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BARIUM IN DEEP-SEA SEDIMENT: A GEOCHEMICAL PROXY FOR PALEOPRODUCTIVITY

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Abstract. We used sediment traps to define the particulate fluxes of barium and organic carbon and investigate the use of barium as a proxy for ocean fertility. Strong correlations between C_{org} and Ba fluxes indicate a link between upper ocean biological processes and barium flux to the seafloor. The ratio of organic carbon to barium decreases systematically with water depth. Data from 10 sites indicate that organic debris settling from the 200-m depth has a C_{org}/Ba ratio of approximately 200. The systematic decrease in this ratio with increasing water depth results from the simultaneous decay of organic matter and uptake of Ba in settling particles. This behavior provides additional evidence that the formation of barite in oceanic particles is a consequence of decomposition/uptake in microenvironments rather than the secretion of barite by specific organisms. The decrease of the Corg/Ba ratio with depth is greatest in the North Pacific followed by the equatorial Pacific and is lowest in the western Atlantic. Since this spatial pattern is consistent with the variations in the deep-ocean barium contents which increase along the path of bottom water flow from the Atlantic to the North Pacific, it suggests that the particulate barium uptake and flux is enhanced by higher barium contents in the intermediate and deep waters of the ocean. Consequently, we have combined our particle flux data with existing water column Ba data to define an algorithm relating new productivity, dissolved barium contents, water depth, and particulate barium flux. This relationship provides a basis of applying barium flux measurements in sediments to estimating new production. In order to use barium as an indicator of productivity, it will be necessary to evaluate inputs from hydrothermal and aluminosilicate sources and xenophyophors. The application of a sequential leach procedure to the trap material indicates that 50-70% of the Ba in settling particles is in the form of barite and the remaining is adsorbed or bound to carbonates. Normative analysis demonstrates that in nearshore areas the contribution of barium from aluminosilicate sources can dominate that from biogenic inputs. It appears that normative estimates of biogenic barium contents can be made with accuracy if less than 50% of the Ba is associated with aluminosilicates; i.e., is of terrigenous origin. Since diagenetic mobilization of Ba can occur in reduced and suboxic sediments, highly productive nearshore areas also are likely to be inappropriate sites to use Ba measurements as productivity indicators. Comparisons between the rain rates of particulate Ba to the seafloor and the burial rate indicate that approximately 30% of the Ba rain is preserved. Although the preservation factor does not appear to be constant, it may be possible to predict the extent of preservation from an empirical relationship with the mass accumulation rate. These observations indicate that measurement of Ba burial fluxes in sediments can provide quantitative information on the paleoproductivity of the oceans. Joining the relationship between barium rain and burial with the barium and organic carbon algorithm, we make estimates of the new production in the northern

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California Current during the last 18,000 years. This calculation suggests that new production was at least a factor of 2 lower at this site during the last glacial maximum.

INTRODUCTION

Since the discovery of fluctuations of calcium carbonate in equatorial Pacific cores [Arrhenius, 1952], there has been continuing discussion of productivity changes in the surface ocean due to changing global climate. The importance of oceanic productivity and the biogeochemical cycle of carbon in regulating global climate change has been reinforced by studies which have defined large ice age variations in atmospheric CO_2 [Berner et al., 1979; Delmas et al., 1980; Neftel et al., 1982; Barnola et al., 1987]. The observation of Shackleton and Pisias [1985] that the CO_2 changes preceded ice volume changes suggests that the CO_2 decrease is a forcing mechanism for rather than a response to glaciation. Studies of marine sediments, which indicate productivity changes during glacial and interglacial times [see Berger et al., 1989 and references therein], suggest that the ice age changes in atmospheric CO_2 arose primarily from perturbations in oceanic biogeochemical processes. These results demonstrate the usefulness of the marine paleoclimatic record in understanding of the Earth's climate system.

The search for chemical proxies for biological productivity preserved in deep-sea sediments has continued for many years. Concentrations of organic carbon, calcium carbonate, and opal have collectively and individually been used to infer past changes in biological productivity. These studies, while instrumental in focusing attention on the climate record contained within deep sea sediments, have all suffered from a common problem, distinguishing between preservation and productivity signals. Marine biological systems have evolved so that components and elements of critical life processes are easily recycled. For example, major nutrient elements, phosphorus and nitrogen, are rapidly and almost completely recycled within the water column. Bulk organic matter, opal, and $CaCO_3$ are recycled to varying degrees within the water column and within the sediment. Therefore any remaining productivity signal is highly diminished, filtered and biased.

In this paper we will explore the possibility that a more refractive chemical species, barium, is strongly linked to productivity—just as the variably recycled components, opal and calcium carbonate—and consequently exhibits more predictable preservation patterns. Chemical tracers of paleoproductivity and preservation, other than the major biogenic components, have not been extensively explored. The development of this approach is possible because of the recent widespread use of sediment traps, which is necessary to defining both the linkages to ocean productivity and the degree of preservation of any potential tracer. Through this approach we will evaluate: (1) the relationship between the flux of organic carbon and the flux of barium and evaluate the consistency of that relationship; (2) possible sources of barium which are not related to upper ocean productivity; (3) the degree to which barium is preserved in the sediments in a predictable manner. Assessing these issues will determine the usefulness of barium as a paleoproductivity proxy.

SAMPLES AND PROCEDURES

Data from sediment trap experiments conducted by our group between 1980 and 1988 form the basis for this paper. Sediment trap samples and fluxes were obtained by mooring sediment traps of the Oregon State University design, a single-cone modification of a trap originally developed by Andrew Soutar [Soutar et al., 1977]. It features all-plastic or all-fiberglass construction, a two-to-one height-to- diameter cone, a 1 cm x 5 cm baffle at the top of the cone, and a 10 cm-wide-lip at the top of the cone to limit turbulence at the mouth of the cone. The trap has evolved from a five-cup, sequential collector to the current model, which has a 15-cup collector for enhanced temporal resolution of the particle flux. In this study, however, we will report only average fluxes over the trap deployment intervals. In general, the deployment periods are for 1 year (Table 1), the minimum deployment necessary to encompass the known seasonal flux changes [Deuser and Ross, 1980].

Sodium azide concentrations of 15 g/L in the sample cups preserve the trap samples. Azide at these concentrations is an effective bactericide, and, because of the high alkalinity of the cup solutions, $CaCO_3$ tests (even aragonite) are very well preserved. Fischer [1984] discusses the sample preparation procedures in detail. Organic carbon was measured by sulfuric/dichromic acid evolution of CO_2 and detection with a Leco carbon analyzer [Weliky et al., 1983]. Instrumental neutron activation analysis was performed to measure of Ba and Al [Laul, 1979].

We report data for 10 sites (Figure 1; Table 1). Four are equatorial Pacific sites: H, M, S, and C. Flux data from sites H and M have previously been reported by Dymond and Lyle [1985], Murphy and Dymond [1984], Fischer et al. [1986], and Walsh et al. [1988a,b]. Data from sites C and S have been reported by Dymond and Collier [1988]. Another four are off the west coast of the United States: MFZ is a California Current site just north of the Mendocino Fracture Zone [Fischer et al., 1983]; Nearshore (NS), Midway (MW), and Gyre (G) form a California Current transect (42°N), which ranges from highly productive waters influenced by coastal upwelling to the relatively unproductive, North Pacific central gyre waters. The two other sites are

TABLE 1. Sample Locations and Carbon, Barium, and Aluminum Flux Data

Site	Latitude, °N	Longitude, °W	Water Depth, m	Date of Experiment	Trap Depth, m	Corg Flux, μg/cm2/yr	Ba Flux, μg/cm2/yr	Al Flux, μg/cm2/yr	Corg/Ba-bio*
Atlantic									
NAP	23.2	63.98	5847	Aug. 21, 1983 to	1464	46	0.7	25.8	96
				Sept. 27, 1984	4832	48	0.9	45.8	80
HAP-2	32.78	70.8	5410	July 9, 1981 to	1285	53	0.5	5.6	123
				June, 2, 1982	2835	60	0.9	13.0	77
					3985	58	0.8	15.4	84
HAP-4	32.73	70.82	5400	June 7, 1982 to	1285	62	0.6	10.4	120
				Apr. 28, 1983	2835	72	1.0	20.1	87
					3985	67	1.0	23.8	84
Equatorial Pacific									
M	8.83	103.98	3150	Sept. 12, 1980 to	635	91	0.8	1.5	109
				Oct. 23, 1981	1565	127	1.9	3.4	67
					2700	135	3.0	11.9	46
H	6.57	92.77	3565	Sept. 20, 1980 to	505	136	1.4	1.9	97
				Oct. 17, 1981	1465	189	3.6	6.3	54
					3075	113	3.3	6.6	35
S	11.06	140.14	4620	Dec. 29, 1982 to	700	114	1.3	1.4	88
				Feb. 14, 1984	1600	87	2.0	1.8	44
					2500	81	2.2	1.9	36
					3400	59	2.0	1.8	30
C-2	1.04	138.94	4445	Dec. 23, 1982 to	1095	108	1.7	1.0	63
				Feb. 24, 1984	1895	155	3.5	2.0	45
					2695	163	4.4	2.4	37
					3495	119	3.2	1.8	37
C-3	1.06	138.98	4450	Feb. 22, 1984 to	1083	196	3.3	1.9	59
				May, 1, 1985	1883	247	5.5	4.0	45
					2908	189	4.4	3.0	43
					3920	169	6.3	5.5	27
California Current									
MFZ-10	39.47	127.68	4233	Sept. 25, 1982 to	585	131	1.1	4.2	122
				Sept. 2, 1984	1235	107	2.8	21.8	41
MFZ-11	39.49	127.69	4230	Sept. 9, 1983 to	1235	59	1.65	14.9	38
				Sept. 1, 1984	2985	37	2.0	41.5	23
					3785	95	5.6	126.5	20
NS-1	42.09	125.77	2829	Sept. 22, 1987 to	1000	471	13.3	675.3	57
				Sept. 16, 1988	1750	469	16.2	768.8	45
					2329	498	15.1	857.0	57
MW-1	42.19	127.58	2830	Sept. 28, 1987 to	500	199	2.3	38.3	99
				Sept. 14, 1988	1000	230	4.5	110.2	63
					1750	211	7.3	165.6	35
					2330	178	7.1	167.8	30
G	41.55	132	3663	Sept. 25, 1987 to	1000	114	3.0	14.9	39
				Sept. 23, 1988	1750	153	2.9	20.0	56
					3164	64	3.0	15.6	23

