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## The effect of grain size and surface area on organic matter, lignin and carbohydrate concentration, and molecular compositions in Peru Margin sediments

BRIAN A. BERGAMASCHI,<sup>1,\*</sup> ELIZABETH TSAMAKIS,<sup>1</sup> RICHARD G. KEIL,<sup>1</sup> TIMOTHY I. EGLINTON,<sup>2</sup>  
DANIEL B. MONTLUÇON,<sup>1,†</sup> and JOHN I. HEDGES<sup>1</sup><sup>1</sup>School of Oceanography, University of Washington, Seattle, Washington 98195, USA<sup>2</sup>Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, USA

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**Abstract**—A C-rich sediment sample from the Peru Margin was sorted into nine hydrodynamically-determined grain size fractions to explore the effect of grain size distribution and sediment surface area on organic matter content and composition. The neutral monomeric carbohydrate composition, lignin oxidation product yields, total organic carbon, and total nitrogen contents were determined independently for each size fraction, in addition to sediment surface area and abundance of biogenic opal.

The percent organic carbon and percent total nitrogen were strongly related to surface area in these sediments. In turn, the distribution of surface area closely followed mass distribution among the textural size classes, suggesting hydrodynamic controls on grain size also control organic carbon content. Nevertheless, organic compositional distinctions were observed between textural size classes.

Total neutral carbohydrate yields in the Peru Margin sediments were found to closely parallel trends in total organic carbon, increasing in abundance among grain size fractions in proportion to sediment surface area. Coincident with the increases in absolute abundance, rhamnose and mannose increased as a fraction of the total carbohydrate yield in concert with surface area, indicating these monomers were preferentially represented in carbohydrates associated with surfaces. Lignin oxidation product yields varied with surface area when normalized to organic carbon, suggesting that the terrestrially-derived component may be diluted by sorption of marine derived material. Lignin-based parameters suggest a separate source for terrestrially derived material associated with sand-size material as opposed to that associated with silts and clays. Copyright © 1997 Elsevier Science Ltd

### 1. INTRODUCTION

Identifying the environmental factors which control the content and molecular composition of organic material in marine sediments is essential to understanding the global cycles of C, O, and S, as well as interpreting the sedimentary record of organic carbon (OC), paleoproductivity, organic chemical fossils, and redox-sensitive metals (Engel and Macko, 1993). Many factors extrinsic and intrinsic to the organic material have been suggested which may exert some level of control on the quantity and type of OC found in marine sediments. Extrinsic factors include oxygen concentration in overlying waters, local sedimentation rate, hydrodynamic sorting of sediments during deposition, and total productivity of the overlying waters. Intrinsic factors include the association of organic material with surfaces, resistance of certain types of biopolymers to degradation, input of highly degraded refractory terrestrial organic material, and in situ geopolymerization of reactive organic compounds into amorphous recalcitrant material (Canfield, 1994; Henrichs, 1992; Pedersen et al., 1992; Mayer, 1994; De Leeuw and Largeau, 1993; Kohlen et al., 1989). It seems likely that many or all of these factors have varying degrees of influence depending on the depositional regime.

Mayer (1994) and Hedges and Keil (1995) have suggested that association with mineral surfaces protects OC from remineralization and thus may provide a control on OC preservation in sediments. In general, there is a worldwide correlation between OC content and surface area in coastal sediments corresponding to between 0.5 and 1 mg OC per m<sup>2</sup> surface. Sediments which do not conform to the general relationship are found largely in pelagic and deltaic environments which are significantly below the typical coastal range and in dysaerobic sediments ([O<sub>2</sub>] < 0.1 mL/L) which are significantly above it. Mayer (1994) made the observation that high carbon sediments from dysaerobic zones possess an intrinsic correlation between OC content and bulk sediment surface area, similar to typical coastal sediments, suggesting that surface area association may play a significant role in carbon preservation, even in deposits containing high levels of OC. The reasons that surface association may promote preservation are not well understood, but Keil et al. (1994b) provided direct evidence for the protective nature of surface association in coastal sediments by showing that sedimentary organic material stable for hundreds of years in situ was rapidly degraded by aerobic bacteria once desorbed. This implies that intrinsically labile biochemicals may be preserved and suggests that chemically intrinsic recalcitrance may not be necessary to preserve surface-associated organic material.

Sediments from beneath oxygen minimums provide ideal locations to study mechanisms controlling the content and composition of sedimentary organic material although only

\*Author to whom correspondence should be addressed.

<sup>†</sup>Present address: USGS, Placer Hall, California State University, Sacramento, California 95819, USA.

<sup>‡</sup>Present address: Marine Science Research Center, State University of New York, Stony Brook, New York 11794, USA.

a small portion of globally integrated OC burial in marine sediments occurs in these deposits (<8%; Hedges and Keil, 1995). OC content of sediments from beneath oxygen minimum zones range from 4 → 20% as compared to the global average of 0.5–1%. Interest in dysaerobic sediments is particularly high because many believe that these areas represent modern analogs of the environmental conditions which form petroleum source rocks and because the organic fossil record is generally regarded to be better preserved in these areas (Demaison and Moore, 1980; Eglinton et al., 1993; McCaffrey et al., 1989a).

The environmental conditions specifically promoting elevated C content in dysaerobic sediments are thought to be a combination of high productivity in the overlying water column which provides elevated carbon inputs, shallow depths which limit water column remineralization, and low oxygen bottom waters which, when combined with relatively high sedimentation rate, limits sedimentary remineralization (Summerhayes, 1983). In addition, the hydrogen sulfide formed by the action of sulfate reducing bacteria may react with some forms of organic material to render it resistant to remineralization (Kohnen et al., 1989). Although the above are all potentially important factors in carbon preservation, the effect of sediment-organic interactions has seldom been investigated.

Direct investigations of the influence of sediment-organic interactions in natural environments and bulk sediments are confounded by the wide variety of organic matter types and sources, the presence of discrete organic-rich particles in sediments, and poor sorting of sediments in general. In order to minimize these complications, Keil et al. (1994a) applied split flow, thin cell, lateral transport (SPLITT; Giddings, 1986) fractionation to marine sediments and found that sediments fractionated into hydrodynamically-defined grain sizes maintained a high correlation between surface area and OC, similar to the results of Mayer (1994) on bulk samples. SPLITT fractionation sorts bulk sediments hydrodynamically into nominal size classes based on size-density relationships and thus effectively mimics sediment sorting during natural deposition. SPLITT fractionation offers the advantage that kilogram quantities of sediment may be rapidly fractionated, permitting a wide variety of previously impractical intensive molecular and mineralogical studies of individual grain sizes.

This study examines the organic molecular characteristics of SPLITT fractionated sediments from the Peru Margin to explore the possible relationship between sediment surface area and the high sedimentary carbon loadings typical of dysaerobic zones. Specifically, the central goal was to determine whether grain size distribution and the corresponding distribution of surface area among sedimentary particles affected the amount and type of organic material passing the sediment-water interface and, thus, the first step toward preservation. This is the first study characterizing the molecular organic composition of SPLITT fractionated sediments. The results show that there are distinct differences in the organic material associated with individual grain size fractions corresponding to differences in composition, source, and amount of diagenetic alteration. Grain size and surface area are independently revealed to be principal factors determining both

the amount of organic material in the bulk sediment and the composition of that organic material.

## 2. EXPERIMENTAL

### 2.1. Study Area

The sediment sample was collected by Soutar-type box core on the upper slope of the East Pico Basin (13°31.13'S, 76°27.15'E; Fig. 1) at water depth of 106 m during cruise SJ1092 on R/V *Seaward Johnson*. The studied sediment was the 10–15 cm depth interval. This nearshore coastal environment located just south of Lima on the Peruvian coast from about 11–15°S is characterized by intense primary production (1–10 g C m<sup>-2</sup>d<sup>-1</sup>) driven by nearshore upwelling. One result is a permanent O minimum zone ([O<sub>2</sub>] < 0.1 mL/L) spanning 75 m to 500 m in the underlying waters which impinges on the seafloor of this region. Sediments depositing in the dysaerobic zone are high in organic carbon (4–19 wt%) relative to other coastal deposits (1–3 wt% OC) and deep-sea sediments (0.1–1% OC).

As for all coastal environments, the sources of organic material to the region are both terrestrial and marine. However, the Peruvian coast is thought to be dominated by marine inputs because of its high productivity combined with locally limited river runoff. There is a pronounced offshore gradient in productivity, with nearshore zones being dominated by the diatoms *Chaetoceros* sp. and *Schroederella delectulata* (Sellner et al., 1983). Importantly, the shallow depth of the sampling site combined with intense productivity prevent extensive remineralization of organic material in the water column.

No sediment accumulation studies were undertaken at the sampling station. Regional (11–15°S) estimates of the sediment accumulation rates from <sup>210</sup>Pb activity profiles average 0.5 cm/y for the 7–20 cm horizon, ranging from 1.1 to 0.23 cm/y. (Summarized by McCaffrey et al., 1989a) The estimated mean age of the 10–15 cm sample is therefore between 10 and 50 y.

