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The role of biominerals in the sinking flux and preservation of amino acids in the Southern Ocean along 170°W

Anitra E. Ingalls^{a,*}, Cindy Lee^a, Stuart G. Wakeham^b, John I. Hedges^c

^a Marine Sciences Research Center, Stony Brook University, Stony Brook, NY 11794-5000, USA

^b Skidaway Institute of Oceanography, 10 Ocean Sciences Circle, Savannah, GA 31411, USA

^c School of Oceanography, University of Washington, Box 357940, Seattle, WA 98195-7940, USA

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Abstract

In a study of the transport and transformation of particulate amino acids in the Southern Ocean, we found that silicate and calcium carbonate biominerals play an important role in the preservation of amino acids throughout the water column and surface sediments. Plankton, sinking particle and sediment samples were collected during the USJGOFS AESOPS transect across the Antarctic Polar Front (APF) along 170°W. Total hydrolyzable amino acids (THAA) made up of 17–27% of total organic carbon (C_{org}) in sinking particles and 6–23% of C_{org} in surface sediments. In addition to THAA, we measured amino acids bound in silicate (SiTHAA) and calcium carbonate (CaTHAA) biominerals. Although the fraction of biomineral bound to total amino acids in plankton was small, <1%, the ratio of mineral-bound to non-mineral-bound amino acids increased with depth in the water column and sediments. Mineral-bound amino acids often dominated the total amino acid pool in biomineral-rich sediments beneath the Antarctic Circumpolar Current. SiTHAA were enriched in glycine and threonine relative to THAA and were similar in composition to SiTHAA in diatom frustules isolated from APF sediments. CaTHAA were enriched in aspartic acid relative to THAA. The difference in composition between mineral-bound amino acids and non-mineral-bound amino acids increased with depth.

Amino acid composition has been used to develop a Degradation Index (sensu Dauwe and Middelburg, 1998). The unusual amino acid composition of Southern Ocean plankton, i.e., dominated by diatom cell walls, resulted in an apparent mismatch between the absolute value of the Degradation Index and the presumed extent of degradation. However, changes in amino acid composition that accompanied degradation were similar to those found in previous studies. Principal components analysis suggests that the greatest change in THAA composition occurred between the sediment surface floc layer and deeper sediments where particles had the longest residence time. Compositional changes observed in the water column suggested that degradation processes resulted in complete removal of amino acids, whereas changes in sediments were consistent both with selective degradation of plankton amino acids with depth and with the conversion of primarily phytoplankton biomass to that of bacterial biomass.

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*Corresponding author. Tel.: +1-617-496-4297; fax: +1-617-496-4387.

E-mail address: ingalls@eps.harvard.edu (A.E. Ingalls).

¹ Present address: Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, MA 02138, USA.

1. Introduction

Sinking particles in the ocean are a major vehicle for the transport of organic carbon from surface water to depth. Because of the high level of

new production and the large size of the Southern Ocean, the “biological pump” in this region is important to carbon cycling on a global scale (e.g., Sigman and Boyle, 2000). One important driving mechanism behind particle sinking is the “ballast” effect whereby mineral phases provide the excess density required to promote the sinking of organic matter out of the euphotic zone (McCave, 1975; Honjo, 1996; Armstrong et al., 2002). In the Southern Ocean, greater than 85% of the mass of sinking material collected in sediment traps at 1000 m is biogenic opal and CaCO₃ (Honjo et al., 2000). Therefore, biominerals are the major source of ballast in this region, and mineral-forming plankton in the Southern Ocean contribute to the high new production observed there (Eppley and Peterson, 1979).

In addition to promoting sinking, there are other ways in which minerals influence the fate of organic matter. Biominerals in both plants and animals are deposited on a glycoprotein scaffold that is trapped within the skeleton during biomineralization (Lowenstam and Weiner, 1989; Swift and Wheeler, 1991). The genetically determined amino acid sequence and composition of the glycoprotein template determine the morphology and mineralogy (e.g., calcite vs. aragonite) of the resulting biomineral. In general, proteins associated with biogenic opal are rich in glycine, serine and threonine (King, 1974, 1977; Kröger et al., 1996, 1999), and CaCO₃-associated proteins are rich in aspartic acid (King, 1977; Constantz and Weiner, 1988). The relative abundance of these amino acids in plankton, sinking particles and sediment also can indicate the relative importance of calcifying and silicifying organisms (Ittekkot et al., 1984a, b; Müller et al., 1986; Gupta and Kawahata, 2000). Despite wide recognition of the association of amino acids with biominerals, previous studies of amino acids in sediment-trap material have not investigated the role of biominerals in preserving organic matter in the water column, nor quantified the contribution of mineral-bound amino acids or organic carbon to the sinking flux of organic matter.

Changes in the absolute amount and relative abundance of amino acids in sinking particles and sediments can indicate source and diagenesis of

marine organic matter (e.g., Lee and Cronin, 1982; Cowie and Hedges, 1994; Lee et al., 2000). Mineral-bound amino acids may be particularly useful as source indicators, as they are well protected from diagenesis and therefore remain relatively unaltered chemically (King and Hare, 1972; Collins et al., 1991) and isotopically (Shemesh et al., 1993; Sigman et al., 1999; Rosenthal et al., 2000), even after long time periods in sediments. In contrast to the physically protected biomineral-bound amino acids, cellular amino acids are among the most labile compounds in living plankton (e.g., Wakeham and Lee, 1993). In the Equatorial Pacific, >99% of amino acids produced in the surface ocean are lost from sinking particles prior to settling to the seafloor (Lee et al., 2000). The large difference in the relative reactivity of mineral-bound and non-mineral-bound amino acids suggests that amino acids protected by minerals should comprise a larger portion of the amino acid pool as particles are progressively more degraded.

Here we report concentrations, fluxes and compositions of amino acids in plankton, sinking particles and sediments in the Pacific sector of the Southern Ocean between 56°S and 66°S along 170°W. We quantify the contribution of mineral-bound (silicate and calcium carbonate) amino acids to total amino acids and characterize their composition. In addition, we calculate the degradation state of organic matter in each sample using the amino-acid-based Degradation Index developed by Dauwe and Middelburg (1998) and compare these results to an independent principal components analysis (PCA) of the amino acid composition of each sample. This study was part of an overall characterization of major biochemical components of organic matter in plankton, sediment traps, and sediments undertaken during the Antarctic Environmental Southern Ocean Process Study (AESOPS) of the US Joint Global Ocean Flux Study (US JGOFS) (Smith et al., 2000). Results of analysis of lipids, carbohydrates and chloropigments will be reported separately. Data from this study are available on the USJGOFS web page at <http://usjgofs.whoi.edu/jg/dir/jgofs/southern>.

2. Methods

2.1. Sample collection

Five mooring stations (Table 1) were located in the western Pacific section of the Southern Ocean along 170°W as part of the AESOPS study (Smith et al., 2000). Mooring stations (MS) were located as follows: MS-1 in the Subantarctic Zone (SAZ); MS-2 in the Polar Front Zone (PFZ); MS-3 in the Antarctic Polar Front (APF); MS-4 in the Antarctic Circumpolar Current (ACC); and MS-5 south of the ACC.

Net plankton samples were collected from all five mooring stations between March 4–30, 1998, beginning with MS-5. Sampling was during late austral summer at which time the northern stations (MS-1 to MS-4) had dissolved Si(OH)₄ below 10 μM, but MS-5 was still silica replete (Hiscock, et al., 2003). Net plankton samples (phytoplankton and zooplankton) were collected by vertically towing a 26-μm net between 40–120 m water depth. Samples were passed through a 850-μm sieve, and then split into 10 subsamples for multiple organic-compound analyses using a wet sample divider (McLane WSD-10). One subsample (1/10 fraction) was filtered (GFF) and frozen for amino acid analysis. The plankton sample was removed from the GFF filter with a spatula and except for MS-5 was divided into two portions and weighed. Half the sample was used for analysis of total hydrolyzed amino acids (THAA) and silicate-bound amino acids (SiTHAA) as described below. The second half was used for analysis of CaCO₃-bound amino acids (CaTHAA). The MS-5 sample

was not divided, and CaTHAA was not analyzed in plankton from that site. For comparison with collected plankton samples, three common diatom species (*Coscinodiscus radiatus*, *Thalassiosira pseudonana* and *Chaetoceros gracilis*) were cultured in the lab in artificial seawater amended with F/2 nutrients. Cells were concentrated by centrifugation and then collected onto GFF filters without rinsing and frozen until later THAA analysis. Biomineral-bound amino acids were not measured in diatom culture samples.

Our IRS sediment traps were deployed as described by Honjo et al. (2000) at four of the AESOPS mooring stations from November 1996 (NBP96-05) until March of 1998 (NBP98-2). We generally followed the same protocol as in earlier studies (Hernes et al., 2001; Lee et al., 2000). As our northernmost sediment traps (MS-1) were compromised due to accidental early recovery, we report results from the 3 mooring stations (MS-2, MS-3 and MS-5) where relatively complete sediment-trap collections were obtained. In addition, we analyzed samples from PARFLUX traps deployed at MS-4 provided by S. Honjo. PARFLUX samples were preserved with formalin and treated as described in Honjo et al. (2000).

IRS sediment traps at each station collected sinking particles for up to 480 d at two depths, ~1300 m below the sea surface and ~1000 m above the seafloor. All traps were equipped with indented rotating sphere valves (IRS; Peterson et al., 1993) and poisoned with mercuric chloride (5 mg/l in NaCl brine; Lee et al., 1992). Each sediment-trap array included one composite and two time-series traps. Composite traps were

Table 1
Sediment trap mooring station locations, trap depths and seafloor depth

Station	Zones	Location	Shallow trap (m)	Deep trap (m)	Bottom depth (m)
MS-1	Subantarctic Zone (SAZ)	53°02'S, 174°44'W	—	—	5441
MS-2	Polar Front Zone (PFZ)	56°54'S, 170°10'W	1325 (481)	4024 (429) ^a	4924
MS-3	Antarctic Polar Front (APF)	60°17'S, 170°03'W	1344 (476)	3057 (444)	3957
MS-4	Antarctic Zone (ACC)	63°09'S, 169°54'W	1031 (425) ^b	—	2885
MS-5	Antarctic Zone (South of ACC)	66°10'S, 169°40'W	1274 (232)	2107 (190)	3015

^aTime-series traps were used since the composite trap failed after seven days.

^bSince no IRS traps were deployed at MS-4, we analyzed splits obtained from the PARFLUX traps at this location (Honjo et al., 2000).

Values in parenthesis are the number of days that composite traps collected sample.

intended to collect a single sample over the entire 480 d sampling time. The actual number of days during which composite traps collected sinking particles are summarized in [Table 1](#). Time-series traps collected sample in individual sample cups beginning November 28, 1996. Each cup collected sinking particles for between 5 and 152 d (duration was based on expected flux throughout the year). Composite and time-series traps were baffled to exclude very large particles (e.g., fish) and had collection areas of 0.033 m². Composite trap samples were split into 10 subsamples using the WSD-10 as above. Time-series trap samples were split into 5 subsamples for organic compound analyses. Subsamples (1/5 or 1/10 fraction) were filtered (GFF) and frozen for later analysis. Prior to analysis, filters containing composite trap samples were cut in half with a razor. Half was analyzed for THAA and silicate-bound amino acids and half analyzed for CaCO₃-bound amino acids (see below for details).

Sediment cores (~45 cm in length) were collected from each mooring station between March 4 and 30, 1998, with a multiple corer ([Barnett et al., 1984](#)). A 147-cm gravity core also was collected at MS-3. Cores were sectioned into 0.5–5.0 cm intervals and frozen on board the ship. Floc samples from the water-sediment interface were collected by suction from the top of the core before sectioning. Samples were later thawed in the laboratory prior to analysis for THAA and SiTHAA. CaTHAA in sediments were analyzed only at MS-3. Wet and dry (freeze-dried) weights were measured; no salt correction was made. In addition to the bulk sediment samples we collected, P. Froelich provided 50 mg of diatom frustules that had been isolated from sediments at the APF and pre-cleaned using a series of acids and organic matter oxidants according to [Shemesh et al. \(1993\)](#). These were analyzed for THAA and SiTHAA.

