

Element and phase composition of particulate matter from the circumpolar current between New Zealand and Antarctica

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ABSTRACT	Elemental analyses and phase determinations of suspended matter, >75 μ m in diameter, from surface waters of the Circumpolar Current show characteristic distribution patterns for different water masses. Suspended matter is high in silica and calcium carbonate in subantarctic waters north of 50°S latitude. At 55°S organic matter is the dominant phase accounting for > 50 wt% of the particulates > 75 μ m. In the surface waters between the Polar Front and the Antarctic Divergence biogenous opal (SiO ₂) dominates the coarse standing stock in distinct latitudinal bands. Implications are that transfer of biogenous constituents to the sediment are significantly affected by particle sizes and their composition in surface waters. Opal and CaCO ₃ are relatively more abundant in the coarse size classes and thus are preferentially transferred to the sediment. However, organic matter and its associated elements are more prevalent in the small size classes and are thus subject to more rapid recycling in part due to their				
· ·	Size effects may also lead to over estimation of global biological silica production by as much as 20-times, depending on whether composition of "coarse" (>75 μ m) or "fine" (0.4-75 μ m) plankton is used in coupling carbon production to silica fixation.				
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RÉSUMÉ	Éléments et phases des matières particulaires en suspension dans le courant circumpolaire entre la Nouvelle-Zélande et l'Antarctique				
	Les analyses d'éléments et les études de phases de la matière en suspension (plus de 75 μ m de diamètre) des eaux de surface du courant circumpolaire montrent que celle-ci présente une répartition caractéristique différente dans chaque masse d'eau traversée. A une latitude d'environ 50°S dans les eaux subantarctiques, la matière en suspension a un fort taux de silice et de carbonate de calcium. A 55°S, la matière organique est la phase dominante, constituant plus de 50 % en poids des particules de diamètre supérieur à 75 μ m. Dans les eaux de surface entre le Front Polaire et la Divergence Antarctique, le stock de grosses particules (>75 μ m) en place est constitué principalement d'opale biogénique, dans deux bandes de latitudes distinctes. Ceci implique que le transfert de constituants biogéniques aux sédiments du fond de l'océan est très influencé par la taille et la composition des particules dans les eaux de				

l'océan est très influencé par la taille et la composition des particules dans les eaux de surface. SiO₂ et CaCO₃ forment l'essentiel des classes de particules de grosse taille et constituent donc l'essentiel du transport aux sédiments. Cependant, la matière organique et ses éléments associés forment l'essentiel des classes de particules de taille fine et sont donc sujets à un recyclage plus rapide.

Les effets de la taille des particules peuvent aussi conduire à surestimer jusqu'à 20 fois la production globale de silice biologique, suivant que l'on se réfère à la composition du plancton de grande taille (>75 μ m) ou de petite taille (0,4-75 μ m) pour associer la production de carbone à la fixation de silice.

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INTRODUCTION

Element cycling in the oceans and pelagic sediment formation are largely controlled by biologically mediated particle production, transfer and decomposition (Mac-Kenzie, 1975; Berger, 1976; Sackett, 1978; among others). Geographical variations in the chemistry of surface particulates are reflected in characteristic bottom sediment distribution patterns, modified by regional water column properties. Of these, dissolved nutrients, oxygen content and degree of calcium carbonate saturation exert the strongest influence.

Quantification of the relation between biological production and bottom sediment accumulation presently depends on direct vertical flux measurements from sediment trap deployments and on inferences from elemental relationships of suspended biological matter (Müller, Suess, 1979; Dymond vet al., in press; Honjo, 1980; Suess, 1980). The waters of the Circumpolar Current are unique in that they sustain the oceans largest biological production where diatoms and other marine algae with and without silica requirements dominate primary production. Their skeletal debris accumulate at the sea floor and form a wide belt of siliceous ooze bordering the Antarctic continent (Lisitzin, 1972; Goodell et al., 1973; Cooke, Hays, 1981).

In this paper we report on element and phase composition of suspended matter from surface waters of the Circumpolar Current between New Zealand and Antarctica. This is to aid attempts in relating production of biogenous matter to sediment accumulation, establishing the regional variability of suspended matter composition, quantifying the standing stock of the coarse particulates and identifying compositional characteristics unique to large size classes of >0.075 mm in diameter.

