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Diagenetic Transformation of Nitrogenous Organic Matter in The Southwest Atlantic Shelf

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Abstract

Amino Acids (AA) and Amino Sugars (AS) were assessed in seston from inner and shelf break waters of the Argentine Sea, and in sediment cores from the inner shelf. Glutamine, asparagine, alanine, serine, glycine and leucine accounted for ~60% of Total Particulate AA (TPAA) in surface waters. The mol percentage of AA from algal frustules (e.g. glycine and serine) increased with depth, while cytoplasmic AA (e.g. alanine and asparagine) decreased, indicating selective bacterial AA uptake. Protein degradation products ornitine (orn), Beta-alanine (β-ala), and Gamma-Amino Butyric Acid (γ-ABA) doubled their mol percentage from the surface to deep water. Percentage contribution of glucosamine to Total Particulate AS (TPAS) decreased with depth from ~74% to ~60%. Galactosamine followed an inverse trend, reflecting an increase in bacterial nitrogen during seston sinking and degradation. TPAA/TPAS ratios increased from ~30% at surface indicating mixed phyto- and zooplanktonic sources, to ~63% in bottom layers as result of an increasing contribution of phytoplankton-derived detritus. Diagenetically fresh material predominated from surface to ~50 m depth, changing to still relatively immature POM at 75 m-120 m. At depths >750 m, POM reached higher maturity due to bacterial turnover, reflected in a diminished mol percentage of proteinogenic AA and a higher of non-proteinogenic. Organic matter from surface sediments is diagenetically similar to seston at depths > 1000 m, suggesting that POM attained a fairly stable condition shortly after deposition. Most parameters barely changed between surface (5 cm) and deep (>250 cm) sediment layers, likely due to much lower rates of OM transformation in the anoxic environment.

Keywords

Amino acids; Amino Sugars; Diagenesis; Seston; Organic Matter

Introduction

Most of the Organic Matter (OM) produced by autotrophic organisms in the euphotic zone is remineralized and recycled in the upper part of the water column, where the concentration of dissolved oxygen is elevated and consumption of Particulate Organic Matter (POM) by heterotrophic bacteria and zooplankton is high [1]. Detrital POM, along with phytoplankton and suspended inorganic matter makes up most of the marine seston [2], and plays a key role in marine trophic webs as it exports carbon and nitrogen from the surface to deep water layers and bottom sediments by sinking [3]. As POM descends to the bottom, its composition changes depending on the variable origins, as well as the metabolic and structural characteristics of the microbial communities associated with the sinking particles [4]. Besides identifiable components from vegetal and animal cells, such as proteins, lipids and carbohydrates, a fraction of seston and sedimentary organic matter is composed of a complex mixture of compounds collectively called humic matter, which are refractory (i.e. resistant to degradation) products of organic matter diagenesis. While labile and refractory compounds coexist in surface water layers, the proportion of slowly degradable components increases with depth, and dominates the organic matter pool in deep waters [4-6].

Similarly, in vegetal and animal cells there are nitrogen-containing organic compounds readily available for heterotrophic organisms, such as cytoplasmic components, as well as those with structural functions, which are inherently more resistant to bacterial attack. The transformation processes of sinking POM are relevant for the organic nitrogen cycling and nutrient regeneration in the water column, and can be assessed through the identification and quantification of different components, such as relevant proteinogenic and non-proteinogenic Amino Acids (AA), and Aminosugars (AS). Proteinogenic AA those incorporated biosynthetically into proteins during translation are essential metabolic components of all plankton types. These compounds make up the largest amount of nitrogen in living organisms, as well as most of the identifiable organic nitrogen in POM and dissolved OM [7]. Along with AS and carbohydrates, proteinogenic AA account for 60%-80% of the dry weight of plankton and are easily degradable constituents of the organic matter, especially cytoplasmic AA (e.g. tyrosine and phenylalanine) that are preferentially consumed [8]. Yet, some proteinogenic AAs are differentially utilized or even preserved during particle sinking [9]. For example, contents of tyrosine, histidine, and methionine decrease rapidly during POM sinking, while leucine, isoleucine, and phenylalanine only slightly decrease with depth. In contrast, the molar fractions of glycine and threonine tend to increase as sinking proceeds [10], likely because they are constituents of cell walls that are preserved during degradation. Non-proteinogenic AA, such as beta-alanine (b-ala), gamma-aminobutyric acid (g-aba), and ornithine, result from the degradation of aspartic acid, glutamic acid, and arginine, respectively [9,11]. The percent molar contribution of these compounds to the total AA indicates the degree of relative "freshness" of the POM pool [12]. Elevated molar percentages of non-proteinogenic AA (>1%) in the OM pool result from advanced stages of diagenetic modification, and these degradation products may represent up to 40% of the total AA pool in bottom sediments, after long periods under diagenetic transformation [13].

Regarding AS, glucosamine is part of the structure of chitin, the main component of the cell walls of fungi and the exoskeletons of arthropods such as crustaceans and insects, and galactosamine is part of the bacterial cell wall polymer peptidoglycan [14]. Thus, changes in the proportions of these monomers in the organic matter during sinking may reflect the activity of the different biological groups involved in its diagenesis. POM sources in detritic material can be also traced back with the ratio between the concentrations in the particulate material of total AA (TPAA) and total AS (TPAS). The

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ratio between glucosamine and galactosamine can help differentiate POM from microbial or zooplanktonic sources [15]. Thus, differences in the rate of change of specific AA and AS concentrations and molar percentages can be used as indicators of metabolism, solubilization, and humification processes of POM as it sinks to the bottom, as well as the preservation of its components in the sediment [16].

Shelf regions play a major role in the ocean carbon cycling and budget [17], as they provide up to 30% of the global marine primary production and about 50% of the organic carbon that reaches deep waters in the open ocean [18,19]. The Patagonian Shelf Large Marine Ecosystem is one of the widest continental shelves worldwide [20]. The area encompasses several frontal systems, including an extended shelf-break front that supports high concentrations of phytoplankton and feeds trophic webs and valuable fisheries [21-25]. Mesoscale frontal systems within the shelf include the Valdes tidal front (Figure 1), that forms during spring and summer and represents the boundary between stratified shelf waters during the warm season and tidally mixed coastal waters [21]. Yet, very little is known about the dynamics of organic matter in these regions [26-30].

The present work examines the distribution patterns of particulate AA and AS in two productive areas of the Patagonian Shelf, and discusses their relevance for the understanding of the POM transformation processes in the water column and sediments, as well as the possible biological mechanisms involved. To our knowledge, this is a pioneer study in the Southwest Atlantic on the utilization of organic nitrogen compounds as indicators of the dynamics and nutritional quality of POM.

