

Export production in the Bay of Biscay as estimated from barium - barite in settling material: a comparison with new production

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Abstract

We present barium data for sediment traps deployed in a northeast Atlantic margin environment (Bay of Biscay). Fluxes of excess barium were measured with the objective of calculating carbon export production rates from the surface mixed layer and thus contribute to the understanding of organic carbon transport in a margin environment. Therefore, it was necessary to properly understand the different processes that affected the barium fluxes in this margin environment. Seasonal variability of POC/Ba flux ratios and decrease of barium solubilisation in the trap cups with increasing depth in the water column probably indicate that the efficiency of barite formation in the organic micro-environment varies with season and that the process is relatively slow and not yet completed in the upper 600 m of water column. Thus barite presence in biogenic aggregates will significantly depend on water column transit time of these aggregates. Furthermore, it was observed that significant lateral input of excess-Ba can occur, probably associated with residual currents leaving the margin. This advected excess-Ba affected especially the recorded fluxes in the deeper traps (> 1000 m) of the outer slope region. We have attempted to correct for this advected excess-Ba component, using Th (reported by others for the same samples) as an indicator of enhanced lateral flux and assigning a characteristic Ba/Th ratio to advected material. Using transfer functions relating excess-Ba flux with export production characteristic of margin areas, observed Ba fluxes indicate an export production between 7 and 18 g C m⁻² yr⁻¹. Such values are 3-7 times lower than estimates based on N-nutrient uptake and nutrient mass balances, but larger and more realistic than is obtained when a transfer function characteristic of open ocean systems is applied. The discrepancy between export production estimates based on excess-Ba fluxes and nutrient uptake could be resolved if part of the carbon is exported as dissolved organic matter. Results suggest that margin systems function differently from open ocean systems, and therefore Ba-proxy rationales developed for open ocean sites might not be applicable in margin areas.

Keywords : Ba-proxy ; carbon export ; margin system

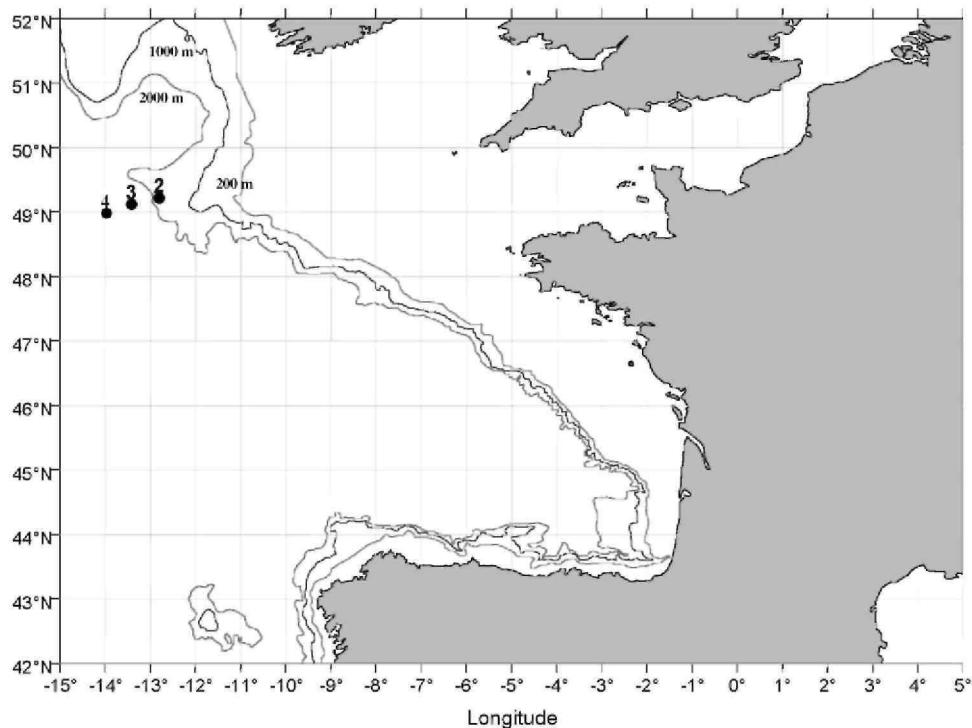
1. Introduction

In the pelagic oceanic environment, microcrystalline barite (~1 µm in size) accounts for 50-100% of the total Ba in oceanic suspended matter (Dehairs et al., 1980; Stroobants et al., 1991). Although the exact mechanism of barite formation is not fully understood, it has been suggested that during degradation of planktonic protein material sufficient sulphate is produced to reach BaSO₄ saturation (Bishop, 1988a). Precipitation of barite appears to be confined to micro-environments composed of aggregates of biogenic detritus (Bishop, 1988a; Dehairs et al., 1980), confirming an original idea formulated by Chow and Goldberg (1960). Supersaturation inside micro-environments can explain the presence of barite in seawater undersaturated with respect to BaSO₄. Bernstein et al. (1992) proposed such supersaturation inside micro-environments to be driven by dissolution of Ba-enriched celestite skeletons of Acantharia. BaSO₄ undersaturation of seawater appears to prevail for the whole Atlantic Ocean water column and surface waters worldwide, except in the Southern Ocean (Church, 1970; Church and Wolgemuth, 1972; Jeandel et al., 1996; Monnin et al., 1999). The settling of biogenic detritus with associated barite to the deep sea and the sediments explains the relationship between barite accumulation in the sediments and biological production in overlying surface waters observed originally by Turekian and Tausch (1964). More recently, observations of particulate barium fluxes in the water column and the sediments highlight the correlation between barite and primary production and stress the potential for sedimentary barite fluxes to provide quantitative information on the (paleo)-productivity of the oceans (Dymond et al., 1992; Ginge and

Dahmke, 1994; Francois et al., 1995; Nürnberg, 1995; Frank, 1996; Paytan et al., 1996). Furthermore, it was observed that part of the detrital aggregates formed in surface waters decompose at mesopelagic depths and that barite is released as discrete crystals into the ambient seawater (Bishop, 1988a,b; Stroobants et al., 1991; Dehairs et al., 1992,1997). This induces a maximum in the particulate barium concentrations in the mesopelagic depth range, i.e. between 100 and 600 m. Such a maximum was reported in various sections of the World Ocean, including the Southern Ocean (Bishop, 1988b; Dehairs et al., 1980,1990-1992,1997), and is closely related to both the surface water productivity and the mesopelagic oxidation of settling detritus (Dehairs et al., 1997).