METHODS

Surface particulate matter was collected during R/VKnorr's cruise 73 leg 13 from December 16, 1978 to January 4, 1979 while underway between New Zealand and the Antarctic Circle. Large volumes of seawater from the ship's contamination free system were continuously pumped through a set of two screens. The screens were ASTM stainless steel standard sieves 12 cm in diameter and 150 and 75 µm in mesh size enclosed by an all-plastic pressure housing with a water meter installed upstream (Fig. 1). The sampling approach taken here by employing a set of screens rather than the conventional 0.45 µm filters prefers the large size classes and will not

easily be converted into total standing stock. However, material flux from the sea surface to the sea floor is dominated by large particles, and therefore it was felt that these samples and their composition as a first approximation are more representative of the actual matter involved in mass transfer than that of total standing stock of particles. Although it is realized that various mechanisms easily convert small particles into larger ones in the surface layer. However, the large volumes of seawater sampled makes this approach more attractive; particularly because large particles are so infrequent that conventional small-volume filtration inadequately represents this important part of the particle size spectrum (McCave, 1975). Also compositional characteristics of certain large sized taxa of plankton are revealed by this sampling procedure.



Figure 1

Continuous filtration system used underway at a rate of $\approx 3 \text{ gal/min}$; stainless steel screens were 150 and 75 µm in mesh size, respectively and the sieves 12 cm in diameter.

Collection of surface suspended matter lasted for 6-10 hours averaging material over long segments of the ship's track of up to 100 nautical miles as well as over periods of changing light intensities. The yield was on the order of several tens to hundreds of milligrams of material per sample. Each sample was poisoned with \geq 100 ppm Hg as HgCl₂ and refrigerated. Samples were subsequently washed salt-free and freeze dried. Large amounts of material were collected thus sacrificing spatial and diurnal resolution of samples for more accurate chemical and phase analyses. The analytical scheme used emphasizes partitioning of elements among phases rather than bulk elemental composition which has traditionally been the case (Boström et al., 1974; Martin, Knauer, 1973; Boström et al., 1978; Moore, Boström, 1978; Copin-Montegut, Copin-Montegut, 1978; Emery, Honjo, 1979). The methods employed here and schematically illustrated in Figure 2 consists of separately determining organic carbon, carbonate carbon, organic and phosphate phosphorus, total silica and



Figure 2

Analytical scheme used for combined element and phase analyses of suspended matter; the minimum amounts required for this procedure are $\approx 50 \text{ mg}$ of dry weight.

nitrogen, and HCl-soluble and residual calcium. Organic carbon and organic phosphorus were determined from the difference between their respective total and HClsoluble element concentrations. Whereby it is assumed that the soluble calcium represents largely particulate calcium carbonate and soluble PO_4 apatitic skeletal phases. Replicate determinations were carried out on a few selected samples (Table 1); the variability is due to inhomogeneities among the splits rather than reflecting the precision of the analytical techniques. The ash content, obtained in the process of converting organically-bound phosphorus to phosphate by ignition at 500°C, proved to be a useful variable.

Table 1

Replicate analyses of suspended matter samples as obtained by the scheme illustrated in Figure 2; the variations are due to inhomogeneities among sample splits rather than to analytical imprecision.

	K	N 17 a	KN 27 a 62°04'-61°26'S 171°07'-171°45'W						
Latitude Longitude	65°30 174°23	′-66°48′S ′-174°14′E							
(wt%)									
Ash ,	69.3	73.3	75.0	75.7					
Silica	64.2	66.0	71.8	67.0					
Nitrogen total	1.73	1.93	0.89	0.92					
Carbon total	9.47 ± 0.42	9.67 ± 0.20	6.96 ± 0.02	9.27 ± 0.60					
		(ppm)							
Phosphorus total	540 [°]	610	270	4 70 [°]					
Phosphorus soluble	60	70	70	80					
Calcium soluble	1 680	1 780	3 000	3 470					
Calcium residual	360	390	480	440					
Barium soluble	45	81	31	31					
Barium residual	19	8	15	10					
Magnesium soluble	800	1 100	400	680					
Magnesium residual	470.	430	120	160					
Aluminium soluble	50	40	80	60					
Aluminium residual	570	, 530	200	240					
Barium residual Magnesium soluble Magnesium residual Aluminium soluble Aluminium residual	19 800 470 50 570	8 1 100 430 40 530	15 400 120 80 200	10 680 160 60 240					