Material and Methods

Field sampling

Seston and bottom sediment samples were collected in the late austral spring (12 to 29 November 2009) on board the RV "Puerto Deseado". Water samples were obtained in two sectors; the shallow inner shelf close to the Valdes Front and San Matías Gulf and a deeper zone close to the shelf break, totalizing 11 stations between 39.77°S- 43.75°S and 55.79°W-64.79°W. Two sediment cores were obtained in the San Matías Gulf (PD19 at 41.58°S- 64.45°W, 2.5 m length) and the Nuevo Gulf (PD33 at 42.48°S-64.37°W, 6 m length) (Figure 1).

Water samples were obtained with 5 L Niskin bottles at 3 m-4 m depths between surface and bottom, according to the depth of each station. Vertical profiles of temperature and salinity were determined with a CTD (Conductivity, Temperature and Depth) probe (Seabird Electronics 911) and continuous surface measurements were carried out with a thermosalinometer. Suspended particulate matter (seston) was collected by filtering 1 L of water under mild vacuum on precombusted (450°C, 3 h) 0.7 µm glassfiber filters (Whatman GF/F). Filters were dried 12 h at 50°C and stored in desiccators until chemical analysis. The sediment cores PD 19 and PD 33 (2.5 m and 6 m length, respectively) were cut in 1m segments, sealed, and stored at 4°C until sampling and analysis.

The determination of monomeric AA and AS in seston and sediment samples was performed after hydrolysis of polymeric material with 6 N HCl under N_2) during 22 h at 105°C [31]. The hydrolysates were evaporated under vacuum and the residue was taken up in sodium citrate buffer (pH 2.65). After precolumn derivatization with o-phthaldialdehyde, monomers were separated and quantified by HPLC with fluorometric detection following [4]. The peaks of the fluorescent products were converted to concentrations with an external standard containing the AA aspartic acid (asp), glutamic acid (glu), serine (ser), histidine (his), glycine (gly), threonine (thr), arginine (arg), alanine (ala), tyrosine (tyr), valine (val), methionine (met), phenylalanine (phe), isoleucine (ile), leucine (leu), lysine (lys), ornithine (orn), taurine (tau), beta-alanine (b-ala) and gamma-aminobutyric acid (g-aba), and the amino sugars glucosamine (gluam) and galactosamine (galam).

Satellite chlorophyll (CSAT) was used as a proxy for the surface concentration of chlorophyll a (chl *a*) during the sampling period. CSAT was estimated from daily MODIS Aqua (AQ) images with 1 km

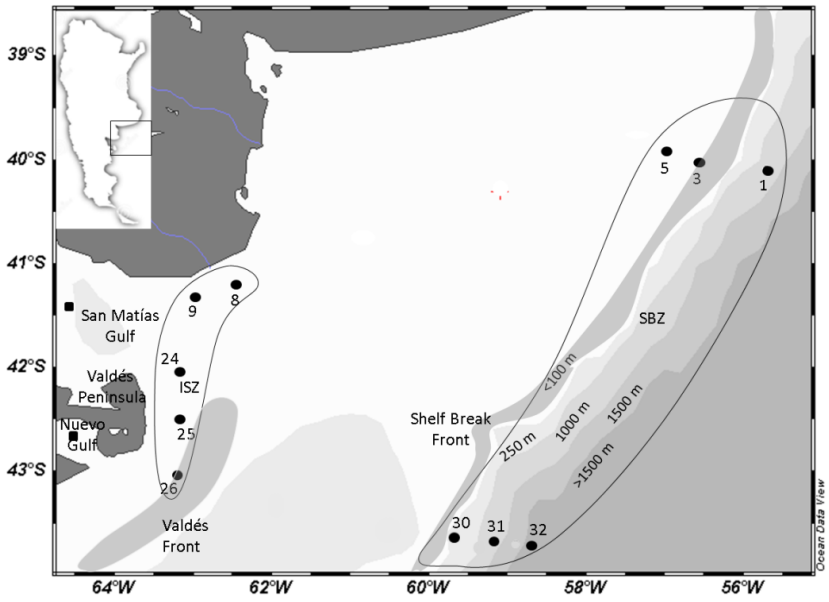

Figure 1: Study region in the Argentine Sea. Seston stations (circles) in the inner shelf and shelf break zones, and sediment cores (squares) taken in the San Matías and Nuevo Gulfs.

×1 km spatial resolution, downloaded from the Ocean Color web site. All available images were processed with the standard flags and the empirical algorithm OC3M and surface chlorophyll concentrations (chl, mg m^{-3}) were averaged over a box of (3 × 3) pixels, centered at the locations of the in situ measurements, in the image corresponding to the closest date [32].

Data Analysis

For visualization of vertical trends within each sampling zone, averages of molar concentrations, molar percentages, and concentration ratios were calculated over the following mean depths (number of samples in brackets): inner shelf 5 m (5), 40 m (3), and 75 m (2); shelf break: 5 m (8), 40 m (9), 95 m (9), and 1225 m (4). One-way ANOVAs were used to test for statistically significant differences between values in surface (5 m) and deep waters, within each sampling zone. For deep waters, samples obtained were those close to the bottom (23 m to 75 m) in the inner shelf, and between 750 m and 1800 m in the shelf break. Deep water sample collection depths were 23 m, 36 m, 40 m, 65 m and 75 m for stations in the inner shelf, and 750 m, 1100 m, 1250 m and 1800 m in the shelf break.

Results and Discussion

Hydrographic conditions

Salinity in surface waters of the inner shelf (5 stations) varied from 33.45 ± 0.01 near the Valdés Peninsula to 34.12 ± 0.01 close to the northern mouth of the San Matías Gulf. Temperature in turn ranged from 10.64 ± 0.06°C near the Valdés Peninsula to 13.96 ± 0.02°C close to San Matias Gulf. In the shelf break zone (6 stations) a north-to-south gradient was observed, with salinity ranging from 33.66 ± 0.02 to 34.14 ± 0.01 and temperature decreasing from 9.85 ± 1.33°C to 7.91 ± 0.85°C. This is in general agreement with previously published values and trends for shelf waters within the same latitudinal range and season.

Typical depth profiles of salinity and temperature acquired in four stations are presented in (Figure 2). In the inner shelf, surface water temperatures ranged 10.9°C to 10.7°C, and values kept almost constant with depth (Figure 2a, Figure 2b). Maximum depth in this zone is ~70 m and temperature profiles are indicative of complete vertical mixing. In the shelf break, on the other hand, temperatures decreased from ~8°C at the surface to ~3°C, with strong stratification down to ~250 m, and a less pronounced cooling from ~500 m to the bottom (Figure 2c, Figure 2d). Salinities in the inner shelf showed a similar pattern than temperature, with values of 33.44 and 33.47 at the surface and little variations with depth (Figure 2a, Figure 2b). In the shelf break (Figure 2c, Figure 2d) salinity was ~34.05 at the surface, and clear signs of stratification were not observed in the upper 250 m, thereafter salinity steadily increased to 34.5-34.6 at depths >1250 m.

