principal Component Analysis (=PCA) Dauwe and Middelburg (1998) quantitatively assessed the variation in amino acid composition. From their analysis, where the first axis of the PCA was used to estimate the Degradation Index (DI), they observed systematic compositional changes upon progressive degradation (i.e., decrease in DI).

Our DI estimates were based on the amino acid composition (mole-% of the different amino acids) of the 105 samples from the 7 stations investigated (Table 3). In accordance with Dauwe and Middelburg (1998) we only used the first axis of the PCA in our analysis to estimate the Degradation Index (DI) of individual samples on this axis. The first component of our analysis of Chile samples explained 44.7% of the variance (Table 6). Surprisingly, DI increased with sediment depth at all the northern stations with the down-core changes in DI being the most extreme at GeoB 7104 (Fig. 11A). At this station DI remained <0.745 in the upper 6 cm of sediment and increased to 1.576–2.678 at depth >6 cm. In contrast, the other diagenetic indicators such as $\%T_{AA}N$, $\%T_{AA}C$ and asp: β-ala indicate that the diagenetic status increased down-core at GeoB 7104, as all three parameters decreased with

Table 6
Parameters of the PCA based on the mole-% composition of THAA from all depths and stations given in Table 3[a]

Amino acid	Factor coefficient	Average	Standard deviation
Asp	0.002	10.02	1.09
Glu	−0.036	7.63	0.81
Ser	−0.106	7.97	1.47
His	−0.076	1.36	0.20
Gly	−0.068	21.59	2.24
Thr	−0.091	6.35	0.72
β-Ala	−0.086	1.01	0.22
Tau	0.055	0.44	0.10
Ala	0.076	10.09	0.37
Arg	0.098	4.18	0.73
Tyr	0.102	1.70	0.59
Val	0.098	5.58	0.51
Phe	0.110	3.12	0.65
Ileu	0.112	3.24	0.42
Leu	0.107	5.02	0.67
Orn	−0.007	0.96	0.30
Lys	0.096	5.57	0.76
Others	−0.037	4.16	1.19

[a] 44.7% of the variation was explained by the first axis.

sediment depth (Figs. 4 and 6). Each of these other diagenetic parameters is considered sensitive to different stages of diagenetic alteration, and they appear to be uncompromised by source variations (Cowie and Hedges, 1994). The uniquely high proportion of glycine in the upper 6 cm of GeoB 7104 (22–31 mole-%) compared to the lower mole-% of glycine at depth >6 cm (14–24 mole-%) undoubtedly contributed to the lower DI values in the upper 6 cm of the sediment. The feeding biology of the foraminifera *Nonionidae*, which was observed in high abundances at GeoB 7104, might be responsible for the accumulation of glycine in the upper part of the sediment and thus the low observed DI values. The foraminifera family *Nonionidae* is known to retain diatom chloroplasts (Grzymski et al., 2002), which indirectly lead to the accumulation of glycine in the form of glycine-rich empty diatom cells. Similarly, Ingalls et al. (2003) explained low DI values for Southern Ocean plankton THAA with the high proportion of glycine in diatom-rich plankton and the presence of a large number of empty diatom frustules. The presence of foraminifera may also explain the peak in the mole-% of aspartate in the upper part of GeoB 7104, as foraminifera shells are know to be rich in aspartic acid (King, 1977).

Bacterial cell-wall peptidoglycan can also be rich in glycine (Koch, 1990), but not serine or threonine (Ingalls et al., 2003). Despite the fact that glycine was more enriched than glycine + serine + threonine in the upper 6 cm of GeoB 7104 (Fig. 12A), there were no indications of peptidoglycan being the source of glycine in the upper part of GeoB 7104. The maximum concentration of the

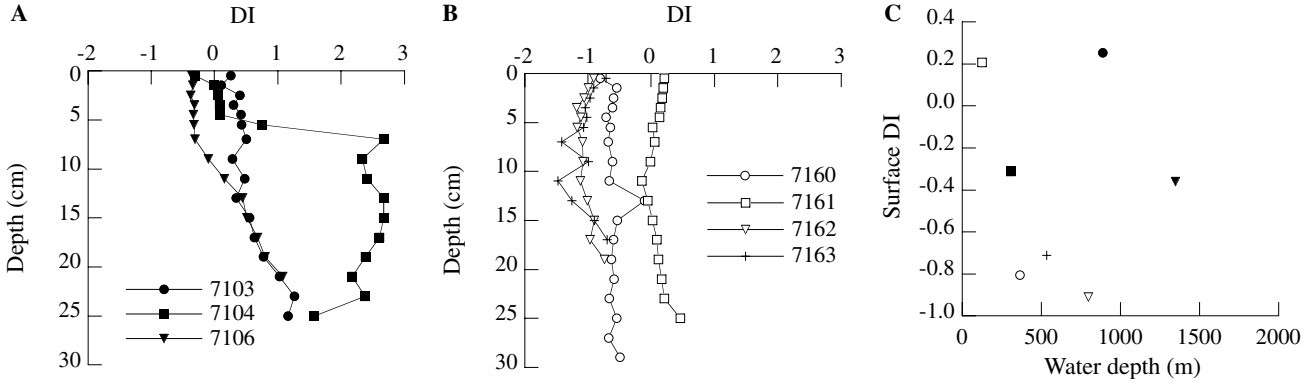

Fig. 11. Profiles of the estimated degradation index (DI) based on the molar composition of THAA off Antofagasta (A) and Concepción (B). Surface DI values versus water depth (C).