Presently it remains uncertain how much of the quite labile organically-bound phosphorus was leaked from the cells of the plankton during sampling on the screens or when washed with distilled water prior to freeze drying and how much continued to be solubilized in the subsequent acid treatment, the step that was designed to attack apatitic phases only. Organic phosphorus concentrations obtained by this method were quite low, in many cases yielding C-org : P-org atomic ratios = 106 : $\ll 1$; this could be an artifact of the procedure or be a characteristic feature of "coarse" surface suspended matter.

SAMPLING TRANSECTS AND GENERAL HYDROGRAPHY

The cruise track crossed the Campbell Plateau, the SW Pacific Basin and the Pacific Antarctic Ridge thereby traversing the Circumpolar Current twice in a N-S direction between 165°W and 170°E longitude. Major water masses encountered were those of the Subantarctic zone, Polar Front and Antarctic Divergence as judged from surface temperature readings (Fig. 3). No other hydrographic parameters were measured. The western transect was run between December 16-26, 1978, the eastern transect between December 26 of 1978 and January 4 of 1979. The southern extent of the cruise track was limited by pack ice. Sample points represent the approximate midpoints of each sampling transect.



Figure 3

Surface temperature between 16 December 1978 and 4 January 1979; the steep gradient between 60° and 55°S marks the position of the Polar Front at that time of the year. The numbered sample points represent the approximate mid points of each individual sampling transect.

Table 2

Suspended matter composition from surface waters of the Circumpolar Current; the numbers preceded by KN refer to the sampling transects shown in Figure 3, a = the size class $\ge 150 \,\mu\text{m}$ and $b = 75-150 \,\mu\text{m}$ in diameter; all concentrations are in (%) of dry weight of desalted and freeze-dried suspended matter; in several cases samples were combined for phase analyses.