In the present study, we investigate the relationship between the Ba-barite water column flux and the export of organic carbon from the euphotic layer for a margin ecosystem in the Bay of Biscay, northeast Atlantic Ocean (Fig. 1). It is investigated through the seasonal variability and the variability with depth in the water column of the Ba-barite component in the settling matter. The significance of different processes or mechanisms affecting the primary, vertical, Ba flux is discussed in an attempt to evaluate the transfer functions proposed by others (Francois et al., 1995; Nürnberg et al., 1997). Finally, calculated export production is compared with new production data for the same area and observed discrepancies are discussed.

Fig. 1. Map of Goban Spur area in the Bay of Biscay showing position of OMEX sediment trap moorings 2, 3 and 4.



2. Material and methods

2.1. Sediment trap sampling

Details of the sediment trap moorings are given in Antia et al. (1999b) and of sample treatment in Bodungen von et al. (1991). Data are presented for three sediment trap moorings deployed at the continental margin of the Bay of Biscay (Goban Spur area) between July 1993 and September 1995 (Fig. 1). Material was trapped at intervals of 9-14 d. Cup solutions were poisoned with mercuric chloride and stored cold and dark.

Two moorings were operated from July 1993 to September 1994: (1) OMEX 2, 49°11'N 12°49'W; water column depth 1425 m; traps at 600 and 1050 m; (2) OMEX 3, 49°05'N 13°25'W; water column depth 3650 m; traps at 580, 1440 and 3260 m. A third mooring was operated between September 1994 and September 1995: OMEX 4, 49°N-13°45'W; water column depth 4470 m; trap at 4000 m. Due to clogging of the 580 m trap at OMEX 3

during spring 1994, the seasonal record is incomplete at this depth.

2.2. Analysis of Ba and Al

Splits of suspended trap material (1/16th; 1/64th or 1/128th of original cup contents) were filtered under pressure of filtered air through polycarbonate membranes (Nuclepore: 47 mm Ø, 0.4 µm pore size). After filtration, the membranes were rinsed with deionized water to eliminate residual sea salt and were dried at 60°C. Samples were stored in polycarbonate petri-dishes at ambient temperature until analysis. The filtered material was transferred to teflon digestion bombs and mineralised overnight by acid digestion using a mixture of HNO₃, HCl and HF (Merck Suprapur; 4/2/1 volume ratio) at 80°C. The acid was then partially evaporated and HF neutralised with boric acid (Merck Suprapur). Final solutions were 0.4% in H₃BO₃. Ba, Ca, Sr and Al were determined by simultaneous and sequential inductively coupled plasma atomic emission spectrometry (Jobin-Yvon 48 and 38). The lithogenic fraction of barium, associated with aluminosilicates, was calculated using the Ba/Al ratio for mean crust (Ba/Al mass ratio = 0.61×10^{-2} ; Bowen, 1979) and assuming all Al in the sample is lithogenic (see also Dymond et al., 1992):

$$[\text{Ba}]_{\text{aluminosilicates}} = [\text{Al}]_{\text{sample}} [\text{Ba/Al}]_{\text{crust}} \quad (1)$$

The use of Al as the lithogenic reference element for oceanic sedimentary material has been questioned by others, who have shown a significant component of Al scavenged from seawater under regimes of high biogenic particle flux (Murray and Leinen, 1996). This was confirmed by Dymond et al. (1997), who furthermore demonstrated the important role of diatom skeletons as conveyors of this excess-Al signal. These studies indicate that it is preferable to use Ti as the lithogenic reference element. Ti was not measured in the present study, but Fagel et al. (1999) analysed both Al and Zr on several of the trap samples discussed in the present work. From these data it appeared that excess-Ba calculated from Al is on an average about 92% of the value calculated with Zr as the lithogenic reference, suggesting Al in the trap samples indeed to be enriched relative to crustal composition. As a result we underestimated the excess-Ba fraction by some 8% using Al as the lithogenic reference. This bias, however, does not alter the conclusions of the present work.

Barium in aluminosilicates represented $\leq 20\%$ of the total barium content (see below, Table 1). Henceforth, Ba data corrected for the lithogenic fraction will be identified as excess-Ba, or Ba_{xs}.

Scanning electron microscope (SEM) investigations were carried out on Au- or C-coated subsamples of Nuclepore filtered material using a JEOL (733 Superprobe) instrument. The presence of barite was checked using the back-scattered electron observation mode for easy spotting of dense particles. Then selected particles were analysed for Ba, S and Sr content, using a Noran-Voyager energy dispersive X-ray detector (Si(Li) semiconductor).

3. Results

3.1. Barite in sedimenting material

SEM-EMP investigations of the OMEX sites 2 and 3 sediment trap samples showed ubiquitous presence of discrete microcrystals of barite $\sim 0.8\text{-}3\ \mu\text{m}$ in size (average size $\sim 2\ \mu\text{m}$). Occasionally barite crystals were observed to contain minor amounts of Sr (up to 5%). The crystals were frequently found associated with aggregates of biogenic detritus that, in some occasions, could be clearly identified as copepod-type faecal pellets.

This association of barite crystals with biogenic aggregates corroborates earlier findings suggesting barite formation to be confined to micro-environments with physico-chemical conditions distinct from those present in the ambient seawater (Chow and Goldberg, 1960; Dehairs et al., 1980; Bishop, 1988a).

To document this micro-environment hypothesis further we looked for barite presence in large marine aggregates sampled with the Marine Snow Catcher device at the lower boundary of the surface mixed layer (i.e. at about 60 m) in the Goban Spur area during R/V *Discovery* cruise D-217 (27 September to 22 October, 1995). The Marine Snow Catcher avoids disintegration of fragile aggregates during sampling (Lampitt et al, 1993). SEM-EMP observations showed the presence of large ($\leq 100\ \mu\text{m}$), thin, low density flake-like particles (marine snow?) carrying numerous coccoliths and barite crystals. Barite crystals were relatively large, between 2 and 5 µm. These observations again corroborate existing conclusions concerning the role played by biogenic micro-environments in the synthesis of marine barite.