*Ba-bio is computed by assuming the Ba/Al in nonbiogenic material is 0.0075.

in the western Atlantic: Hatteras Abyssal Plain (HAP) site is approximately 300 km off the east coast of the United States. Particle flux data from this site have been reported by Heggie et al. [1987]; the Nares Abyssal Plain (NAP) is a deepwater site in the western Atlantic [Thomson et al., 1984].

A number of studies that have demonstrated systematic relationships between measured primary

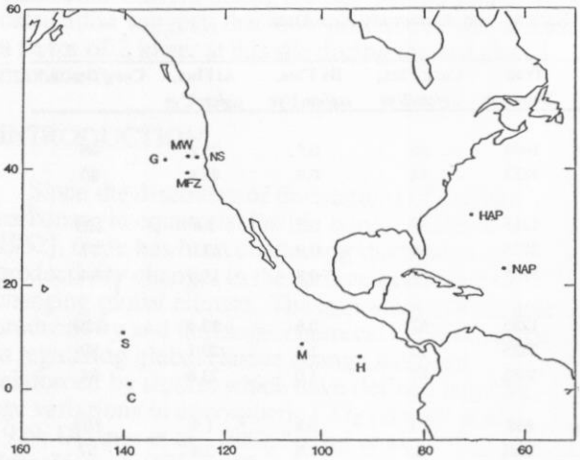

Fig. 1. Location of sediment trap experiments. Exact locations, depths, and date of the experiment is given in Table 1.

productivity and particulate organic carbon flux rates [Suess, 1980; Suess and Müller, 1980; Betzer et al., 1984; Lee and Cronin, 1984; Martin et al., 1987; Pace et al., 1987]. These results give us confidence that sediment trap data reflect ocean fertility. Our focus differs from these previous studies in that we do not attempt to relate tracer flux rates directly to primary productivity but rather to "export-productivity" and to the rain rate of organic carbon to the seafloor.

Sediment traps measure the export flux of organic carbon, which over long time scales approximates "new productivity"—the fraction of total primary production supported by the input of nutrients into the euphotic zone rather than by the recycling of nutrients from particulate organic matter within the euphotic zone [Dugdale and Goering, 1967; Eppley and Petersen, 1979]. This important shift in focus was also recognized by Sarnthein et al. [1988] for the organic carbon flux versus depth relationship. These authors combined an expanded set of sediment trap data and primary productivity estimates with a relationship between total and new primary production to predict the new production from the carbon flux data. Their predictive equation is as follows:

$$F_c = 20.563\ (P_{new})^{0.6648}\ z^{-0.5537} \qquad (1)$$

where P_{new} is the new productivity (which Sarnthein et al. equate to the export flux of carbon), F_c is the flux of organic carbon, and z is the depth in meters in the water column. Both F_c and P_{new} have units of $gCm^{-2}yr^{-1}$. The use of export productivity as a measure of ocean fertility avoids the problem that particulate carbon fluxes represent a poorly known fraction of total primary productivity [Eppley and Petersen, 1979]. Moreover, because the export flux of particulate organic matter over appropriate time scales must be balanced by an input of essential nutrients, new production is the net output of the system which is stimulated by physical oceanographic and meteorological forcing. Thus variations in new production may directly indicate climatic changes.

BARIUM AS A PRODUCTIVITY INDICATOR

In a normative model which identifies the major sources of deep-sea sediments, Dymond [1981] uses Ba contents to characterize a fraction of the sediments as a residue from dissolution and oxidation of hard and soft parts of carbonate and siliceous organisms. The model documents that for the variety of sediments types found on the Nazca Plate, which is in the eastern subtropical and equatorial portions of the Pacific, generally less than 10% of the Ba contents can be accounted for by contributions from hydrogenous, biogeneous, aluminosilicates, or hydrothermal components. At distances within 100 km of the spreading center, however, hydrothermal sources are significant. For most samples, greater than 90% of the sediment barium was proposed to be a residue of recycled biogenic material [Dymond, 1981]. The concept of barium as a "dissolution residue" of biogenic debris is compatible with earlier studies that indicated that indeed Ba has strong biogenic associations [Chow and Goldberg, 1960; Church, 1970] and with subsequent studies showing Ba to be taken up by sinking biogenic particles in the ocean [Bishop, 1988].

The nutrientlike distribution of dissolved Ba suggests biological cycling [Chan et al., 1976; Collier and Edmond, 1984], and Dehairs et al. [1980] provide evidence for the importance of biological processes in their study of suspended matter at GEOSECS stations. They find that the Ba in suspended particles is dominantly in the form of barite and so conclude that it formed in the upper water column by the breakdown of organic matter, release of Ba, and formation of barite in a microenvironment. More recently, detailed data on ocean particles collected by large volume filtration techniques [Bishop, 1988] indicate that barite forms in microenvironments by decomposition of organic matter and is not actively precipitated by haptophyte microalgae [Fresnel et al., 1979].

A comparison of particulate organic carbon and Ba fluxes measured with the OSU sediment trap system provides evidence for the utility of Ba as a productivity indicator (Figure 2). The strong correlation between the two variables for sediment traps deployed at different seasons and in different biological environments suggests that Ba is a potential proxy for productivity.

It might be argued, however, that the correlation of Ba with productivity is an artifact of filtering and packaging by zooplankton, which indiscriminately ingest Ba as part of the suspended load, and therefore has nothing to do with a productivity linkage. For example, strong correlations between

C_{org} and aluminosilicate [Honjo, 1982] and Al fluxes [Deuser et al., 1983; Jickells et al., 1984] have been previously demonstrated. Since the source of particulate Al is clearly nonbiogenic, does correlation between Ba and C_{org} necessarily indicate productivity? The dramatic contrast between Ba and Al (Figure 2 versus Figure 3) shows the difference between direct functional relationships and common carrier relationships. While the C_{org}/Ba values vary by less than a factor of 2, the site-to-site variations in the C_{org}/Al values vary by approximately 100. However, strong intersite correlations for Al and C_{org} are present. The common process which relates C_{org} and Al flux may well be zooplankton filtering; however, the quantity of available aluminosilicate debris is strongly dependent on the location and independent of productivity. Sites near continental sources or those with strong eolian fluxes, such as at our Nares Abyssal Plain site, have relatively low C_{org}/Al values.

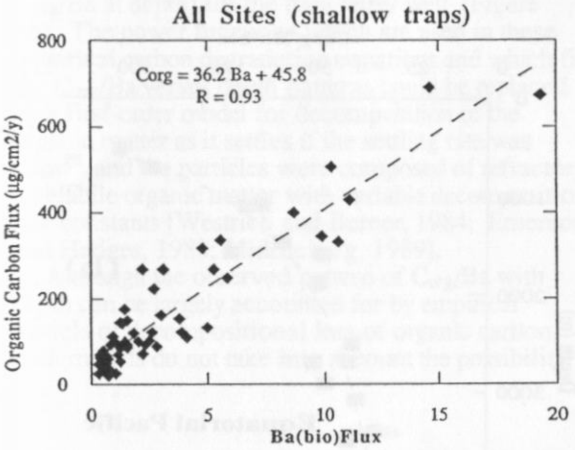

Fig. 2. The flux of barium versus the flux of organic carbon for the 10 sites shown in Figure 1. The data shown are for the seasonal sampling cups at each site; as a result two to six samples represent each site. Also, in order to minimize effects of different sample depths on the C_{org}/Ba values, only data from the shallowest depths at each site are shown. The depths range from 505-m to 1465-m depth. $Ba_{(bio)}$ flux is computed from the total barium by correcting for aluminosilicate barium assuming a constant Ba/Al in the aluminosilicate fraction. In most cases the $Ba_{(bio)}$ composes >90% of the total barium in the sample. Units are in $\mu g/cm^2/yr$.