·	Sample (Nr.)	Concentration (µg.kg)	Ash (wt%)	SiO ₂ (wt%)	CaCO ₃ (wt%)	C-org (wt%)	N-total (wt%)	P-total (wt%)	P-org (wt%)	
	KN2 a	19.6 6.48	58.0 56.2	45.2 43.9	1.4 0.8	15.4 15.7	2.64 2.77	0.420 0.373	0.112 n.d.	-
• ,	KN3 a b KN4 a	6.92	68.1 → 31.2	n.d. n.d.	1.0 6.3	10.0 29.0	1.44	0.137 0.401	0.082 n.d.	
	b KN5 a	No sample	-	-	-	-	-	-	<i></i>	
	KN6 a b	1.74 5.41	• 41.1	n.d.	2.4	21.4	4.31	0.202	n.d.	
•	KN7 a b KN8 a	5.97 10.3 4.59	41.1	n.d.	4.8	23.8	4.43	0.544	n.d.	
	KN9 a	7.48 1.93	46.2	33.0	5.2	19.6	3.53	0.324	n.d.	
•	b KN 10 a	2.73	• 25.4	10.2 n.d	10	31.6	4.77	0.310	n.d.	• .
	KN11 a b	7.56	+ 50.9	n.d.	15	21.6	4.46	0.356	0.160	,
	KN 12 a b KN 13 a	4.30 25.0 24.3	51.8 74.8 62 5	n.d. n.d. 51.6	3.4 1.7 2.9	23.6 9.7	5.80 1.60 2.96	0.575 0.196 0.090	n.d. 0.033 0.082	
	b KN 14 a	35.8 35.6	66.5 68.8	58.4 60.4	2.7	13.3 12.2	2.41 2.17	0.083	0.075 0.053	
	KN 15 a b	21.1 39.5	74.6 69.6 70 <i>.</i> 6	63.0 62.7 64.9	2.0 0.9 0.7	12.5 11.6	2.62 2.46	0.080 0.084 0.076	0.030 0.074 0.065	
	KN 16 a b KN 17 a	52.6 41.6 67.5	71.1 66.8 69.3	61.3 60.6 64.2	1.2 · 1.0 0.4	10.5 10.9 9.5	1.92 . n.d. 1.73	0.149 0.106 0.054	n.d. n.d. 0.048	
	6 KN 18 a	43.2 9.7	71.2 56.2	65.6 44.6	0.4 1.5	10.4 25.6	1.95 5.25	0.071 0.144	0.063 0.099	
	ь КN 19 а b	6.1 7.1	68.5 • 48.3	60.2 43.2	1.9 . 1.0	13.1 23.6	2.26 2.93	0.066 0.119	0.055	
	KN 20 a b KN 21 a	14.9 9.0 12.0	55.8 64.6 57.1	46.1 56.2	0.3 0.3	25.5 13.9 19.7	5.68 2.44 3.26	0.206 n.d.	n.d. n.d. 0.088	
	$\frac{b}{KN 22 a}$	11.0 22.8	65.6 67.1	57.2 n.d.	0.8 · 0.6	14.6 14.0	2.58 2.36	0.097 0.127	0.073 0.045	
	ь КN 23 а b	24.7 25.4 34.1	73.2 73.1 71.3	n.d. n.d. n.d.	0.8 0.7 1.0	10.8 12.7 11.5	1.99 2.06 1.98	0.378 0.328 0.199	0.015 n.d. 0.050	
	KN 24 a b KN 25 a	7.2	72.8	62.5 54 5	0.2	11.3	1.98	0.357	0.202	
	KN 26 a	24.9 65.5	73.4	61.7 47 1	0.6	9.9 14.6	2.10	0.068	0.056 n.d	
	ь KN 27 а b	45.4 82.7 No sample	75.0	71.8	1.1	6.8	0.89	0.027	0.020	
	KN 28 a b KN 29 a	9.8 38.3 20.6	56.5 •73.7	41.8	6.6 1 4	16.1 9 1	3.01 1.27	0.257	n.d. 0.041	
	KN 30 a KN 31 a	5.1 4.7	15.4	5.6	12	n.d.	4.78	0.250	n.d.	
	KN 32 a KN 33 a KN 34 a	3.5 2.8	>30.2	3.2	27	n.d.	5.15	0.201	n.d. ^{ź.}	
	KN 35 a KN 36 a KN 37 a	4.5	12.9	4.8	9.0 8.1	n.d.	4.19	0.360	n.d.	
	KN 38 a	1.3	712.0	4.0	0.1	n.u.	3.00	0.339	n.a. ,	

SUSPENDED MATTER CONCENTRATIONS AND COMPOSITION

The suspended matter concentration in dry weight per kg of seawater of the two size classes are listed in Table 2 along with the results of elemental and phase analyses as obtained from the analytical scheme shown in Figure 2. Based on these data the distribution patterns were constructed for the various biogenic phases with the exception of $CaCO_3$ (Fig. 10)-whose distribution is shown as relative concentration in wt.-% of dry suspended matter-all other phases are shown in absolute concentrations; i. e. wt./kg of seawater (Fig. 4, 5 and 8). In some instances data from only one size class were available and in others pooled samples were analyzed as indicated by brackets in Table 2.

This information was subsequently interpolated by comparison with adjacent samples and samples from the same latitude of the second transect. Such interpolation affected only samples to the north of the Polar Front. Between the Polar Front and the Antarctic Divergence sufficient material for complete analyses was recovered for each station and for each of the two size classes.