3.2. Vertical fluxes

Table 1 shows the monthly averaged daily fluxes for Ba (F_{Ba}), excess-Ba (F_{Baxs}), Al and POC (F_{POC}), based on an original set of 210 cups. The POC data are from Antia et al. (1999b). The average excess-Ba flux values range from 0.4 to 2.4 $\mu\text{g cm}^{-2} \text{yr}^{-1}$. Such values fall well within the range observed for other sites in the Pacific and Atlantic Ocean (Dymond et al., 1992; Francois et al., 1995), but the overall average of our data is about a factor two lower than for data presented by Dymond et al. and Francois et al. Our confidence in the Ba results presented here rests on the good coherence obtained for a reduced number of cups duplicated in the work by Fagel et al. (1999; $r^2 = 0.88$; slope = 1.09; $n = 70$).

The POC/Ba flux ratios at sites 2 and 3 are highest in the shallowest traps (the case of site 3 is shown in Fig. 2). The decrease of the POC/Ba flux ratio in the deeper traps at sites 2 and 3 results from a proportionally larger increase of the Ba flux relative to the POC flux. At site 3 the highest Ba and POC fluxes occur at the intermediate depth of 1440 m while the Al flux increases further between 1440 and 3260 m.

Table 1. Monthly average fluxes of total mass, Ba, excess-Ba, Al and POC at OMEX 2, 3 and 4 sediment trap sites

Site/depth	Mid-day	Mass flux ^a ($\text{mg m}^{-2} \text{d}^{-1}$)	Ba ($\text{nM m}^{-2} \text{d}^{-1}$)	Excess-Ba ($\text{nM m}^{-2} \text{d}^{-1}$)	Al ($\mu\text{M m}^{-2} \text{d}^{-1}$)	POC ^a ($\text{mg m}^{-2} \text{d}^{-1}$)	
OMEX 2, 600 m 1993	July	86.6	85	82	2.8	7.2	
	August	110.9	196	184	10.6	17.7	
	September	44.7	60	56	3.5	6.3	
	October	41.8	68	63	3.6	3.6	
	November	74.6	208	193	13.0	5.6	
	December	26.1	75	69	5.4	3.4	
	1994	January	7.9	64	43	17.3	2.9
		February	11.7	29	26	3.0	2.0
		March	8.8	30	26	3.0	0.7
		April	30.0	82	67	12.5	2.6
		May	102.2	259	214	37.3	8.3
		June	48.8	66	64	2.1	4.9
		July	38.1	20	20	0.1	2.3
		August	5.6	7	7	<0.1	0.4
	Average ^b		49.6	98	88	9.1	5.3
	OMEX 2, 1050 m 1993	July	49.3	123	116	6.0	8.6
August		201.4	482	444	32.5	22.0	
September		66.7	167	141	21.3	7.2	
October		121.6	214	193	17.2	5.5	
November		43.8	210	193	14.8	4.8	
December		39.9	156	106	42.2	2.3	
1994		January	14.4	160	140	17.0	0.7
		February	17.1	71	56	12.7	0.3
		March	5.2	15	14	1.0	0.2
		April	13.3	74	68	5.0	2.5
		May	142.2	484	406	65.7	6.7
		June	75.6	676	584	77.7	7.7
		July	86.3	497	408	75.1	4.9
		August	68.2	347	289	49.2	5.0
September		21.2	64	48	13.7	3.6	
Average ^b			72.1	244	210	28.8	5.9
OMEX 3, 580 m 1993	July	54.0	96	82	12.1	8.7	
	August	74.7	180	160	16.9	12.6	
	September	48.9	105	75	25.7	7.0	
	October	53.9	82	64	14.5	6.6	
	November	11.7	37	24	11.0	1.5	
	December	11.2	32	20	9.7	1.3	
	1994	January ^c	6.9	166	160	—	1.7

	February ^c	6.9	53	49	—	1.6
	March ^c	14.7	90	88	—	2.2
	April ^c	43.8	415	407	—	3.9
	May ^c	74.4	288	205	—	5.5
Average ^b		37.0	134	122	14.9	4.9
OMEX 3, 1440 m 1993	July	132.0	569	517	44.1	12.0
	August	148.8	609	567	35.5	20.1
	September	150.4	402	367	29.6	9.9
	October	123.7	582	544	32.2	9.8
	November	49.1	301	288	10.6	2.7
	December	110.2	849	742	89.9	5.5
	January	49.1	330	309	18.0	3.1
1994	February	44.1	223	195	24.1	3.7
	March	55.0	389	331	49.0	2.8
	April	72.2	502	469	27.8	5.5
	May	265.5	985	909	63.9	21.5
	June	160.1	359	309	42.3	14.9
	July	86.0	407	344	53.2	8.8
	August	102.1	449	343	89.3	10.6
	September	121.8	1406	1213	163.6	14.0
Average ^b		112.0	536	479	48.2	9.9
OMEX 3, 3260 m 1993	July	118.1	571	484	73.2	6.9
	August	107.2	407	357	42.3	7.3
	September	100.1	383	343	34.0	5.7
	October	41.7	180	160	17.3	2.5
	November	88.4	366	321	38.2	2.9
	December	90.8	475	394	69.1	3.1
	January	63.2	425	386	66.0	3.1
1994	February	33.1	423	332	—	2.5
	March	49.3	301	252	41.3	2.3
	April	49.2	235	193	18.8	3.7
	May	218.0	441	345	—	8.8
	June	231.0	745	575	225.6	9.1
	July	222.0	806	598	314.8	14.6
	August	138.1	782	599	147.6	8.3
	September	100.3	495	388	—	5.5
Average ^b		113.0	472	380	68.5	5.9
OMEX 4C, 4000 m 1994	September	96.5	339	302	—	—
	October	74.9	286	253	—	—
	November	54.6	184	160	—	—
	December	72.2	224	194	—	—
1995	January	66.0	147	118	—	—
	February	57.6	204	171	—	—
	March	51.9	226	186	—	—
	April	76.8	216	178	—	—
	May	79.1	211	178	—	—
	June	160.0	184	157	—	—
	July	76.0	188	163	—	—
	August	93.4	221	190	—	—
	September	106.4	277	234	—	—
Average ^b		82.1	224	190	—	—