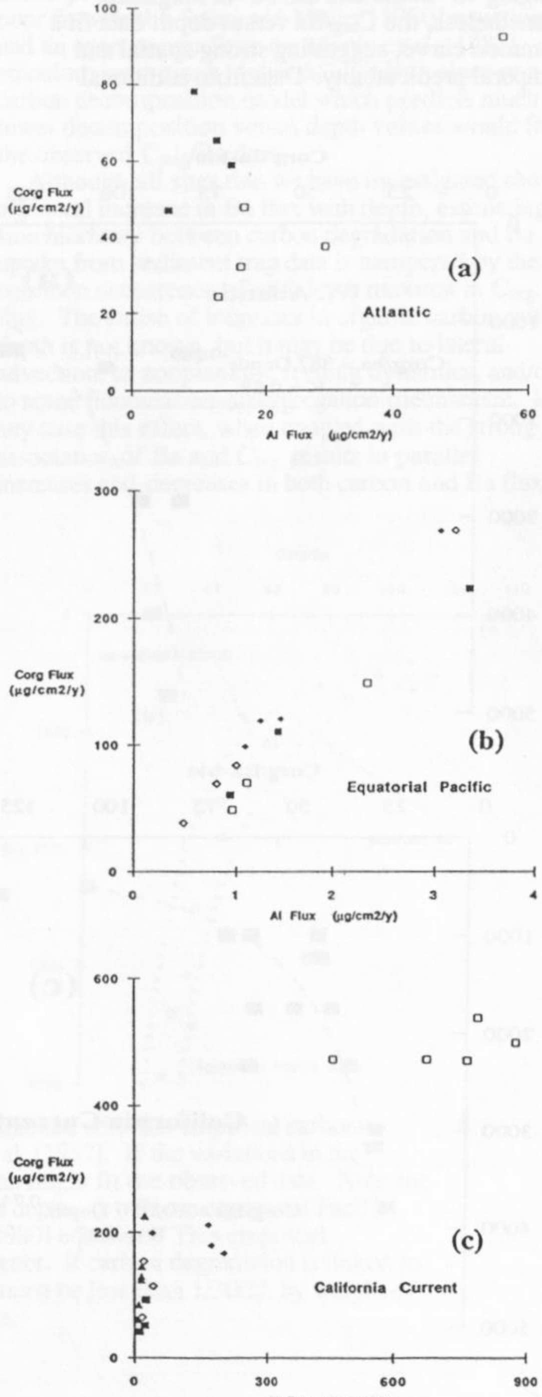

Fig. 3. Al flux versus C_{org} flux at all sites shown in Figure 1. The data shown are for the seasonal sampling cups at each site. Note the scales differ by more than 2 orders of magnitude in the different figures. In general, there is good correlation between the two variables at a single site, but no correlation if the data are considered for multiple sites. Seasonal cups are used and only the shallowest data from each site is used. (a) Data for the two Atlantic sites. Open squares are for the Nares Abyssal Plain (NAP); Filled squares are for the Hatteras Abyssal Plain (HAP). (b) Data for the four equatorial Pacific sites. (c) Data for the four California Current sites.

In addition to the strong correlation between C_{org} and Ba in oceanic particles (Figure 2) the C_{org}:Ba ratios in settling particles exhibit systematic changes with depth (Figure 4). All four equatorial sites fit nearly the same power function of C_{org}/Ba versus depth (Figure 4a), which indicates that the C_{org}/Ba value of particles leaving the euphotic zone is predictable. The equatorial Pacific traps were deployed in different years and at different locations ranging 10° in latitude and 50° in longitude. Nonetheless, the C_{org}/Ba versus depth data fit a common curve, suggesting strong spatial and temporal predictability. Data from additional deployments in the California Current and western Atlantic are fit by different power functions (Figures 4b and 4c). Power function curve fitting at the three sites results in predicted C_{org}/Ba values at 200-m depth that only varies between 185 and 200.

Water column measurements provide additional support for a common C_{org}:Ba ratio of approximately 200 in particles leaving the euphotic zone. The ubiquitous depletion of dissolved Ba in the euphotic zone can, on average, be accounted for by the removal of one Ba atom for every 3000 C atoms [Broecker and Peng, 1982], a value which is equivalent to a C_{org}:Ba weight ratio of 260.

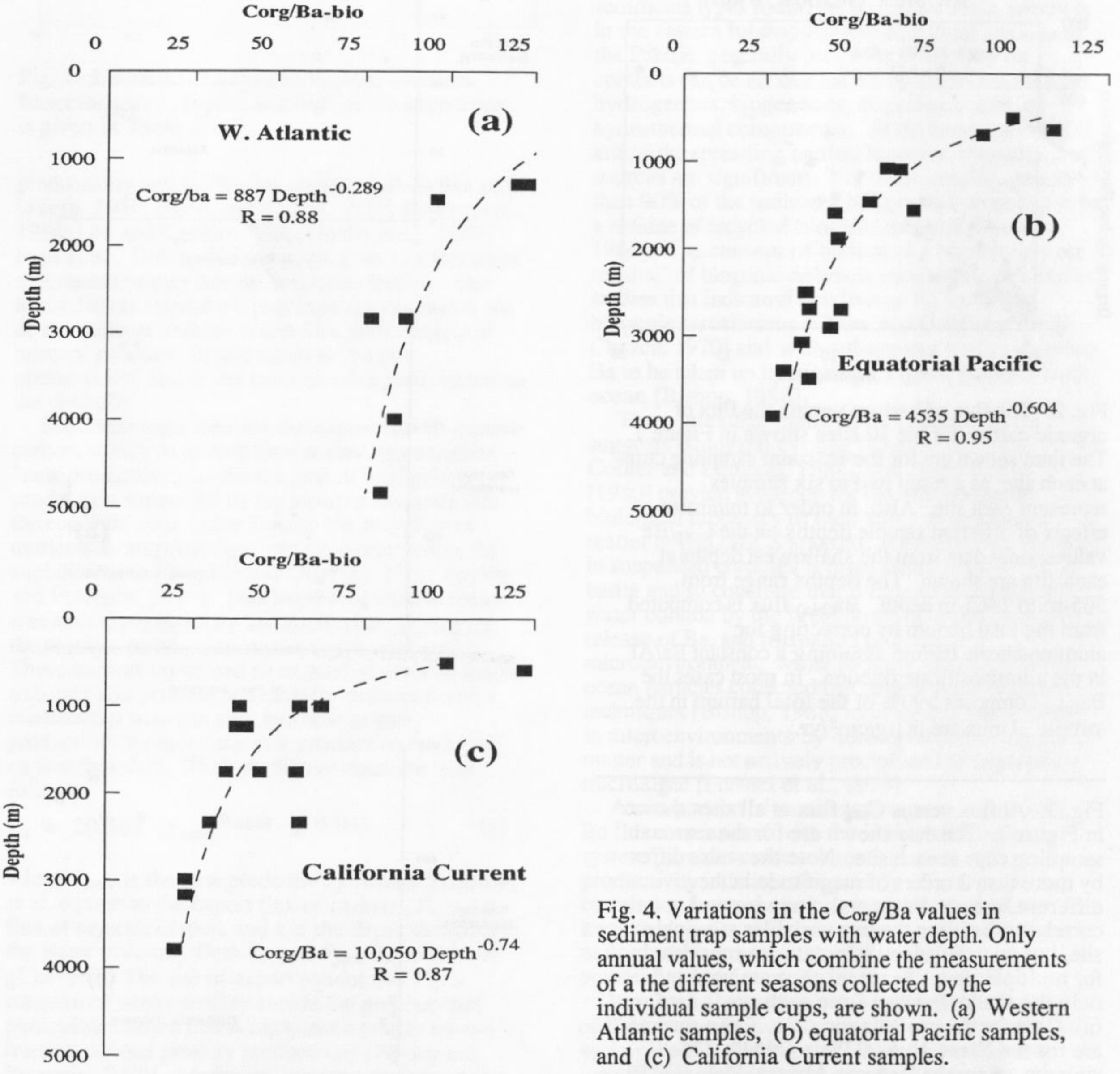

Fig. 4. Variations in the C_{org}/Ba values in sediment trap samples with water depth. Only annual values, which combine the measurements of a the different seasons collected by the individual sample cups, are shown. (a) Western Atlantic samples, (b) equatorial Pacific samples, and (c) California Current samples.

CONTROLS ON THE BARIUM CONCENTRATIONS AND C_{org}/Ba IN SETTLING PARTICLES

The systematics of the C_{org}/Ba relationship demonstrated by Figure 4 could be accounted for by the degradation of organic carbon with depth and by the conservative behavior of barium fixed in the upper water column. In Figure 5 we compare two empirical carbon degradation equations with the C_{org}/Ba data from the equatorial Pacific. The Martin et al. [1987] equation (Figure 5a) underestimates the ratio at depth, whereas the Suess and Müller [1980] equation (with some suggestion of overestimation of C_{org}/Ba at depth) fits the data fairly well (Figure 5b). The power functions which are used in these empirical carbon degradation equations and which fit the C_{org}/Ba versus depth patterns could be replaced by a first-order model for decomposition of the organic matter as it settles if the settling rate was known and the particles were composed of refractory and labile organic matter with variable decomposition rate constants [Westrich and Berner, 1984; Emerson and Hedges, 1988; Middleburg, 1989].

Although the observed pattern of C_{org}/Ba with depth can be largely accounted for by empirical models of decompositional loss of organic carbon, such models do not take into account the possibility of Ba addition during the settling and decomposition of organic carbon. Our data document, however, that the decrease in C_{org}/Ba is a result both of a decrease in the flux of organic carbon (Figure 6a) and of an increase in the flux of Ba (Figure 6b) with increasing depth. For the example shown in Figure 6 we estimate an average $\Delta C_{org}/\Delta Ba$ over the depth interval shown to be approximately 70 on a weight-weight basis. This stoichiometry for carbon decomposition to Ba addition would result in a very poor fit with the Suess and Müller [1980] equation and an even poorer fit to the Martin et al. [1987] equation; only much higher $\Delta C_{org}/\Delta Ba$ values or a carbon decomposition model which predicts much lower decomposition versus depth values would fit the observed C_{org}/Ba data.