Total suspended matter concentrations of $> 50 \,\mu g \,kg^{-1}$ of the combined size classes >150 and $150-75 \,\mu m$ delineate the zone of high productivity between the Polar Front and the Antarctic Divergence (Fig. 4). Within this zone maximum concentrations of more than $100 \,\mu g. kg^{-1}$ indicate patchiness in standing stock distribution rather than continuous bands of extremely high productivity. This interpretation guided the contouring of the data; clearly though, concentrations of $> 50 \,\mu g. kg^{-1}$ are typical for the entire belt of maximum productivity of the Circumpolar Current. Concentrations between $20-50 \,\mu g \,kg^{-1}$ characterize the waters over the Campbell Plateau and a narrow transition zone between the less fertile subantarctic waters $(<20 \,\mu g. kg^{-1})$ over the Southwest Pacific Basin and the Polar Front. The same distribution pattern, although with concentrations exactly 20 times higher (Table 3) was observed by Lisitzin (1972), Lisitzin et al. (1966) and Bogdanov (1965). These concentrations were obtained by ultrafiltration through 0.7 µm filters and presumably represent the total suspended load. A similar factor (i.e. 15 times) is suggested for converting particulate load $>75\,\mu\text{m}$ in diameter to total load from comparisons of Lisitzin's work to the data recently obtained by Copin-Montegut (1978) from the Indian Ocean sector of the Circumpolar Current.

Organic matter

Of all the elements and phases analyzed, organic carbon shows the least fluctuations (Fig. 5). Lowest standing stocks of organic carbon ($< 2.5 \,\mu g. kg^{-1}$) are characteris-

Table 3

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Relationship between total standing stock $(>0.7 \mu m) > 0.45 \mu m)$ and concentrations of the coarse size class $>75 \mu m$; included for comparison are mass concentrations of a poorly defined group of size classes separated from surface waters by continuous centrifugation.

	Particle size (µm)				
Concentration in surface waters	>75 (µg.kg ⁻¹)	Suspensate (*) (µg.kg ⁻¹)	>0.7 (*) (µg.kg ⁻¹)	>0.8 (**) (µg.kg ⁻¹)	
Subantarctic waters:					
Campbell Plateau	20-50	_	1 000-2 500	-	••
SW Pacific Basin	<20	-	500-1 000	-	
SE Indian Ocean Polar Front:	-	<100	250- 500	- .	
SW Pacific Ocean	50-100	-	2 500-5 000	-	
SE Indian Ocean	_	100-200	500-1 000	150-200	· .

(*) After Lisitzin (1972) obtained by continuous centrifugation and ultra-filtration. (**) After Copin-Montegut, C. and G. (1978) obtained by filtration.



Figure 4

Suspended matter concentrations in $\mu g/kg$ of the combined size classes $>150\,\mu m$ and $75\text{-}150\,\mu m$ in diameter.

tic for waters north of the Polar Front overlying the southwest Pacific Basin. At the northernmost portion of the transect increased productivity of the relatively shallow waters overlying the Campbell Plateau was picked up. Maximum concentrations were again determined for the waters between the Polar Front and Antarctic Divergence with $>7.5 \,\mu g \, \text{C-org. kg}^{-1}$. The distribution pattern appeared less patchy than that of total suspended matter and has more continuous elongated features in the direction of the main water movement.

Total nitrogen co-varies closely with the organic carbon distribution pattern (Fig. 6). The elemental ratio of C-

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Figure 5

Suspended organic carbon concentrations in $\mu g/kg$ of the combined size classes $>150\,\mu m$ and 75-150 μm in diameter.

org : N-total is close to the Redfield ratio for total plankton of 106 : 16 in all samples; however, more nitrogen-rich samples were found north of the Polar Front than in the high productivity zone between the Polar Front and the Antarctic Divergence. This presumably reflects a change in zooplankton and phytoplankton abundance, whereby nitrogen-rich zooplankton dominate coarse size classes of particulates in waters north of the Polar Front. The lowest C/N-ratios are from samples highest in phytoplankton. Linear regression of all samples emphasizes the importance of



Figure 6

Total nitrogen and organic carbon contents of all suspended matter samples; the line indicates the C/N wt.-ratio corresponding to the Redfield ratio of C-org: N-org=106: 16; deviations from this value reflect varying proportions of zooplankton and phytoplankton north and south of the Polar Front, respectively. nitrogen-poor phytoplankton material in a positive Corg intercept of the relationship:

C-org =
$$4.43$$
. N_{total} + 3.05 ; $n = 39$, $r = 0.92$.

The C/N ratios are consistent with those reported for other size classes of total suspended matter from numerous studies (Anita *et al.*, 1963; Fraga, 1966; Chester, Stoner, 1974; Copin-Montegut, Copin-Montegut, 1978; among others).