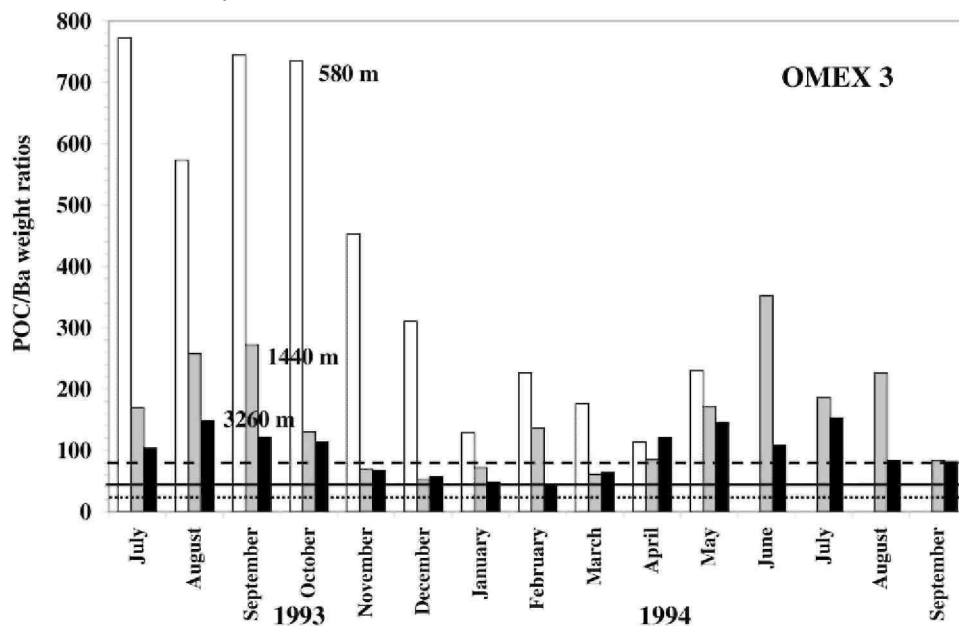
^aData from Antia et al. (1999b)

^bWeighted averages, taking into account sampling time (between 9 and 14 d).

^cData from Fagel et al. (1999); excess-Ba calculated using Zr as the lithogenic reference element.

— means no data.

Fig. 2. Seasonal evolution of POC/excess-Ba ratio (W/W) in sediment trap material at 580 m (white bars), 1440 m (grey bars) and 3260 m (black bars) at OMEX 3. Horizontal lines represent ratios obtained from Eq. (4): broken line (580 m), full line (1440 m) and dotted line (3260 m).



3.3. Seasonal variability

Seasonality in bulk and organic matter fluxes is characterised by elevated fluxes during spring and summer and lowest fluxes between November and March (Antia et al., 1999b). Opal and autotrophic pigment flux are highest during April-May, associated with sedimentation of the spring bloom (Antia et al., 1999a). This is seen at all depths, though a decrease in seasonality is registered with increasing water depth. At 580 m, site 3, smallest mass and element fluxes are generally observed from November 1993 until March 1994. In April-May 1994 fluxes increase probably as a result of the spring bloom. A similar pattern is observed for the deep traps at site 3, but in addition these show an intermediate peak for December 1993. After June 1994 deep trap fluxes decrease again. Moderate fluxes persist until September 1994. The same picture generally holds for site 2, but without the December 1993 peak in the deep trap. At site 4 (4000 m) there is little apparent seasonal variability.

POC/Ba flux ratios are highest during spring and summer. This seasonal variability is apparent at all depths, but the deepest traps show the smallest variation (case of OMEX site 3 shown in Fig. 2). Nevertheless the decrease of the flux ratios during winter (November to February) is still clearly visible in the deepest traps.