Although all sites that we have investigated show a general increase in Ba flux with depth, estimating a stoichiometry between carbon degradation and Ba uptake from sediment trap data is hampered by the common occurrence of mid-depth maxima in C_{org} flux. The cause of increases in organic carbon with depth is not known, but it may be due to lateral advection, to zooplankton feeding dynamics, and/or to some flocculation-disaggregation mechanism. In any case this effect, when coupled with the strong association of Ba and C_{org}, results in parallel increases and decreases in both carbon and Ba flux

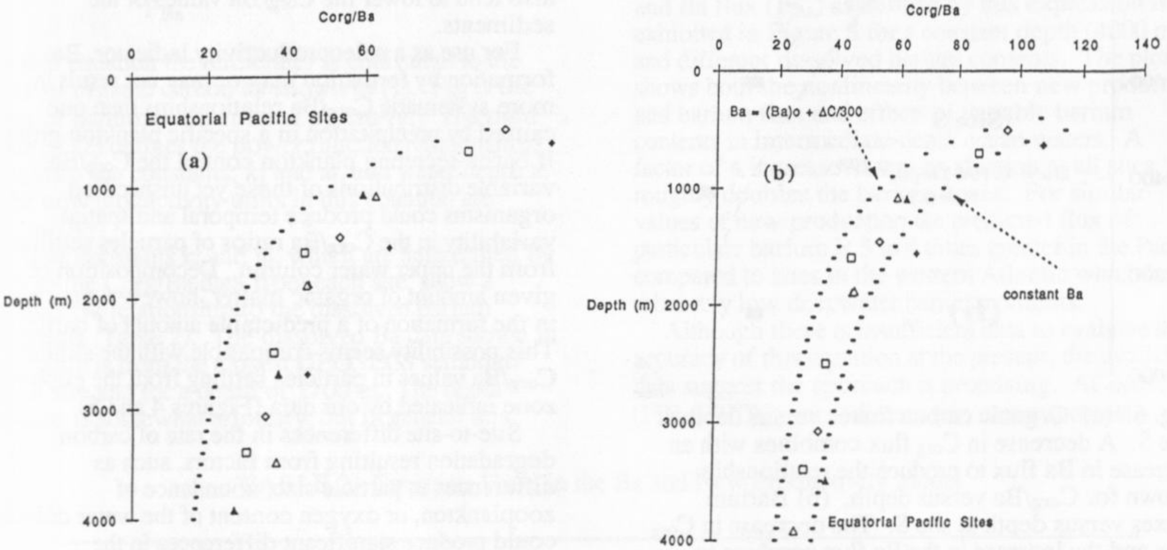

Fig. 5. (a) Equatorial Pacific C_{org}/Ba values exhibited with the empirical carbon degradation equation (dashed line) of Martin et al. [1987]. If the variations in the C_{org}/Ba were due to C_{org} loss alone, the equation might fit the observed data. Note the equation underestimates the C_{org}/Ba values with depth. (b) Same equatorial Pacific data, but exhibited with the Suess and Müller [1980] equation. This empirical relationship fits the observed variations much better. If carbon degradation is linked to Ba uptake [Bishop, 1988], the barium addition must be less than 1/300th by weight of the C_{org} loss to still fit the equatorial Pacific data.

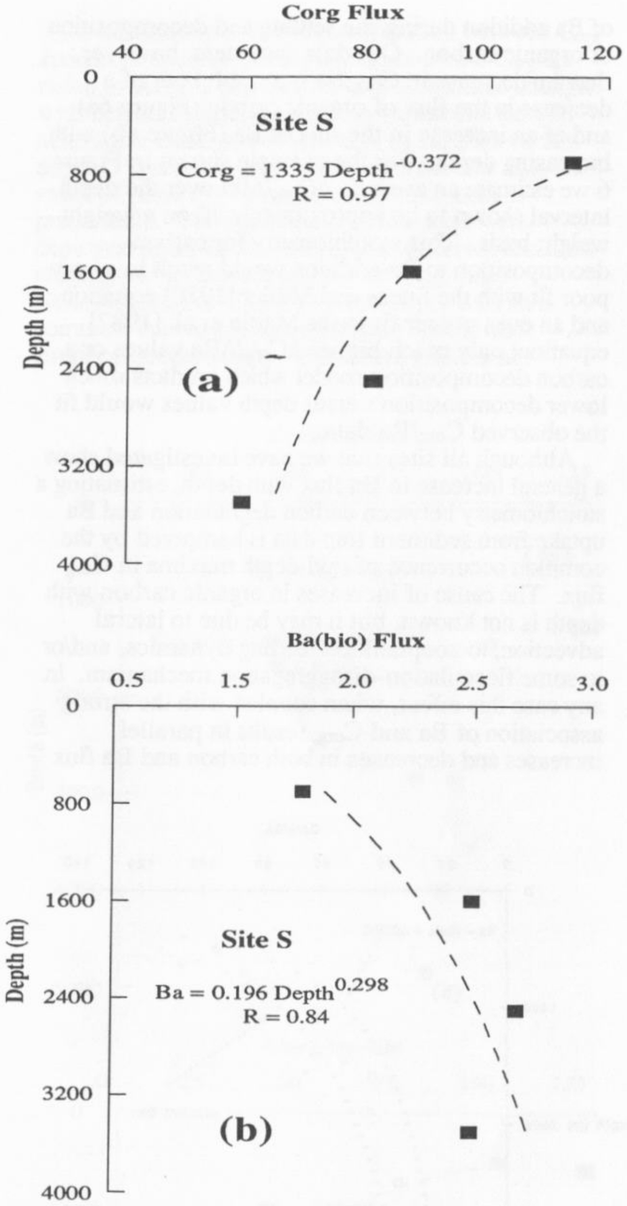

Fig. 6. (a) Organic carbon fluxes versus depth at site S. A decrease in C_{org} flux combines with an increase in Ba flux to produce the relationship shown for C_{org}/Ba versus depth. (b) Barium fluxes versus depth at site S. The decrease in C_{org} flux and the increase in the Ba flux combine to produce the C_{org}/Ba-depth relationships show in Figures 4 and 5. Flux units are in µg/cm²/yr.

with depth for many profiles, rather than an expected C_{org} flux decrease and an associated Ba flux increase.

Consequently, although we cannot define the specific processes which result in the observed systematic decrease in the C_{org}/Ba with depth, it appears to be both a consequence of carbon degradation and of Ba addition with depth. These observations are further evidence for the continued formation of barite by decomposition in a microenvironment [Dehairs et al., 1980; Bishop, 1988] rather than through formation by barite-secreting organisms.

Von Breymann et al. [1989] also suggest that syngenetic formation of barite during settling/aging of biogenic particles, as proposed by Bishop [1988], can account for the low concentrations of barium in shelf deposits as compared to slope and abyssal plain deposits. The shelf deposits, which have equal or greater concentrations of organic matter, are conspicuously poor in barium and have C_{org}/Ba values of 200 compared to values of 20 to 50 on the middle slope. Von Breymann et al. [1989] suggest particle settling and decomposition throughout the greater slope depths result in more barium uptake by the organic debris. Our sediment trap data (Figure 4) show systematic decreases in C_{org}/Ba from values of approximately 200 to values of < 50 at depths >3000 m. While this pattern could account for the observed differences in C_{org}/Ba values of the shelf versus the slope, variations in the preservation of C_{org} that are related to differences in mass accumulation rate [Dymond and Lyle, 1992] could also influence the sediment C_{org}/Ba values. Thus enhanced preservation of organic carbon in rapidly accumulating shelf and upper slope sediments would also tend to lower the C_{org}/Ba values of the sediments.

For use as a paleoproductivity indicator, Ba formation by formation may or may not result in more systematic C_{org}/Ba relationships than one caused by precipitation in a specific plankton group. If barite-secreting plankton control the C_{org}/Ba, variable distributions of these yet unspecified organisms could produce temporal and spatial variability in the C_{org}/Ba ratios of particles settling from the upper water column. Decomposition of a given amount of organic matter, however, may result in the formation of a predictable amount of barite. This possibility seems compatible with the similar C_{org}/Ba values in particles settling from the euphotic zone indicated by our data (Figures 4 and 5).

Site-to-site differences in the rate of carbon degradation resulting from factors, such as differences in particle size, abundance of zooplankton, or oxygen content of the water column, could produce significant differences in the relationship between C_{org}/Ba and water depth. In addition, the Ba uptake through the decomposition process may be dependent on the Ba content of the water through which decomposing biogenic debris settles. Barium follows a typical nutrient profile with greater Ba contents in deep water and increasingly higher Ba contents along the flow path of bottom water through the Atlantic and into the Pacific and North Pacific. Consequently, the amount of Ba uptake for a given carbon degradation may be greater in the Pacific than in the Atlantic. Our data are compatible with this suggestion (Figure 7) because the curvature of the C_{org}/Ba with depth follows the pattern of the North Pacific (MFZ) > equatorial Pacific > Atlantic (HAP).