2.2. Total hydrolyzable amino acids (THAA)

THAA were analyzed in all samples by HPLC using pre-column OPA derivatization after acid hydrolysis ([Lee and Cronin, 1982](#); [Lee et al., 2000](#)). Thawed filters (usually half of each filter contain-

ing plankton and sediment-trap samples) and sediments were sealed in glass tubes under N₂ with 6 N HCl and 0.25 wt% phenol added and hydrolyzed at 150°C for 90 min. All samples were between 0.5 and 2.0 g. Hydrolyzates were centrifuged to remove particles. The supernatant was transferred to a combusted glass vial, evaporated, and dissolved in MilliQ water, and the residue retained for analysis of SiTHAA. Hydrolysis releases amino acids that are in peptide bonds and adsorbed onto surfaces, but not those bound within opal. HCl dissolves CaCO₃, so that proteins and peptides protected by CaCO₃ are also released. As is traditionally done, we will refer to this fraction as THAA; it includes both non-mineral-bound and CaCO₃-bound amino acids. The procedure for the isolation of CaCO₃-bound amino acids is described later.

Amino acids were analyzed by HPLC using a modification of [Lindroth and Mopper \(1979\)](#). An Alltech Alltima C-18 250-mm 5- μ m column equipped with a guard column was eluted at a flow rate of 0.95 ml/min. A binary gradient of 0.05 M sodium acetate (pH 5.7) and 5% THF (eluant A) and methanol (eluant B) was used, ramping from 22% B to 50% B in 40 min, then to 100% B in 20 min. OPA-derivatized amino acids were detected by fluorescence and identified by comparison to retention times of authentic standards, amino acid identifications were verified in a few samples by GC-MS. An amino acid mixture (Pierce Chemical, Standard H) was used as the standard. The non-protein amino acids, β -alanine, and γ -aminobutyric acid (β -Ala and γ -aba) were added individually to the standard mixture. Aspartic acid and glutamic acid measurements include the hydrolysis products of asparagine and glutamine. Where lysine is not reported, this peak was not detected.

Samples of plankton, sinking particles and diatom isolates were consumed in a single hydrolysis. Hydrolysis of these individual samples were analyzed in duplicate, which agreed within $\pm 5\%$. Duplicate composite trap samples were not available; however, where both time-series and composite traps were collected, averages are reported (See [Table 7](#)). Time series and composite trap fluxes agreed within $\pm 15\%$. Several sediment samples

from each batch of 10–20 samples were hydrolyzed in duplicate. Duplicate hydrolyzates agreed with $\pm 10\%$. The isolated diatom sample was analyzed in a single hydrolysis.

2.3. Silicate-bound THAA (SiTHAA)

Silicate-bound amino acids (SiTHAA) were measured in all samples. After the first hydrolysis removed THAA, sample residues were rinsed with MilliQ water. Silicate minerals are not dissolved by HCl hydrolysis; therefore, the sample residue was composed mainly of biogenic opal (Si_{bio}) and detrital minerals (Table 2). HCl (6 N) was added to the rinsed residue and the samples hydrolyzed a second time. Analysis of this second hydrolyzate (THAA2) was carried out on several samples from the diatom cultures, plankton, sediment traps, and sediments, and represented between 0.3% and 2.7% of THAA. In plankton, THAA2 was enriched in aspartic acid (by 5–10 mol%) and depleted in serine, valine, phenylalanine, isoleucine and leucine (by ~ 5 mol%) and glycine (by 10–15 mol%) relative to THAA. In sediment-trap material, THAA2 was depleted in serine (by 10 mol%) and glycine (by 5–10 mol%) and enriched in valine, phenylalanine, isoleucine and leucine (by 5 mol%) relative to THAA. Sediment THAA and THAA2 compositions were similar; sediment samples were the only samples in which

β -ala was detected in THAA2. γ -Ala was not present in THAA2 in any samples.

Due to the small contribution of THAA2 to THAA, this second hydrolysis was carried out as a cleaning procedure on all samples, but analyses of this fraction were not made on all samples. After the second HCl hydrolysis, sample residues were rinsed with MilliQ water onto a GFF filter. The filter and sample were placed in a Teflon beaker that had first been cleaned by soaking in detergent, chromic acid, and then 6 N HCl, and rinsed with MilliQ water, methanol and then acetone. Samples were then dissolved in cold concentrated hydrofluoric acid (HF) to release silicate-bound amino acids (King, 1974). The HF was slowly evaporated on a hot plate at a temperature below the boiling point of HF (108°C). Once HF was completely evaporated, the residue was hydrolyzed with 6 N HCl, and the resulting SiTHAA analyzed by HPLC as described above. Standard amino acid mixtures were treated exactly as samples to determine if HF treatment altered the composition or concentration of amino acids. These experiments indicated that very little alteration of amino acids occurred during HF treatment. Neither HF nor GFF filters were a significant source of amino acid contamination. In addition, the dissolution of the glass GFF filters did not alter the composition of amino acids, suggesting that there was no artifact associated with their use. Here we define

Table 2

Composition (wt%) and mass flux of sinking particles in sediment traps (Honjo et al., 2000) and sediment cores (average of top 15 cm) from F. Sayles and W. Martin (data available at http://usjgofs.whoi.edu/jg/serv/jgofs/southern/nbp98_2/)

Station	SiO ₂	CaCO ₃	Detrital	C _{org}	N	Mass flux (g/m ² /yr)	PP ^a (mmol C/m ² d)
MS-2							
982 m trap	52	41	0.40	5.7	1.0	33.5	14
Sediment	27	0.25	72	0.5			
MS-3							
1003 m trap	64	30	0.30	5.4	0.9	36.9	20
Sediment	61	32	6.1	0.3			
MS-4							
1031 m trap	81	15	0.20	3.2	0.6	80.6	17
Sediment	93	10	—	0.37			
MS-5							
937 m trap	85	3.3	0.30	10	1.4	27.6	9.6
Sediment	31	16	52	0.4			

^a Estimated annual average primary production based on primary productivity measurements made between mid-October and April by Hiscock et al. (2003).

THAA plus SiTHAA as total THAA (TotTHAA) to denote amino acid concentrations that include all hydrolyzable amino acids in the sample, including those that are silicate, as well as carbonate, mineral bound.

2.4. Calcium carbonate-bound THAA (CaTHAA)

THAA analysis included CaCO₃-bound amino acids (CaTHAA) as mentioned above. To quantify CaTHAA separately, one half of selected samples (0.5–2 g) was placed in a 15-ml combusted glass vial with ~10 ml of 5% NaOCl (commercial bleach) and shaken for 8 d. Sediment-trap samples were placed in the vials on one half of a 47-mm GFF filter. Previous studies have shown that bleach removes non-mineral-bound organic matter but leaves CaCO₃-protected organic matter intact (Gaffey and Bronnimann, 1993). Bleach was replaced twice during the 8 d. After rinsing samples thoroughly with MilliQ water, CaCO₃ was dissolved with 6 N HCl. Hydrolysis and HPLC analysis of CaTHAA were as described above. CaTHAA were only measured in samples that were large enough and had a relatively large carbonate component; thus, plankton (MS-2, MS-

3 and MS-4), all composite traps, and sediment (MS-3) were analyzed for CaTHAA.

3. Results

3.1. Amino acid composition

3.1.1. Net plankton THAA

The small standard deviation in the mole percentages (mol%) of each amino acid averaged over all plankton samples demonstrates that the amino acid composition of plankton THAA had a similar general pattern at all latitudes (Table 3, Fig. 1). Amino acid abundance followed the order: glycine > alanine ~ glutamic acid > aspartic acid ~ serine > leucine > threonine > valine ~ arginine. All other amino acids were present at <5 mol%. Glycine was enriched in plankton collected at and south of the Polar Front (MS-3, 4 and 5) relative to plankton from north of the APF (MS-1 and 2). The percentages of glycine (16–23 mol%) in the diatom-dominated plankton mixture from the Southern Ocean were higher than previously reported for THAA in several species of diatoms (Hecky et al., 1973). They were also higher than in

Table 3
Amino acid composition (mol%) of plankton and cultured diatoms

	Asp	Glu	His	Ser	Gly	Arg	Thr	β -Ala	Ala	Tyr	γ -Aba	Met	Val	Phe	Ile	Leu	Lys
THAA																	
Cultures																	
<i>C. gracilis</i>	13.7	12.6	1.4	12.4	10.9	3.3	5.4	0.0	9.1	2.5	0.0	2.0	5.9	3.8	4.2	7.7	5.0
<i>C. gradiatus</i>	12.3	15.1	1.2	8.2	10.6	4.8	6.3	0.0	11.8	2.5	0.0	1.8	5.8	4.0	4.8	8.2	2.5
<i>T. pseudonana</i>	12.6	11.5	2.1	10.0	14.1	4.3	6.3	0.0	12.3	3.2	0.0	2.1	5.6	4.1	4.3	7.6	0.0
Plankton																	
MS-1	9.2	14.0	2.8	6.9	17.9	4.7	6.4	0.0	13.8	1.7	0.0	1.3	7.6	3.0	3.6	7.2	—
MS-2	11.5	15.1	1.7	8.0	16.4	5.3	6.6	0.0	11.4	1.5	0.0	1.4	5.4	3.6	4.0	8.0	—
MS-3	8.9	10.5	1.9	10.5	22.5	5.8	7.6	0.0	11.1	0.4	0.0	1.5	4.9	3.6	4.1	6.8	—
MS-4	9.6	12.2	1.9	8.9	20.0	5.6	6.8	0.0	11.1	1.6	0.0	2.2	5.3	3.5	4.0	7.4	—
MS-5	8.9	12.8	1.4	10.3	20.5	5.2	7.2	0.0	11.9	0.0	0.0	1.6	5.5	3.4	3.9	7.5	—
SiTHAA																	
MS-2	13.2	13.4	0.6	11.3	21.6	3.6	3.9	0.0	6.6	2.5	0.0	0.0	4.8	4.2	7.4	6.9	—
MS-3	11.8	12.3	0.6	9.1	16.5	2.5	4.4	0.0	7.7	3.0	0.0	0.0	8.1	4.7	9.8	9.5	—
MS-4	8.6	12.6	0.7	9.8	24.7	2.4	13.8	0.0	6.1	3.1	0.0	0.0	3.7	2.7	6.1	5.5	—
CaTHAA																	
MS-2	11.8	10.0	1.1	5.5	3.6	1.5	4.1	0.0	19.3	2.0	0.0	0.0	14.0	8.0	1.1	18.2	—
MS-3	8.5	13.9	2.3	10.1	8.4	3.2	8.9	0.0	22.5	1.1	0.0	0.0	5.6	10.2	5.3	0.0	—
MS-4	9.2	9.1	6.9	4.5	2.4	0.9	3.7	0.0	15.5	2.5	0.0	0.0	13.6	6.7	9.6	15.2	—

—Lysine peak was not detected chromatographically.

similar plankton tow samples from the Equatorial Pacific (Lee et al., 2000) or in phytoplankton, zooplankton, bacteria, and fungi from coastal areas (Cowie et al., 1992). High proportions of glycine (up to 22 mol%) have been reported in diatom cell walls isolated from two species of cultured *Cyclotella* (one estuarine and one freshwater) (Hecky et al., 1973). However, whole cells of these species are only 11 mol% glycine. Serine (7–11 mol%) was present in Southern Ocean plankton in an amount similar to other reports of diatoms (Chuecas and Riley, 1969; Hecky et al., 1973). However, mol% aspartic acid was generally lower than in the above studies.