4. Discussion

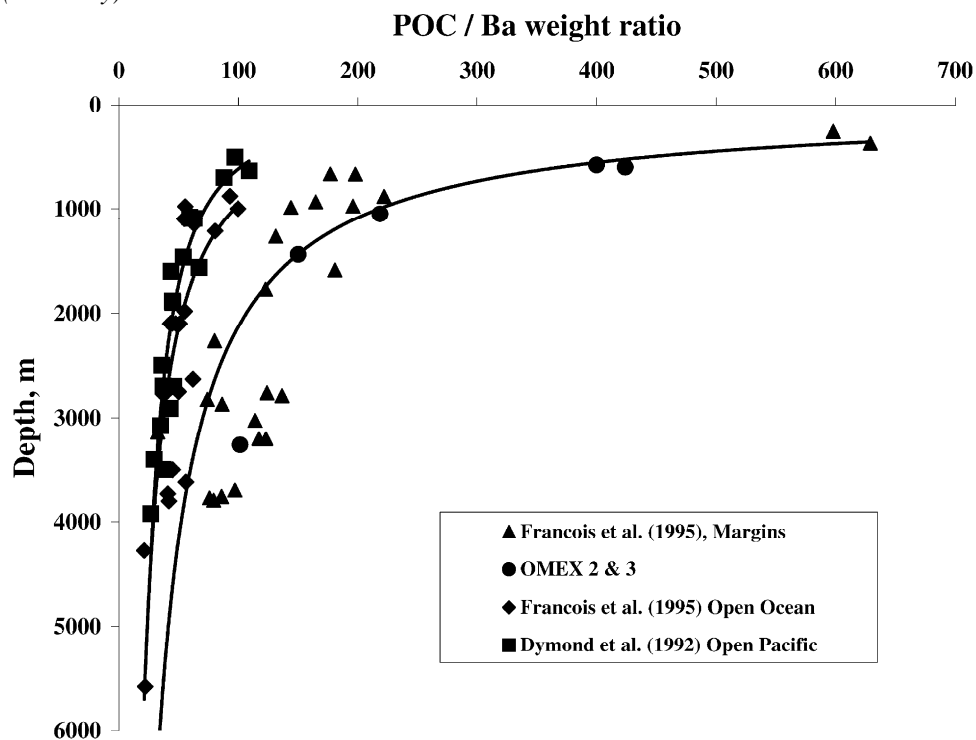
4.1. The nature of the excess-Ba pool

Based on numerous sediment trap data from the major oceanic basins, Francois et al. (1995) proposed an algorithm that relates the POC/Ba flux ratio to depth in the water column and forms the basis of the transfer function between Ba flux and export production (ExP) discussed further below. In their paper, Francois et al. were able to differentiate between oceanic stations that were minimally affected by input of advected detrital carbon and stations closer to continental slopes and shelves. Fig. 3 reproduces the depth distribution of the POC/Ba ratios for these two situations as taken from the papers by Francois et al. (1995) and Dymond et al. (1992). We have included our OMEX data in this figure, and it appears clearly that these are similar to data reported for stations affected by input of advected detrital carbon from slope and shelf regions. The rationale developed by Francois et al. considers advection of detrital carbon to occur without significant advection of excess-Ba, because barite preservation in continental shelf sediments is poor in the prevailing anoxic conditions (e.g. Von Breyman et al., 1992) and also because organic matter resuspended from shelf sediments would be free of labile sulphur, precluding further precipitation of barite. Thus, the trapped flux of excess-Ba would be associated with degradation of organic matter produced in local surface waters and, therefore, the excess-Ba flux

rather than the POC flux would allow for proper estimation of export production (Francois et al., 1995). We investigate this basic assumption using our OMEX data.

First we look into the nature of this excess-Ba phase. We have seen in the results section that barite microcrystals are present in the trap material and are frequently associated with biogenic detritus. While other studies on oceanic suspended matter have demonstrated barite is indeed the major contributor to the excess-Ba pool (Dehairs et al., 1980), this has not been verified for fast settling trap material. To verify whether there were any differences in the composition of the excess-Ba pools in trapped materials between different depths we compared their susceptibility to dissolution by looking into the dissolved Ba content of the cup solutions. This was done only for site 3 traps. Dissolved Ba concentrations, as determined by isotope-dilution ICP-MS, were $\leq 148 \text{ nmol l}^{-1}$ and remained below conditions of BaSO_4 saturation (Church and Wolgemuth, 1972; Monnin and Galinier, 1988; Monnin et al., 1999; Jeandel et al., 1996). The absolute amount of dissolved Ba, corrected for dissolved Ba present in the seawater that filled the cups, was compared with the absolute particulate Ba content of the cups. We thus calculated that 12.5, 3 and 1.5% of the original Ba flux was solubilised in cups of the traps at 580, 1440 and 3260 m, respectively. Such a decrease in the fraction of Ba solubilised with depth was observed also by Dymond and Collier (1996). This enhanced fraction of labile Ba in the 600 m trap is relatively small but suggests there are differences in the type of main Ba phase between the shallow and deep traps. The relatively larger dissolution of the sampled F_{Ba} at 600 m might result from incomplete formation of barite at this depth. Here Ba may still occur, to a significant extent, adsorbed on or chemically bound to organic and other biogenic matter such as carbonate, opal and celestite (e.g. Bernstein et al., 1992). These would be more prone to rapid redissolution in the cups than barite. Complete barite formation is then reached only after a certain maturation period. It is probable that such a vertical gradient in the progress of barite formation is actually a function of the amount of time the carrier micro-environment has spent settling through the water column, and thus of the settling speed of the aggregate.

Fig. 3. Comparison of depth distributions of POC/Ba ratios between OMEX and other areas reported in literature. Triangles = sites close to margins (from Francois et al., 1995); diamonds = open ocean sites (from Francois et al., 1995); squares = open Pacific Ocean sites (from Dymond et al., 1992); circles = OMEX sites (this study).



Next we look into the variability of the POC/Ba ratio with changing season: during spring and summer POC/Ba ratios are higher than during winter. We speculate that during spring and summer conditions exist for which the

organic matter trapped at the shallow depths would be relatively fresh. Under these conditions the bacterial degradation processes, including the oxidation of reduced organic sulphur to sulphate, would not yet be completed and thus barite not yet fully synthesised. During winter the POC/Ba ratios at all depths approach those expected from the rationale outlined by Francois et al. (1995) (see Eq. (4)). This winter - summer variability in POC/Ba ratios may reflect the fact that during the phytoplankton growth season transfer of surface water organic detritus to depth is more efficient (less recycling) and faster (it would reach greater depths before being eventually recycled) as suggested by Bishop et al. (1980) and Boyle (1988). A similar possibility was put forward by Dymond and Collier (1996) to explain the variability of the Ba/POC flux ratios in their Equatorial Pacific sediment traps. Also, a decoupling of herbivore (copepod) grazing from spring phytoplankton growth, as observed for temperate shallow water systems, would result in mass sedimentation after nutrient depletion (Peinert et al., 1989). Evidence for seasonal differences in the quality and composition of sedimenting material at the OMEX sites is seen in the pattern of autotrophic pigment and intact diatom and faecal pellet fluxes reported elsewhere (Antia et al., 1999a). Whereas fast-sinking aggregates and faecal pellets were presumably important vehicles for particle sedimentation in spring and summer, respectively, material collected during winter consisted largely of unidentifiable detritus. However, this is not conclusive evidence, since aggregates and faecal pellets seldom contribute more than a few % of total POC flux.

4.2. Variability of excess-Ba flux with depth

We have seen that excess-Ba fluxes increase considerably between the 600 m traps and the deeper ones. Furthermore, at site 3, the intermediate trap at 1440 m shows the highest flux in the profile. Such variability needs to be understood to verify the usefulness of barite as a tracer of export production.