These results appear to be compatible with a model in which Ba is removed from the upper two kilometers of the ocean by barite precipitation that is associated with particulate organic matter decomposition. Dissolution of barite and diagenesis of labile barium-enriched particles at the sediment-water interface would release barium to deep ocean water. In this way barium behaves like Si and alkalinity which are removed by carbonate and opal-bearing species in the upper water column and returned to seawater through dissolution which primarily occurs at the seafloor.

Despite the variability in the relationship between C_{org}/Ba and water depth, we propose an algorithm to predict new production from the Ba flux and a knowledge of the dissolved Ba contents at each of these three oceanic environments. We begin by substituting the organic carbon flux predicted by equation (1) into the power function relationships used to fit the C_{org}/Ba versus depth relationships shown in Figure 7. This substitution yields the following equality:

$$\frac{2056\ (P_{new})^{0.6648}\ z^{-0.5537}}{F_{Ba}} = k_i\, z^{a} \qquad (2)$$

In this equation the numerator is equivalent to the flux of organic carbon as shown in (1). F_{Ba} is the flux of barium (with units of μg/cm²/yr) The right side of (2) defines the power function relationship between the constants, k_i and a_i, and water depth z. The new productivity units in this equation are gC/m²/yr.

The constants k_i and a_i, which are determined by fits to the Corg/Ba data from each site, show a consistent relationship to the dissolved barium contents (Table 2). The dissolved Ba data shown in the table is from the closest GEOSECS station to each site and for a depth of 1700 m. The depth choice is somewhat arbitrary, but in general this depth maximizes the differences in the dissolved Ba contents between the three sites. The choice seems plausible because it is deep enough to characterize the first-order differences between these ocean basins based on ventilation age but is also shallow enough for the downward flux of organic particles to acquire their major barium contents.

Hence general expressions for k and a can be obtained by fitting the respective values for k_i and a_i defined by Figure 7 to the dissolved Ba contents estimated from GEOSECS barium data. Using the category of fit with the highest statistical significance, as the best approximation, yields the following:

$$k = 0.171\ \mathrm{Ba}^{2.218} \qquad (3)$$

$$a = -0.0774 - 0.00478\ \mathrm{Ba} \qquad (4)$$

Substituting these expressions into (2), the flux of particulate biogenic barium as a function of depth, new production, and dissolved Ba contents is as follows:

$$F_{Ba} = \frac{2056\ (P_{new})^{0.665}\ z^{-0.476 + 0.00478\,\mathrm{Ba}}}{0.171\ \mathrm{Ba}^{2.218}} \qquad (5)$$

The relationship between new production (P_{new}) and Ba flux (F_{Ba}) as defined by this expression is exhibited in Figure 8 for a constant depth (4000 m) and different dissolved barium contents. The plot shows both the nonlinearity between new production and barium flux and effects of variable barium contents in intermediate-depth ocean waters. A factor of 4 increase in new production at all sites roughly doubles the barium fluxes. For similar values of new production the predicted flux of particulate barium is 3 to 4 times greater in the Pacific compared to sites in the western Atlantic which have relatively low deepwater barium contents.

Although there is insufficient data to evaluate the accuracy of this equation at the present, the available data suggest the approach is promising. At site C (1°N, 139°W) our sediment trap measurements

TABLE 2. Constants Used in the Ba and New Productivity Model

Location	Ba, (μm/kg†)	k_i	a_i
Western Atlantic	50	1,003	-0.3045
Equatorial Pacific	110	5,761	-0.6361
California Current	145	10,633	-0.7504

† Data from nearest GEOSECS station to the mooring sites. Values shown are from 1700-m depth [GEOSECS, 1987].

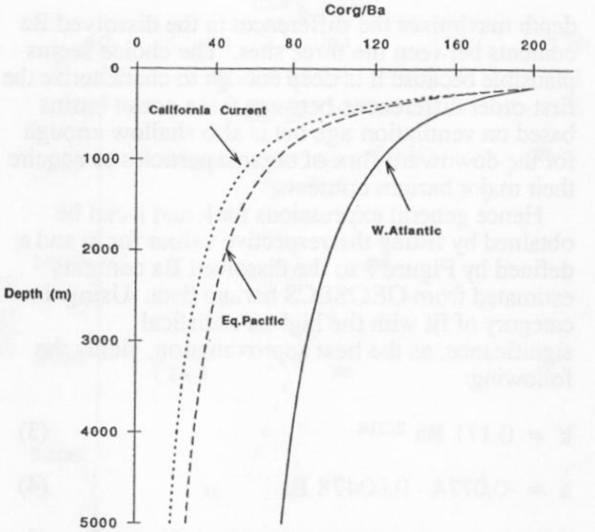

Fig. 7. A comparison between the best fit lines for C_{org}/Ba versus depth in trap samples from the three primary areas studied. In contrast to Figures 4a-4c, the power function fits have been forced through a Corg/Ba value of 200 at a water depth of 200 m. There are systematic variations in the rate of decrease in the C_{org}/Ba values with depth. The decrease for the California Current > equatorial Pacific > Atlantic. This pattern follows the increase in Ba in deep waters and could be a consequence of enhanced barite formation in the more Ba-enriched waters. The relationship between Corg/Ba and depth for each site is as follows: Western Atlantic — Corg/Ba = 1,003 $z^{-0.3045}$; equatorial Pacific — Corg/Ba = 5,761 $z^{-0.6361}$; California Current — Corg/Ba = 10,633 $z^{-0.7504}$.

indicate a flux of particulate barium to the bottom (4445 m) of 5 μg/cm²/y, which indicates a new production of 28 gC/m²/y from (5). This value lies within the range of estimates of new production made for this location. Berger et al. [1988] suggests a value of 6 to 9 gC/m²/y for the site based on their synthetic productivity map and an export flux at 200 m of 0.1 times the total primary production. Chavez and Barber [1987] suggest an average new production of 77 gC/m²/yr for the equatorial Pacific based on a number of primary productivity measurements and a f ratio of 0.44. For the California Current sites our estimate of new production decreases systematically from the Nearshore site, which is strongly influenced by coastal upwelling, to the Midway site (220 km from the coast), and the Gyre site. Equation (5) predicts a new production at Nearshore of 93 gC/m²/y. Midway is predicted to be a factor of 5 lower (18 gC/m²/y), and Gyre is another factor of 5 lower (4 gC/m²/y). These decreases seem reasonable from what is known about the general oceanography along the transect; however, we can only compare these estimates with a few single-point measurements made by P. Wheeler (personal communication, 1991) at each of the sites. These data reveal a range of measured new production across the Multitracers Transect that varies between 48 and 240 gC/m²/y. These values are higher than our predictions, however, the measured new productions were made in late summer, at a time of peak coastal upwelling and high light levels. The barium-based estimate is for an integrated annual value of new production.

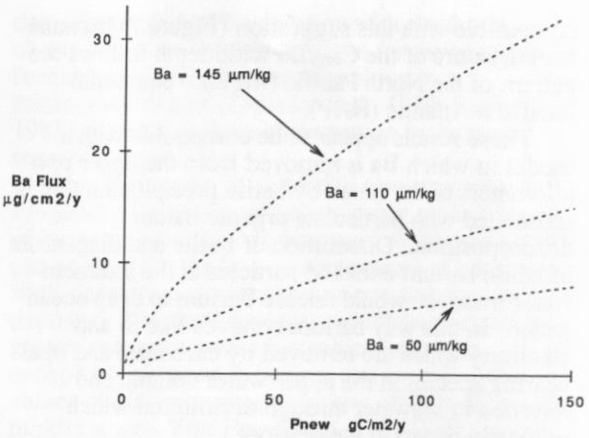

Fig. 8. Barium flux (F_{Ba}) as a function of new production (P_{new}) as computed by (5). The lines shown are for the flux at a constant depth of 4000 m. The three lines define the effects of different mid-depth barium contents on the barium flux. The water column barium contents chosen in this example are those estimated from GEOSECS data at the three general oceanic regions where we have data.

MULTIPLE Ba CARRIERS

Introduction

Barite has been shown to be an important carrier of the barium found in oceanic particulate matter. As discussed above, overwhelming evidence indicates that this phase forms syngenetically after the suspended load leaves the euphotic zone. The usefulness of C_{org}/Ba relationships as paleoproductivity indicators depends on whether the syngenetically formed barite is the predominant contribution to the barium flux and there is little postdepositional mobilization of barium. Since sediment pore waters are saturated with respect to barite [Church and Wolgemuth, 1972], good preservation of this phase in oxic and suboxic sediments is possible. Anoxic sediments, however, with any degree of sulfate reduction would not be suitable for paleoproductivity reconstructions from Ba accumulation.

TABLE 3. Selective Leaching Results on Sediment Trap Samples

	Depth, m	% Ba Acetic Acid	% Ba NH_2OH-HCl	% Residual
Site H	505	43	0	57
	1465	37	0.5	63
	3075	30	0	70
	3414*	24	15	61
Site M				
	1565	42	0	58
	2883*	22	30	48

* These samples are within the resuspension zone [Walsh et al., 1988].