In contrast to the carbon-nitrogen characteristics, the C/P ratios of coarse particulate matter vary widely (Fig. 7). The most pronounced feature is the strong depletion of P-org relative to carbon of all samples, with the mean atomic ratio being C-org : P-org = 106 : 0.3. As pointed out in the description of methods, this may be due to phosphorus leakage from phytoplankton cells during sampling, desalting or acid-treatment or may be a characteristic of coarse particulate matter. Knauer et al. (1979), however, also report significant P-depletion in coarse sediment trap material at rather shallow depths; i.e. C-org : P-org = 106 : 0.4 (at 50 m). In several instances the C-org/P-org atomic ratio of the Antarctic surface particulates approached 106:1, the value expected from the Redfield-Ketchum-Richards elemental relationships of plankton thus discounting possible sampling artifacts. The question is raised whether or not it is advantageous to partition total phosphorus into an organic and an inorganic fraction, since this is not an easy analytical task, is not standard procedure in plankton analyses, nor was taken into consideration when the characteristic elemental plankton composition was first established (Redfield et al., 1963).

In no instance, however, was an excess of phosphorus observed in the Antarctic surface particulates (i.e. Corg : P-org=106>1) which was reported by Copin-Montegut and Copin-Montegut (*op. cit.*). Their analyses were performed on total suspended matter (>0.8 μ m) thus including essentially all of the bacterial biomass. If these differences are not due to seasonal changes, it is possible that the C-org : P-org relationship is here





Organic phosphorus and organic carbon contents of all suspended matter samples; the low atomic ratio of C-org: P-org = 106: <0.3 reflects either P-depleted organic matter in coarse size classes >75 µm or is due to P-leakage during sample treatment.

strongly controlled by particle sizes, whereby the small size classes $(0.8-75\,\mu\text{m})$ are rich in organically-bound phosphorus and coarse particulates (>75 μ m) are depleted. This relationship cannot be further explored from the data presented here because of possible phosphorus leakage, but it warrants special consideration in future studies. Such size-controlled chemistry would strongly affect the phosphorus flux to the sea floor because of rapid transfer of large, phosphorus depleted particles.

Inorganic skeletal remains

High particulate SiO₂ of phytoplankton are confined to the fertile waters between the Antarctic Divergence and the Polar Front. Standing stocks there increase from $\sim 10 \,\mu g. kg^{-1}$ of SiO₂ to > 60 $\mu g. kg^{-1}$, where extremely high concentrations (> 100 $\mu g. kg^{-1}$) indicate patchiness in phytoplankton distribution and are contoured accordingly (Fig. 8). Waters overlying the southwest



Figure 8

Suspended silica concentrations in $\mu g/kg$ of the combined size classes $>150\,\mu m$ and $75\text{-}150\,\mu m$ in diameter.

Pacific Basin typically contain $<10 \,\mu g. kg^{-1}$ of suspended SiO₂ in the coarse size classes. The distribution within the fertile belt of surface water generally increases southward with decreasing temperature, an observation also reported by Copin-Montegut (1978). Comparison to their data from the Indian Ocean sector of the Circumpolar Current allows estimates of total particulate SiO₂ stock, i.e. silica fraction of particles > 0.45 μm in diameter and that contained in the larger size classes (75-

Table 4

Variations in SiO_2 -to-organic carbon ratios of different size classes of suspended matter and from different surface water masses.

Sample	Carbon (ng-at./l)	Silica (ng-at./l)	Size Class (µm)	$\frac{\text{SiO}_2}{\text{C-org}} \text{wt.}$
	Temperat	ure 5-7°C, Pol	ar Front	
C-M 1978 (*)	5113	103	> 0.8	0.1
KN9	123	8	> 75.	0.3
. 1	Femperature 3	-5°C, south o	f Polar Front	
C M 1079	(4555	305	> 0.8	0.3
C-M 19/8	120	95	> 75.	4.0
KN 11	256	118	> 75.	2.3
	Temperature	1-3°C, north c	of Divergence	
C-M 1978	3 523	1 4 3 8	> 0.8	2.0
KN 13	701	630	> 75.	4.5
KN 27	468	990	>150.	10.6

(*) Copin-Montegut, Copin-Montegut (1978).