Undersampling by shallow traps has been reported in the literature as inferred from observed imbalances between sediment trap $^{230}\text{Th}_{\text{exc}}$ and $^{231}\text{Pa}_{\text{exc}}$ fluxes and water column production rates at depths shallower than 1000 m (e.g. Bacon, 1996). From excess ^{230}Th and ^{231}Pa measurements discussed in Antia et al. (1999c), it appeared that the shallow traps had poor trapping efficiencies. These were of 35 and 38% at 580 m at site 2 and 600 m at site 3, respectively. For the deeper traps, however, efficiency was 85% for the site 2 trap at 1050 m and close to 100% for both deep traps at site 3. When corrected for trapping efficiency we note that yearly averaged excess-Ba fluxes now range between 1.2 and 2.4 $\mu\text{g cm}^{-2} \text{yr}^{-1}$ (Table 2). Furthermore, F_{Baxs} values now remain relatively constant with depth at site 2 between 580 and 3260 m at site 3. The only exception is the higher F_{Baxs} value at 1440 m, site 3. These findings would indicate that the process of excess-Ba uptake by the detrital organic matter is essentially completed in the upper 600 m of water column. However, this does not necessarily imply all excess-Ba is present as barite, and indeed our observations concerning enhanced solubilisation of Ba in the shallow traps suggest the presence of a larger labile component of the excess-Ba pool in the shallow traps than in the deeper traps.

Table 2. Annual average POC and excess-Ba fluxes corrected for trapping efficiency; annual average excess-Ba fluxes corrected for trapping efficiency and advection; calculated export productions

Site and depth	Trapping efficiency ^a	F_{POC} (1) ($\text{gC m}^{-2} \text{yr}^{-1}$)	F_{Baxs} (1) ($\mu\text{g cm yr}^{-1}$)	Adverted fraction of F_{Baxs}	F_{Baxs} (2) ($\mu\text{g cm}^{-2} \text{yr}^{-1}$)	ExP (1) ($\text{gCm}^{-2} \text{yr}^{-1}$)	ExP (2) ($\text{gC m}^{-2} \text{yr}^{-1}$)
Site 2							
600	0.38	1.95	1.2	0.27	0.8	1.6	7.2
1050	0.85	2.10	1.2	0.47	0.7	1.2	4.6
Site 3							
580	0.34	1.79	1.8	0.08	1.7	3.5	20.0
1440	0.98	3.53	2.4	0.34	1.6	3.3	16.5
3260	1.05	2.14	1.9	0.33	1.3	2.6	10.6
Site 4							
4000	0.7	—	1.4	0	1.4	2.8	11.4

(1) = observed POC and excess-Ba fluxes corrected for trapping efficiency.

$F_{\text{Baxs}}(2)$ = observed excess-Ba flux corrected for trapping efficiency and advection of excess-Ba.

ExP(1) = export production obtained using $F_{\text{Baxs}}(2)$ and Eq. (5); $\text{ExP} = 1.95 (F_{\text{Baxs}})^{1.41}$

ExP(2) = export production obtained using $F_{\text{Baxs}}(2)$ and $\text{ExP} = 22.7 (F_{\text{Baxs}})^{1.504} Z^{0.139}$ (from Eqs. (7) and (3)).

^aTrapping efficiency as given in Antia et al. (1999c).

One must keep in mind that the trapping efficiency expresses the capacity of the trap to sample the vertical flux of $^{230}\text{Th}_{\text{exc}}$ but does not, however, inform on the degree of lateral advection, if present. Since we deal here with a continental slope setting, advection of shelf and slope material to the traps is likely to have occurred. Advective transport of slope material at depths > 1000 m was indeed demonstrated by McCave et al. (1999), and input of this material to the deep traps is discussed by Antia et al. (1999b), Fagel et al. (1999) and Wollast and Chou (1998). Antia et al. (1999b) conclude that significant lateral POC flux occurs at depths below 1000 m at OMEX 3, most probably due to the detachment of benthic nepheloid layers from the sea bed and the formation of intermediate nepheloid layers carrying suspended material into the water column. For the 1440 m trap at site 3, Antia et al. (1999c) estimate that about 40% of the POC trapped comes from a source other than vertical export from the mixed layer. Since the organic detritus in this trap was observed to be relatively fresh as inferred from low C/N ratios and the presence of labile algal pigments (Antia et al., 1999b), it is likely that advected organic detritus also brought freshly synthesised barite with it.

For winter (January-February) and summer (July-August) 1994, Fagel et al. (1999) observed high and covarying fluxes of excess-Ba, Th, ΣREE and lithogenic matter in the deep traps at OMEX sites 2 and 3. For instance, during these four months, monthly averaged Th fluxes at 3260 m (site 3) ranged between 0.7 and 2.4 $\text{nmol m}^{-2} \text{d}^{-1}$, and such values are about 10 times higher than the average Th fluxes for other periods and depths (Fagel et al., 1999). In spring, however, enhanced excess-Ba fluxes stand alone, not accompanied by enhanced Th and ΣREE fluxes. These observations suggest that in winter and summer 1994 slope material, consisting of both a lithogenic and a Ba-enriched biogenic component (the latter probably resulting from previous plankton blooms) was advected to the sediment trap sites. In spring, the occurrence of an enhanced excess-Ba flux without a lithogenic component indicates coincidence with the phytoplankton bloom.

Differentiating between the two fluxes of excess-Ba seems quite impossible. We have attempted to estimate the fraction of advected excess-Ba at sites 2 and 3 using the Th data reported by Fagel et al. (1999). Based on the Th and ΣREE composition, they report that of all OMEX traps, the site 4 trap (4000 m) is least affected by an advected lithogenic influx. For site 4 trap they report an average Th concentration of 0.25 ppm, which is lower than the averages recorded for the other traps at sites 2 and 3, which range from 0.6 ppm (site 2, 600 m) to 1.8 ppm (site 3, 3260 m). Next, we have assumed that the 4000 m trap at site 4 remained free of an advective input of Th and took the average Th composition for this trap as representative for the true vertical component of the Th flux in the OMEX area in general. For sites 2 and 3 traps we subtracted the average Th concentration obtained for site 4 (0.25 ppm) from the measured total Th concentration to obtain the Th concentration in the advected component. Next, we assumed that all excess-Ba associated with the very high Th flux events in January, February, July and August 1994 at 3260 m, site 3, was entirely of advected origin. Furthermore, we considered the average Ba/Th ratio for these 4 months as representative of the Ba/Th ratio in particulate material advected to the traps. This allowed us to correct the observed total excess-Ba flux values for the advected component. The latter were calculated to range from 8% (site 3, 580 m) to 47% (site 2, 1050 m). In Table 2 we give our best estimate of excess-Ba fluxes, after correction for trapping efficiency and advection. In the following we calculate export production of carbon using our corrected excess-Ba fluxes.