Diatoms cultured in the lab for this study each had a distinct THAA composition (Table 3). *Coscinodiscus graditatus* was dominated by glutamic acid (15 mol%) and relatively depleted in serine (8 mol%) and glycine (10 mol%). *Thalassiosira pseudonana* was enriched in glycine (14 mol%) relative to the other species cultured. *Chaetoceros gracilis* was most enriched in serine (14 mol%) and contained 10 mol% glycine. Some of the variability in THAA composition may have been due to culture conditions at the time of cell harvest; no particular care was taken to harvest cells at a set time or in a particular growth phase. The THAA of cultured species were not enriched in glycine to the extent found in Southern Ocean plankton tow collections.

3.1.2. Net plankton SiTHAA and CaTHAA

SiTHAA in net plankton at MS-2, MS-3 and MS-4 were a tiny fraction (0.02–0.05%) of TotTHAA carbon. SiTHAA in plankton were characterized by high percentages of glycine (17–25 mol%), and in one case threonine (MS-4, 13.8 mol%), although glycine, serine and threonine showed little enrichment relative to bulk THAA. Alanine was much less important in SiTHAA (6–8 mol%) than in THAA (11–14 mol%). Methionine was undetectable in SiTHAA.

CaTHAA in plankton were a somewhat larger percent (0.2–1.0%) of THAA than were SiTHAA. This higher contribution could be due to a higher concentration of mineral-bound organic matter in carbonates relative to opal. Alternatively, the higher contribution of CaTHAA may reflect error

due to small sample size or to bleach not being completely effective in removing non-mineral-bound amino acids in these organic carbon-rich samples. The composition of CaTHAA (Table 3, Fig. 1) tends to support the suggestion that bleach does not remove all the cellular material since the enrichment of aspartic acid generally found in CaCO₃-bound organic matter relative to cellular material was not observed. However, pteropods were abundant in sinking particles at these sites (Honjo et al., 2000), and their skeletons have been shown to contain only 11.3 mol% aspartic acid, much lower than other calcareous shells (King, 1977), and similar to typical values found in net plankton (e.g., Lee et al., 2000). Glycine was significantly lower (~2–8 mol%) in the CaTHAA fraction and alanine was higher (19–23 mol%) than in SiTHAA or THAA.

3.1.3. Sediment-trap THAA

The small standard deviation in mol% of each amino acid among annually averaged sinking particle THAA at all locations and depths suggests a relatively similar general pattern in amino acid compositions throughout the region (Fig. 1, Table 4). In two cases, composite trap samples were not available (MS-2 deep trap, MS-4 shallow trap), so time-series data were summed by adding the μmol amino acid/trap for each time interval and dividing by the total number of days deployed; annual fluxes and average compositions were calculated from these totals. Detailed results from time-series traps will be reported elsewhere (Ingalls et al., in prep.). Sinking particle THAA were enriched in glycine relative to plankton (except MS-5), particularly in the deep traps. Aspartic acid was also enriched in trap samples relative to plankton (except MS-4 shallow). Trap samples were depleted in glutamic acid, alanine and methionine relative to plankton, particularly in deep traps. Although plankton THAA contained undetectable concentrations of the non-protein amino acids, β -Ala and γ -Aba, small amounts (0.1–0.6 mol%) of β -Ala were present in all sinking particles, and γ -Aba (0.2–0.7 mol%) was present at MS-2 and MS-5. The highest mol% glycine was at MS-3 in both shallow and deep traps. MS-3 was at

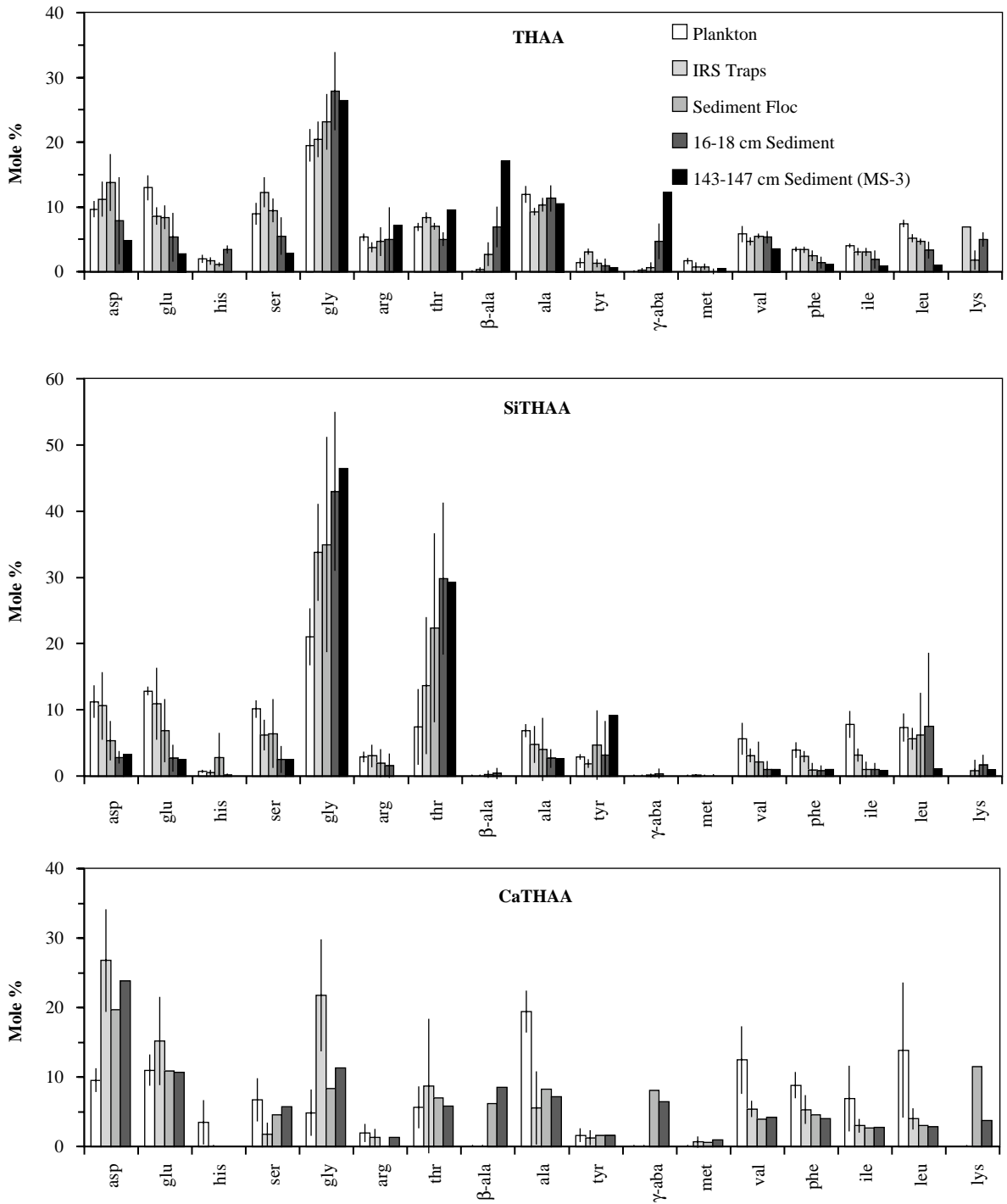


Table 4

Amino acid composition (mol%) and flux ($\mu\text{mol THAA C/m}^2\text{d}$) in composite sediment traps except where noted

Sediment traps	Asp	Glu	His	Ser	Gly	Arg	Thr	β -Ala	Ala	Tyr	γ -Aba	Met	Val	Phe	Ile	Leu	Lys	Flux
THAA																		
MS-2 1325 m	12.2	8.9	1.9	11.1	18.6	3.6	8.4	0.5	9.4	2.8	0.7	0.0	4.7	3.1	3.0	4.9	6.1	71
MS-2 4024 m ^a	15.1	10.0	2.2	11.3	18.9	4.1	8.7	0.6	8.8	3.0	0.2	1.6	4.3	3.3	2.8	5.2	8.5	38
MS-3 1344 m	11.2	9.5	2.0	11.5	22.7	4.0	8.3	0.3	9.5	3.5	0.0	0.2	4.8	3.6	3.3	5.6	7.3	100
MS-3 3057 m	10.2	7.1	1.7	11.8	24.4	3.7	7.9	0.4	8.6	3.1	0.0	0.3	4.1	3.0	2.7	4.4	6.7	52
MS-4 1031 m ^b	10.8	9.0	1.0	10.7	21.7	4.6	7.1	0.1	8.9	2.4	0.0	1.2	5.6	3.8	3.8	5.6	3.5	122
MS-5 1274 m	6.6	6.9	1.3	17.0	17.1	3.0	9.2	0.1	9.8	3.1	0.2	0.6	4.8	3.4	2.9	5.5	8.7	118
MS-5 2107 m	12.0	8.5	1.2	12.2	19.2	2.8	8.7	0.1	9.2	3.2	0.2	0.7	4.4	3.1	2.7	4.7	7.1	69
SiTHAA																		
MS-2 1325 m	14.9	16.3	0.4	6.6	28.0	4.2	7.6	0.0	4.2	1.6	0.0	0.0	3.2	2.9	3.5	6.6	—	0.63
MS-2 4024 m ^a	14.9	16.4	0.9	8.7	26.7	4.9	3.7	0.0	4.1	2.6	0.0	0.1	3.2	3.3	3.6	6.7	—	0.56
MS-3 1344 m	9.1	6.7	0.4	5.8	43.3	2.0	17.4	0.0	2.8	1.9	0.0	0.0	2.1	2.2	2.3	3.8	—	2.76
MS-3 3057 m	6.8	7.2	0.3	4.9	44.3	1.5	21.8	0.0	3.0	1.7	0.0	0.0	1.7	1.7	1.8	3.0	—	2.48
MS-4 1031 m ^b	1.6	3.0	0.4	2.1	33.3	0.9	31.1	0.1	4.1	0.8	0.0	0.2	4.5	3.8	4.5	6.9	2.7	3.98
MS-5 1274 m	13.6	12.1	0.6	7.0	29.7	3.9	4.6	0.0	10.5	2.1	0.0	0.0	3.5	3.1	3.1	6.2	—	0.82
MS-5 2107 m	12.9	14.4	0.0	7.9	31.0	3.4	8.9	0.0	3.9	2.1	0.0	0.0	3.1	3.2	3.2	5.9	—	0.68
CaTHAA																		
MS-2 1325 m	37.0	11.1	0.0	1.6	10.3	1.4	6.9	0.0	8.5	2.0	0.0	1.4	6.9	4.0	4.0	4.8	—	0.30
MS-2 4024 m ^a	NA																	
MS-3 1344 m	29.3	13.1	0.0	1.9	17.3	1.8	6.0	0.0	12.6	1.7	0.0	1.1	4.8	4.1	2.8	3.6	—	0.30
MS-3 3057 m	28.7	10.2	0.0	3.7	23.1	2.6	6.2	0.0	6.6	1.9	0.0	0.0	5.0	4.2	3.2	4.6	—	0.21
MS-4 1031 m ^b	NA																	
MS-5 1274 m	26.3	18.8	0.0	3.0	23.5	1.5	4.6	0.0	6.0	1.2	0.0	0.0	3.7	4.8	2.6	3.8	—	0.64
MS-5 2107 m	22.5	—	0.0	—	46.5	0.0	0.0	0.0	—	0.1	0.0	0.0	7.6	12.3	4.2	6.7	—	0.07

^aSum of time-series traps cups.^bPARFLUX time-series trap.

—Peak was not detected chromatographically.

NA Samples were not analyzed due to small size of time-series traps.

the APF and had a high weight% of biogenic silica in the underlying sediment (Table 2; Honjo et al., 2000). MS-4 had the highest weight% of sedimentary Si_{bio} , but no deep trap data were available for this station. Overall, the composition of THAA was similar to that found in other sediment-trap studies. Mol% serine and glycine were slightly higher than in the equatorial Pacific (Lee et al., 2000).