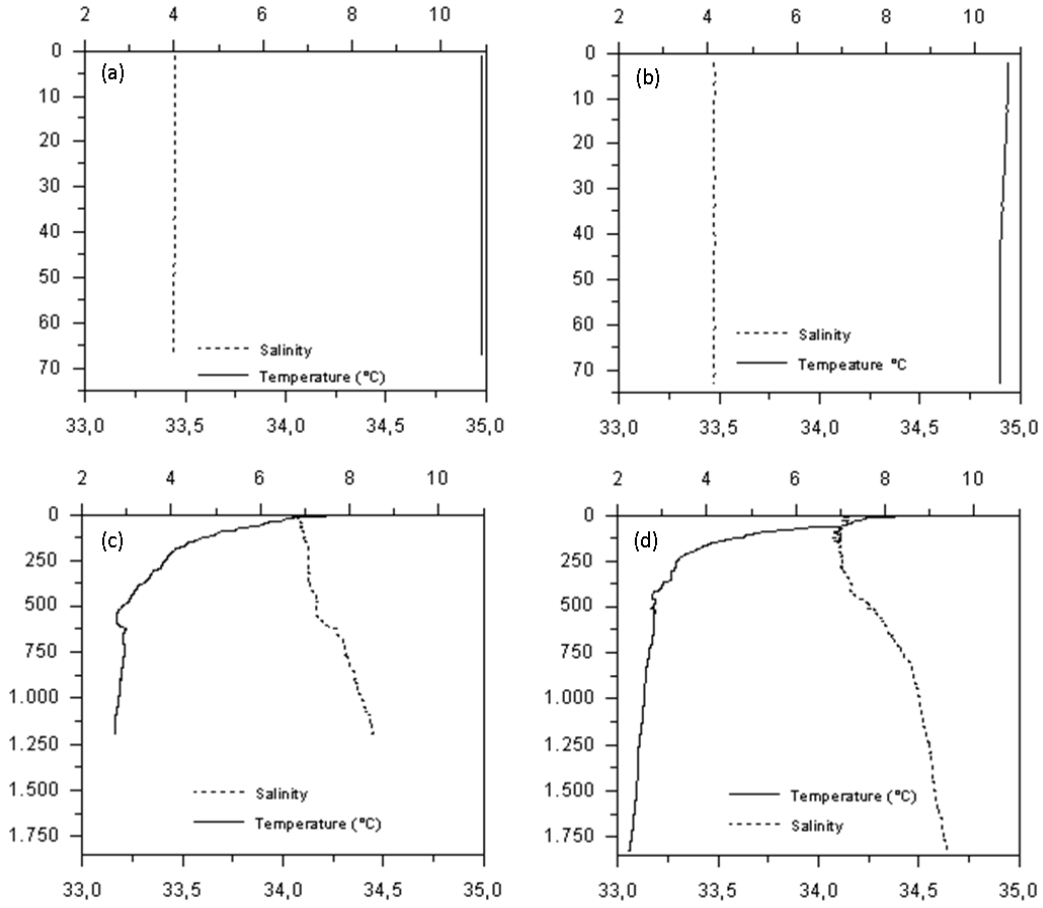

Figure 2: Examples of (a): Salinity; (b): Temperature vertical profiles at stations of the internal shelf, Station 25 Station 26 respectively, Shelf break zone; (c): Station 31; (d): Station 32.

Particulate amino acids and amino sugars in surface and bottom waters

Table 1: The main trends of molar concentrations (μM, mean ± standard deviation) of Total Particulate AA (TPAA) and AS (TPAS) are described.

TPAA and TPAS (mol%)	Surface layer (5 m), Inner shelf, n=5	Deep stratum (20 m-75 m*), Inner shelf, n=5	Surface layer (5 m), Shelf break, n=6	Deep stratum (>750 m-1800 m**) Shelf break, n=4
Glutamine	12.5 ± 0.6	12.4 ± 0.5	12.4 ± 0.5	13.1 ± 0.9
Glycine	12.1 ± 0.7	12.9 ± 0.7	11.9 ± 0.7	17.6 ± 1.5
Asparagine	11.3 ± 0.4	10.8 ± 0.7	10.8 ± 0.45	8.7 ± 0.5
Serine	7.8 ± 0.3	8.2 ± 0.8	7.2 ± 0.5	11.7 ± 1.2
Leucine	7.6 ± 0.3	7.6 ± 0.3	7.7 ± 0.3	6.5 ± 0.4
Arginine	4.5 ± 0.3	4.5 ± 0.2	4.6 ± 0.3	4.2 ± 0.3
Ornithine	2.3 ± 0.6	2.4 ± 0.6	2.0 ± 0.3	5.2 ± 1.6
B-alanine	0.5 ± 0.2	0.5 ± 0.1	0.5 ± 0.1	0.9 ± 0.4
G-aminobutyric acid	0.5 ± 0.2	0.5 ± 0.1	0.5 ± 0.1	1.5 ± 0.5
Glucosamine	67.9 ± 5.6	69.1 ± 4.9	73.7 ± 10.5	60.5 ± 11.1
Galactosamine	32.1 ± 5.6	30.9 ± 4.9	26.3 ± 10.5	39.5 ± 11.1
TPAA (μM)	1.3 ± 0.3	1.5 ± 0.5	1.6 ± 0.1	0.3 ± 0.2
TPAS (μM)	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.0 ± 0.0

Molar percentages (mol % ± s.d.) and mean concentrations (μM ± s.d.) of total particulate amino acids (TPAA) and amino sugars (TPAS).

Average (mol % ± s.d.) of individual AA and AS in seston of the shallow Inner Shelf Zone (ISZ) and the deeper Shelf Break Zone (SBZ) of the North Patagonian Argentine Sea in surface waters (ISZ and SBZ, 5 m), close to the bottom in ISZ (23 m to 75 m) and between 750 m and 1800 m in SBZ. Deep stratum sample collection depths were 23, 36, 40, 65 and 75 m at ISZ stations (*), and 750 (Station 31), 1100 (Station 1), 1250 (Station 31) and 1800 (Station 32) m at SBZ stations.