4.3. Flux of excess-Ba and export production

Sarnthein et al. (1988) proposed the following algorithm relating export production (ExP) with water column POC flux (F_{POC}) and depth (Z):

$$F_{\text{POC}} = 20.56 \text{ExP}^{0.6648} Z^{-0.5537}. \quad (2)$$

solving for ExP, Eq. (2) can be written (Francois et al, 1995) as

$$\text{ExP} = \exp[(\ln F_{\text{POC}} + (0.5537 \ln Z) - 3.023)/0.6648] \quad (3)$$

with ExP and F_{POC} in $\text{gCm}^{-2} \text{yr}^{-1}$ and Z in m. This empirical relationship ($r = 0.92$), widely used by others in later studies, is based on a set of 67 Atlantic and Pacific Ocean sediment trap POC flux data and on measured and literature data of primary production (Sarnthein et al., 1988). Updating of this data set has, to our knowledge, not been attempted. For areas under the influence of advection from the margins, Francois et al. (1995) argued that Eq. (3) would not be applicable because of advected POC contributing to the sediment trap fluxes. Considering only oceanic stations well outside any influence of slope regions, they proposed the following algorithm relating the annual average POC/Ba flux ratios to depth:

$$F_{\text{POC}}/F_{\text{Baxs}} = 4787Z^{-0.616}. \quad (4)$$

This empirical relationship, based on numerous sediment trap data from the Pacific and the Atlantic Ocean, reflects the fact that organic matter breakdown and barite formation are fairly homogenous processes worldwide. In the case of no advection of excess-Ba this relationship allows one to assess the fraction of total POC flux advected into the traps and to calculate the true vertical component of the POC flux. Using yearly averaged data for sediment traps from open ocean sites (Pacific and Atlantic Oceans) well outside the influence of margins, Francois et al. (1995) observed an excellent agreement between observed excess-Ba flux and export production calculated from observed POC fluxes via Eq. (3). This resulted in the following empirical relationship:

$$\text{ExP} = 1.95 (F_{\text{Baxs}})^{1.41} \quad (5)$$

with ExP in $\text{g C m}^{-2} \text{ yr}^{-1}$ and F_{Baxs} in $\mu\text{g C cm}^{-2} \text{ yr}^{-1}$.

ExP and F_{Baxs} are of course also related through the combination of Eqs. (3) and (4). Indeed, solving Eq. (4) for F_{POC} and substituting into Eq. (3) allows one to write export production as a function of F_{Baxs} and depth (Nürnberg, 1995; Frank, 1996):

$$\text{ExP} = 3.56 (F_{\text{Baxs}})^{1.504} Z^{-0.0937} \quad (6)$$

with ExP in $\text{g C m}^{-2} \text{ yr}^{-1}$, F_{Baxs} in $\mu\text{g C cm}^{-2} \text{ yr}^{-1}$ and Z in m.

The export production computed using Eq. (6) is relatively insensitive to Z and is equivalent to the outcome of Eq. (5). Assuming that advective transport of matter remains free of excess-Ba, these equations would allow one to estimate export production also in situations where the trapped POC flux integrates vertical and advected components. In the present study we showed, however, that advection of excess-Ba occurs, and we attempted to correct for this effect (see above). In the following we will use our F_{Baxs} data, corrected for trapping efficiency and advective input, to estimate export production.

We applied Eq. (5) to our yearly averaged excess-Ba flux data (Table 2) and obtained annual average export production values ranging from $1.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ (600 m, site 2) to $3.5 \text{ g C m}^{-2} \text{ yr}^{-1}$ (580 m, site 3). We now compare estimated export production with information on new production obtained for the same area. Joint et al. (1999) report that the yearly averaged new production in the OMEX area amounts to $80 \text{ g C m}^{-2} \text{ yr}^{-1}$ 50% of total production. Wollast and Chou (1998) propose a value of $54 \text{ g C m}^{-2} \text{ yr}^{-1}$ for ExP at site 3 and a value of $30 \text{ g C m}^{-2} \text{ yr}^{-1}$ at site 4. Antia et al. (1999c) propose a value of $49 \text{ g C m}^{-2} \text{ yr}^{-1}$ at the outer slope (site 3). Whatever the value chosen, we face a major problem, with the Ba-proxy approach, outlined here, resulting in much lower values for carbon export. Several explanations can be offered to account for this discrepancy, which can reach a factor of 40.

To account for an export production of the order of $50 \text{ g C m}^{-2} \text{ yr}^{-1}$, the flux of excess-Ba should be of the order of $9 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ (equivalent to $1800 \text{ nmol m}^{-2} \text{ d}^{-1}$), up to 8 times larger than the observed F_{Baxs} values. While such high values can occur and have occasionally been observed elsewhere (e.g. California Current, 42°N - 126°W , Dymond et al. (1992); Barents Sea 74°N - 15°E , Francois et al. (1995)), they are the exception, and overall averages of the values reported by Dymond et al. (1992) and Francois et al. (1995) are lower by a factor of 4. This suggests that either the carbon export production values put forward by others for the OMEX area are too high or that the relationship between F_{Baxs} and ExP deduced for open ocean systems is not applicable in this margin environment. In the following we will look more carefully into the different empirical relationships used to develop the F_{Baxs} -ExP transfer function (Eq. (5)) and check whether these relationships, developed from open ocean data sets, apply to a margin system.