Direct observation by submarine reconnaissance revealed that the sediment sampling area was dominated by *Thioploca* sp. mats, although occasional worms were also observed (T. Eglinton, pers. commun.). *Thioploca* is a genus of colorless, filamentous, sulfur-oxidizing bacteria found exclusively in dysaerobic sediments. They are usually aggregated into bundles up to a few cm long and surrounded by a mucilaginous sheath (McCaffrey et al., 1989b). The mats are usually confined to the upper few centimeters of sediment where they may constitute as much as 80% of the biomass.

### 2.2. Methods

#### 2.2.1. Size fractionation

Sediments were thawed, thrice suspended in distilled water to remove salts, and centrifuged. Removing salt is essential to limit

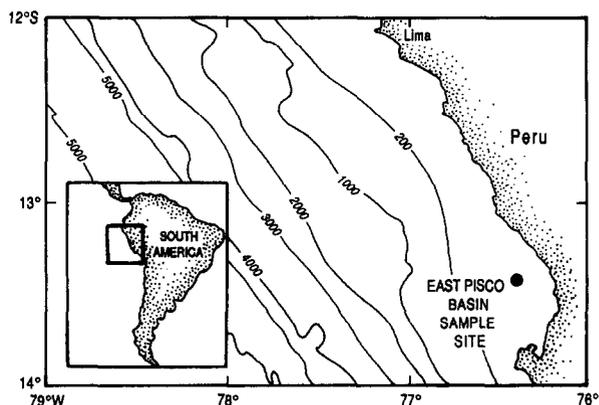


Fig. 1. East Pico Basin and its relation to Peru. Inset locates study site on the coast of South America. Water depths in meters.

clay mineral interactions during disaggregation and sorting. Washed sediments were sequentially passed through 250  $\mu\text{m}$ , 64  $\mu\text{m}$ , and 38  $\mu\text{m}$  stainless steel sieves to collect sand-sized material. Material passing the 38  $\mu\text{m}$  sieve was hydrodynamically sorted into classes corresponding to nominal cutoffs of 15  $\mu\text{m}$ , 8  $\mu\text{m}$ , 3  $\mu\text{m}$ , and 1  $\mu\text{m}$ . The nominal grain size in any fraction is therefore taken to be the median between upper and lower cutoffs. For material below the 1  $\mu\text{m}$  cutoff, the 0.8  $\mu\text{m}$  fraction was recovered by centrifugation (11,000 rpm, 30 min), and the 0.5  $\mu\text{m}$  fraction, recovered from the supernatant by addition of 5 g NaCl/L and subsequent centrifugation. Losses during this process are discussed later.

The theory of SPLITT fractionation and its application to sediments has been presented elsewhere (Giddings, 1986; Springston et al., 1987; Keil et al., 1994a). Briefly, bulk sediments are sonicated and suspended in distilled water, they continuously introduced into the upper inlet of the SPLITT cell by peristaltic pump to form the upper laminar flow stream. A lower laminar flow stream of distilled water is simultaneously introduced through the bottom inlet. As particles are swept through the SPLITT cell, those with high sedimentation coefficients fall from the upper laminar flow stream to the lower laminar flow stream, where they may be isolated from the bulk material. Careful calibration of inlet and outlet flows permits precise determination of cut-off sedimentation coefficients. Sediments were sequentially sorted into finer nominal grain sizes until settling velocities dropped below those necessary for separation.

#### 2.2.2. Organic carbon and nitrogen

Weight percent of organic carbon, inorganic carbon, and total nitrogen was determined in duplicate using a Carlo Erba model 1106 CHN analyzer. Carbonate was removed from the samples prior to analysis by vapor phase acidification (Hedges and Stern, 1984). Weight percent carbonate was taken to be the difference in measured carbon value between untreated and acid treated samples.

#### 2.2.3. Silica

Biogenic silica was determined using the method of DeMaster (1981), as modified by Mortlock and Froelich (1989). Briefly, samples (~50 mg) were hydrolyzed at 85°C in 10 mL of a 5 wt% sodium carbonate solution. Aliquots (250  $\mu\text{L}$ ) were removed after 2, 3, 4, and 5.5 h, and two 50  $\mu\text{L}$  subsamples analyzed separately using the standard paramolybdate technique. Biogenic silica was determined by regression of the four concentration values to zero time. Average precision for the ten duplicate measurements in this study was  $\pm 6\%$ .

#### 2.2.4. Surface area

Surface area determinations were made on a Quantchrome surface area analyzer using the one-point BET method described by Mayer et al. (1988). Freeze-dried samples were heated to 350°C for several days to remove water prior to analysis, and repeated desorption measurements were made using 0.3 mole fraction  $\text{N}_2$  in He. Replicate samples had a standard error of  $\pm 4\%$ .

#### 2.2.5. Density fractionation

Approximately 250 mg bulk, unwashed sediment was thawed, disaggregated, and slurried in 10 mL of a saturated solution of cesium chloride (density = 1.9  $\text{g}/\text{cm}^3$ ; Sigma Chemicals). The slurry was allowed to settle overnight at 25°C, then centrifuged (11,000 g, 30 min). The supernatant then was removed, the pellet disaggregated, washed three times in distilled water, and freeze-dried.

#### 2.2.6. Carbohydrates

Monomeric abundances of neutral carbohydrates were determined using the alditol acetate method (Fox et al., 1989) modified to accommodate pretreatment with liquid anhydrous HF. All analyses were conducted in an apparatus specially constructed for HF solvolysis experiments (Bergamaschi and Hedges, 1995). Briefly, the appa-

ratus is comprised of six independent, fully closed and pressurized reaction vessels, along with a network of valves which provides means to measure liquid HF into each reaction vessel and carefully control the temperature and duration of the reaction. Each sample (10–20 mg) was weighed directly into the reaction vessel, then the reaction vessel capped and installed in the solvolysis apparatus. The reactor was equilibrated in a 0°C cold bath for 15 min; liquid HF (1 mL) was added sequentially to each sample and allowed to react for 30 min. Addition of cold trifluoroacetic acid (3 mL) terminated the anhydrous solvolysis, and the reactor was warmed to 100°C without opening for 30 min. The reactor was again cooled to 0°C; samples were removed and dried in an evacuating centrifuge (SpecdVac, Savant Instruments, Farmingdale, NY, USA) equipped with both calcium sulfate and liquid nitrogen traps. The following day, samples were suspended in 0.1 M  $\text{NaCO}_3$ , internal recovery standard added, and the pH corrected to 7. After 30 min at 25°C, samples were centrifuged, and  $\text{NaBH}_4$  (0.5 mL, 0.5M) was added to the supernatant to reduce aldoses to alditols. Following 90 min reduction, excess  $\text{NaBH}_4$  was converted to borate by dropwise addition of 25% acetic acid. Cations were removed by passing the samples over 2 mL AG 50W-X8 resin (200–400 mesh; Biorad, Hercules, CA, USA) and eluting with 3 mL distilled water. Samples were dried completely under vacuum on a Hakke-Buchler Vortexing Exasperator (50°C), then rinsed with 3 mL methanol and dried three times to remove borate. To convert to per-O-acetate derivatives, the resulting syrup was dissolved in 0.5 mL pyridine and 0.5 mL acetic anhydride, and the vials were securely capped and placed in a heating block at 80°C for one h. The samples were then dried under a stream of nitrogen to remove the acetic anhydride and taken up in 200  $\mu\text{L}$  pyridine.

Quantification of individual monosaccharides was accomplished by gas chromatography using a Hewlett Packard 5890a gas chromatograph (Hewlett Packard Scientific Instruments, Santa Clara, CA, USA) fitted with a 0.25 mm i.d.  $\times$  30 m 14% cyanopropylphenylmethylpolysiloxane bonded-phase capillary column (DB-1701, J&W Scientific, Folsom, CA, USA) and a split/splitless injector operating in split mode with a split ratio of 10:1. Flame ionization detector output was collected and integrated on a personal computer running Lab Calc chromatography software (Galactic Industries, Salem, NH, USA). Baseline separation of all analytes was accomplished in 30 min by programming the oven to increase temperature from 200°C to 240°C at 2°C/min after an initial time of 10 min. Absolute abundances were calculated by normalizing to a known amount of recovery standard using a separately determined relative response ratio. Average reproducibility for the eleven duplicate measurements in this study was  $\pm 14\%$ . Individual aldose yields from select samples were also analyzed for carbohydrates using an earlier sulfuric acid pretreatment method (Cowie and Hedges, 1984a) and agreed relatively well ( $\pm 18\%$ ).

#### 2.2.7. Lignin

Lignin phenols were liberated by cupric oxide oxidation using the method of Hedges and Ertel (1982). Vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, p-coumaric acid, and ferulic acid were quantified as their trimethylsilyl derivatives by simultaneous gas chromatography (instrument as above) on a 0.25 mm i.d.  $\times$  30 m 100% methylpolysiloxane bonded-phase capillary column (DB-1) and a 0.25 mm i.d.  $\times$  30 m 14% cyanopropylphenylmethylpolysiloxane bonded-phase capillary column (DB-1701, J&W Scientific, Folsom, CA, USA), using a 20:1 split ratio. For these lignin-poor samples, analysis on two columns was necessary to minimize errors resulting from coelution. For all analyses, the column oven temperature was increased at 4°C/min from an initial setting of 100°C to 270°C and held for 16 min. Flame ionization detector output was collected and integrated on two stand-alone integrators (HP3394a; Hewlett-Packard, Santa Clara, CA, USA). Yields were calculated by normalizing peak areas to a known amount of internal standard whose relative response to analyte peaks was characterized separately. Average reproducibility for lignin phenol yield is typically  $\pm 5\text{--}10\%$  (Hedges and Ertel, 1982).