In the inner shelf there were no significant differences between surface and bottom waters, neither in TPAA nor TPAS concentrations ($p<0.05$). In surface samples TPAA concentration was 1.33 ± 0.29 μM and TPAS averaged 0.04 ± 0.01μM. Close to the bottom (20 m- 75 m), TPAA and TPAS concentrations were 1.52 ± 0.50 μM and 0.04 ± 0.02 μM, respectively). In the shelf break, TPAA and TPAS concentrations were significantly higher in surface than in deep waters ($p<0.05$). From surface to bottom, TPAA concentrations changed from 1.59 ± 0.11 μM to 0.31 ± 0.18 μM, and TPAS changed from 0.05 ± 0.01 μM to 0.005 ± 0.003 μM. TPAA/TPAS ratios in the inner shelf averaged 35 ± 7 and there were no significant differences between surface and bottom waters. TPAA/TPAS ratios in surface waters of the shelf break were similar to those in the inner shelf (29 ± 6) but significantly higher values were obtained from deep deep-water samples (63 ± 1.7). These ratios reflect mixed phyto- and zooplanktonic sources to seston in surface waters, and a higher proportion of phytoplankton-derived detritus in the deep sea [16].

In the shelf break, satellite estimates of chl a concentrations increased from north to south, with a maximum of 6.73 mg m^{-3} in the northern transect (station 5) and a peak value of 2.62 mg m^{-3} in the southern transect (station 31). TPAA concentrations measured in situ were significantly correlated with chl *a* estimates ($r=0.85$, $n=5$, $p<0.05$), suggesting a high proportion of phytoplanktonic sources in surface seston composition and their influence in TPAA/TPAS ratios. Regarding TPAS, there was no significant correlation with chl a estimates.

In the following sections we discuss trends of the molar percentages (mol percentage) of individual AA and AS, as their individual percentage contribution to the pool of all quantified monomers. These contributions will be used to describe the modifications of sestonic OM during its sinking from the source in the surface layers to the bottom.

Particulate amino acids in the water column

In the inner shelf, surface and bottom concentrations of TPAA were similar, likely due to shallow depths and good mixing of the water column. In the shelf break, the pattern of decreasing TPAA concentrations with increasing depth (Table 1) is likely a result of the preferential heterotrophic utilization of readily available AA [10]. Most changes in composition commonly occur within the first 300 m, and significantly slow down below 1000 m [33-36]. This diagenetic deceleration is mostly due to lower temperatures and heterotrophic activity [37,38]. Accordingly, we discussed differences in composition of "fresh" and "mature" POM (Figure 2) in the shelf break between 5 m and 1225 m depths (see ** in Table 1). Stations 1, 30, 31 and 32 were sampled to greater depths, and thus considered for the analysis.

Glutamine (glu), glycine (gly), alanine (ala), asparagine (asp), leucine (leu), and serine (ser) were the most abundant AA in the shelf break, and made up to ~55% and ~60% of TPAA in surface and deep waters, respectively. At a mean depth of 1225 m there was a significant increase in the molar percentage of gly and ser; ala and asp decreased, while leu did not notoriously change. A similar pattern was reported by Hubberten, et al. in the Greenland Sea and Antarctic waters [10,39].

Another pattern observed in the shelf break was that gly mol percentage consistently increased with depth, from 12% at 5 m to 14% at 95 m, reaching ~18% at 1225 m. Van Mooy, et al. reported for the eastern tropical North Pacific Ocean that POM was enriched in gly and ser from 75 m to 500 m [40]. Also Lee, et al. and Hannides, et al. found that gly proportions increase with depth [41,42]. Gly is one of the most abundant AA in the inner, planar protein layer of diatom frustules and is protected from a rapid degradation during sinking due to the tight association with the siliceous frustule structure [43,44]. Bacterial proteases would not be able to degrade these proteins [45], and particularly gly molecules. As gly molecules are inserted as spacers in the protein structure, they would not be easily accessible to enzymatic attack [46]. Thus, structural protection would produce a percentage increment of gly during sinking in the water column, due to the faster degradation of the other AA.

The sulfur-containing components taurine, methionine and methionine sulfone showed average molar percentage around 1% or lower. Methionine is not efficiently recovered during acidic hydrolysis and is partially oxidized to the corresponding sulfone, thus the reported values of these two AA should be considered only a rough estimate and are not further discussed. Regarding taurine, this is a compound of predominantly animal origin, and hence despite its low percentages a valuable indicator of organic matter origin and processing [47]. In our samples, taurine decreased from surface values of 1.0 ± 0.8% to 0.4 ± 0.4% at 1225 m (Figure 3), reflecting the degradation of material of zooplanktonic origin in the water column.

Degradation of the proteinogenic AA arginine (arg), asparagine (asp), and glutamine (glu), produces the non-proteinogeinc AA ornithine (orn), beta-alanine (b-ala), and gamma-aminobutyric acid (g-aba). Since non-proteinogenic AA are not DNA-coded, they are good indicators of organic matter diagenesis [16,48]. Arg, the precursor of

orn, decreases marginally with depth from 4.6 ± 0.3% in the surface to 4.2 ± 0.3% at 1225 m depth (Figure 3). Despite this slight decrease, the molar percentage of its degradation product, orn, increases from 2.0 ± 0.3% in the surface to 5.2 ± 1.6% at 1225 m depth (Figure 3). The increase of orn in seston indicates that dead phytoplankton cells are decomposing [49]. Further, orn can be synthesized by some bacteria from glutamate [50], what might explain the high values found, in comparison to arg mol percentage decrease.

Asp is one of the most abundant AA in the ocean and generates b-ala by metabolic decarboxylation during POM sinking [11]. In the present study we observed a slight decrease in asp mol percentage with depth, with relatively constant values of about 10% from the surface to 95 m, reaching 8.7 ± 0.5% (Figure 3) at 1225 m, which is a similar trend to that observed by Hubberten, et al. (1995) in Antarctic waters [10,39]. Average b-ala mol percentage increased from 0.5 ± 0.1% in the surface to 0.8 ± 0.4% at depths of 1225 m (Figure 3). This increment, though moderate, would be consistent with the inverse trend showed by its precursor asp.

The molar percentage of glu did not considerably change with depth, and kept an average value of 13.1 ± 0.9% from surface to 1225 m. On the other hand, g-aba, the product of the diagenetic decarboxilation of glu [51], increased from 0.5 ± 0.1% in the surface to 1.5 ± 0.5% at 1225 m (Figure 3).

The percentage increase of the non-proteinogenic AA b-ala and g-aba would reflect the preferential consumption of their precursors during POM sinking in the water column [37]. On the contrary, the mol % increment of gly and ser would be due to protection from enzymatic attack in the protein layer in algal frustules or by the diagenetic formation of new macromolecular structures [52,53], and additionally by the utilization of the more easily available cytoplasmic AA [10]. Therefore, b-ala and g-aba appear as more direct indicators of OM degradation, since their production depends on the bacterial uptake of two major protein AA such as glu and asp [11,53] stated that the only AA that showed a net increase in organic carbon from surface to deep waters were the non-proteinogenic b-ala and g-aba and to a lower extent, orn, therefore constituting univocal indicators of bacterial transformation processes of POM during its sinking in the water column. This is partly in agreement with our observations in the shelf break, since mol percentage of b-ala and g-aba significantly increased with depth, yet orn showed a large mol percentage increase with depth. Net concentrations of these three non-proteinogenic AAs showed an increasing trend starting at depths ~100 m, and their increments might be attributed to a longer residence time of particles at those depths, allowing a more extensive degradation of the precursor protein AA, likely due to physical retention mechanisms such as e.g. vertical stratification.