 $150 \,\mu\text{m}$ and $> 150 \,\mu\text{m}$; Table 4). As a first approximation about one-half of the particulate SiO₂ is contained in the size classes $>75 \,\mu\text{m}$ and one-half in the classes $<75 \,\mu\text{m}$. A more pronounced effect, however, of particle size control on chemical composition, is revealed, comparing carbon and silicon contents from classe. $>0.8\,\mu\text{m}$ to those from classes $>75\,\mu\text{m}$ within three distinct bands of the highly fertile surface waters (Table 4). First, at the Polar Front (5-7°C) only about 3% of the total organic carbon and <10% of the total particulate silica are contained in the coarse size classes; second, in the temperature band (3-5°C) the respective elemental proportions increase from 3 to 6% for C-org and from 30-40% for SiO₂. Third, in the band of highest productivity $(1-3^{\circ}C) > 20\%$ of the organic carbon and >50% of the silica are found in the size class $>75\,\mu m$. These differences presumably reflect a zonation in the primary producers whereby larger marine algae with high silica requirements (diatoms) dominate the coldest and most recently upwelled waters near the Antarctic Divergence. With increasing temperature and aging of the water other marine algae, smaller in size and less heavily silicified (silicoflagellates) or with no silica requirements at all (dinoflagellates), become increasingly more important.

It is interesting to note that the suspended SiO₂ contents of the coarse size classes measured here are almost identical to those reported by Lisitzin (1966; 1972) for the total range of particle sizes whereas the bulk weights between coarse (>75 µm) and total (>0.7 µm) particulates differed by a factor of 20. Although the sampling and contour grid employed by Lisitzin *et al.* is much coarser than ours, it shows changes in SiO₂-contents from <10 µg.1⁻¹ to >10 µg.1⁻¹ at 60°S and from <100 µg.1⁻¹ to >100 µg.1⁻¹ at ~63°S.

Again, size control on chemical composition of particulate potentially has a strong effect on vertical flux of biogenous elements to the sea floor because of rapid transfer of large particles having a composition different from that of the bulk matter.



Figure 9

Calcium carbonate of suspended matter in % of dry weight for the combined size classes >150 μm and 75-150 μm in diameter.

Suspended calcium carbonate (Fig. 9) is also controlled by particle size and biological production in surface waters. Both the highest standing stock of suspended $CaCO_3$ (>2µg.kg⁻¹) and the highest wt.-% of CaCO₃ in the particulate matter are confined to a band between 55°-60°S just south of the Polar Front (3-7°C) and right over the deepest part of the southwest Pacific Basin. Again, it should be noted that in Figure 9 the relative concentrations of CaCO₃ are shown, whereas all other figures show absolute concentrations of constituents. The mean CaCO₃-content is >10 wt.-% for the size class >75µm, whereby on the average the fraction >150µm has about twice as much CaCO₃ than the fraction 150-75µm (Fig. 10). The results by Lisitzin (*op. cit.*) show the



Figure 10

Calcium carbonate content of individual size classes >150 μm (O) and 75-150 μm (Δ) in a composite N-S transect.

same narrow CaCO₃ band between $56^{\circ}-58^{\circ}S$, although based on one data point only. A second CaCO₃maximum – but less pronounced – was recorded in the smaller size classes further south ($65^{\circ}S$); there the CaCO₃-content of the small size class was equal to or even exceeded that of the large size fraction. We did not determine what taxa of carbonate secreting organisms are controlling this distribution. Undoubtedly, though, forams make up the coarse CaCO₃-maximum to the north and perhaps smaller cold-water forms the maximum in the south (Bé, 1969).

SUMMARY AND IMPLICATIONS

Proportions of the three major phases of particulates, organic matter, calcium carbonate and silica in the coarse size classes vary systematically with the surface water masses between New Zealand and Antarctica (Fig. 11).





Variations in phase composition of coarse suspended matter in circumpolar waters; N-S composite transect shows high biogenous silica in waters over the Campbell Plateau and between the Polar Front and Antarctic Divergence.