Table 1. Elemental compositions of Peru Margin size-fractionated sediments. Abbreviations: %OC, weight percent organic carbon; %TN, weight percent total nitrogen; C/N, atomic carbon to nitrogen ratio; %Si, weight percent opal-derived silica; SA, N<sub>2</sub> specific sediment surface area; n.d., not determined; Bulk, freeze-dried unfractionated sediment; Rinsed, sediment washed in preparation for SPLITT fractionation (see text). Note that bulk %OC and %TN values are not salt corrected.

Sample	Mass %	%OC Wt%	%TN Wt%	C/N (atomic)	%Si (OPAL)	SA m <sup>2</sup> /g
Bulk	—	6.6	0.7	10.7	n.d.	n.d.
Rinsed	—	8.3	0.9	11.2	24	24
0.5 μm	1.7	21.6	2.4	10.5	16	95
0.8 μm	5.3	12.9	1.5	10.2	24	60
2 μm	6.4	7.1	0.8	10.4	32	40
5 μm	34.0	9.8	1.2	9.5	21	30
11 μm	32.4	7.8	0.9	10.2	19	27
26 μm	15.8	4.3	0.5	10.0	13	16
50 μm	2.4	1.5	0.2	8.8	3	4
156 μm	1.5	7.9	1.2	8.0	5	28
500 μm	0.6	8.6	2.3	4.4	6	20

### 2.2.8. Statistics

All differences and correlations discussed were statistically tested and found significant at the 95% confidence interval or greater. The Games and Howell method was used for comparison of means, and the Mann-Whitney U-test, for ranking. Values of the correlation coefficient and test level for the all correlations discussed are reported in the text.

## 3. RESULTS AND DISCUSSION

### 3.1. Analysis of Bulk Sediments

#### 3.1.1. Elemental composition

The measured OC content of the bulk rinsed sediment is 8.41% (Table 1; rinsed in distilled water; see section 3.3.1.). This value is higher than typical of coastal areas (1–4%; Mayer, 1994), but in the mid to low end of the range (3–20%) found previously for near-surface samples in the region (Reimers and Suess, 1983). Total nitrogen yields for the bulk sample are 0.87%, conferring an atomic carbon to nitrogen ratio (C/N<sub>a</sub>) of 10.7. The C/N<sub>a</sub> of these sediments

is within the range observed in fresh planktonic material (4–12) and much lower than terrestrial plant material (18–>100). However, a C/N<sub>a</sub> near 11 is also within the range typical of soil organic matter and highly degraded marine material and is therefore an ambiguous source indicator.

#### 3.1.2. Lignin composition

The terrestrial component of sediments may be inferred by examination of their lignin content. Lignins are phenolic polymers produced uniquely by vascular plants as part of their structural matrix (Sarkanen and Ludwig, 1971). The suite of simple phenols produced by the cupric oxide oxidation of lignin is therefore an unambiguous tracer of terrestrial organic material in the marine environment and useful for inferring the relative amount of terrestrial material preserved (e.g., Hamilton and Hedges, 1988). Compound-specific lignin yields also permit differentiation between vascular plant and tissue sources and inference of the diagenetic state of lignin-bearing materials.

Total lignin yields for a sample are conventionally expressed as the sum of the eight most abundant phenols recovered from 10 g sediment (Σ8). Analysis of the bulk Peru sample resulted in Σ8 values of 4.2 mg/10 g SED (Table 2), in the range (~3–7) normally observed in other coastal regimes. Another common lignin parameter, Λ, is Σ8 normalized to the amount of OC present in the sample. Evaluation of this parameter provides insight into the contribution of terrestrial carbon to the total OC pool. The Λ value for bulk Peru sediment is 0.50 mg/100 mg OC, near the lower end of the range (0.2–6.8) observed in other coastal marine environments (Hamilton and Hedges, 1988; Hedges et al., 1988; Hedges and Mann, 1979b). Such a low Λ suggests extensive dilution of lignin-bearing terrestrial OC by autochthonous material.

The diagenetic freshness of lignin-bearing tissues may be inferred from the relative quantities of acidic vs. aldehydic phenols (e.g., Hedges et al., 1988). A higher acid to aldehyde ratio corresponds to more severely degraded material. The vanillic acid to aldehydic phenol ratio, (Ad/Al)<sub>v</sub>, of bulk Peru sediment is 0.9, as compared to ~0.3 for other coastal regimes (Hamilton and Hedges, 1988; Hedges et al.,

Table 2. Lignin compositions of Peru Margin size fractionated sediments. Abbreviations: V, S, and C; mg of total syringyl, total vanillyl, and total cinnamyl phenols, respectively, per 100 mg OC; Σ8, sum of V, S and C normalized to 10 g dry sediment; Λ, sum of V, S and C normalized to 100 mg OC; C/V and S/V, weight ratios of C and S over V, respectively; (Ad/Al)<sub>v</sub>, weight ratio of vanillic acid to vanillin; b.d., below detection.

Sample	V	S	C	Σ8	Λ	C/V	S/V	(Ad/Al) <sub>v</sub>
Bulk	0.14	0.37	0.07	3.8	0.58	0.49	2.66	1.0
Rinsed	0.11	0.29	0.09	4.2	0.50	0.83	2.66	0.9
0.5 μm	0.04	0.06	0.02	2.7	0.13	0.57	5.54	b.d.
0.8 μm	0.15	0.26	0.03	5.7	0.45	0.21	1.73	2.8
2 μm	0.21	0.19	0.13	3.7	0.52	0.61	0.92	2.3
5 μm	0.19	0.20	0.16	5.3	0.54	0.82	1.05	3.8
11 μm	0.19	0.19	0.15	4.2	0.54	0.79	0.98	3.3
26 μm	0.22	0.38	0.13	3.1	0.73	0.58	1.68	3.9
50 μm	0.55	0.39	0.06	1.5	1.00	0.11	0.71	0.4
156 μm	0.57	0.39	0.06	7.9	1.01	0.10	0.69	0.9
500 μm	0.61	0.54	0.05	10.3	1.19	0.08	0.89	0.5

Table 3. Carbohydrate compositions of Peru Margin sediment size fractions. All monosaccharide values are percentages by weight of total carbohydrate yield. Abbreviations: RHA, rhamnose; FUC, fucose; RIB, ribose; ARA, arabinose; XYL, xylose; MAN, mannose; GAL, galactose; GLC, glucose;  $tCH_2O$ , total neutral carbohydrate yield (mg) normalized to 100 mg OC;  $\Sigma CH_2O$ , total neutral carbohydrate yield (mg) normalized to 100 mg sediment.

Sample	RHA	FUC	RIB	ARA	XYL	MAN	GAL	GLC	$tCH_2O$	$\Sigma CH_2O$
Bulk	7.6	7.8	5.1	11.0	14.1	15.0	23.0	16.5	8.2	0.54
Rinsed	8.8	5.9	3.1	8.5	11.3	17.6	25.4	19.3	7.4	0.61
0.5 $\mu m$	11.3	5.8	2.7	6.2	11.7	21.5	21.9	18.8	9.4	2.03
0.8 $\mu m$	8.2	4.8	3.6	7.1	12.6	19.8	23.3	20.7	7.3	0.94
2 $\mu m$	6.4	4.8	3.8	7.5	11.1	19.5	25.8	21.0	5.6	0.40
5 $\mu m$	7.8	5.9	3.8	8.2	11.4	18.4	26.2	18.2	6.0	0.59
11 $\mu m$	7.1	5.4	4.1	8.7	11.7	17.9	27.2	17.8	6.8	0.53
26 $\mu m$	9.8	7.5	4.8	9.9	14.0	16.2	23.7	14.0	7.9	0.34
50 $\mu m$	5.8	4.3	4.7	7.0	10.2	10.9	17.4	39.5	13.7	0.21
156 $\mu m$	7.8	5.3	4.0	13.3	13.8	13.3	18.7	23.6	8.5	0.67
500 $\mu m$	7.8	3.8	2.5	11.2	10.5	12.4	19.1	32.5	3.6	0.31

1988), near 0.2 for fresh woody plant debris (Hedges and Mann, 1979a), and between 0.3 and 0.6 for degraded plant tissue (Opsahl and Benner, 1995). (Ad/Al)<sub>v</sub> values greater than one are typically associated with highly degraded dissolved humic materials and soil organic material (Ertel and Hedges, 1984; Ertel et al., 1986).

### 3.1.3. Carbohydrate composition

Carbohydrate yields have the advantage of providing information on a much larger fraction of total organic material than lignins because saccharides encompass virtually all potential sources, including terrestrial plants, plankton, and bacteria (Cowie and Hedges, 1984b). However, due to this universal distribution, aggregate carbohydrate composition provides fewer specific diagnostic clues as to the source and diagenetic state of carbohydrate-bearing material.