Particulate amino sugars in the water column

The concentrations of the individual AS glucosamine (gluam) and galactosamine (galam) showed a general a decrease with depth (data not shown). In the following we focus on the discussion of the mol percentage variation of these compounds, where 100% represents the sum of the molar concentrations of gluam and galam, as indicators of the relative contribution of zooplankton and bacteria derived organic matter respectively.

Gluam surface mol percentage values were 67.9 ± 5.6 (mean ± standard deviation) in the inner shelf, with no significant differences between surface and bottom waters. In the shelf break, on the other hand, mol percentage values decreased from 73.7 ± 10.5% in the surface to 60.5 ± 11.1% at 1225 m. This is in agreement with degradation of detritus from chitinaceous zooplankton and its pellets during sinking [54].

Similarly, galam mol percentage showed little variations with depth in the inner shelf (32.1 ± 5.6% in surface to 30.9 ± 4.9% in bottom waters). However, in the shelf break, galam mol % increased from 26.3 ± 10.5% in the surface to 39.5 ± 11.1% at 1225 m, indicating a larger proportion of bacterial biomass in POM during its degradation and consumption with depth. Variability of galam mol percentage was higher in the shelf break, with standard deviations doubling those in the inner shelf break. These larger variations may be due to differences in bacterial biomass in the shelf break stations.

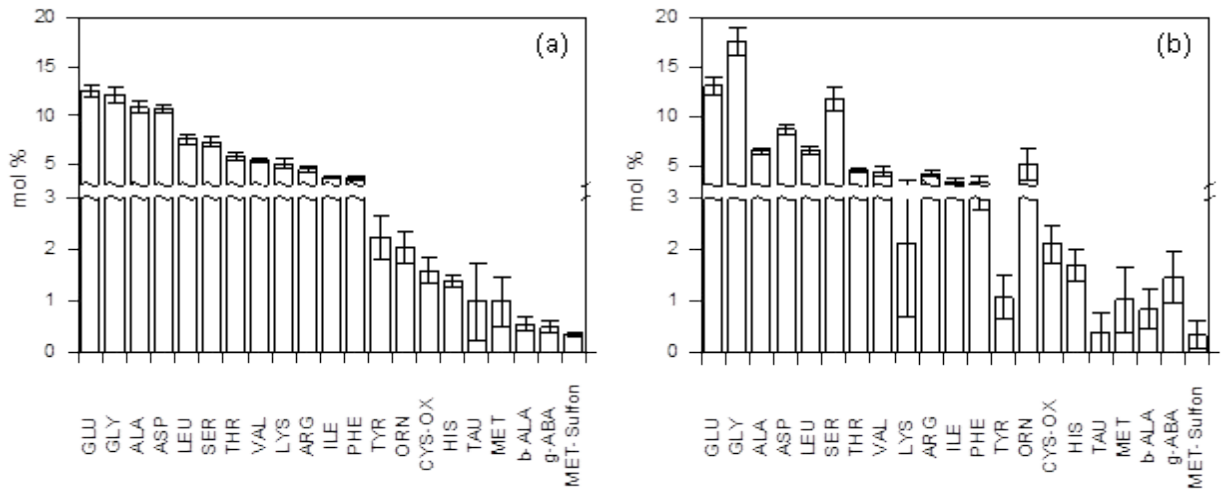

Figure 3: Modifications in the composition pattern of Amno Acids (in mol percentage) in seston samples from stations in the shelf break zone at (a): 5 m (n=6); (b): 1225 m mean depth (n=4, depth range from 750 m to 1800 m).

Amino acid and amino sugar indicators of POM transformation in the water column

Changing ratios of proteinogenic/non-proteinogenic AA with depth reflect POM transformations while sinking, as well as changing ratios between AS, as a result of bacterial activity on "fresh" source material from phyto- and zooplankton (Figure 4).

All ratios arg/orn, asp/b-ala, glu/g-aba and gluam/galam displayed similar ranges and decreasing trends with depth in both sampling sectors. However, for many ratios there was a large variability between samples, as evidenced by dispersion bars in (Figure 4). Therefore, those ratios that showed the lowest variability within a given region were selected for the analysis, and considered more robust indicators of the degree of organic matter transformation in their respective environments. In the shallower inner shelf, gluam/galam ratios were those that showed the smallest dispersions. In the shelf break, on the other hand, glu/g-aba was the less variable ratio for all depths.

The ratio gluam/galam is useful to differentiate seston of predominantly microbial biomass from that of zooplanktonic origin. Values >8 are found in chitin-rich fresh POM and decrease during biodegradation. In general, gluam/galam values <4 indicate a significant proportion of microbial biomass, and ratios <2 point to bacterial sources of POM and/or strong diagenetic alteration [16]. In the present study, gluam/galam in the inner shelf ranged from 2 ± 0.5 to 3 ± 0.7, with little dispersion and no clear vertical trend. In the shelf break the gluam/galam ratio changed from 3.6 ± 2 in the surface to 1.7 ± 0.7 in bottom waters. This ratio showed much larger variability in surface waters (range 1.7 to 6.8) and its standard deviations decreased with depth. This pattern would relate to the presence of a diagenetically more heterogeneous POM pool close to the surface, relatively enriched in chitin from zooplankton as well as particles with significant heterotrophic degradation and/or abundant bacterial biomass. This composition is in agreement with the environmental context, within a productive zone characterized by an intense turnover of the organic matter. Both trends of mean and standard deviations decreasing with depth strongly suggest that POM degradation begins within the surface layers where it is produced, and that it becomes diagenetically more homogeneous throughout sinking, with progressively less contribution of zooplankton-derived detritus and increasing proportions of bacterial-derived organic matter.

In the shelf break, the glu/g-aba ratio diminished from 19.48 ± 4.35 in surface waters to 7.05 ± 3.33 at 1225 m. Surface ratios in the inner shelf were similar to those in the shelf break, and decreased to 14 ± 2 close to the bottom (~70 m depth). Noteworthy, these glu/g-aba ratios were comparable to those observed in the shelf break at a similar depth. Thus, provided its shallow depth, a significant proportion of POM in shelf waters would be in a diagenetically immature, relatively "fresh" state [55].