Using Eq. (3) we tuned the value of ExP to obtain F_{POC} values similar to those observed in the OMEX traps after correcting for trapping efficiency and advective supply. For POC, the impact of advection is difficult to assess, but based on the discussion in Antia et al. (1999c) we considered advective POC supply to represent 40% of total F_{POC} in the 1440 and 3260 m traps at site 3, but to be negligible in the other traps. It then appears that in order for Eq. (3) to produce F_{POC} values similar to the (corrected) observed F_{POC} values, ExP should be reduced to about $18 \text{ g C m}^{-2} \text{ yr}^{-1}$. We can now wonder what should be the values of F_{Baxs} required to sustain such an ExP value? Using the calculated F_{POC} values, obtained via Eq. (3) for $\text{ExP} = 18 \text{ g C m}^{-2} \text{ yr}^{-1}$, we calculated F_{Baxs} via Eq. (4). These calculated F_{Baxs} values are still up to 7 times higher than the observed values. This raises the question about the applicability of the Eq. (4) relationship to non-open-ocean systems. Fig. 3 compares the evolution of the $F_{\text{POC}}/F_{\text{Baxs}}$ ratio with depth between open ocean and margin systems. We recall that these $F_{\text{POC}}/F_{\text{Baxs}}$ ratios in Fig. 3 were obtained for fluxes not corrected for advective input. It can be seen from Fig. 3 that OMEX data evolve in a way very similar to those reported by Francois et al. (1995) for margin areas and that for any given

depth, $F_{\text{POC}}/F_{\text{Baxs}}$ ratios for margin areas are larger than for open ocean systems. Of course, for the OMEX sites we know that F_{POC} and F_{Baxs} fluxes need to be corrected for advective inputs. However, for the traps at 1440 and 3260 m at OMEX site 3 the magnitude of advective input is similar for POC and excess-Ba (about 40%), and thus advection is not expected to impact considerably on the $F_{\text{POC}}/F_{\text{Baxs}}$ ratios, at least for these traps. For site 2 correction for advective input would concern only F_{Baxs} (no POC advection assumed, see above), increasing even more the discrepancy with the open ocean systems. Thus, it is likely that margin systems function differently from open ocean systems with regard to the yield of excess-Ba during organic matter degradation. Francois et al. (1995) give an overview of available sediment trap data sets (their Table 1), and they identify the following data sets as characteristic of margin systems: Bering Sea; Okhotsk; Panama Basin; De-marara; Sargasso; Sohm; Lofoten; Bear Island; Fram Strait; Greenland Basin; Aegir Ridge; Barents Shelf; Barents Sea; Arabian Sea. We have complemented this data set with the Atlantic Ocean data reported by Dymond et al. (1992), which, according to Francois et al. (1995), also are more characteristic of margin systems. The following power function describes the $F_{\text{POC}}/F_{\text{Baxs}}$ evolution with depth in the water column for the whole of this margin data set:

$$F_{\text{POC}}/F_{\text{Baxs}} = 16\,360Z^{-0.646}. \quad (7)$$

If we substitute for F_{POC} in Eq. (7) the values obtained from Eq. (3) with ExP taken as $18\text{ g C m}^{-2}\text{ yr}^{-1}$, we obtain F_{Baxs} values between 1.6 and $1.8\ \mu\text{g cm}^{-2}\text{ yr}^{-1}$. Such values are similar to those observed for the traps at sites 3 and 4 (between 1 and $1.6\ \mu\text{g cm}^{-2}\text{ yr}^{-1}$; Table 2). For site 2, observed F_{Baxs} values are lower (between 0.6 and $0.8\ \mu\text{g cm}^{-2}\text{ yr}^{-1}$), possibly indicative of an even lower ExP value (closer to $7\text{ g C m}^{-2}\text{ yr}^{-1}$) for the inner slope region.

It thus appears that the regression describing the evolution of $F_{\text{POC}}/F_{\text{Baxs}}$ ratio with depth in open ocean systems may indeed not be applicable to margin systems. Margin systems and open ocean systems operate differently, with margin systems characterised by a proportionally smaller excess-Ba flux for a given POC flux. The reasons for this remain to be explained, but we speculate that differences in water column transit of exported POM (faster for margin systems) and maturation time for barite synthesis (shorter for margin systems) between margin and open ocean systems could be responsible.

Our findings also suggest that export production in the OMEX outer slope region is rather closer to $18\text{ g C m}^{-2}\text{ yr}^{-1}$ than to $50\text{ g C m}^{-2}\text{ yr}^{-1}$, a value put forward by others using different approaches. It could be that a major fraction of new organic carbon does not settle out of the upper mixed layer, possibly because of (i) the diversion of a fraction of the new production into dissolved organic matter instead of particulate organic matter, or (ii) the advective transport of export production out of the margin area.

5. Conclusions

We have documented further the presence of barite in sedimenting oceanic suspended matter. A close association of barite crystals with aggregates of biogenic detritus was observed, stressing the potential of such crystals to trace export production.

The proportionally smaller solubilisation of Ba in the deep traps relative to the shallow traps is taken as an indication that barite synthesis in degrading organic matter is not completed when organic matter exits the surface mixed layer, but goes on during transit through the upper 1000 m of water column. However, the similarity of excess-Ba fluxes between shallow and deep traps (after correcting for trapping efficiency) suggests that the reservoir of excess-Ba was already constituted in the material sampled by the shallow traps.

Trapped fluxes of sedimenting material in this OMEX area were affected by advection of material from the upper slope region. Taking Th as a tracer of advective input we estimated the true vertical component of the excess-Ba flux. Using excess-Ba fluxes corrected for trapping efficiency and advection and a depth evolution of the POC over excess-Ba flux ratios, typical for margin areas, our data suggest particulate carbon export in the OMEX slope region to be of the order $8\text{-}18\text{ g C m}^{-2}\text{ yr}^{-1}$. Such values are lower by a factor 3-6 than estimates of new production based on nutrient uptake studies. Both approaches would converge, however, if a significant fraction of new production ends up as dissolved organic matter instead of particulate organic matter. Further studies are required to verify this proposed differential behaviour of the Ba-proxy in margin systems relative to open ocean systems.

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