The total neutral carbohydrate yield in milligrams normalized to 100 milligrams sediment ( $\Sigma CH_2O$ ) from the bulk Peru sediments was 0.61 mg/100 mg SED (Table 3), corresponding to 7.4 mg/100 mg OC ( $tCH_2O$ ). This is similar to a sum of 7.9% reported by Lewis and Rowland (1993) from a nearby station (10°58.7'S 11°57.5'W) as determined by colorimetric methods. The absolute abundance of total carbohydrates in Peru sediments is similar to (or slightly higher than) that found in other coastal sediments ( $\Sigma CH_2O = \sim 0.3\text{--}1.0$  mg/100 mg SED; Cowie and Hedges, 1984b; Hamilton and Hedges, 1988), but represents only about half the usually observed fraction of total OC ( $tCH_2O = \sim 12\text{--}25$  mg/100 mg OC).

The relative concentration of neutral carbohydrate monomers in bulk Peru Margin sediments (Fig. 2) is unusual. Galactose is the most abundant monomer, accounting for 23% of the total aldose yields, followed by glucose, mannose, and xylose, each of which account for over 14%. The deoxy sugars rhamnose and fucose represent 9% and 6% of total aldose yields, respectively. Most marine sediments exhibit higher relative abundances of glucose than other monomers (e.g., Cowie and Hedges, 1984b; Moers et al., 1990) and higher abundances of hexoses (glucose, galactose, and mannose) than pentoses (ribose, arabinose, and xylose) or deoxy hexoses (rhamnose and fucose). An extensive liter-

ature search found only one similarly composed sediment: a diatom ooze sample from the Namibian shelf (Klok et al., 1984). Influence of the bulk carbohydrate composition by terrestrial inputs is unlikely in view of the low abundance and highly degraded nature of the associated lignins. Previous studies of the occurrence and abundance of minor sugars (Bergamaschi, 1995; Klok, 1984) indicate that the majority of neutral carbohydrates present in coastal sediments are predominantly of autochthonous origin.

### 3.2. Grain Size Distribution

In order to examine the relationships between grain size, sediment surface area, and organic content, the bulk sediment sample was separated into nine fractions with the following nominal sizes: clay-sized (0.5  $\mu m$ , 0.8  $\mu m$ , 2  $\mu m$ ), silt-sized (5  $\mu m$ , 11  $\mu m$ , 26  $\mu m$ ), and sand-sized material (50  $\mu m$ , 156  $\mu m$ , 500  $\mu m$ ). The sand-sizes were sieve fractionated and the remainder hydrodynamically separated using the SPLITT system. One should note that the clay- and silt-size classes are operationally defined by the hydrodynamics within the SPLITT process. Larger, low density particles such as diatom frustules or organic rich particles will

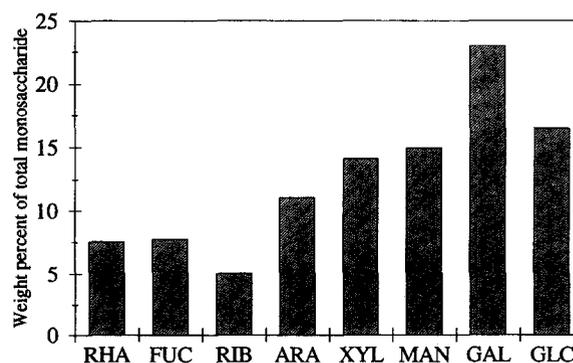


Fig. 2. Histogram of individual monosaccharides from Peru Margin sediment washed in distilled water (see text). Values are percentages by weight of total carbohydrate yield. Abbreviations are as in Table 3.

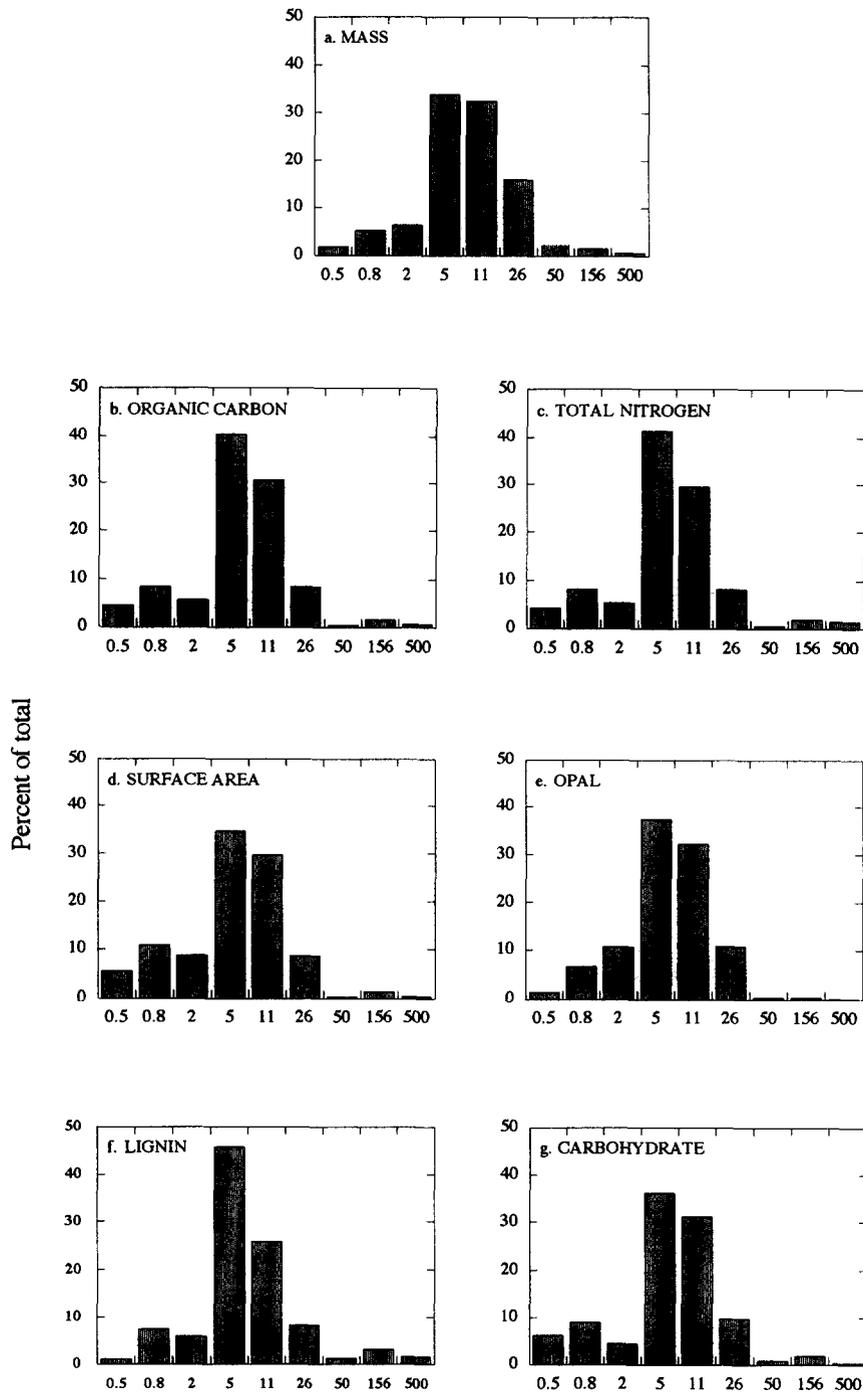


Fig. 3. Histograms of elemental and molecular parameters for individual size fractions in Peru Margin sediments. Values are percentages of integrated total yield from grain size fractions.

sort with smaller, denser mineral grains. Further explanation of mineral-equivalent size ranges associated with each of the nominal size classes is presented in the Methods section.

### 3.2.1. Mass distribution

The majority of sediment mass occurred in the 5  $\mu\text{m}$  and 11  $\mu\text{m}$  sizes (Fig. 3; Table 1), accounting for 34% and 32%,

respectively, of the bulk sample. The 26  $\mu\text{m}$  fraction was next most abundant, accounting for 16% of the mass. Thus, together the silt-size grains comprised 82% of sediment mass. Of the residual, 13% resided in clay-size and 5%, in the sand-size fractions. The Peru mass distribution is skewed toward the finer size ranges in comparison to the relatively few SPLITT-fractionated sediments previously analyzed (Keil et al., 1994a). For example, the median grain size in

the Washington coast silt deposit was the 50  $\mu\text{m}$  fraction, as opposed to the 11  $\mu\text{m}$  fraction seen here.

### 3.2.2. Visual inspection

Microscopic examination of the sedimentary size fractions revealed four general types of debris which dominated the particle distribution: clastic mineral grains, granular amorphous material, diatom fragments, and other structured debris of apparent biogenic origin. Particle types were not evenly distributed among sediment size fractions. Mineral grain abundances appeared to be highest in the 50  $\mu\text{m}$ , 26  $\mu\text{m}$ , and 11  $\mu\text{m}$  fractions and none were observed in the 500  $\mu\text{m}$  fraction. Intact diatom tests, frustules, and fragments appeared to be most abundant in the 11, 5, and 2  $\mu\text{m}$  fractions, but present in all. Granular amorphous material appeared in increasing abundance from the 50  $\mu\text{m}$  through the 0.5  $\mu\text{m}$  fraction. The dominant particle type in the 500  $\mu\text{m}$  fraction was structured debris characterized by a striated pattern. The most likely source for this material is *Thioploca* sheath material. Smaller amounts of this material were found in the two remaining sand-sized fractions. Fragments of similar material, but without characteristic striations, were also found in the 0.5  $\mu\text{m}$  fraction, likely sorted there because of low density.