Particulate amino acids in sediments

In this section, both sediment cores obtained in the inner shelf are considered. The top (5 cm) and bottom (250 and 550 cm) sections are compared in terms of the mol % of AA with particular diagenetic interest (Figure 5). Further, the OM composition of the top sections is contrasted with the POM composition in bottom waters of the inner shelf. Due to the shallow water depths (<100 m) that characterize the inner shelf, water samples of the shelf break, corresponding to a mean depth of 1225 m were included to provide a broader perspective on the influence of longer sinking times on the diagenetic status and

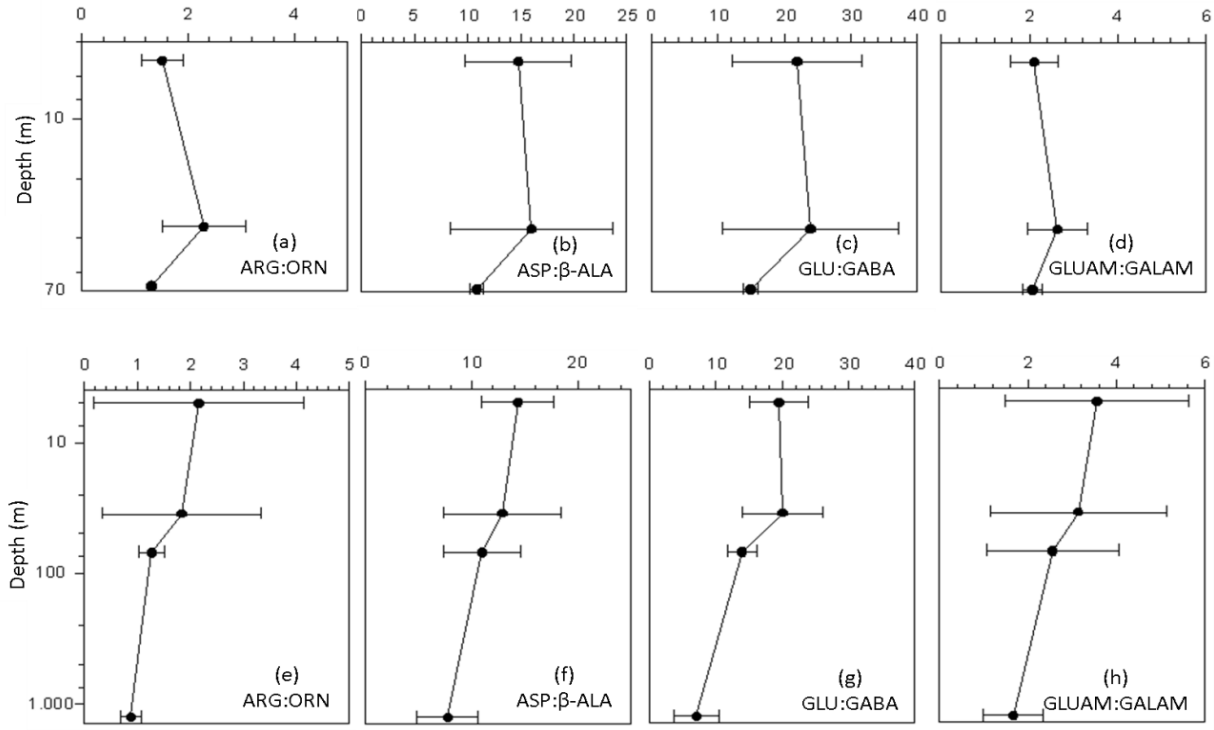

Figure 4: Ratios of amino acids and amino sugars (mean ± standard deviation) as indicators of organic matter degradation at different depths in the water column of the stations; (a,b,c,d): shallow (<100 m) inner shelf; (e,f,g,h): shelf break sectors.

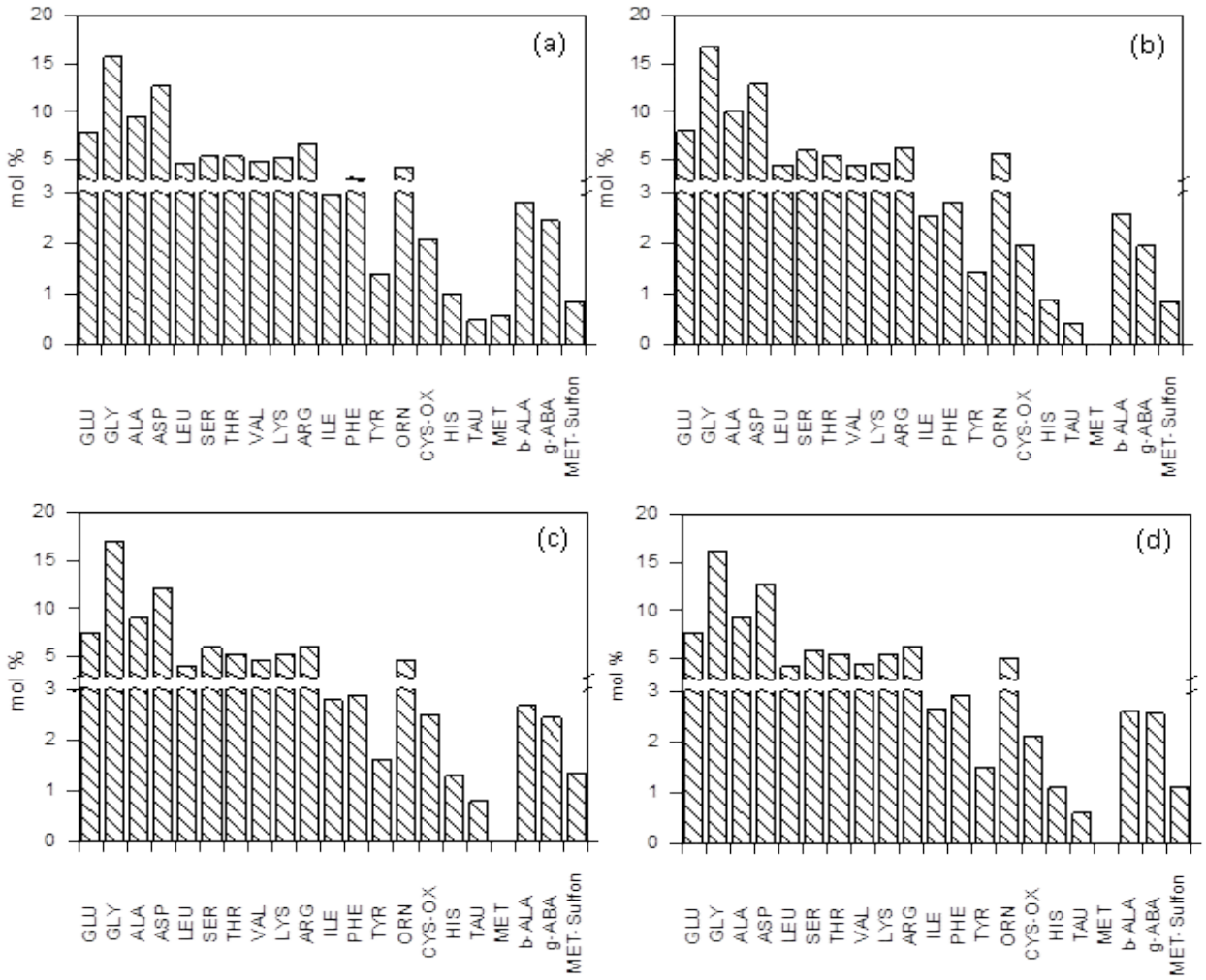

Figure 5: Modifications in the molar percentage pattern of amino acids in inner shelf sediment cores at surface 5 cm in (a): PD19; (b): PD33 Deeper layers 250 cm; (c): PD19 550 cm; (d): PD33.

stability of the POM in the study region.