3.1.4. Sediment-trap SiTHAA and CaTHAA

The composition of SiTHAA was more distinct from that of THAA in sinking particles compared to plankton. Mol% glycine in trap SiTHAA (27–44 mol%) was enriched by a factor of 1.5–2.0 relative to THAA, with the highest values at the APF (MS-3) (Table 4). North and south of the APF, glutamic acid was enriched in the SiTHAA pool relative to THAA but was relatively depleted

Fig. 1. Average amino acid composition measured in net plankton, sediment trap material, and sediment at all stations, and the composition of deeper sediment at MS-3. Total hydrolyzable amino acids (THAA) include both non-mineral-bound amino acids and calcium carbonate-bound amino acids. SiTHAA are silicate-bound amino acids. CaTHAA are calcium carbonate-bound amino acids. Vertical bars are plus or minus one standard deviation of the average mol% for each amino acid among all mooring stations, not error bars. Abbreviations for amino acids are as follows: Asp, aspartic acid; Glu, glutamic acid; His, histidine; Ser, serine; Gly, glycine; Arg, arginine; Thr, threonine; β -Ala, β -alanine; Ala, alanine; Tyr, tyrosine; γ -Aba, γ -aminobutyric acid; Met, methionine; Val, valine; Phe, phenylalanine; Ile, isoleucine; Leu, leucine; Lys, lysine.

Table 5

Amino acid fluxes, contribution of amino acids to the total carbon and nitrogen flux, amino acid in biogenic mineral phases and proportion of primary production exported and preserved as amino acids

Sample	THAA C ($\mu\text{mol}/\text{m}^2\text{d}$)	%C org from THAA	%N from amino acids	%TotTHAA as SiTHAA C	%TotTHAA as CaTHAA C	TotTHAA C ($\mu\text{mol}/\text{m}^2\text{d}$)	%PP Exported as TotTHAA C
Sinking particles							
<i>Shallow trap</i>							
MS-2 ^a	71	18	41	0.9	0.42	71.9	0.5
MS-3 ^a	100	21	43	2.7	0.29	103.1	0.52
MS-4 ^b	122	24	50	3.2	—	126.0	0.73
MS-5	118	27	60	0.7	0.54	119.5	1.2
<i>Deep trap</i>							
MS-2 ^c	38	26	51	1.4	—	38.9	0.29
MS-3 ^a	52	17	34	4.5	0.38	54.7	0.28
MS-5 ^a	69	20	42	1.0	0.10	69.7	0.7
	THAA C ($\mu\text{mol}/\text{gdw}$)					TotTHAA C ($\mu\text{mol}/\text{gdw}$)	
Sediment							
<i>Floc</i>							
MS-2	30.4	22.7		5.4	—	32.2	
MS-3	15.3	12.0		7.3	10.8	16.5	
MS-4	33.1	6.5		11.9	—	—	
MS-5	20.0	10.9		13.5	—	23.1	
<i>16–18 cm</i>							
MS-2	9.6	6.7		5.4	—	10.2	
MS-3	7.2	4.5		47.8	16.0	13.8	
MS-4	3.5	2.1		62.4	—	9.3	
MS-5	4.8	8.9		0.4	—	4.8	
<i>145 cm</i>							
MS-3	9.0			44.1		16.1	
Diatom frustules^d							
MS-3	5.2			58.4		12.5	

^a Values based on average of time-series and composite traps (SD $\pm 15\%$).

^b Values based on PARFLUX traps.

^c Values based on time-series traps.

^d Diatom frustules separated and chemically cleaned according to Shemesh et al. (1993).

at MS-3 and MS-4. MS-3 and MS-4 were enriched by a factor of 2.0–4.5 in threonine (17–33 mol%) and depleted by a factor of 2–5 in serine (2–6 mol%) relative to other stations. We know of no data on SiTHAA in sediment traps for comparison; however, enrichments of serine, threonine and/or glycine are commonly reported for this fraction in diatomaceous materials (King, 1977; Montani et al., 1982; Shemesh et al., 1993).

CaTHAA in sinking particles also differed more in composition from THAA than in plankton. CaTHAA were enriched in aspartic acid by up to a factor of 3 relative to bulk THAA. Glutamic acid was also enriched, and serine and alanine depleted (Table 4). The contribution of aspartic acid in the CaTHAA pool (23–37%) is similar to other reports of amino acids in biogenic carbonates (e.g., King, 1977; Carter and Mitterer, 1978;

Table 6

Amino acid composition (mol%) and total concentration ($\mu\text{mol THAA C/gdw}$) of sediment samples and isolated and cleaned diatom frustules

Sample	Asp	Glu	His	Ser	Gly	Arg	Thr	β -Ala	Ala	Tyr	γ -Aba	Met	Val	Phe	Ile	Leu	Lys	Conc.
THAA																		
MS-2 Floc	9.5	6.7	1.0	11.8	20.6	7.3	7.5	3.1	10.8	1.0	1.1	0.4	5.6	2.3	3.3	4.9	3.2	30.4
MS-3 Floc	19.2	10.5	1.0	7.7	19.1	4.5	6.7	2.2	9.2	1.8	0.0	1.1	5.7	3.2	3.5	4.7	0.0	15.3
MS-4 0.0–0.5 cm	14.8	9.0	1.0	8.9	24.2	4.5	7.0	0.6	9.9	1.5	0.2	1.0	5.1	2.6	2.7	4.8	2.2	33.1
MS-5 Floc	15.3	12.0	1.3	9.5	18.6	4.3	7.5	1.2	10.6	2.6	0.0	0.0	5.2	3.0	4.2	4.7	1.5	20.0
THAA																		
MS-2 16–18 cm	4.6	3.9	0.2	5.1	28.7	14.9	5.8	6.2	11.1	0.3	3.6	0.4	5.4	1.5	1.5	2.8	4.3	9.6
MS-3 16–18 cm	19.8	7.2	0.9	3.4	21.2	5.8	7.4	7.7	9.1	1.1	5.7	0.6	4.6	1.7	1.8	2.0	—	7.2
MS-4 16–18 cm	10.1	4.7	0.9	7.8	30.9	6.1	6.2	3.0	13.7	0.8	0.9	0.3	6.5	1.4	1.8	2.5	2.4	3.5
MS-5 16–18 cm	7.8	5.3	3.4	5.4	27.9	5.0	5.0	6.9	11.3	0.9	4.7	0.0	5.3	1.3	1.8	3.3	4.9	4.8
MS-3 143–147 cm	6.5	4.7	0.0	6.4	29.5	7.8	9.4	7.8	8.7	0.7	4.5	0.6	3.6	1.3	0.2	1.2	7.3	9.0
Diatom frustules	10.7	16.3	1.4	6.5	19.3	5.1	3.8	0.6	6.6	3.2	0.5	0.2	4.5	3.4	4.3	9.5	4.2	5.2
SiTHAA																		
MS-2 Floc	8.3	10.7	2.6	3.8	24.0	3.9	12.9	0.9	10.3	1.7	0.2	0.0	6.4	2.1	2.4	6.7	3.1	1.2
MS-3 Floc	5.0	4.2	0.0	5.2	47.0	0.0	28.2	0.0	0.0	4.9	0.0	0.0	1.5	1.0	0.7	2.2	0.0	1.3
MS-4 0.0–0.5 cm	1.6	1.5	0.3	2.6	50.3	0.3	39.4	0.0	1.0	0.3	0.0	0.0	0.6	0.4	0.6	1.1	0.0	4.9
MS-5 Floc	6.3	10.6	7.9	13.8	18.3	3.2	8.8	0.0	4.5	11.8	0.0	0.0	0.0	0.0	0.0	14.7	0.0	3.1
SiTHAA																		
MS-2 16–18 cm	3.0	4.9	0.2	4.6	44.8	3.8	18.8	1.4	4.5	0.4	1.2	0.0	2.5	1.4	1.2	4.5	2.9	0.6
MS-3 16–18 cm	3.6	3.5	0.0	2.6	52.7	0.0	21.3	0.0	2.4	10.6	0.0	0.0	0.9	1.1	0.2	1.1	—	6.6
MS-4 16–18 cm	1.7	1.6	0.2	2.5	48.3	0.3	38.7	0.0	2.0	0.4	0.0	0.1	0.5	0.5	0.6	0.8	2.0	6.1
MS-5 16–18 cm	2.7	0.7	0.0	0.0	25.8	2.0	40.4	0.0	1.6	1.2	0.0	0.0	0.0	0.0	1.9	23.6	0.0	0.5
MS-3 143–147 cm	3.2	2.5	0.0	2.4	46.4	0.0	29.2	0.0	2.6	9.1	0.0	0.0	0.9	0.9	0.8	1.1	0.9	7.7
Diatom frustules	1.6	2.9	0.1	1.7	54.2	0.4	31.4	0.3	2.7	0.0	0.1	0.0	0.8	0.7	0.4	1.8	0.9	7.3
CaTHAA																		
MS-3 0–0.5 cm	25.3	10.6	0.0	4.6	8.4	0.0	6.8	7.1	8.0	1.6	11.6	0.6	3.3	3.3	2.1	2.7	4.1	1.5
MS-3 16–18 cm	23.8	10.7	0.0	5.7	11.2	1.2	5.8	8.5	7.1	1.6	6.4	0.9	4.1	3.9	2.7	2.8	3.7	2.2

Lowenstam and Weiner, 1989). The composition of bleached samples (CaTHAA) was more variable than either THAA or SiTHAA (Table 4). This variability may be due to inconsistency in the removal of amino acids by bleach treatment. However, since the entire plankton sample was consumed during analysis, this variability was not investigated. Aspartic acid was most enriched at MS-2 and decreased southward along with weight % CaCO_3 in the traps (Table 2). The small sample size in the deep trap at MS-5 undoubtedly resulted in erroneous compositional data in this sample (Table 4).

SiTHAA were 0.70–3.2% of TotTHAA concentrations in shallow traps (Table 5) with the highest values at MS-4. Deep traps had slightly higher proportions of SiTHAA than shallow traps. CaTHAA were 0.01–0.54% of TotTHAA (Table 5).

3.1.5. Sediment THAA

The amino acid composition of the surficial sediment floc differed from that of trap samples in several ways (Table 6, Fig. 1). At MS-2, the floc was depleted in aspartic acid and enriched in glycine relative to overlying trap material, reflecting the low CaCO_3 content of sediments at this site (Table 2). Mol% aspartic acid was highest at MS-3 (19 mol%) where wt% CaCO_3 was highest. Aspartic acid was enriched in the floc layer relative to traps at both MS-3 and 5. In addition, β -Ala (2.2–3.1 mol%) and γ -Aba (0.0–1.1 mol%) were enriched in floc samples relative to traps, with higher values at the northern station, MS-2, and lower values southward at MS-3 and MS-5.

The compositional changes in THAA in deeper sediments indicated progressively more degradation. These compositional changes were

similar to those found in previous studies (e.g., Whelan, 1977; Keil et al., 2000) with decreases in mol% aspartic and glutamic acids and increases in mol% β -Ala and γ -Aba (Fig. 1, Table 6). The ratio of aspartic acid to β -Ala and glutamic acid to γ -Aba generally decreased with depth (Table 7). Mol% serine, tyrosine, methionine, glutamic acid, phenylalanine, isoleucine and leucine decreased, while mol% glycine and arginine increased with depth in the sediment. Mol% threonine increased with depth at MS-3, which also had the highest Si_{bio} , but decreased with depth at MS-2 and MS-5.