### 3.2.3. Distribution of extensive parameters

Figure 3 shows the distribution among sedimentary grain size fractions of sediment mass, sediment surface area, organic carbon, total nitrogen, biogenic silica (opal), lignin, and total neutral carbohydrate. Each parameter is measured independently and presented as the percentage of integrated component mass which occurs in each grain size. All parameters measured correlate with the weight distribution of total particles among the sedimentary size classes, indicating mass distribution is a dominant factor in determining bulk sediment properties for these sediments. The question remains as to how grain size distribution affects the quantity of OC preserved in the 12 cm horizon and whether texture affects the type of organic material preserved.

## 3.3. Compositional Trends Among Grain Sizes

### 3.3.1. Elemental trends

Comparison of %OC and %TN values for nontreated bulk samples and samples rinsed with distilled water shows that approximately 5% of the OC was lost during initial rinsing and disaggregation (Table 1). The  $C/N_a$  ratio of the sediment changes measurably after rinsing from 10.7 to 11.2, indicating a slight preferential loss of N-rich material. Mass balance of the losses, however, yields a  $C/N_a$  ratio for the lost material of 1.5, unreasonably low for any organic substance and likely due to loss of inorganic nitrogen. Losses following disaggregation during sediment splitting are minimal (<2%) as determined by comparison of integrated OC in the grain size fractions with initial bulk values.

The carbon to nitrogen relationship changes between size fractions in a remarkably systematic fashion (Fig. 4: Table

1). All sediment size fractions, except the largest (500  $\mu\text{m}$ ), plot on a single line ( $r = 0.99$ ) with a slope of 9.1. The slope of the line corresponds to a  $C/N_a$  of 10.6. The linear relationship between %OC and %TN is most simply explained by the occurrence of progressively varying amounts of similar materials within each grain size fraction. The regression line linking the size fractions intercepts the %OC axis near zero, indicating total nitrogen is predominantly organic. An intercept appreciably above zero on the carbon axis would be evidence for the contribution of C-rich material such as terrestrial plant material, plankton storage polysaccharides, or microbial exopolysaccharides.

The 500  $\mu\text{m}$  sample has an unusually low  $C/N_a$  of 4.4. Low  $C/N_a$  is characteristic of fresh phytoplankton or bacterial biomass. In these sediments, either relatively intact diatom cells or *Thioploca* filaments may account for low  $C/N_a$  material in this size range. Measured diatom  $C/N_a$  values from a nearby station (10°S) average 5.3 (Sellner et al., 1983). The low  $C/N_a$  in this size fraction is consistent with a microbial source as suggested by visual identification of fragments. Since this fraction is coarse and relatively organic rich, there is little chance the low measured  $C/N_a$  is due to inorganic nitrogen.

Despite the effect of grain size distribution on OC, the changes in  $C/N_a$  are evidence of compositional differences among the organic material associated with each of the grain size fractions. There are considerable differences in %OC and %TN content between textural classes (Table 1). Percent OC was highest (21.6%) in the smallest (0.5  $\mu\text{m}$ ) fraction, decreased systematically to a minimum (1.5%) in the 50  $\mu\text{m}$  fraction, and rebounded to near bulk values in the remaining sand fractions. As would be expected from the consistent changes in  $C/N_a$ , %TN exhibits a closely parallel trend. In general, the organic material associated with the three sand-sized grains has lower  $C/N_a$  values than finer fractions (Table 1). This difference and attendant differences in molecular compositions described in the next section will clearly show that the organic material associated with sand-size grains is distinctly different from that associated with finer material and thus represents material of distinct origins or diagenetic history.

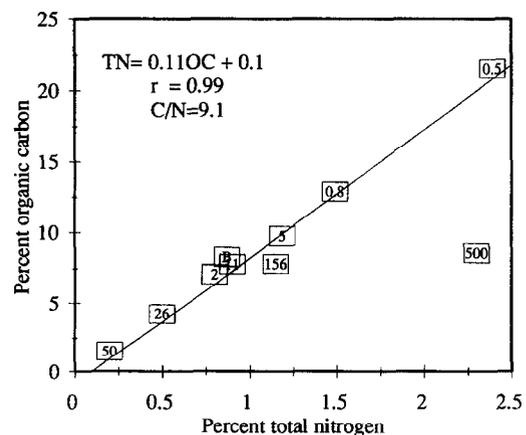


Fig. 4. Plot of %OC against %TN for individual particle size fractions. Data labels correspond to nominal size fraction ( $\mu\text{m}$ ).

### 3.3.2. Lignin compositional trends

The most obvious and easily interpreted distinction between organic material in different grain size fractions is the total lignin yields from sand-sized sediments, compared to the finer fractions (Table 2). The  $\Lambda$  values for all three sand-size fractions is in the range of 1.0–1.19, while  $\Lambda$  values for the silt and clay fractions range are lower, ranging from only 0.13 to 0.73. These values are all appreciably below the range observed in fresh vascular plant samples (3–25; Hedges and Mann, 1979a). Thus, chemically intact vascular plant material must be a minor component of the organic material in all fractions. However, the significantly different levels imply organic material associated with sand-sized fractions has a higher terrestrial contribution.

Similarly, (Ad/Al)<sub>v</sub> values are different for the sand-sized fractions vs. the finer ones (Table 2). (Ad/Al)<sub>v</sub> in the sand-size fractions range from 0.9 to 0.4, while the clay and silt values range from 2.3 to 3.9. These ratios indicate lignin is highly degraded in all fractions, but extremely so in the fine fractions, whose (Ad/Al)<sub>v</sub> ratios are higher than may be expected from intact plant debris, soil organic matter, dissolved humic material (Ertel et al., 1986), or degraded plant matter (Opsahl and Benner, 1995).

Compositional patterns among lignin phenols may be used to reconstruct vascular type and tissue plant sources (e.g., Hedges et al., 1988; Hedges and Mann, 1979b). However, because over-all lignin abundances were low and the evident lignin degradation may alter compositional relationships, source assignments of the individual fractions should be regarded as rudimentary. Relative phenolic monomer abundances point to a different provenance for lignin associated with the sand-sized fractions. For example, vanillyl phenols are produced in high yield by all lignin-bearing tissues, but are the only major products from CuO oxidation of gymnosperm woody tissues. In contrast, syringyl phenols are produced in high yield almost exclusively by angiosperms, while cinnamyl phenols are produced in high yield only by nonwoody gymnosperm and angiosperm tissues. Thus, plots of syringyl to vanillyl yield ratios (S/V) against cinnamyl to vanillyl yield ratios (C/V) helps distinguish the contribution of both the plant tissue and the plant type to the sample.

When presented in this way (Fig. 5) the three sand-size fractions plot closest to the origin, while the remaining silt and clay fractions are elevated in syringyl and cinnamyl phenols. The sand-sized fractions fall outside the range obtained from fresh angiosperm material. Since gymnosperm woody tissues are depleted in syringyl and cinnamyl phenols, low values in both S/V and C/V may be interpreted as contribution of gymnosperm woody tissues to the lignin-bearing material. Much lower values than these have been found in coastal sediments adjoining land masses with coniferous forests (Hamilton and Hedges, 1988; Hedges et al., 1988; Hedges and Mann, 1979) where the contribution of gymnosperm material is likely to be great. The remaining finer fractions plot away from the sands, suggesting a different source. With the exception of the 0.8  $\mu\text{m}$  sample, all have C/V values in the range of lignin found in angiosperm soft tissues. The 0.8  $\mu\text{m}$  sample has a lower C/V and plots in the range of fresh angiosperm wood. Diagenesis is known

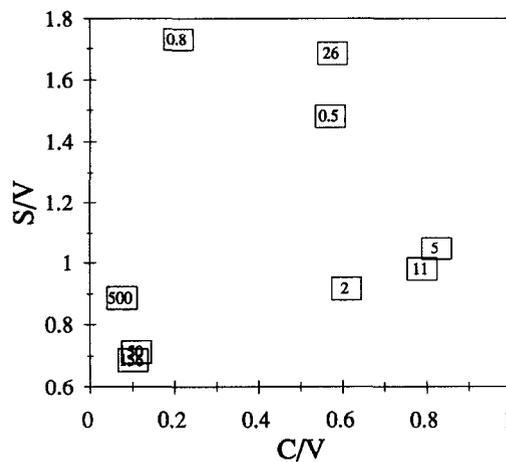


Fig. 5. Plot of the weight ratio of syringyl to vanillyl phenols (S/V) against the weight ratio of cinnamyl to vanillyl phenols (C/V) for all size fractions. Data labels are as in Fig. 4.

to alter S/V and C/V by selectively removing cinnamyl and syringyl phenols over vanillyl phenols. The alteration of these ratios confound source determinations by progressively lowering ratios into the gymnosperm range. The lower values observed in the sand-sized grains, however, are unlikely to have resulted from diagenesis because the Ad/Al ratios indicate fresher material associated with this size class.