The proteinogenic AA arg, asp, and glu were compared with their respective non-proteinogenic degradation products orn, b-ala, and g-aba, which were previously considered good indicators of OM diagenesis. Values of mol percentage arg were very similar in both cores, averaging 6.6% and 6.1% in the top and bottom layers, respectively (Figure 5). These values were higher than the average value of 4.5% in bottom waters of the inner shelf and the average of 4.2% at 1225 m depth in the shelf break. Although the sedimentary enrichment of arg has been previously reported elsewhere, no clear biological sources were proposed [56]. Instead, the arg enrichment in sediments could be indicative of non-biological partitioning, through selective interactions of basic, positively charged AA with the negatively charged mineral surface of particles [13]. Orn values were similar in both cores with maximum values of 5.7% at 5 cm and 5.0% at the bottom of core PD33 (550 cm) (Figure 5). These values are much higher than those reported for bottom waters of the inner shelf (2.4%) but similar to those in the deep water layers of the shelf break (5.2%). Besides being a degradation product of POM, ornithine orn can also be a constituent of microorganisms living in suboxic environments [57]. Thus, the high orn mol percentage found in sediment cores could also result from the additional contribution of *in situ* organic matter turnover by sediment bacteria, and orn incorporation into bacterial biomass. Hence, we hypothesize that the resuspension of surface sediments by bottom currents in the shelf break could influence the composition of POM in bottom waters of this area and could, to some extent, explain the high orn mol percentage observed in those samples.

In both cores, asp mol percentage was 12% and 13% in the top and bottom layers respectively (Figure 5), which is only slightly higher than 10.8%, the value reported for bottom waters of the inner shelf. However, it is 40% higher than the mol percentage in deep waters of the shelf brek (8% at 1225 m depth). The asp enrichment in sediments was also reported by Keil, et al. [13]. In the sediment surface the mol percentage of b-ala was 2.8%, essentially the same as in the deepest sediment layers [58,59], about five times larger than in bottom waters of the inner shelf (0.53%) and also higher than in deep waters of the shelf break (~0.9%).

Glu surface values were ~8% in the top layers of both cores. This value was, in contrast to arg and asp, lower than in bottom waters of the inner shelf (12.4%) and deep waters of the shelf break (13.0%). Also, in both cores, g-aba mol percentage was 2.6 in the top and deep sediment layers, about five times larger than values in bottom waters of the inner shelf (0.5%) and also higher, yet closer, to values of deep waters in the shelf break (1.5%). Glu and g-aba were fairly constant with depth in both cores, with 7.5% in PD19 at 250 cm and 7.7% in PD33 at 550 cm (Figure 5).

The comparison of the non-proteinogenic b-ala, g-aba, and orn between sediments and deep waters showed another interesting difference to previous work. According to Keil and Kirchman, sediments containing highly degraded AA (pooled mol percentage of all non-proteinogenic AA >5) are rare [56]. However, in our sediment cores, the sum largely exceeds that value, reaching 11%. This is supported by the high proportions of orn in our samples, which comprise more than half of the non-proteinogenic AA. Furthermore, the sum of non-proteinogenic AA in deep waters of the shelf break is 7.5% (>5), while it reached only 3.42% in deep waters of the inner shelf. The contrasting values between sediments and water column would be due to to their different sensitivities depending on the specific diagenetic stages in each substrate [16].

The ratios arg/orn in cores PD19 and PD 33 were 1.5 and 1.1 in the top, and 1.3 and 1.2 in the deeper sections, respectively. These values are very similar to those in bottom waters of the inner shelf and deep waters of the shelf break (1.0 ± 0.2). Overall, these ratios do not clearly show an enrichment of orn in sediments directly derived from arg modification in the water column. This supports the assumption made above that the high orn mol percentage in sediment could be partly due to the biomass contribution of microorganisms living in a suboxic environment [57].

In both cores, asp/b-ala ranged 4.5-5.2 with no major differences between top and deep layers. In bottom waters of the inner shelf the ratio was 10 ± 2 and 8 ± 3 in deep waters of the shelf break. Extending the comparison to the whole water column of both study zones suggests a diagenetical transition model departing from fresh OM with an average asp/b-ala of ~15 in surface waters to mature OM in sediments characterized by values of ~5.

The ratio glu/g-aba was on average ~4 in both cores with the lowest value on the top section of PD 19 (3.2) and a maximum value of 4.7 in the bottom section of PD33. In each core, the ratio increased only ~14% from top to deep strata. In bottom waters of the inner shelf it was 14 ± 2 and in deep waters of the shelf break it averaged 7 ± 4. Alike asp/b-ala, the ratio glu/g-aba showed a trend that can be roughly described as starting with high and variable values around 20 in fresh surface seston, to much lower and stable values of ~4 in mature sedimentary OM.

Since it was not possible to take sediment cores in the shelf break, and compositional changes in sinking OM considerably slow down below a water depth of 1000 m, we contrasted gly mol percentage data from inner shelf sediments with those in the water column, in an attempt to gain some additional insight into its overall OM diagenetic status. As elevated gly mol percentage values are characteristic of highly modified, more stable OM, we compared this indicator of diagenetic progress in seston from surface waters (the primary OM source) of the inner shelf and shelf break with values from the deepest sampled stations, as well as with surface and deep sediment sections of sediment cores from the inner shelf (Figure 6).

Average gly mol percentage in surface waters was ~12.5 %, and did not show significant differences between inner shelf and shelf break zones, while gly mol percentage in deeper layers of the shelf break (between 750 m and 1800 m) was significantly higher and ranged 16%-18%. In the sediment samples gly mol percentage was 16% in the top of both cores, being much closer to values in deep waters of the shelf break than those at surface or deep layers of inner shelf. Furthermore, in both cores there were virtually no differences between top and base or between locations, with gly mol % about 16%-17% at surface (5 cm) and at the deeper sediment layers (250 cm and 550 cm).