3.1.6. Sediment SiTHAA

SiTHAA composition was most distinct from THAA in sediments as compared to plankton and

sinking particles. SiTHAA were almost always enriched in glycine and threonine relative to bulk amino acids, reaching a high of 53 mol% glycine (Table 6). The mol% glycine+threonine in the SiTHAA pool (upper 18 cm) was positively correlated ($p = 0.016$, $n = 5$) with wt% biogenic silica (Fig. 2); this was not the case in the THAA pool ($p = 0.72$, $n = 4$). While the large enrichments of glycine and threonine observed in the HF-extractable amino acids in this study are unusual, reports of high proportions of glycine and threonine are not without precedence. King (1974) reported that HF-digested modern and fossil radiolaria tests contained ~ 20 mol% glycine, 15 mol% aspartic acid and 5–10 mol% serine and threonine, similar to the ~ 22 mol% glycine in diatom cell walls

Table 7
Amino acid indicators of source or diagenesis in THAA

Sample	Ser + Thr (mol%)	Asp/Gly	Asp/ β -Ala	Glu/ γ -Aba	DI	SO-PC1 Site Score
<i>MS-2</i>						
Plankton	14.5	0.70	—	—	0.59	4.64
1325 m	19.5	0.66	27.0	12.5	-0.11	2.82
4024 m	20.0	0.80	26.6	62.0	0.10	4.07
Floc	19.3	0.46	3.05	6.40	-0.79	1.80
16–18 cm	10.9	0.16	0.73	1.08	-2.08	-1.72
<i>MS-3</i>						
Plankton	18.1	0.39	—	—	0.11	3.80
1344 m	19.8	0.49	37.7	—	0.14	3.43
3057 m	19.6	0.42	23.7	166	-0.21	2.35
Floc	14.4	1.00	8.74	—	-0.42	3.25
16–18 cm	10.9	0.93	2.57	1.27	-1.66	-0.62
143–147 cm	15.7	0.22	0.84	1.04	-2.28	-4.09
<i>MS-4</i>						
Plankton	15.7	0.48	—	—	0.54	4.65
1031 m	17.8	0.50	94.1	278	0.14	3.99
0.0–0.5 cm	15.8	0.61	24.7	48.2	-0.70	2.38
16–18 cm	14.0	0.33	3.39	5.30	-1.87	-0.50
<i>MS-5</i>						
Plankton	17.5	0.43	—	—	0.10	4.02
1274 m	26.1	0.39	67.6	42.3	0.14	3.91
2107 m	20.9	0.62	119	48.3	-0.15	3.30
Floc	17.1	0.82	2.46	5.68	-0.20	3.12
16–18 cm	10.4	0.28	1.14	1.14	-0.82	-1.54
<i>Diatom frustules</i>	10.2	0.55	18.2	31.4		

— β -Ala and/or γ -Aba were not present in these samples, so no ratio could be calculated.

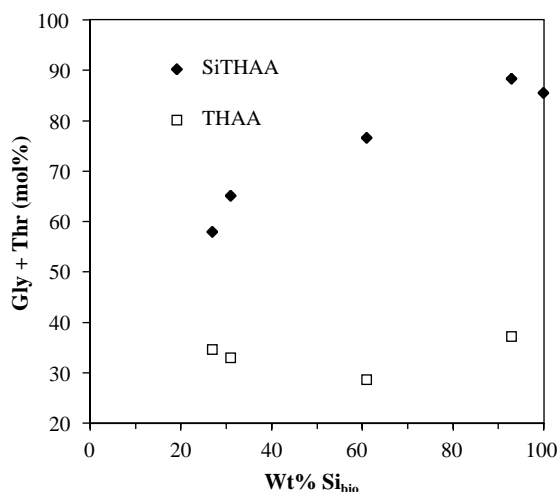


Fig. 2. Wt% Si_{bio} and mol% glycine + threonine in the THAA ($r^2 = 0.079$) and SiTHAA ($r^2 = 0.95$) pools in the upper 18 cm of sediment. MS-2 through MS-5 plus diatom isolates from MS-3 (100% Si_{bio}) are plotted.

reported by Hecky et al. (1973). King (1977) reported that biogenic opals were all enriched in glycine (35 mol%); however, he found enrichment of threonine (26 mol%) only in diatoms. Montani et al. (1982) found 54 and 22 mol% glycine and threonine, respectively, in the upper 10 cm of HF-digested (SiTHAA) Okhotsk Sea sediment that contained 50 wt% Si_{bio}. Deeper sediment horizons in the Okhotsk Sea contained <10% Si_{bio}, and in these samples, SiTHAA was <30 mol% glycine, <8 mol% threonine, and 18–24 mol% serine. Diatom frustules isolated from APF sediments had very high proportions of glycine (54 mol%) and threonine (31 mol%) in the SiTHAA fraction (Table 6).

Studies of HF-extractable proteins and amino acids rely on a spectrum of methods to remove non-silicate-bound amino acids. Differences in these methods may account for some of the differences in the amino acid composition found between studies. For example, acid hydrolysis of diatom frustules pre-cleaned by the Shemesh et al. (1993) method showed that the THAA composition of pre-cleaned diatoms was similar to that of bulk sediment THAA (Table 5). In addition, the THAA and SiTHAA concentrations of pre-

cleaned diatom isolates were similar (Table 5), suggesting that the Shemesh cleaning method as it was used here did not remove all surficial amino acids, and that acid hydrolysis releases additional amino acids from these samples. Montani et al. (1982) also acid-hydrolyzed sediments before digesting them with HF and found the composition of the SiTHAA fraction to be similar to what we report here. In addition to these differences due to cleaning methods, King (1977) found that SiTHAA compositions were highly species specific.

3.1.7. Sediment CaTHAA

Sedimentary CaTHAA (measured only at MS-3) were relatively enriched in aspartic acid (Table 6). Mol% aspartic acid was variable with depth (10–33 mol% between 0 and 25 cm) with most values between 20–33 mol%; some of this variability was probably related to the changing CaCO₃ content with depth in the sediment core (0–35%). Elevated mol% aspartic acid in CaCO₃-rich sediments has been previously reported and is thought to be due to the presence of proteins that aid mineral precipitation or to preferential adsorption of aspartic acid to CaCO₃ surfaces (Carter and Mitterer, 1978). Presumably, surface-sorbed amino acids are removed by bleach; however, some mineral-precipitating proteins are not (Gaffey and Bronnimann, 1993). Unlike bleached plankton and trap samples, bleached sediment contained significant β -Ala and γ -Aba (5–10 mol%) (Table 6).

3.2. Amino acid fluxes in sediment traps

THAA fluxes measured in ~1300 m traps ranged narrowly between 71–122 $\mu\text{mol C/m}^2\text{d}$ (1.9–3.5 mg amino acid/m²d) (Table 5). The similar values at all stations indicate relatively uniform export of amino acids across the region, with the lowest flux north of the APF at MS-2 (Table 4; Fig. 3). Honjo et al. (2000) also found relatively uniform fluxes of total organic carbon across the region at 1000 m water depth. Our deeper traps collected 38–69 $\mu\text{mol THAA C/m}^2\text{d}$ (0.78–2.0 mg amino acid/m²d) (Table 5). These amino acid fluxes are comparable to those in many

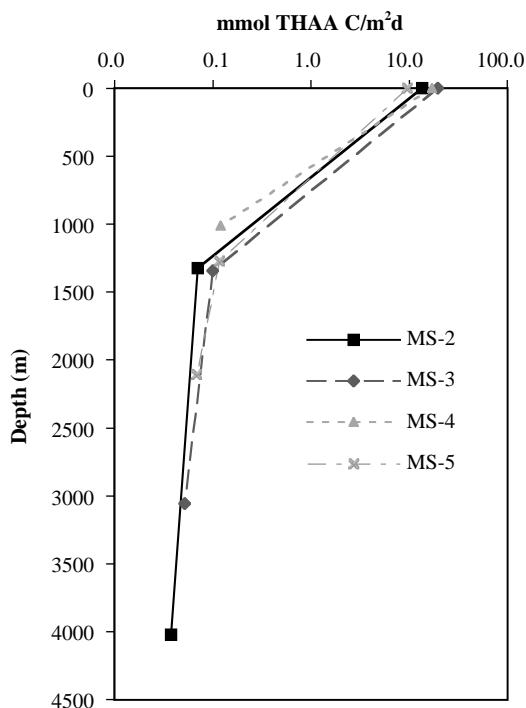


Fig. 3. Total amino acid fluxes in shallow and deep traps. Points at zero depth represent primary production estimated from average primary production (Hiscock, et al., 2003) and assuming that 30% of the carbon in plankton is in amino acids. Fluxes are plotted on a log scale.

previous reports, e.g., in the equatorial Pacific ($4.5 \text{ mg/m}^2 \text{ d}$ at 1000 m and $1.9 \text{ mg/m}^2 \text{ d}$ at 3600 m; Lee et al., 2000), North Atlantic ($14 \text{ mg/m}^2 \text{ d}$ at 1000 m and $3.3 \text{ mg/m}^2 \text{ d}$ at 3500 m; Lundgreen and Duinke, 1998), and the Brazil coast ($0.6\text{--}4.0 \text{ mg/m}^2 \text{ d}$; Jennerjahn et al., 1999). They are small compared to highly productive coastal and Peru upwelling sites ($260\text{--}630 \text{ mg/m}^2 \text{ d}$; Lee and Cronin, 1982), and large compared to fluxes at 3400 m in the oligotrophic Sargasso Sea ($0.12\text{--}1.7 \text{ mg/m}^2 \text{ d}$; Ittekkot et al., 1984b).

We can only estimate the contribution of amino acids to total carbon flux, since total organic carbon (C_{org}) fluxes have not yet been measured in our trap samples. We can use C_{org} fluxes reported at nearby depths from PARFLUX sediment traps that were on the same moorings and that began collecting at the same time as ours (Honjo et al., 2000). However, trap depths and collection peri-

ods were different from ours; this results in additional uncertainty in these calculations since analysis of time-series traps showed changes in flux on a seasonal timescale (Ingalls et al., in prep.). Using C_{org} and N fluxes from PARFLUX traps ($\sim 1000 \text{ m}$ for shallow traps and 700 m above bottom for deep traps), we estimate that THAA contributed 18–27% of C_{org} and 41–60% of N_{tot} fluxes in shallow traps (Table 5). THAA in deep traps were 17–26% of C_{org} and 34–51% of N_{tot} . Fluxes of amino acids to deep traps were 52–59% of those in shallow traps. For comparison, in the equatorial Pacific, the flux of THAA to 3600 m traps was less than half that at 1000 m, and 24% of C_{org} was in amino acids in both 1000 and 3600 m samples (Lee et al., 2000). Ittekkot et al. (1984b) found 13–34% C_{org} in amino acids and 30–53% of N in amino acids in the Sargasso Sea. Müller et al. (1986) found 32–51% of C_{org} in amino acids and 23–77% of N in amino acids in the Scotia Sea.

3.3. Sediment amino acid concentration

Sedimentary THAA concentrations ranged from $3.5\text{--}33.1 \mu\text{mol THAA C/gdw}$ ($0.098\text{--}0.93 \text{ mg amino acid/gdw}$) between 0–43 cm at MS-2 and MS-5, 0–143 cm at MS-3 (Fig. 4, Table 6), and at two depths between 0–20 cm at MS-4 (Table 6). Surface sediment concentrations were higher and more variable than in deeper samples, with concentrations relatively constant below 20 cm. Polar Front (MS-3) sediment contained the highest concentration of amino acids below 15–20 cm ($10\text{--}15 \mu\text{mol THAA C/gdw}$), more than twice the concentration north and south (MS-2 and MS-5) of the APF (Fig. 4). THAA contributed 7–23% C_{org} at the sediment water interface and 2–9% C_{org} in 16–18 cm sediment (Table 5). These values are similar to those found in other open-ocean sediments, i.e. the deep Atlantic ($12 \pm 10\%$; Whelan, 1977), equatorial Pacific surface sediments ($\sim 16\%$ of C_{org} ; Lee et al., 2000), and the Atlantic continental slope (10–13%; Grutters et al., 2001).