### 3.3.3. Carbohydrate compositional trends

The sand fractions contain both the highest and lowest total carbohydrate yields normalized to OC ( $\text{rCH}_2\text{O}$ ; Table 3). The highest  $\text{rCH}_2\text{O}$  value (13.7 mg/100 mg OC) was found in the 50  $\mu\text{m}$  fraction (the sample with the lowest %OC). The lowest value (3.6 mg/100 mg OC) was found in the 500  $\mu\text{m}$  fraction, consistent with its low C/N<sub>s</sub> value. The remaining  $\text{rCH}_2\text{O}$  values were relatively uniform, ranging from 5.5 to 9.39 mg/100 mg OC. There was no consistent trend with grain size in  $\text{rCH}_2\text{O}$ . However, due to variations in organic C, there is a consistent trend of increasing  $\Sigma\text{CH}_2\text{O}$  (total carbohydrate normalized to sediment mass) with decreasing grain size. This relationship will be discussed in greater detail in section 3.4.

Within the neutral carbohydrate pool there are several constant compositional changes across the grain size fractions (Table 3). Again, the sand-size fractions appear distinct from the smaller grains. Glucose is the most abundant aldose in the three largest grain sizes, accounting for 32, 24, and 39 wt% of total carbohydrates for the 500  $\mu\text{m}$ , 156  $\mu\text{m}$ , and 50  $\mu\text{m}$  fractions, respectively. The remaining size fractions range from 21 to 14 wt% glucose, averaging 18 wt%. Galactose is the predominant sugar in the finer fractions, accounting for 22–27 wt% of total aldose. In contrast to the behavior of glucose and arabinose, mannose and rhamnose decline in relative abundance with increasing grain size. Mannose declines from a high of 21 wt% on the finest fraction to 12 wt% in the largest. Similarly, rhamnose declines from 11 wt% in the finest fraction to 8 wt% in the largest. This compositional variability within the aldoses indicates a

Table 3. Carbohydrate compositions of Peru Margin sediment size fractions. All monosaccharide values are percentages by weight of total carbohydrate yield. Abbreviations: RHA, rhamnose; FUC, fucose; RIB, ribose; ARA, arabinose; XYL, xylose; MAN, mannose; GAL, galactose; GLC, glucose;  $\Sigma\text{CH}_2\text{O}$ , total neutral carbohydrate yield (mg) normalized to 100 mg OC;  $\Sigma\text{CH}_2\text{O}$ , total neutral carbohydrate yield (mg) normalized to 100 mg sediment.

Sample	RHA	FUC	RIB	ARA	XYL	MAN	GAL	GLC	$\Sigma\text{CH}_2\text{O}$	$\Sigma\text{CH}_2\text{O}$
Bulk	7.6	7.8	5.1	11.0	14.1	15.0	23.0	16.5	8.2	0.54
Rinsed	8.8	5.9	3.1	8.5	11.3	17.6	25.4	19.3	7.4	0.61
0.5 $\mu\text{m}$	11.3	5.8	2.7	6.2	11.7	21.5	21.9	18.8	9.4	2.03
0.8 $\mu\text{m}$	8.2	4.8	3.6	7.1	12.6	19.8	23.3	20.7	7.3	0.94
2 $\mu\text{m}$	6.4	4.8	3.8	7.5	11.1	19.5	25.8	21.0	5.6	0.40
5 $\mu\text{m}$	7.8	5.9	3.8	8.2	11.4	18.4	26.2	18.2	6.0	0.59
11 $\mu\text{m}$	7.1	5.4	4.1	8.7	11.7	17.9	27.2	17.8	6.8	0.53
26 $\mu\text{m}$	9.8	7.5	4.8	9.9	14.0	16.2	23.7	14.0	7.9	0.34
50 $\mu\text{m}$	5.8	4.3	4.7	7.0	10.2	10.9	17.4	39.5	13.7	0.21
156 $\mu\text{m}$	7.8	5.3	4.0	13.3	13.8	13.3	18.7	23.6	8.5	0.67
500 $\mu\text{m}$	7.8	3.8	2.5	11.2	10.5	12.4	19.1	32.5	3.6	0.31

different source or diagenetic state of carbohydrate-bearing material among size fractions. The opposing trends which concentrate glucose and arabinose in the larger grain sizes and concentrate mannose and rhamnose in the smaller ones suggest that the system may be dominated by simple mixing of two carbohydrate sources. It is important to note that the observed trends in carbohydrate composition are too large to be artefacts caused by changes in glucose alone, but reflect systematic changes in the absolute amount of material.

Clues to the origin of these compositional trends among the size fractions, and thus to the source of the carbohydrates, may be obtained by comparing the composition of the fraction with the highest absolute yield of carbohydrate (0.5  $\mu\text{m}$ ) to the one with the lowest (50  $\mu\text{m}$ ). These two samples represent the continuum of change through the size classes (Table 3). The simplest way to effect this comparison on a mass-free basis is to normalize the yields of the individual aldoses within each sample to glucose, the most abundant monomer in the 50  $\mu\text{m}$  fraction (Fig. 6a). Glucose was chosen in order to limit the introduction of passive trends which may occur due to the dramatic difference in its abundance between samples. The difference between these two spectra represents the compositional dissimilarities between the two samples (Fig. 6b).

From this compositional comparison it is evident that the 0.5  $\mu\text{m}$  fraction is particularly elevated in mannose, galactose, and rhamnose, relative to the 50  $\mu\text{m}$  fraction. Such a compositional shift would require addition of material richer in these monomers than glucose to the more C-rich fine fraction sediments. Gross carbohydrate monomeric abundances of phytoplankton and bacteria are typically elevated in glucose (Cowie and Hedges, 1984b). Isolated diatom cell walls, however, are relatively unique in having carbohydrate monomeric distribution high in mannose, galactose, and rhamnose (Fig. 6c; data from Cowie and Hedges, submitted). For eleven species where diatom cell wall material has been isolated and analyzed, all exhibit similar carbohydrate molecular compositions (Cowie and Hedges, in press; Darley, 1977; Hecky et al., 1973; Haug and Myklestad, 1976) despite considerably different extraction methods and methods of analysis. Addition of cell wall material to the 50  $\mu\text{m}$  fraction would cause compositional changes in the direction

observed in finer fractions. Thus, diatom cell wall material is potentially a progressively more important contributor to carbohydrate yields with decreasing grain size.

#### 3.4. Surface Area Relationships

The bulk specific surface area (SA) of the sediment is 23.7  $\text{m}^2/\text{g}$ , well within the global range (2–55  $\text{m}^2/\text{g}$ ) of

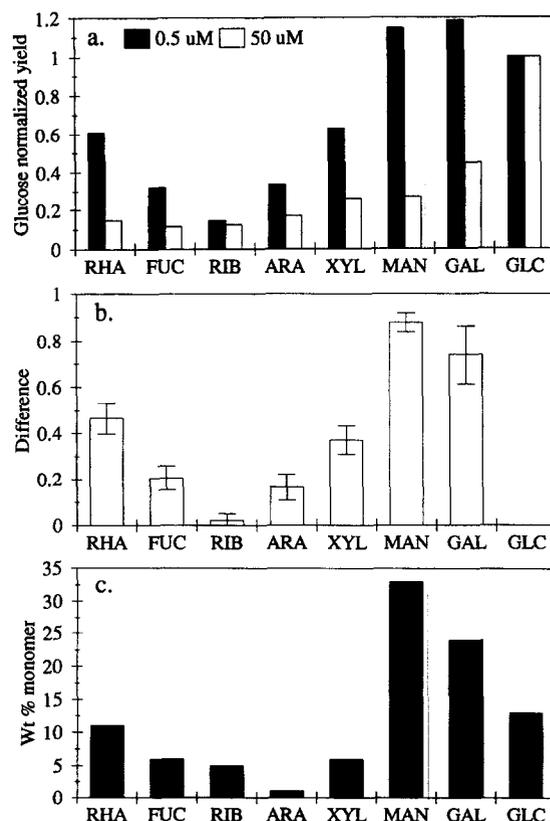


Fig. 6. Histograms of (a) aldose abundances in 0.5  $\mu\text{m}$  and 50  $\mu\text{m}$  size fractions normalized to glucose yield, (b) difference between values in panel a, (c) average diatom cell wall composition normalized to total carbohydrate yield. Diatom cell wall data are from Cowie and Hedges (1996) and abbreviations are as in Table 3.

surface area in bulk sediments (Mayer, 1994). Surface area of the grain size fractions increases exponentially from 3.7 m<sup>2</sup>/g in the 50 μm fraction to 95 m<sup>2</sup>/g in the 0.5 μm fraction (Table 1). The rate of increase is much greater than for theoretical SA values calculated based on smooth particles of the same nominal size, indicating rough sediment surfaces. These SA values are generally similar to those measured in identical size fractions in coastal sediments (Keil et al., 1994). However, the two largest fractions do not conform to the trend of increasing SA with decreasing size and possess SA values 2–3 times greater than previously observed for sediments of similar size, attesting to their different nature.