Selective leaching [Wefer et al., 1982] tentatively established that both an acid-soluble and a refractory Ba phase existed in settling particles of the Drake Passage. We have refined this method of characterizing forms of barium in settling particles by using multiple sequential leachings on selected samples from sites M and H. The procedure [Lyle et al., 1984; Robbins et al., 1984] subjects trap samples to a pH 5 acetic acid extraction in order to remove adsorbed and calcite-bound elements, then to a pH 9 sodium dodecyl sulfate extraction to remove organically bound elements, and a final treatment with a pH 5 hydroxylamine hydrochloride solution to remove elements bound by poorly crystalline ferromanganese oxyhydroxides. Refractory or residual barium is determined as the difference between total Ba (measured by dissolution of a separate split with HF-HNO_3) and the sum of the three partial extractions. Table 3 lists the results of this sequential extraction for two of the equatorial Pacific trap sites. Because the level of Ba was undetectable in the organic extraction, this data column is omitted.

Barium in sediment trap materials is almost exclusively in two forms: the adsorbed/calcite-bound extract (22-43% of total Ba) and the residual (48-70% of total Ba). Only near the bottom, where resuspension becomes important [Walsh et al., 1988a], is there significant oxyhydroxide-associated barium. On the basis of typical Ba/Al values of aluminosilicate material we can partition the residual Ba in sediment trap samples into an aluminosilicate fraction and a barite fraction. The aluminosilicate fraction is typically 1-2% of the total, except for the two deepest samples, which have more aluminosilicate barium because of the contribution by resuspension. The adsorbed/calcite bound fraction of the barium is similar to the nonbarite fraction estimated by Dehairs et al. [1980] and to the soluble Ba estimated by Wefer et al. [1982] in suspended particles and in trap material, respectively. Both groups of researchers found the mass of refractory barite to account for 75±20% of the total barium.

The observation that significant barium is associated with the hydrated oxide fraction of the sediment samples suggests that the Ba concentrations in sediments may be affected by redox mobilization of sediments. This issue will be discussed more completely below.

Other Sources of Barium

Although our data seem to suggest particulate Ba fluxes are dominated by biogenic sources, other sources may contribute significantly to the Ba that is preserved in deep-sea sediments. We will consider the following: (1) the role of detrital aluminosilicates as barium carriers, (2) hydrothermal precipitates as a source for barium, (3) secretion by a group of benthic organisms, (4) diagenetic mobilization and loss from anoxic sediments, and (5) effects of suboxic diagenesis on preservation. Future studies which apply barium as a paleoproductivity indicator will require more detailed study of each of these topics.

Detrital aluminosilicates contain 300 to 1000 ppm Ba, comparable to the content (1000-2000 ppm) we observe in trapped particles from regions of the ocean dominated by biological debris. Since barium in aluminosilicate material is likely to be preserved during burial, this source could dominate the preserved Ba flux in some regions of the ocean. For example, normative chemical analysis [Dymond, 1981] indicates that sediments from the eastern Nazca plate are composed of more than 90% detrital aluminosilicate. Approximately two thirds of the Ba contained in these sediments is detrital, with the rest of the Ba being of biological origin. In contrast, more than 90% of the barium in sediment samples collected from more than 500 km from the South American coast has a biogenic origin [Dymond, 1981]. Similarly, normative analyses of sediment trap data collected at a site located at the base of the slope at 42°N latitude in the California Current indicate as much as 50% of the total barium is associated with aluminosilicates. In contrast, more than 95% of the barium in samples from a trap mooring at the same latitude but 600 km from the coast is biobarium. These data suggest that for most of the pelagic environments of the world's ocean, aluminosilicate barium in sediments will be insignificant. In nearshore areas and at other sites with strong inputs of continental debris, however, the preserved barium signal in sediments may be strongly influenced by aluminosilicates.

Although we have no definite solution unraveling aluminosilicate contributions, several approaches seem promising. Since the biogenic Ba seems to be predominantly in the form of barite [Dehairs et al., 1980], quantitative mineralogical analyses might distinguish between the nonbarite forms of Ba, which predominate in detrital sources to the sediments. Alternatively, normative analysis of bulk sediment chemical compositions [Dymond, 1981; Leinen and Pisias, 1984; Dymond et al., 1984] could define the aluminosilicate contribution. For example,

$$Ba_{(bio)} = Ba_{(total)} - (Al \times Ba/Al_{aluminosilicate}) \qquad (6)$$

This equation assumes that all the aluminum in sediments is of aluminosilicate origin and that the $Ba/Al_{aluminosilicate}$ ratio can be estimated independently. Various compilations of elemental abundances in crustal rocks [Taylor, 1964; Rösler and Lange, 1972] suggest that the Ba/Al of aluminosilicate detritus should range between 0.005 and 0.01. If one assumes an average value of 0.0075, this degree of uncertainty could produce approximately ±15% error in a sample with 30% aluminosilicate barium, ±50% error with 50% aluminosilicate barium, and nearly a factor of 10 uncertainty with 75% aluminosilicate. Consequently, to define the biobarium by normative analysis in sites with abundant aluminosilicate sources would require accurate knowledge of the composition of the aluminosilicate source or sources.

The influence of a normative aluminosilicate correction on the biogenic Ba accumulation rate in sediments is illustrated by data from cores taken along the Multitracers transect across the California Current (42°N). The Nearshore site is 120 km from shore and receives large quantities of detrital aluminosilicates, while the Midway site (270 km) and the Gyre site (630 km) receive significantly less terrestrial input. Since independent measurements of opal and marine organic carbon indicate that primary productivity has doubled from the last glacial maximum to the present (M. Lyle et al., Paleoproductivity and carbon burial across the California Current: The Multitracers transect, 42°N, submitted to Paleoceanography, 1992), increases in Ba accumulation rate over this interval are expected. A clear increase in Ba accumulation rate over the past 15 ka are apparent for the Midway and Gyre sites, regardless of the Ba/Al value used in the normative correction (Figure 9). At the Gyre site the aluminosilicate correction is minor. Nearer to the coast, at Midway, the correction is larger but still does not change the shape of the curve. At Nearshore, however, the correction can change the interpretation completely (Figure 9). With no correction the Ba flux dropped by about a third from the glacial to the interglacial period. Different aluminosilicate Ba/Al corrections can either flatten the curve or reverse its slope. It appears that the aluminosilicate contribution to the total Ba flux is larger in sediments older than 15 ka.

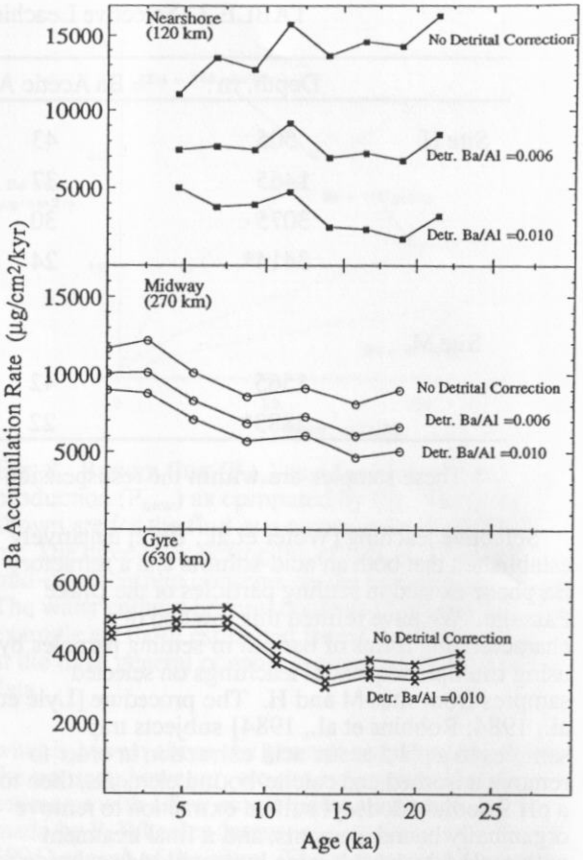

Fig. 9. Barium burial rate in sediments at the three Multitracers sites which comprise a transect across the California Current at 42°N. The effects of different Ba/Al values for computing the biological Ba (using equation (6) are shown for different depths (ages) in the cores. Because the aluminosilicate contribution for the Nearshore site is approximately 50% of the total Ba, the assumed Ba/Al value has a large effect on the computed biological Ba.

Mineralogical analyses may not help to distinguish between hydrothermal and biogenic barite, since barite is a common precipitate from hydrothermal solutions. Nonetheless, hydrothermal Ba may pose a problem only near venting sites. For example, the Ba in sediments deposited within 100 km of the East Pacific Rise, is on average only 19% from hydrothermal sources [Dymond, 1981]. Sediments in the basins adjacent to the Rise Crest, contain less than 5% hydrothermal barium, in spite of the fact that they are dominated by iron and manganese oxyhydroxides of hydrothermal origin. Normative analyses can be used to distinguish between hydrothermal and biobarite [Dymond, 1981].

Another possible source of barium in sediments is a peculiar group of barite-secreting deep-sea benthic organisms known as xenophyophorans. This phylum of protozoans produces fossilizable barite crystals in large quantities [Schulze, 1905; Tendal and Gooday, 1981]. The organisms are widely distributed in the deep sea, particularly in equatorial Pacific sediments, and it is unclear whether their barium sulfate crystalites differ from those forming from organic matter decay and what quantities they generate. Jumars et al. [1989] speculate that the population of xenophyophorans might depend on the flux of particulate debris arriving at the seafloor. Their production of biobarite might therefore augment the barium flux from the euphotic zone. The significance of this potential source remains unclear.

Diagenetic Redistribution

The degree of saturation of bottom water and pore fluids with respect to barite is the first-order parameter controlling mobilization and redistribution of Ba in sediments. Undersaturation therefore may obliterate the paleoproductivity signal. In pelagic sediments interstitial, dissolved sulfate rarely deviates from that of normal oceanic waters. This maintains the barite saturation and minimizes Ba remobilization. Such an environment is best suited for Ba-based paleoproductivity studies.