SiTHAA concentrations were measured at all depths sampled in cores from MS-2, MS-3 and MS-5 (Table 6, Fig. 4). The core from MS-4 was only analyzed at two depth intervals (Table 6). Concentrations of SiTHAA were highest at MS-3

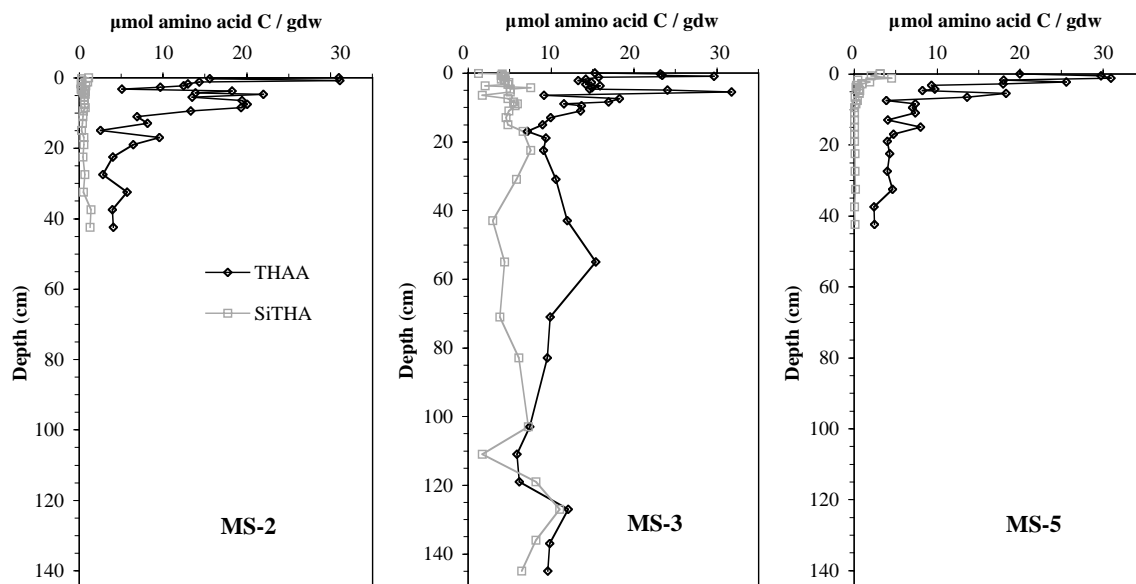


Fig. 4. Total hydrolyzable amino acids (THAA) and silicate-bound THAA (SiTHAA) concentrations in sediment cores from MS-2, MS-3 and MS-5. MS-4 data is not shown because only 2 depths were analyzed (see Table 5).

and MS-4 and ranged between 2 and 11 μmol SiTHAA C/gdw. SiTHAA equaled or exceeded THAA at several depths in the sediment at MS-3 and in the 16–18 cm interval of MS-4. At MS-2 and MS-5, SiTHAA never exceeded 5 μmol SiTHAA C/gdw and was less than 1 μmol SiTHAA C/gdw in most samples. SiTHAA was positively correlated ($p = 0.033$, $n = 5$) with wt% Si_{bio} . At MS-3, CaTHAA was 11% of THAA in surface sediment and 16% of THAA in deeper sediment (Table 5).

4. Discussion

4.1. Amino acid sources

4.1.1. THAA sources

The amino acid composition of plankton collected in early March at all stations reflected both the high proportion of diatoms and the physiological status of the diatoms present. Primary productivity during AESOPS peaked in Subantarctic waters near MS-2 in December 1997 (Hiscock, et al., 2003). Small diatom cells dominated the phytoplankton bloom communities at

MS-1 and MS-2 where silicic acid was in short supply. Phytoplankton THAA at these stations had the lowest mol% glycine values relative to those at stations further south (Table 3). At stations at and south of the APF (MS-3 and MS-4), silicic acid was abundant throughout January, and large centric and pennate diatoms dominated the phytoplankton bloom community (Brown and Landry, 2001). Plankton at these stations were enriched in glycine (Table 3). The peak in productivity migrated south over time (Franck et al., 2000). By March 1998, the peak in productivity subsided as diatom populations became nutrient-limited by silicic acid in the north and iron in the south (Franck et al., 2000).

While substantial variations in amino acid composition exist among diatom species, glycine contents of 22.5 mol% observed in Southern Ocean plankton THAA are extremely high. This high glycine content might in part be due to the presence of a large number of diatoms lacking cytoplasm and chloroplasts during the summer when nutrient supplies are lower (Brown and Landry, 2001). Compared to intact diatom cells, empty cells contain a high proportion of their total cellular protein in their cell walls. Diatom cell

walls include both a glycoprotein outer coating and a siliceous frustule (Preisig et al., 1994). During silicification, the frustule is laid down on a protein template, some of which appears to be closely associated with the frustule and is inaccessible unless the opal frustule is dissolved (Swift and Wheeler, 1991; Kröger et al., 1997, 2001). In general, the term “cell wall amino acids” is used to refer to amino acids in the glycoprotein coating (analyzed as THAA), but not the template proteins (analyzed as SiTHAA). Glycine, serine and sometimes threonine can be enriched in the THAA of diatom cell walls relative to total phytoplankton (Hecky et al 1973; Cowie et al., 1992; Cowie and Hedges, 1996).

Other mechanisms besides nutritional status could be responsible for the formation of empty diatom cells, and thus the enrichment in cell wall proteins we observed. The chain-forming diatom, *Fragilariopsis kerguelensis*, which dominates the plankton and sediment of the APF (Smetacek, 1999), can contain numerous empty cells within chains (DeBaar, 1997; Smetacek et al., 1997). Laboratory investigations suggest that protozoa can consume diatoms by extracting their cellular contents, leaving behind empty cell walls (Kühn, 1997). Another common Southern Ocean diatom, *Corethron criophilum*, is known to discard its cell walls during sexual reproduction (Crawford, 1995; Smetacek et al., 1997). Although cell wall proteins are remineralized more slowly than other cellular proteins, they eventually can be consumed by microbes (Bidle and Azam, 1999, 2001). However, some portion of cell wall proteins may be protected from hydrolytic enzymes in small micropores on diatom surfaces or within inaccessible compartments of frustules (Hurd et al., 1981; Mayer, 1994a; Ransom et al., 1998).

4.1.2. SiTHAA sources

Silaffins are one class of characterized polypeptides that are reported to be a major component of HF extractable proteins (SiTHAA) in a common marine diatom (Kröger et al., 1999). Although these peptides are enriched in glycine and serine, they also contain non-conventional protein amino acids that are not quantified by our HPLC analysis. SiTHAA from Southern Ocean surface

plankton we analyzed were not enriched in glycine and serine. However, both sinking particles and pure diatom frustules isolated from Southern Ocean sediments were enriched in these two amino acids. One explanation for the compositional difference between plankton and the other samples could be the considerable variability in the amino acid composition of template proteins among organism groups. For example, SiTHAA of fossil radiolaria, sponge spicules, and opal phytoliths are not enriched in threonine; however, some species of diatoms contain up to 26 mol% threonine (King, 1977). All these fossils, especially diatoms, are enriched in opal-bound glycine (19.9–34.6 mol%). Another explanation for compositional differences between Southern Ocean plankton, sinking particles and sediment is that the plankton samples collected may not have been representative of sinking material, either because of seasonal differences in species composition or differences in relative opal dissolution. However, the similarity between SiTHAA composition in diatom frustule isolates and sinking particles and sediments suggests that diatoms are the source of SiTHAA to deeper waters. The proteins responsible for the enrichment of glycine and threonine in our samples have not been identified.

4.2. Water column amino acid fluxes

Fluxes of amino acids generally decrease rapidly with depth after these compounds are initially formed by phytoplankton in the euphotic zone. Calculation of amino acid production by plankton in the euphotic zone is difficult in the Southern Ocean. In the equatorial Pacific (Lee et al., 2000), we estimated this flux by multiplying the measured contribution of amino acids to plankton carbon (27%) by the primary productivity. However, the amino acid contribution to total organic carbon in a single algal species, *Thalassiosira pseudonana*, has been shown to range between 30% and 60%, depending on growth phase (logarithmic or stationary) and ambient light levels (Brown et al., 1996). Cells that experience N or Si limitation put more resources into carbohydrates and lipids for energy storage, reducing cellular protein content by up to 50%. Light and nutrient availability vary

greatly throughout the year in the Southern Ocean, so that many more samples than we collected would be needed to determine an annual average amino acid contribution to plankton.

Despite the uncertainty in contribution of amino acids to plankton, we can roughly estimate the annual average fraction of carbon from primary production exported to our sediment traps as amino acids (Table 5). To estimate an average primary productivity, we took seasonally averaged values of daily primary production from October 1997 through March 1998 (Hiscock, et al., 2003) and multiplied by the number of days in each season to get the total flux per season. The total of all seasons was the total annual production (Table 2). No measurements were available during the six months from April to September, during which we assumed that production was zero due to light limitation and/or ice cover.

Using this approximation for annual production, we estimate that 0.50–1.2% of the C_{org} produced in the upper 100 m is exported to ~1300 m as amino acids, and 0.28–0.70% of primary production was exported to deep traps as amino acids (Table 5). MS-5, with the highest trap Si_{bio} content (Table 2), had the highest proportion of primary production exported as amino acids to both shallow (1.2%) and deep traps (0.70%). Larger export at MS-5 may be due to the deep trap being 1000 m shallower than at other stations, so that degradation had less time to occur. However, MS-5 is south of the ACC and is iron-limited all year, which can at times result in higher sinking rates of diatoms if they do not gain enough energy to remain in the surface water (Waite and Nodder, 2001; Waite et al., 1992). Iron limitation also results in higher Si:C of diatoms (Hutchins and Bruland, 1998); more robust frustules also may aid sinking. Rapid sinking of particles can lead to better preservation of organic matter. MS-2 exported the smallest portion of organic matter as amino acids. MS-2 was silica-limited earlier in the season than other stations, and this resulted in smaller diatoms and higher proportions of non-silicifying phytoplankton (Brown and Landry, 2001). Thus, the highest overall proportions of surface amino acid production were exported at the iron-limited station

(MS-5) with the highest proportion of Si_{bio} , and at MS-4, which was characterized by abundant large diatoms.

In the equatorial Pacific, 91% of amino acids produced in the euphotic zone were degraded before leaving that zone, and the flux of amino acids at 3600 m was 42% of the flux at 1000 m (Wakeham et al., 1997; Lee et al., 2000). In the Southern Ocean, deep-trap fluxes ranged between 52–58% of shallow-trap fluxes. The higher rate of preservation of amino acids in MS-5 sediment traps does not continue into the sediment, which had a low THAA concentration relative to other stations, and low contribution from SiTHAA probably due to the poor preservation of Si_{bio} there (Table 2). In EqPac and Arabian Sea sediments, the fractional loss of organic matter at the sediment seawater interface was as great or greater than in the surface waters (Lee et al., 1998, 2000). We did not have surface-sediment accumulation rates for AESOPS samples so we could not estimate this loss at AESOPS sites. However, it is likely that the fractional losses in the euphotic zone and at the sediment surface were also similar in the Southern Ocean.

The contribution of biomineral-bound amino acids (SiTHAA and CaTHAA) to TotTHAA increases with increasing depth (Fig. 5) and therefore extent of degradation at all stations. This increase indicates that amino acids that are trapped in inorganic phases are preferentially preserved relative to amino acids that are not mineral bound. In addition, it reflects the preferential remineralization of organic matter relative to dissolution of biogenic minerals that occurs as particles sink. There were differences in the %SiTHAA/TotTHAA between stations. MS-3 and MS-4 consistently had the highest contribution of SiTHAA, reflecting the higher proportion of Si_{bio} preserved at these stations.