#### 3.4.1. Elemental trends

As has been previously presented (Hedges and Keil, 1995), there is a strong positive correlation ( $r = 0.96$ ,  $\alpha = 0.99$ ) between OC and surface area in these samples (Fig. 7). Thus, surface area appears to be a key factor determining OC content in Peru Margin sediments. The relationship between OC and surface area (Fig. 7) corresponds to approximately 2.3 mg OC/m<sup>2</sup> and is a much higher loading than the range of 0.5–1.0 mg OC/m<sup>2</sup> typically observed in sediments (Mayer, 1994).

OC/SA correlation seems somewhat surprising in view of the substantial compositional variability discussed in the previous section. It is unclear how compositional variability is maintained if a single relationship determines organic content. The heterogeneity of compound types among size classes found in the Peru sediments is similar to that found with molecular level analyses of size fractionated sediments from the Washington Coast (R. J. Keil, unpubl. results). These results imply that the bulk of organic material is sorbed irreversibly to sediments (consistent with the low observed losses upon treatment with distilled water) and the compositional distinction formed prior to deposition. Postdepositional association, reversible sorption, and redistribution during sample processing would all tend to obscure the observed differences.

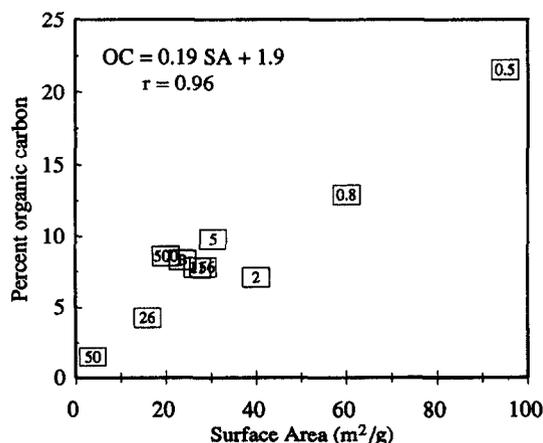


Fig. 7. Plot of weight percent organic C against specific surface area (m<sup>2</sup>/g) for all grain size fractions. Data labels are as in Fig. 4.

Regression of the %OC to SA relationship to zero SA indicates that some organic material remains independent of SA (Fig. 7). However, explicit calculation of the amount remaining is highly susceptible to error given that the grain-size fractions carrying the majority of OC cluster towards the center of the line, and small errors in the outlying data may cause a disproportionate change in the intercept value. Sensitivity of the intercept value to error due to any datum may be determined by calculating the range of intercept values which result following the removal of any single data point from the set. The 500 μm sample is excluded from all regression analyses because microscopic observations and C/N<sub>a</sub> values demonstrate it carries material distinctly different from the remainder of the size fractions. Also, little of the organic material in the bulk sediment is associated with this size fraction, owing to the low mass of material in this size range.

The resulting intercept values range from 0.9 to 1.7% OC, indicating 10–20% of organic matter may not be related to sediment surface area. Mechanistically this may mean that in the large, low carbon grain size fractions (which carry little of the organic material in the bulk sediment), most organic material exists in discrete particles, and surface area is not the dominant factor determining OC content. This is similar to observations in SPLITT-fractionated sediments from the Washington coast (Keil et al., 1994a) and in agreement with fresher lignin values found in sand-sized fractions corresponding to discrete plant debris. Conversely, surface area and OC content are highly correlated in the finest fractions, with 79% to 90% of the OC directly related to surface area, and apparently not found in discrete debris.

The C/N<sub>a</sub> of organic material unrelated to SA may be crudely estimated in a similar fashion by regressing %TN to zero SA and comparison to %OC intercepts. Percent OC and %TN are tightly coupled in these sediments (Fig. 4), so errors causing changes in intercept value will affect both parameters in a like fashion. Regression analysis yields a range of C/N<sub>a</sub> values from 7.8 to 11.0, on average slightly more nitrogen rich than the bulk sediment (Table 1) and encompassing the C/N<sub>a</sub> determined for material mixing among size fractions (Fig. 4).

Several of the other parameters measured correlate well with surface area, and several show little or no correlation. Figure 8 shows the remaining parameters plotted against surface area. Total nitrogen covaries with carbon and thus has a positive correlation with surface area (Fig. 8a).

#### 3.4.2. Lignin

Lignin yields normalized to sediment mass ( $\Sigma 8$ ) do not appear to correlate with surface area (Fig. 8c), indicating SA is not a principal factor determining the lignin content of these sediments and demonstrating that lignin content is uncoupled from the total OC content.  $\Delta$ , however, is negatively correlated with surface area (Fig. 8d,  $r = 0.80$ ,  $\alpha = 0.05$ ), possibly due to dilution of lignin carbon by addition of surface-related autochthonous debris.

#### 3.4.3. Carbohydrates

Several carbohydrate compositional parameters vary in concert with SA demonstrating that previously discussed

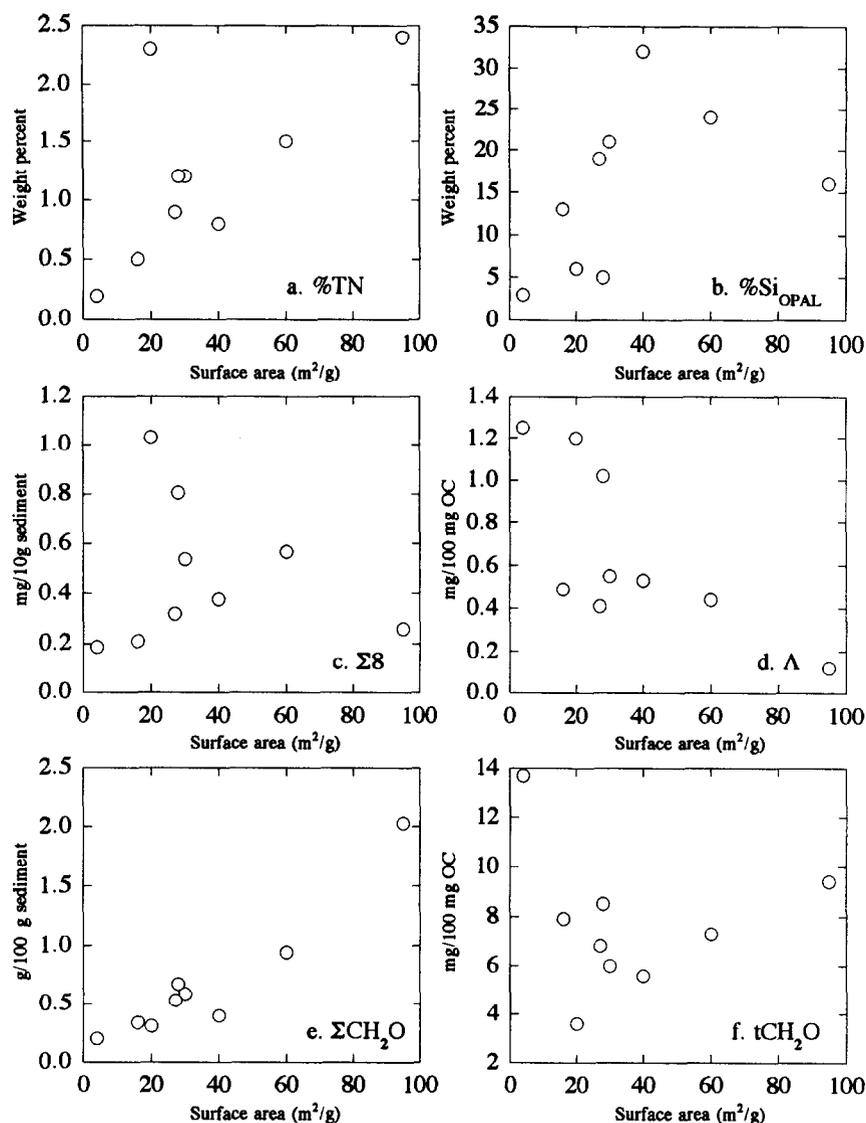


Fig. 8. Plots of molecular and elemental parameters for all grain size fractions against surface area. Abbreviations are as in Tables 1, 2, and 3.

changes among textural classes are related to surface area. Total carbohydrates normalized to sediment mass ( $\Sigma\text{CH}_2\text{O}$ ) correlate positively with SA (Fig. 8e,  $r = .93$ ,  $\alpha = 0.01$ ). The amount of OC present as analyzable carbohydrate ( $t\text{CH}_2\text{O}$ ) remains relatively small but constant (Table 2), and thus  $\Sigma\text{CH}_2\text{O}$  has essentially the same increase with surface area as bulk OC (Fig. 8f). Among individual monomers, wt% rhamnose and mannose positively correlate with SA ( $r_{\text{RHA}} = 0.64$ ,  $r_{\text{MAN}} = 0.79$ ,  $\alpha = 0.05$ ), indicating these monomers are selectively concentrated in the fine fractions in proportion to SA.