Suspended matter is high in silica (>40 wt.-%) in subantarctic waters over the Campbell Plateau and high in calcium carbonate over the southwest Pacific Basin. To the south organic matter is the dominant phase in subantarctic waters accounting for > 50 wt.-% of total particulates larger than 75 µm. In the surface waters between the Polar Front and the Antarctic Divergence two distinct bands were found in which SiO₂ dominates the standing stock. First, between 55° and 60°S, SiO₂ constitutes between 30-50 wt.-% with a substantial amount of CaCO₃ present (>10 wt.-\%). This zone is associated with the steepest temperature gradient immediately south of the Polar Front. Second, south of 60° S, SiO₂ continues to increase to >70 wt.-%, whereas $CaCO_3$ decreases abruptly to well below 5 wt.- %. Within the second band north of 64°S particulate SiO_2 appears evenly divided between coarse and fine size fractions whereas south of this latitude almost all the particulate SiO_2 is contained in the large size classes.

The C/N elemental ratios of organic matter reflect a change from dominantly phytoplankton matter (C : N = 106 : 12) south of the Polar Front to substantial proportions of zooplankton (C : N = 106 : 18) in subantarctic waters north of the Polar Front. Yet, generally they are quite close to those predicted by the Redfield ratios. The strong depletion of coarse organic matter in phosphorous, however, cannot adequately be explained as yet. It could possibly have resulted from preferred P-leakage during sampling and/or pretreatment of the samples.

Processes of element cycling in the ocean and accumulation of biogenous sediment constituents are both significantly affected by size control on element and phase compositions. As shown here for surface plankton from waters of the Circumpolar Current, skeletal phases – opal and $CaCO_3$ – dominate the coarse size classes and thus are preferentially transfered to the sediment. Organic matter and elements associated with it-phosphorus, nitrogen and trace constituents-are dominantly contained in the small size classes and are thus subject to more rapid recycling in the water column. Recent data from particle trap experiments in the deep ocean underline this phenomenon. Honjo (1980) reports a phase composition of this material at depth to be heavily weighted towards the skeletal constituents of opal and CaCO₃ and are more similar in general to the "coarse" particulate matter of surface waters than to the total standing stock. In short: quantification of biogenous sediment accumulation, although reflecting the general fertility pattern of surface waters, appears strongly controlled by size-sorting during vertical transit. More readily discernible and more detailed patterns between production of biogenous constituents in surface waters and their accumulation in the sediment record might become apparent when quantifying the "coarse" particle production and mapping its phase composition. Element recycling on the other hand may be more closely coupled to the composition of total standing stock. On a global scale the problems here are biological ones of species distribution of primary and secondary producers and their geographical variation, yet as a first approximation the silica-to-carbon relationship of plankton standing stock has widely been used to calculate biological silica fixation (Lisitzin, 1972; Heath,

1974; Wollast, 1974; DeMaster, 1979). Berger (1976) pointed out the problems with this approach and recently Copin-Montegut and Copin-Montegut (op. cit.) have emphasized that the commonly accepted conversion factor of SiO₂ opal: C-org=2.3 could possibly overestimate global biological silica fixation by > 20 times. This discrepancy appears to be also related to size-effects of plankton composition. Table 4 lists SiO₂/C-org wt.ratios as a function of particle size. It appears that the plankton analyses by Lisitzin (1972) represent the "coarse" size classes but are used globally to calculate total biological silica fixation. The "coarse" nature of Lisitzin's samples becomes plausible when considering the differences in standing stock measured by ultrafiltration and continuous centrifugation [Table 3 (Gordeev, 1963)]. Clearly the concentrations of suspended matter obtained by ultrafiltration from Lisitzin's work are comparable to those of Copin-Montegut, but Lisitzin's and Gordeev's separates from centrifugation correspond to our "coarse" particulate matter distribution. Therefore the "filterable" suspended matter and its composition should be coupled to primary carbon production to calculate SiO₂-fixation and not that of the coarse separates.

In conclusion then <u>total</u> standing stock of suspended matter may be coupled to the cycle of organic carbon to estimate globally rates of fixation of certain strongly biologically associated elements but characteristics of the <u>coarse</u> particulate standing stock are the controlling factor in accumulation of biologically conveyed elements in the sediment.

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