4.3. Amino acid degradation

4.3.1. THAA and CaTHAA compositional changes

The amino acid composition of organic matter can be indicative of both its source and extent of degradation. Variation in amino acid composition can be quantitatively assessed using principal

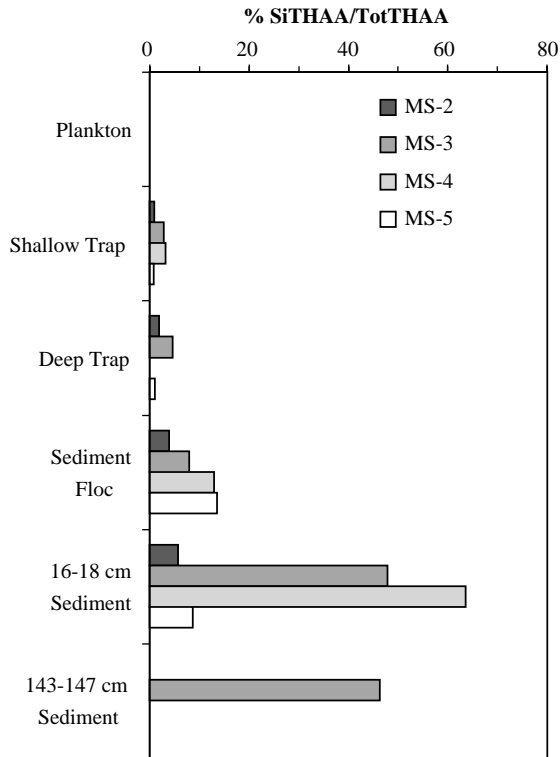


Fig. 5. The fraction of TotTHAA (THAA + SiTHAA) made up by SiTHAA as a function of depth in the water column and sediment. THAA includes calcium carbonate-bound amino acids (CaTHAA). Plankton values are 0.02–0.05%.

components analysis (PCA). We used two PCA-based methods to analyze our data set. First, we used the “Degradation Index” (DI) equation [$DI = \sum_i (var_i - avg\ var_i / std\ var_i) \text{ loading}_i$] derived by Dauwe et al. (1999). In this equation, var_i is the mol% of amino acid i , $avg\ var_i$ and $std\ var_i$ are the mean and standard deviation of the amino acid mol% in a given data set and loading_i is the PCA-derived loading of amino acid i (Table 8). Dauwe et al. (1999) derived these loadings from a PCA of a data set that contained samples of varying degrees of degradation including plankton, particulate matter and sediments. Since the amino acid composition among organisms is so similar, they argue that differences in amino acid composition arise primarily from degradation (Dauwe and Middelburg, 1998; Dauwe et al., 1999). In calculating a DI value, mol% threonine, arginine,

Table 8

Loadings for amino acids in the principal components analysis (SO-PC1) of THAA and SiTHAA in all samples from the Southern Ocean

Amino acid	THAA SO-PC1	SiTHAA SO-PC1	DI*
Asp	0.17	0.36	-0.10
Glu	0.21	0.41	0.065
His	0.013	0.13	0.16
Ser	0.27	0.24	0.015
Gly	-0.30	-0.34	-0.10
Arg	-0.063	0.17	-0.12
Thr	0.14	-0.28	-0.13
β -Ala	-0.31	0.012	
Ala	-0.064	0.15	-0.043
Tyr	0.24	-0.13	0.18
γ -Aba	-0.31	-0.039	
Met	0.26	0.13	0.13
Val	0.22	0.36	-0.044
Phe	0.38	0.27	0.13
Ile	0.34	0.28	0.14
Leu	0.34	0.27	0.17

*THAA loadings used to calculate degradation index (DI) (from Dauwe et al., 1999).

aspartic acid, glycine and valine have negative loadings and are therefore enriched in samples with negative DI values. The more negative the DI, the more degraded the sample. Methionine, phenylalanine, isoleucine, histidine, leucine and tyrosine have positive loadings and are enriched in samples with positive DI values. Positive DI values suggest fresher organic matter. These changes in amino acid composition with degradation generally agree with numerous lab and field based studies of changes in amino acid composition with degradation (e.g., Lee and Cronin, 1984; Cowie and Hedges, 1996; Nguyen and Harvey, 1997).

We also carried out a second, independent PCA using the software package Sirius for Windows (2.1). For our PCA, we chose two data sets. The first consisted of the mol% of individual amino acids in THAA in each sample, and the second included the mol% of individual amino acids in SiTHAA. The axis of the first principal component in our Southern Ocean PCA (SO-PC1) had negative loadings for glycine, arginine, β -Ala, ala and γ -Aba in THAA and for glycine, threonine, and tyrosine and γ -Aba in SiTHAA. All other amino acids had positive loadings (Table 8).

On the Dauwe and Middelburg scale, DI values for Southern Ocean plankton THAA in this study were between 0.0–0.5 (Table 7; Fig. 6a), much lower than those for plankton (DI = 1.0–1.5) and within the range for coastal sediments (DI = –0.4 to 1.0) reported by Dauwe et al. (1999). The uniquely high proportion of glycine in Southern Ocean diatom-rich plankton undoubtedly contributed to the lower DI values. Diatom cell wall THAA can have a DI of <0.5 (Keil et al., 2000); thus, the presence of a large number of empty diatom cells in Southern Ocean plankton samples (as discussed above) would lower the DI. Preferential loss of cytoplasm relative to cell wall

material is also common during organic matter degradation and results in compositional changes that are similar to those observed in diatom-rich samples (e.g., Cowie and Hedges, 1996). Thus, DI does not clearly distinguish between the influences of source and degradation.

Despite the “apparent” degradation of plankton source material suggested by low DI values of THAA, sinking particles and sediments had a progressively lower DI (and were presumably more degraded) with depth at all stations, reaching a low of –2.3 (Table 7; Fig. 6a), similar to the –2.17 reported for the oxidized zone of the MAP f-turbidite beneath 5400 m of water, and the –2.02

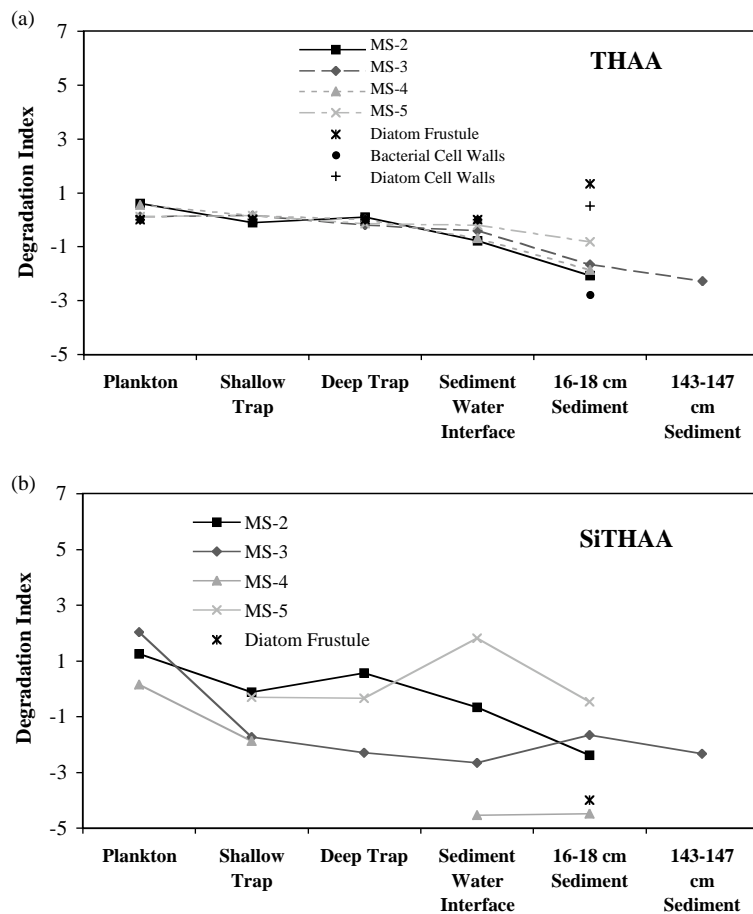


Fig. 6. (a) Degradation Index of THAA in plankton, sinking particles and sediments. DI values for THAA in diatom frustules isolated from MS-3 sediments are shown, as well as for diatom cell walls and bacterial cell wall peptidoglycan (Keil et al., 2000 and references there in). (b) DI values for SiTHAA in plankton, sinking particles, sediments and diatom frustules isolated from MS-3 sediments (diatom isolates are courtesy of P. Froelich).

found in Mediterranean Sea sediment (Dauwe et al., 1999). This result suggests that the absolute value of the DI may not be comparable between data sets that contain samples from diverse sources, but that within a data set, trends in amino acid composition can be attributed to changes in composition that occur as organic matter ages.

PCA of THAA in samples only from the Southern Ocean resulted in decreasing site scores with increasing depth or age of organic matter (Fig. 7a). On the basis of both PCA-based methods, it is clear that a degradation sequence of plankton, sediment-trap material, and sediment occurs. However, the SO-PC1 is more sensitive to

increasing alteration state of the samples than the DI, and gives a better idea of the influence of various processes in changing composition. For example, the first axis in the SO-PC1 accounts for 37% of the variability. The second axis accounted for 17% of the variability (data not shown). The most dramatic drop in SO-PC1 site scores occurred between the sediment floc and 16–18 cm in the sediment. For example, production of β -Ala and γ -Aba from aspartic acid and glutamic acid occur to a significant extent only in the sediments (Table 7).

As mentioned earlier, it is likely that the fractional losses in the euphotic zone and sediment

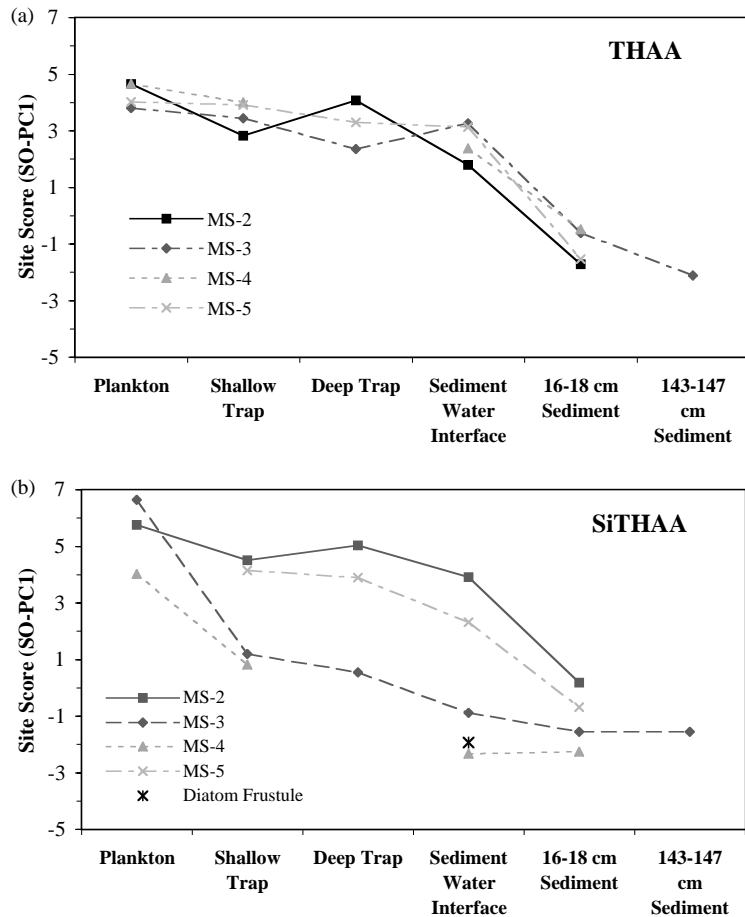


Fig. 7. Site scores for the first axis of the PCA (SO-PC1). Data included plankton, sinking particles and sediments of (a) THAA and (b) SiTHAA. Pure opal from diatom frustules isolated from MS-3 sediments are also included (pure diatoms are courtesy of P. Froelich).

are equally large. Thus, the large drop in site scores in the upper sediment column might indicate that processes responsible for organic matter degradation in the sediment result in a more dramatic alteration of organic matter composition than in the euphotic zone. Organic matter appears to be lost from sinking particles through physical or biochemical processes (such as dissolution and disaggregation) in the water column that do not change the composition of organic matter greatly. On the other hand, in the sediment, where the residence time of particles is much longer and particles reaching the seafloor are more refractory than in the surface waters, degradation is more selective and leads to a greater change in composition.