Burdige and Martens reported an increment with depth of the molar percentage gly in sediments and ascribed it to differences in rates of solubilization, metabolism and humification of proteinaceous material [60]. However, this pattern was not observed in our samples. The constancy of mol percentage gly in cores down to 5 m depth suggest a high stability of sedimentary organic matter in the sampled area. It has been postulated that AA in organic matter rich sediments (> 5% organic carbon) are not markedly altered by past degradation, possibly due to the abundance of substrates for the incorporation

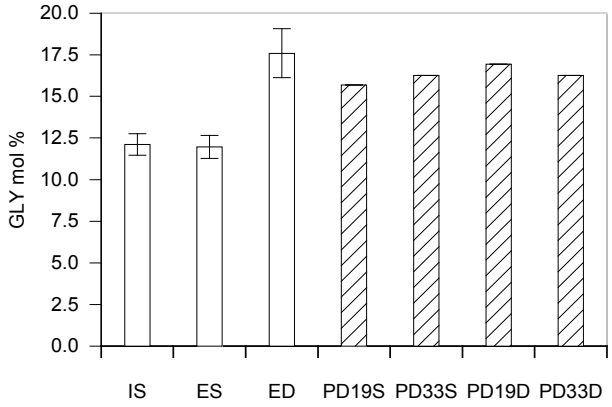

Figure 6: Mean values and standard deviations of glycine molar percentage in seston from the different sampled zones and depths in the water column (IS: inner shelf, surface, 5 m, n=5; ES: external shelf, surface, 5 m, n=6; ED: external shelf, deep, 1225 m mean depth, n=4) and in sediments cores at surface (5 cm in PD19S and PD33S) and deeper layers (250 cm in PD19D and 550 cm in PD33D). An average deep value for the shallow stations of ISZ was not included for not being significantly different from IS.

of AA into humic matter [56,61]. Organic carbon contents in our sediment samples (0.8%-1.2%) are within the range of normal values for coastal marine sediments, thus, they do not support this possibility [62]. Notwithstanding, the abundant brown macroalgae in Nuevo and San Matías Gulfs could be a source of polyphenolic material for the formation of refractory compounds contributing to a high diagenetic stability of AA [53]. Another plausible explanation for the preservation of gly could be a strong sorption on clay material, which protects this AA from bacterial attack, particularly in anoxic sedimentary environments [63]. Besides reporting similar increments with depth of gly contribution to TPAA, Hubberten, et al. found a strong enrichment of this AA in dissolved, refractory humic substances, reaching mol percentage >30 at any depth in Arctic and Antarctic waters [10,39]. Hence, gly seems to be a strong proxy of multiple diagenetical pathways involved in the preservation of particulate and dissolved nitrogenous material, which are not yet fully understood.

The above comparisons suggest that in the study region a significant degree of diagenetic stability could be rapidly reached during particle sinking, at depths ~1000 m in the water column, or also in a relatively short time after deposition on the sediment surface, even in the shallow waters of the inner shelf. This is particularly true for the specific coring area within the inner shelf, where maximum water depth is <100 m.

Particulate amino sugars in the sediment

In surface sediments, gluam mol percentage of 54.8% and 55.4% were registered for cores PD19 and PD33, respectively. In deeper core sections, gluam mol percentage were 52.9% and 54.4% at depths of 250 cm in PD19 and 550 cm in PD33. This is essentially the same trend described for AA in these same cores, where most molar percentages barely changed with depth, indicating a slow turnover or consumption by anaerobic or facultative organisms. These sedimentary AS values were significantly lower than those obtained in surface waters of the inner shelf and the shelf break (~70%) and also in deep waters of the shelf break (~60%) waters, reflecting a relatively rapid chitin consumption in the water column and sediment surface.

Galam mol percentage was 45.3% for the top section of PD19 and 44.7% for PD33 and it marginally increased in the deep sections to 47.1% for PD19 and 45.6% for PD33. These values were higher than those observed in surface and bottom waters of the inner shelf (~30%) and surface waters of the shelf break (~26%), and closer to the average of ~40% at 1225 m mean depth. These higher mol percentage values reflect a more extensive heterotrophic transformation of POM due to a longer period of sinking in the shelf break. In addition, it suggests the occurrence of *in-situ* bacterial sources of sedimentary organic matter.

In both cores the ratio gluam/galam was ~1.22 in top and ~1.15 in deeper sections. In bottom waters of the inner shelf gluam/galam was 3.0 ± 0.7, and a ratio of 1.7 ± 0.7 was obtained in the shelf break at 1225 m mean depth. Like arg/orn ratios, values <2 suggest that OM in sediments suffered significant diagenetic alteration, and also that there might be a significant contribution of OM from bacterial origin [16]. It also supports the former similar assumption that was made based on galam mol percentage.

Conclusion

POM in the surface layer exhibited a homogeneous average diagenetic state, likely due to good mixing. AA and AS indicators point to POM in a relatively fresh condition at depths <100 m, evolving to diagenetically more mature states in deeper layers. These trends were especially clearly reflected by the arg/orn, asp/b-ala, glu/g-aba, and gluam/gala ratios. Particularly the relatively high and constant glu/g-aba ratios in the first 70 m of ISZ and SBZ indicate that a significant proportion of POM in shelf waters is in a diagenetically immature state.

TPAA and TPAS concentrations in surface waters were higher in the shelf break than in the coastal zone, decreasing to about a fifth at ~1000 m depth. TPAA/TPAS ratios reflect mixed phyto- and zooplanktonic sources of OM in the surface, with an increasing relative contribution of phytoplanktonic detritus and bacterial derived components in the deep sea. Also specific components support this view taurine a component of animal origin mol percentage decreased with depth, reflecting the degradation of zooplanktonic material in the upper water column. Further, the increase with depth of the mol percentage of the non-protein AA orn in seston indicates an increase of decomposed phytoplankton cells. The mol percentage increase with depth of b-ala and g-aba, reflect bacterial degradation of OM during its sinking in the water column. Gluam/galam ratios <2 in the deep water of the shelf break indicate a large bacterial derived contribution to OM.

In sediment, most mol percentage of monomeric AA and AS and their concentration ratios showed values consistent with a higher degree of maturity than in the water column. OM diagenetic characteristics in surface (5 cm) sediments in the shallow inner shelf were similar to POM sinking to deep water layers (>1000 m depth) in the shelf break, suggesting that a significant degree of OM stability is reached shortly after its deposition on the sediment surface. In both sediment cores galam mol percentage was with ~46% significantly higher than in surface and deep waters in both regions, pointing to an extensive diagenetic transformation and to in-situ bacterial sources of sedimentary OM. Also a gluam/galam ratio <2 and orn mol percentage of ~6 support this assumption. In deeper sediment layersmost indicators kept fairly constant, suggesting a much slower diagenesis of OM after its burial, most likely due to anaerobic conditions.

An influence of sediment resuspension through bottom currents on the POM composition of deep waters in the shelf break zone cannot be ruled out.

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