In hemipelagic sediments, where sulfate reduction is common, Ba mobilization and diagenetic redistribution are inevitable. A diagenetic Ba front forms at the base of the sulfate zone [Brumsack and Gieskes, 1983; von Breymann et al., 1989] in the anoxic sediments that underlie coastal-upwelling productivity in the Gulf of California and in the Peru margin. Thus the use of barium as a paleoproductivity indicator in nearshore deposits is limited not only by uncertainties in the aluminosilicate contribution but also by remobilization of biobarite. Deposits from these environments should not be used for paleoproductivity reconstruction using Ba accumulation.

Redox mobilization of manganese oxyhyroxides, which results from organic carbon burial under suboxic conditions, could also affect the preservation of barium in sediments. This process commonly results in a near-surface enrichment of manganese oxyhydroxides. These phases typically contain 1000-2000 ppm of barium [Dymond et al., 1984]. Our observation, noted above, that approximately 30% of Ba in surface sediments is removed by a hydroxylamine hydrochloride leach, documents the significance of these phases in sediments. The surficial Mn enrichment can be a steady state feature which migrates upward with sediment deposition and, which in this case, would not affect the preserved barium signal, unless surficial manganese enrichments enhanced the barium preservation factor over that found in totally oxidized sediments. Under conditions of changing carbon rain rate, however, a surficial Mn enrichment can become buried and produce strong downcore variations in manganese concentrations [Finney and Lyle, 1988]. These situations could obscure the strictly biogenic barium signal preserved in the core and complicate a paleoproductivity interpretation.

Application of Barium Fluxes for Defining Paleoproductivity

Estimating paleoproductivity from biogeochemical tracers in the sediment inevitably simplifies a complex set of processes. The arriving flux undergoes large changes at the seafloor, both within the upper layer of sediment which communicates with the bottom water, and also within the deeper sediment which is shut off from bottom water communication. Jumars et al. [1989] have discussed in a general way the complexities for biogenic materials. For the specific case of Ba-organic matter association we have used sediment trap data to define the export of particulate barium and organic carbon from the euphotic zone, the acquisition of barium during settling through the water column, and the chemical characterization of barium carriers. In order to use this information as a paleoproductivity tool, however, the preservation of Ba in sediments must be predictable as well. In a limited fashion this can be tested with data for the sediments underlying our sediment trap moorings.

The preservation of any component or element can be computed by comparing the burial fluxes and the rain rates of material which reaches the seafloor [Dymond and Lyle, 1985; Sarnthein et al., 1988; Dymond and Lyle, 1992]. This approach requires estimates of the sedimentation rate and bulk density of the sediments and assumes that the sediment trap fluxes to the seafloor are an accurate estimate of the long-term flux. An alternative approach involves using ratios of the element of interest to a refractive element, such as aluminium. If we assume the flux of aluminum to the bottom is conservative and the Ba/Al of the raining material remains constant over the time interval integrated by sediment burial rate data, the following relationship is valid:

$$\%\ \text{Ba preserved} = ((\text{Ba/Al})_{\text{sediments}}/(\text{Ba/Al})_{\text{rain}})\ 100 \quad (7)$$

Similar relationships can be written for any of the labile components of the particulate rain.

Figure 10 indicates that approximately 70% of the barium which reaches the seafloor is recycled prior to burial. The accumulation rates represented by these sites vary by more than a factor of 100. Since only one sample falls markedly off the 30% preservation line, the data suggest preservation is consistent in a wide variety of sedimentological regimes. It is also encouraging that the percentage of barium preservation, 30%, is the highest preservation factor of any of the productivity tracers investigated so far. A previous estimate of 15% for the global barium preservation in sediments was based on a model balancing the global particulate flux of Ba with the river input of Ba [Wolgemuth and Broecker, 1970].

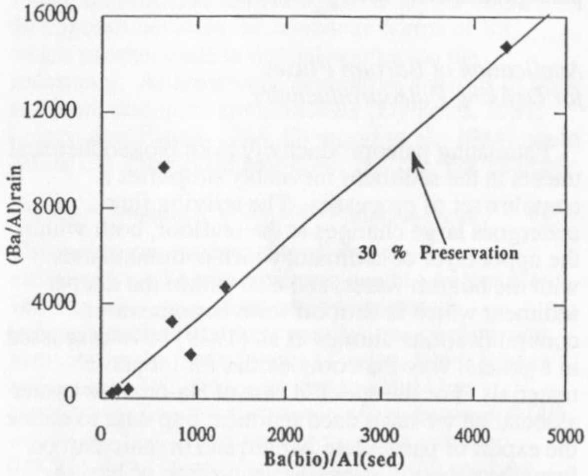

Fig. 10. Ba/Al values in particles that rain to the bottom (estimated from deep sediment traps) versus the same ratio in underlying sediments. The line indicating 30% preservation of biogenic barium provides a reasonably good fit to the data.

A more detailed examination of the extent of barium preservation, however, indicates that preservation is not constant over a wide range of accumulation rates (Figure 11). Such a pattern seems consistent with our observation that there are two forms of biologically related barium in settling particles. Barite is the dominant form and comprises up to 70% of the particulate material (Table 3). The preservation of barite might be expected to be increased both by rapid accumulation rate, which results in less exposure to undersaturated bottom waters, and by greater barium rain rate, which facilitates saturation of the pore waters with respect to barite. Our leaching experiments, however, have demonstrated that absorbed/calcite-bound barium constitutes 22 to 43% of total barium. This relatively labile barium is likely to be lost under even very rapidly accumulating sediments. The resulting nonlinear preservation-mass accumulation rate relationship for barium is analogous to the enhanced preservation of organic carbon observed in more rapidly accumulating sediments [Heath et al., 1977; Müller and Suess, 1979; Henrichs and Reeburgh, 1987; Dymond and Lyle, 1992]. It is probable that the preservation-accumulation rate relationship for organic carbon, like that for barium, is a consequence of the particulate rain being composed of both labile and refractory components [Emerson and Hedges, 1988; Dymond and Lyle, 1992].

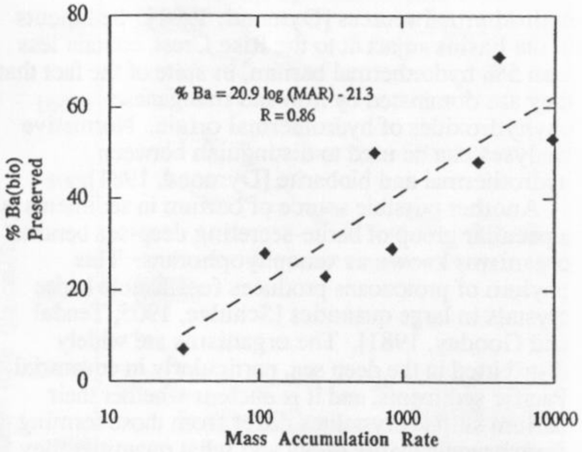

Fig. 11. The percentage of $Ba_{(bio)}$ preserved versus the mass accumulation rate (units of $\mu g/cm^2/yr$). The percentage preserved is computed from the Ba/Al comparison shown in Figure 8. Note the log scale on the abscissa. Only data from the Pacific sites shown because sediments from the Atlantic sites have such high aluminosilicate contents to preclude accurate estimates of their biogenic barium contents.

These considerations are relevant for attempting to define a barium-based productivity algorithm. We have demonstrated that for much of the oceans, barite is the dominant form of particulate barium reaching the seafloor. Contributions of detrital aluminosilicate barium can be accounted for with sufficient accuracy, except in locations where aluminosilicate barium approaches 50% of the total rain. Preservation of barium is a function of the sediment mass accumulation rate; nevertheless, the relationship seems systematic enough to offer hopes of defining the barium rain rate to the bottom from measurements both of total sediment accumulation rate and of barium accumulation rates in sediments. Consequently, the first steps toward defining ocean productivity are as follows:

1. Measure mass accumulation rate of the sediment;
2. Measure barium concentration and aluminium concentration in the sediment;
3. Compute the biobarium from the normative relationship:

$Ba_{(bio)} = Ba_{(total)} - (0.0075\ Al)$.

The constant 0.0075 is a typical Ba/Al value for detrital aluminosilicates but can be adjusted for specific provenances.

4. Compute the degree of preservation from the measured mass accumulation rate and the relationship shown in Figure 11:

% Ba pres. = 20.9 log (MAR) -21.3).

This relationship is tentative and should be confirmed or modified for additional locations.

5. Compute the biobarium rain rate from the % Ba preserved and from the accumulation rate of biobarium in the sediments.

Using this procedure with our data, we suggest the following tentative formulation for predicting the rain of biobarium to the seafloor (i.e., the Ba_{bio} flux):

$$Ba_{bio}flux = (Ba_{bio}\text{-acc.})/[(0.209 \log (MAR)-0.213) \quad (8)$$

where Ba_{bio}-acc. equals the accumulation of barium in sediments after correcting for aluminosilicate barium and MAR equals the mass accumulation rate of the sediments in units of μg/cm²/yr.