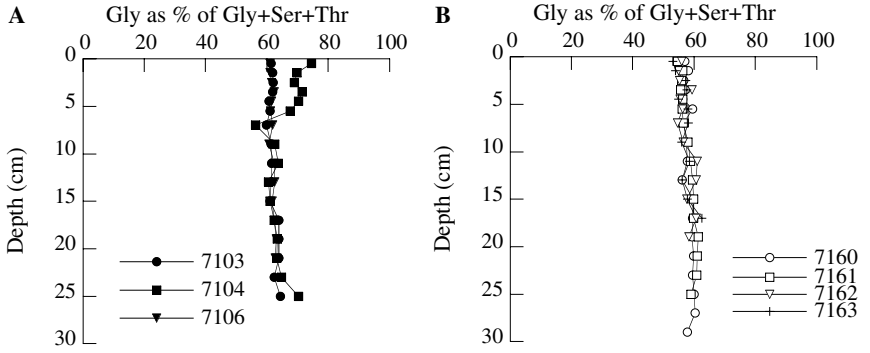

Fig. 12. Profiles on the contribution of glycine to glycine + serine + threonine off Antofagasta (A) and Concepción (B).

four peptidoglycan D-amino acids was recorded at 8–10 cm depth (Figs. 7A, C, E, and G) and thus below the zone of glycine enrichment.

At the southern stations off Concepción DI remained relatively constant with sediment depth (Fig. 11B). We consider that the presence of bioturbating macrofauna (Niggemann, 2005) resulted in such extensive mixing of the sediments, that compositional changes with depth were nearly absent. Similarly, Dauwe and Middelburg (1998) observed that degradation occurred at all their investigated stations, but that it was difficult to trace at most stations because of bioturbation.

Off Concepción there was a decrease in surface DI values from 0.207 at the shallowest station GeoB 7161 to −0.711 to −0.910 at the deeper stations (Figs. 11B and C), which suggested that more degraded material was incorporated into the sediment at the deeper stations. Pantoja and Lee (2003) also obtained the highest DI values (least degraded material) in surface sediments at near-shore stations off Concepción, whereas DI for the deeper stations suggested the presence of more degraded material.

In summary, the abrupt increase in DI below 6 cm depth at GeoB 7104 and the general increase in DI with sediment depth at the northern stations indicate that DI did not clearly distinguish between the influence of source and degradation. Consequently, the absolute values of DI cannot be compared between data sets from the northern and southern stations. Keil et al. (2000) made similar observations on compiled literature data, where they found that sediments from the Peru upwelling region and the Mexican margin contained amino acids that better reflected sources rather than highly altered amino acid remains.

5. Conclusions

The degree of decomposition in sediments underlying the Chilean upwelling cells off Antofagasta and off Concepción was identified from trends in three different biogeochemical compositional characteristics: the percentage of organic carbon in the form of amino acids, the percentage of total nitrogen present as amino acids, and the ratio between aspartate and its degradation product β-alanine. Each of these parameters showed consistent trends with water depth and at the shallowest stations they also showed consistent trends with sediment depth.

The degradation state of the sediment was also evaluated from DI. Off Concepción DI supported trends in the aforementioned compositional characteristics describing the degree of decomposition. The greatest change in DI was related to distance off shore of the sampling stations, as the degradation state of the organic matter appeared to increase with increasing water depth. The unexpected down-core increase in DI with sediment depth at all stations off Antofagasta was contradictory to the aforesaid compositional characteristics and hampered the use of DI in the northern area.

This study successfully examined the contribution of bacterially derived amino acids to bulk THAA, which gives indications on the importance of bacteria in the preservation of organic carbon. Off Antofagasta and off Concepción enumerated bacteria accounted for a relatively insignificant fraction of THAA-N (<7 and 14%, respectively). Estimates on the contribution of enumerated bacteria to the measured D-amino acid concentrations indicated that a large fraction of the measured D-amino acids were from empty cell sacs and cell wall fragments, including peptidoglycan, which persisted in the sediment after cell death. In surface sediments it was estimated that peptidoglycan amino acids contributed 18–25% of THAA and that the relative contribution of $THAA_{pep}$ to THAA increased with increasing water depth. This indicates that bacteria and cell wall remains were degraded at a slower rate than other proteinaceous material during their transfer through the water column. In accordance with this, there was an increase in $THAA_{pep}$/THAA with increased depth and age of the sediments, which shows that THAA becomes progressively enriched with bacterial peptidoglycan as degradation proceeds. Hence, the preservation of peptidoglycan amino acids followed the general trend in the investigated diagenetic indicators, where organic matter in sediments became more refractory at increased water depth and age of the organic matter.

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