Although diatom cell walls and frustules are a major source of glycine, bacterial cell-wall peptidoglycan is also highly enriched in glycine (Salton, 1960), but not serine or threonine; thus, peptidoglycan is a likely source of glycine as particles age. The increasing proportion of THAA glycine and decreasing proportion of serine with depth in the Southern Ocean water column and sediment is consistent with the idea that phytoplankton (diatom) biomass is being converted to bacterial biomass (Bidle and Azam, 1999). In addition, previous work suggests that the D/L ratio of amino acids in Southern Ocean sediment is consistent with a significant contribution from bacterial cell walls (Blunt and Warnke, 1978; Warnke et al., 1980). In this light, the observed changes in composition with depth in the water column are consistent with both selective degradation of plankton THAA and conversion from primarily phytoplankton THAA to microbial THAA. The decrease in DI values with apparent age of Southern Ocean samples from values similar to diatom cell walls to values similar to those of bacterial cell walls (Fig. 6a) is consistent with particulate organic matter being converted from primarily diatom-derived in surface waters to bacterially derived as it sinks and ages. Site scores calculated in the SO-PC1 for amino acid compositions of various bacteria cell wall components confirm this conclusion, and were between -3 and -14.7 . The relative difference in sites scores between plankton and deep sediments was much

greater than the relative difference between DI values, likely because the loadings calculated from the DI were not representative of compositional changes that occurred in our Southern Ocean samples (Table 8).

Preservation of aspartic-acid-rich organic matter associated with calcareous skeletons also can affect THAA compositions (Carter and Mitterer, 1978; Müller et al., 1986; Lee et al., 2000). Coccolith and foram shells have a much higher mol% aspartic acid than do pteropod shells (King, 1977). The high mol% aspartic acid in plankton and trap samples at MS-2 is consistent with the high wt% coccolithophorid-derived CaCO_3 observed there by Honjo et al. (2000). At stations to the south (MS-3 and MS-5), where the CaCO_3 content in trap samples is lower (Table 2), the mol% aspartic acid is also lower. Pteropods were abundant in sinking particles at these southern stations (Honjo et al., 2000), so that the increase in aspartic acid in THAA (and thus CaTHAA) with depth may reflect the preferential dissolution of pteropods relative to calcite. This again shows that source of amino acids can affect the variation in composition (and thus DI) as much as degradation.

Sediment floc THAA at MS-3, MS-4 and MS-5 contained more aspartic acid than deep traps, possibly reflecting the preferential preservation of CaTHAA, particularly at MS-3 where CaCO_3 was relatively abundant (32 wt%). MS-2 and MS-5 had much lower CaCO_3 concentrations, and mol% aspartic acid and glutamic acid were lower in the floc layer relative to deep traps. In situ production of aspartic acid is also a possible explanation for its enrichment in the floc layer. Lee et al. (2000) noted an apparent “freshening” of organic matter in the floc relative to trap material from equatorial Pacific sediments. They suggested that re-synthesis of “fresh” amino acids results from bacterial growth at the sediment water interface. However, bacterial conversion of aspartic acid to β -Ala and of glutamic acid to γ -Aba also occurs with age of a sample (Table 7) and appears to influence THAA composition more than any possible production of aspartic acid. Despite the elevated aspartic acid, DI and SO-PC1 values both suggest that the floc layer was more degraded than the deep traps at

each site except MS-3 (Figs. 6 and 7). The appearance of non-protein amino acids does indicate, however, that bacteria are active and are a source of “fresh” organic matter, as well as being decomposers of detrital organic matter.

Deeper in the sediments, compositional changes in THAA were consistent with increasing degradation of organic matter. At all four stations SO-PC1 site scores decrease most in the upper 10 cm (Fig. 8), in part reflecting the decrease in the ratios of aspartic acid/ β -Ala and glutamic acid/ γ -Aba (Table 7). Deeper sediments at MS-2, MS-3 and MS-5 have similar site scores, resembling those of bacterial cell wall peptidoglycan (Fig. 8). Sediment cores at MS-2 and MS-3 contain relatively recent sediments throughout their entire length of 45 cm (<25,000 ^{14}C years). MS-5, on the other hand, contains much older material (24,700 years at 10–14 cm) due to a lower sediment accumulation rate than at other stations and possible erosion of

surface sediments (Chase et al., 2003). Based on these ages, organic matter in MS-5 sediments is expected to be more degraded than organic matter at other stations, particularly in the upper 10–15 cm. Indeed, the SO-PC1 site scores for this core are lower than those at other stations (Fig. 8), reflecting the older age of this material. The decrease in SO-PC1 site score with depth at all stations likely reflects increasing degradation of organic matter.

4.3.2. SiTHAA compositional changes

Both the DI and the site scores of the SO-PC1 for SiTHAA generally decrease with depth in the water column and sediments (Figs. 6b and 7b). At diatom-rich stations (MS-3 and MS-4), unlike THAA, SiTHAA composition changed between the plankton and shallow trap. This is not surprising given the lack of a clear enrichment of glycine and threonine in plankton SiTHAA as discussed earlier. From Fig. 7b it appears that there was also a large change in composition between the sediment floc and 16–18 cm sediment. However, examination of the entire sediment core reveals that downcore variability in composition is large, and unlike THAA, the decrease in site scores of SiTHAA is not uniform with depth (Fig. 9). Changes in SiTHAA composition are not likely to reflect changes related to degradation as very little decomposition is thought to occur over thousands of years (King, 1974). The consistency of the composition of SiTHAA in sediments at MS-3 suggests that this bound pool of amino acids can be very stable over thousand year timescales (Fig. 9). Differences in composition at the other stations are thus more likely to be due to differences in SiTHAA source with depth. The very low concentrations of SiTHAA at MS-2 and MS-5 also result in greater analytical error. Other possible reasons for variability in SiTHAA composition might include preferential export of diatoms relative to other silicifying organisms, preferential export of more robust diatoms, or preferential export of diatoms with poor nutritional status.

Unlike THAA, the average concentration of SiTHAA in the upper 18 cm of sediment is generally proportional to wt% Si_{bio} of the sediment. However, while the wt% Si_{bio} was only

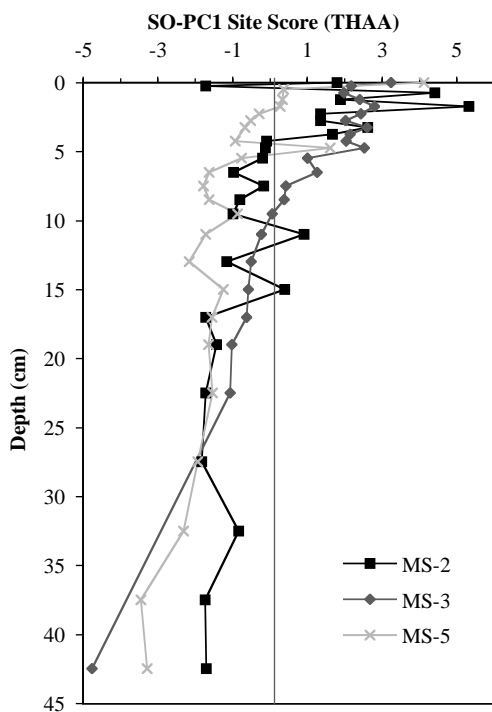


Fig. 8. Site scores for the first axis of the PCA (SO-PC1) of THAA as a function of depth in sediment cores from MS-2, MS-3 and MS-5. Surface points are for the floc layer (sediment water interface).

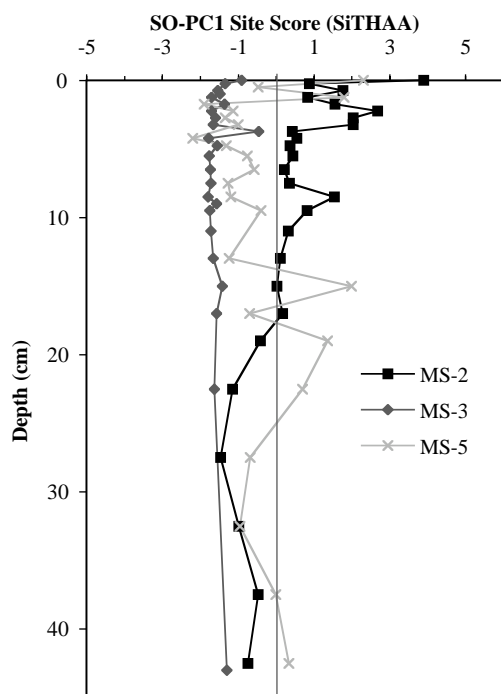


Fig. 9. Site scores for the first axis of the PCA (SO-PC1) of SiTHAA as a function of depth in sediment cores from MS-2, MS-3 and MS-5. Surface points are for the flocc layer (sediment water interface).

~2X greater at MS-3 and MS-4 than at MS-2 and MS-5, the concentration of SiTHAA ($\mu\text{mol SiTHAA C/gdw}$) was up to $10\times$ greater. This suggests that the SiTHAA/Si_{bio} ratio is not necessarily the same within or among diatom species, or that dissolution of Si_{bio} in the sediment may influence this value. The correlation of mol% glycine + threonine of SiTHAA with wt% Si_{bio} among stations (Fig. 2) suggests that non-biogenic-silica (e.g., clay minerals) might be a significant source of amino acids during HF digestion. However, the contribution of SiTHAA to samples with low Si_{bio} was negligible, indicating that detrital material had little or no SiTHAA associated with it. The more likely explanation for the correlation between Si_{bio} and glycine + threonine is that the change in SiTHAA composition reflects changes in species assemblages or other environmental factors. For example, as discussed earlier, nutrient limitation can influence the Si:C in diatoms (Hutchins and Bruland, 1998); perhaps it

also can affect the organic template used in the silicification process by changing the species composition, SiTHAA/Si_{bio} or SiTHAA composition. Additionally, if amino acids within the opal matrix influence the solubility or toughness of the diatom frustules, the preservation of Si_{bio} in sediments may be partially controlled by these proteins. Selective dissolution of less robust frustules (Abelmann and Gersonde, 1991; Leventer, 1991) also may change the concentration or composition of SiTHAA in sinking particles and sediments resulting in the preservation of frustules with a high SiTHAA/Si_{bio} ratio.

5. Conclusions

Amino acids (THAA) in Southern Ocean plankton are highly enriched in glycine and serine. Diatoms and diatom cell walls appear to be the source of this enrichment. Biomineral-bound amino acids (CaTHAA and SiTHAA) are a negligible percent of TotTHAA in plankton. Due to selective preservation of opal relative to organic matter, however, SiTHAA become a larger percentage of TotTHAA (> 50%) as particles sink and are deposited in sediments.

THAA concentrations in sediments with high biogenic mineral contributions are lower than in areas with a higher percent of detrital material. However, TotTHAA concentrations (SiTHAA plus THAA) are highest in diatom-rich sediments. Compositional differences between SiTHAA and THAA increased with depth. The difference among the compositions of SiTHAA in plankton, sinking particles and sediments may reflect shifts in species composition of plankton or selective dissolution of less robust siliceous species as particles sink and are deposited on the seafloor.

The Degradation Index (DI) showed that changes in the composition of amino acids occur with depth in the water column and sediment. However, the unusual amino acid composition of organic matter in the Southern Ocean makes the use of an absolute value of the DI problematic in this location. Principal components analysis was found to be a useful tool in interpreting amino acid compositional differences among samples.

PCA suggests that the greatest change in THAA composition occurred between the sediment surface and deeper sediments rather than in surface waters. Organic matter appears to be lost from sinking particles through processes in the water column that do not change greatly the composition of organic matter. However, in the sediment where particles have a longer residence time and are more refractory than in the surface waters, degradation is more selective and leads to a greater change in composition.

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