### 3.5. Geochemical Implications

Clearly, grain size distribution is a principal determinant of the OC concentration and composition of the Peru Margin sediments. This result alone from an area where controls on carbon preservation are thought to be related to productivity

or oxygen concentration has important implications (e.g., Summerhayes, 1983). The factors which control the depositional process and therefore the grain size distribution may primarily determine the OC composition and distribution. These factors include the current regime in the depositional area, discharge, size, lithology and proximity of nearby river drainages, extent and variability of biogenic inputs, and sediment sorting during deposition or postdepositional redistribution. This result is in agreement with the finding of Pedersen et al. (1992) that postdepositional winnowing lowered the inventory of OC in sediments accumulating on the Oman Margin. Although primary production ( $1.5 \text{ g C m}^{-2} \text{ d}^{-1}$ ), bottom water oxygen concentration and adjoining arid continental environment are similar to that at the Peru Margin, the OC content of Oman Margin sediments averaged 4.11%. Analysis of Cr and Zr as proxies for grain texture revealed selective removal of finer grain fractions resulted in loss of OC and a change in  $\text{C}/\text{N}_s$  values.

The effect of grain size distribution in Peru Margin sediments is evident from a simple heuristic model. The median grain size of the sample is in the 11  $\mu\text{m}$  size fraction (Table 1). If all grain size characteristics and the relative weight distribution remain constant, but the median grain size is shifted to the 26  $\mu\text{m}$  fraction, approximately 27% less organic carbon and nitrogen, and 25% less carbohydrate would be present in the bulk sample, corresponding to a change in %OC from 8.3 to 6.1. Conversely, if the median grain size were shifted to the 5  $\mu\text{m}$  fraction, approximately 10% more organic carbon and nitrogen, and 13% more carbohydrate would be present in the bulk sample.

A mechanism by which grain size distribution may affect total OC content is direct physical association, probably adsorption to mineral surfaces. Mayer (1994) and Hedges and Keil (1995) have suggested adsorptive control of OC content may be the rule in neritic sediments. The high correlation of mineral surface area to %OC suggests direct physical association of organic matter with the mineral matrix may control organic C content of Peru Margin sediments as well, in spite of their much greater carbon content. Organic material sorbed to mineral surfaces at loadings between 0.5 and 1.0 mg OC/m<sup>2</sup> is apparently protected from remineralization (Keil et al., 1994b) and may also be protected at the higher loadings found in the Peru Margin sediments. Physical association of the organic material with the mineral matrix is suggested by small losses of OC during disaggregation and washing (<5%) and subsequent SPLITT fractionation (<2%).

The evidence for adsorption of organic material to surfaces in these sediments, however, is not indisputable. Discerning between physical association and hydrodynamic effects is problematic. Microscopic examination showed increasing abundances of amorphous flocs in finer textural classes. Low density, organic rich material may be selectively concentrated in the finer fractions by hydrodynamic process without physical association, providing a fortuitous correlation with surface area. However, in order to produce the observed trend, the OC content needs to be an exponential function of particle density—an unlikely scenario—since nominal grain size determination during hydrodynamic sorting is a linear function of particle density (Springston et al., 1987).

Independent correlations between SA and organic molecular parameters strengthen the evidence for physical association of bulk organic material with mineral grains. For example,  $\Delta$  correlates negatively with SA. The most plausible explanation for this relationship is that, irrespective of initial values, relict sorbed lignin material is diluted by the addition of organic matter in proportion to surface area. Another example is that  $\Sigma\text{CH}_2\text{O}$  and specific monomeric abundances correlate positively with SA, suggesting possible adsorptive control of the amount and composition of carbohydrates found in these sediments similar to that controlling bulk OC, even though carbohydrates represent a small fraction of total OC.

Aldose compositional changes across textural classes also support physical associative control of carbohydrate abundances. Relative increases in mannose and rhamnose in the fine fraction material require proportionally increasing

amounts of material compositionally similar to diatom cell walls (see section 3.3.3). If cell wall material is preferentially concentrated or preserved in the finer fractions, it is decoupled from opal preservation. Biogenic opal abundances do not correlate with grain size or surface area (Fig. 8b), ruling out the possibility that carbohydrate material resembling cell wall polymers is contained at constant concentrations within the matrix of fine, low density diatom debris.

Preservation of diatom cell wall material in Peru Margin sediments would hardly be surprising given that the bulk sediment is 53% biogenic opal (24 wt% biogenic silica). Sellner et al. (1983) estimate that approximately 90% of the particulate organic carbon in the waters above this region is diatom derived. The important implication is that the degradation of cell wall carbohydrate polymers may be inhibited through sorption to surfaces. Intrinsic properties of diatom cell wall polymers make them likely candidates for surface association: they are self-associative, rich in charged moieties (Kloareg and Quantrano, 1988), and insoluble in water (Darley, 1977). They also form crystalline and pseudocrystalline structures (Rees et al., 1982) which may anchor or form the high organic loading coatings found in these sediments. That the cell wall components of diatoms should be selectively preserved has been demonstrated by Cowie and Hedges (1996), who found that the fecal material of *Calanus pacificus*, fed a diet exclusively composed of diatoms, resembled the carbohydrate composition of cell wall material.

It is possible to crudely estimate the upper bound of the potential contribution of intact diatom cell wall polymers to carbohydrate abundances in the sediments. Mannose is the monomer in highest abundance in diatom cell walls (Fig. 6c), but not in the sediments (Fig. 2). The amount of residual material may be determined by making the arbitrary assumption that all mannose is derived from diatom cell wall debris and using it as a basis for comparison among the remaining monomers. Mannose is a common monomer, so there is no reason to expect it would be solely derived from diatoms. Estimated in this way, the maximal potential contribution of intact diatom cell wall carbohydrates to the bulk sediment is 45%, indicating a minimum of half or more of the carbohydrate has some other source or suffers extensive diagenetic alteration. The potential contribution of intact diatom cell wall polymers systematically rises in the grain size fractions from 32% in the 50  $\mu\text{m}$  fraction to 63% in the 0.5  $\mu\text{m}$  fraction. The increase is in direct proportion to surface area, supporting the notion that diatom cell wall polymers may be surface active.

The compositional distinction of the sand-sized grains despite the continuous nature of the  $\Sigma\text{CH}_2\text{O}/\text{SA}$  relationship (Fig. 8e) may provide insight into the process of preservation. Silt- and clay-sized grains are apparently arriving at the sediment rich in high-mannose carbohydrate material, while sand-sized grains are not. If all sediment grains were equal with respect to carbon loading potential on arrival at the sediments, high-mannose and autochthonous carbohydrate material would compete equally for binding sites and be dispersed in constant proportion among all size fractions according to their distribution coefficient. This is not the case, however. While  $\Sigma\text{CH}_2\text{O}$  maintains a continuous relationship with surface area (Fig. 8e), high-mannose carbohy-

drate is found to be concentrated in fine fractions and high-glucose carbohydrate in the sands. Thus, for mannose-rich material to occur in higher abundance in the finer grains, and do so in constant proportion to surface area, either the high-mannose carbohydrate was selectively absorbed to silt and clay-size particles prior to deposition, or organic matter associated with sand-size grains was selectively altered.

#### 4. CONCLUSIONS

1) SPLITT fractionation provides novel insights into the provenance and distribution of organic matter in Peru Margin sediments. Separate grain size fractions have markedly different elemental and molecular contents and compositions, indicating different processes and sources affect organic material among the textural classes. Organic carbon, nitrogen, and carbohydrate are progressively concentrated in finer-grained sediments, while lignin and biogenic opal do not systematically vary with grain size.

2) There is notable correlation between surface area and total nitrogen total carbohydrates, and fractional abundance of the monomers rhamnose and mannose. These results suggest physical association with mineral surfaces may play an important role, not only in determining the concentration but also the composition of the preserved material.

3) Comparison of the composition of carbohydrates found in sand-sized grains with that found in clay-sized ones on a mass-free basis suggests material compositionally resembling diatom cell walls is progressively concentrated in finer sediments. Two monomers characteristically enriched in diatom cell walls, rhamnose and mannose, increase in proportion to sediment surface area, while biogenic silica did not. Thus, diatom cell wall polymers may be selectively adsorbed to sediment surfaces and thereby preserved. However, intact diatom cell wall polymers probably account for much less than 50% of the observed carbohydrate in bulk sediment.

4) Lignin abundance data indicate terrestrial material contributes only a small, highly degraded fraction of the organic material in these sediments. The source and diagenetic state of the lignin-bearing material associated with sand-sized grains is distinctly different from that associated with the silts and clays as determined by lignin compositional trends. (Ad/Al)<sub>v</sub> ratios in the silts and clays correspond to those found in marine humic material. The fraction of OC found as lignin phenols systematically decreases in proportion to surface area, suggesting relict lignin may be diluted by addition of surface-associated marine-derived material.

5) OC and sediment surface area maintain a nearly constant ratio of  $\sim 2.3$  mol C/m<sup>2</sup>, much higher than the 0.5–1 mol C/m<sup>2</sup> generally observed in coastal sediments. This relationship is continuous despite elemental and organic molecular differences among grain size fractions indicative of differing compositions, sources, and diagenetic histories between grain-size fractions. The majority of organic material in the bulk sediment (79–90%) is apparently related to surface area.

6) Grain size distribution is a principal determinant of the content and distribution of organic carbon, total nitrogen, biogenic opal, carbohydrates, and lignin within these sediments. Therefore, the factors which control grain size distri-

bution likely play a more significant role in determining the type and amount of organic material preserved in texturally heterogeneous sediments than previously thought.

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