The flux of biobarium to the seafloor is the crucial perameter from which to hindcast new production using the Ba-flux equation (5). Rearranging (5) yields the following predictive relationship:

$$P_{new} = \left(\frac{F_{Ba}\, 0.171\ Ba^{2.218}\ z^{0.476 - 0.00478\ Ba}}{2056} \right)^{1.504} \quad (9)$$

where F_{Ba} is the biobarium flux.

This working algorithm takes on a particular significance for paleoceanographic reconstruction because it combines ocean chemistry, defined here as the dissolved Ba content (Ba), with new production (P_{new}). The former is a function of the large-scale deep circulation, more specifically of the ventilation age of the water masses. The latter is a function of climate and surface circulation.

As an example of the application of (9) we have used barium accumulation rate data (Figure 9) for our Midway site in the California Current (Figure 1) to estimate the new productivity during the past 18,000 years (Figure 12). In this calculation we assume that the present-day concentrations of water column barium existed during the last glacial maximum. We have made this simplification because there are no published values of Ba/Ca ratios in foraminifera from North Pacific sediments which could be used to define the paleo-barium concentrations in this part of the ocean (Lea and Boyle, 1990). This assumption, however, is only warranted as a first approximation.

Most recent developments in paleo-ocean chemistry use diagnostic trace element relationships from tests of pelagic and benthic calcareous organisms for the prediction of shallow and deep micronutrient distributions (for review see Elderfield [1990]). The Ba/Ca ratio of benthic forams as well as surface dwelling corals has been used to characterize water masses and their Ba concentrations. Such independently derived paleo-ocean chemistry data are essential to solve (9) for new production. Used this way, the equation is the first algorithm which truly combines multiple tracers for the task of hindcasting paleoproductivity and the ventilation age of water masses.

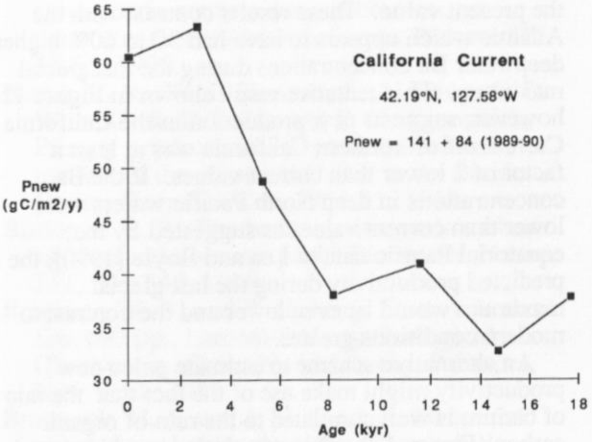

Fig. 12. Estimates of new production during the last 18,000 years at site MW (Figure 1). The new productivity estimate is based on the accumulation of barium at the site (Figure 9) and using (9) as a tentative algorithm. A constant value of deep water barium was assumed (145 μm/kg) which, as discussed in the text, probably over estimates new production during the last glacial maximum. Modern values of new production are shown as well based on ^{15}N uptake experiments at the site (P. Wheeler, personal communication, 1991). The surface sediment estimate is lower than the mean values made during 1989-1990 (although there is overlap in the estimates). The sediment values represent long-term average new productivity but, the ^{15}N uptake-based values were measured during the late summer when productivity is at a maximum at the site.

Following our earlier scheme of listing the necessary steps to obtain the Ba-rain rate to the seafloor from the sediment mass accumulation rate and the partitioning of the biobarium fraction, we now continue this list with the steps needed to estimate new production.

6. Obtain Ba/Ca ratios of benthic calcareous organisms at intermediate water depths of 1500-2000 m.

7. Compute the Ba concentration at 1700-m depth following the relationship of Lea and Boyle [1990].

8. Compute new primary production from (8) using the flux rate of the biobarium to the seafloor (equation 7) and the estimate of dissolved Ba concentration at 1700 m.

Lea and Boyle [1990] present data suggesting that deepwater Ba concentration in the equatorial Pacific during the last glacial maximum is 25% lower than the present value. These results contrast with the Atlantic which appears to have had 30 to 60% higher deepwater Ba concentrations during the last glacial maximum. This tentative result shown in Figure 12, however, suggests new production in the California Current off of northern California was at least a factor of 2 lower than current values. If the Ba concentrations in deep North Pacific waters were lower than current values as suggested by the equatorial Pacific data of Lea and Boyle [1990], the predicted productivity during the last glacial maximum would be even lower and the contrast to modern conditions greater.

An alternative scheme to estimate paleo new productivity might make use of the fact that the rain of barium is well correlated to the rain of organic carbon (Figure 13). This correlation could be used to define the organic carbon flux to the bottom (organic carbon rain) from the barium rain rate computed by (8). Thus

$$F\text{-}C_{org} = 25\ (Ba_{bio}\text{-acc.})/(0.209\ \log\ (MAR) - 0.213) \quad (10)$$

where F-Corg is the organic carbon flux to the bottom.

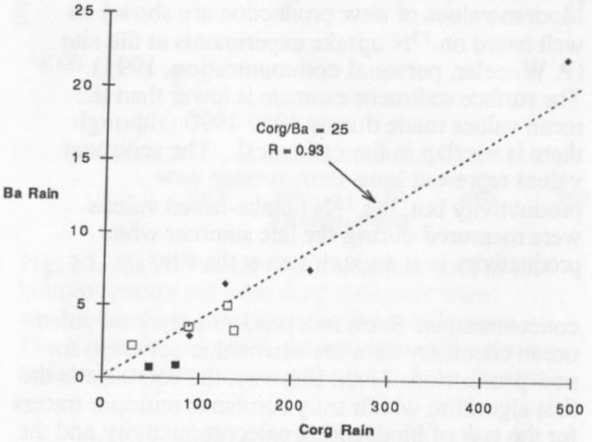

Fig. 13. A comparison between of the organic carbon and barium fluxes in particles which rain to the bottom. Units are in µg/cm²/yr. Filled squares are Atlantic samples. Open squares are equatorial Pacific samples. Filled diamonds are samples from the California Current.

The organic carbon flux to the bottom (C_{org}-Rain) is itself a qualitative measure of surface water productivity. Consequently, estimates of variations in carbon rain computed from variations in barium accumulation in sediment cores could be used to distinguish paleoproductivity from paleo-preservational effects. The organic carbon rain rate to the bottom could also be translated into the export flux of carbon from the euphotic zone ("new productivity"), using the relationship of Sarnthein et al. [1988]. Site-to-site variations in these carbon-depth relationships, however, can introduce errors into estimates of carbon flux at the base of an assumed euphotic zone thickness. These differences may reflect site-to-site variations in carbon degradation and utilization.

We present these approaches to estimating paleoproductivity, not as definitive algorithms, but rather as a demonstration of possible approaches to using barium accumulation rates in marine sediments to define the export of carbon from the ancient oceans. In order to improve the algorithms, it will be necessary to refine the relationship between carbon flux and new production (equation 1). The relationship between barite formation and water column Ba concentration needs additional investigation. Hopefully, this would lead to a better understanding of the specific mechanisms and conditions which result in barite formation and would enhance the confidence of any Ba-productivity algorithm. Also, it is possible that the preservation of barium (Figure 11 and equation 8) is a function both of the barium rain and of the mass accumulation rate. These refinements can be accomplished by determining the flux of particulate barium and its burial in sediments in oceanic environments with contrasting dissolved Ba contents and distinct biological productivities and sedimentological conditions.

CONCLUSIONS

The strong correlation of particulate organic carbon with barium fluxes over broad areas of the ocean provides one more indication of a linkage between barium removal in the oceans and biological processes. The systematic changes in C_{org}/Ba values with water depth indicate that the C_{org}/Ba in particles leaving the euphotic zone is relatively constant in diverse areas of the ocean. The decrease in this ratio with depth is a consequence both of decomposition of settling organic matter and of barium uptake by biogenic particles. This observation further supports a syngenetic origin of barite rather than primary formation by a particular plankton group. The relationship between changes in Corg/Ba values depth and the barium contents of intermediate-depth ocean waters also supports the formation of barite during the decomposition of organic matter. Selective leaching experiments demonstrate that 50-70% of the particulate barium flux is in the form of barite, and that the rest is either adsorbed or bound on carbonates. Normative analysis indicates that detrital aluminosilicate contribution to the barium content of settling particles and sediments is significant in some parts of the ocean. This contribution can be accounted for with reasonable accuracy except at sites in which <50% of the Ba is biobarium.

Diagenetic redistribution of barium introduces a problem when applying barium as a paleoproductivity indicator in reduced and possibly also suboxic sediments. If sulfate reduction is achieved, barite will dissolve and be mobilized. Suboxic diagenesis in which manganese is mobilized can also provide some redistribution of barium although not of biobarite. Under steady state mobilization this process should not significantly affect the preserved barium signal in sediments.

On average, approximately 30% of the biogenic barium flux which reaches the bottom is preserved. Because this preservation factor is the highest of all biogenic components, barium has promise as a tracer of ocean fertility. The degree of preservation of Ba, however, is not constant and appears to be a logarithmic function of the mass accumulation rate. Thus from measurements of the accumulation rate of biobarium it is possible to estimate the rain of barium reaching the bottom. A number of approaches are suggested transform the rain of barium reaching the bottom to the export flux of carbon leaving the euphotic zone (the export flux).

Of these approaches the one which incorporates the dissolved Ba contents seems most promising since new techniques in paleo-ocean chemistry have been successful in independently estimating this parameter from Ba/Ca values of benthic calcareous organisms.

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