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PARTICULATE BARIUM FLUXES ON THE CONTINENTAL MARGIN: A STUDY FROM THE ALBORAN SEA (WESTERN MEDITERRANEAN)

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ABSTRACT

Particulate biogenic barium (bio-Ba) fluxes obtained from three instrumented arrays moored in the Alboran Sea, the westernmost basin in the Mediterranean Sea, are presented in this study. The mooring lines were deployed over almost one year, from July 1997 to May 1998, and were equipped with sediment traps at ~500-700 m depth, ~1000-1200 m depth and 30 m above the sea floor (~1000-2200 m). The results obtained support the growing body of evidence that the relationship between particulate bio-Ba and Corg throughout the water column in margin systems is clearly different from this relation in the open ocean. In the Alboran Sea the annual averaged bio-Ba fluxes range from 0.39 to 1.07 μmol m^{-2} d^{-1}, with mean concentrations of 1.31-1.69 μmol g^{-1} and bio-Ba/Corg ratios lower than in the open ocean. The low bio-Ba values obtained also indicates that calculating bio-Ba is extremely sensitive to the detrital Ba/Al ratio of each sample. The lithogenic Ba fraction in the Alboran Sea continental margin area contributes between 24% to 85% of the total Ba. Increased bio-Ba export efficiency was observed after periods of high primary productivity and suggests that the processes limiting the bio-Ba formation in the study area relate to settling dynamics of organic matter aggregates. Furthermore, the ballasting effect of the abundant lithogenic and carbonate particles may limit decomposition of organic matter aggregates and enhance the transfer of particles rich in Corg and relatively poor in bio-Ba to the deep sea floor. Lateral input of freshly sedimented biogenic material, including particulate bio-Ba, has been observed on the lower continental slope in the western Alboran Sea. These observations emphasize that the use of the bio-Ba as a proxy of export productivity from the surface ocean must be used cautiously in highly dynamic environments such as those in the Alboran Sea.

Keywords: Biogenic barium, Particulate flux, Organic carbon, Export production, Alboran Sea, Mediterranean Sea

5.1. INTRODUCTION

Continental margins play an important role in the biogeochemical cycling of carbon because of the high primary production and sedimentation rates typical of these environments, which cause the burial of substantial amounts of this element. Accurate determinations of modern and paleo-organic carbon fluxes on continental margins is therefore of prime importance to improve our understanding of the global carbon cycle and its response to climate change. However, the recycling of organic carbon while settling through the water column and during early diagenesis in the sediment may reduce its utility as a primary productivity proxy. The apparent relationship between barium from biogenic barite ($BaSO_4$) and organic carbon, and the relatively refractory nature of biogenic barium in non sulfate reducing sediments, have led to the consideration of biogenic barium as a proxy for both modern (Dymond et al., 1992; Francois et al., 1995) and past (Schmitz, 1987; Dymond et al., 1992; Gingele and Dahmke, 1994; Paytan et al., 1996) biological processes. Although seawater is usually undersaturated with respect to barite (Monnin et al., 1999), this mineral is thought to precipitate within saturated microenvironments within settling particles as a result of the oxidation of organic sulphur to sulphate into the decaying organic matter (Bishop, 1988), the release of both barium and sulphur from the dissolution of acantharian-derived celestite (Bernstein et al., 1992), or the release of barium during plankton decomposition (Ganeshram et al., 2003).

Recent studies have revealed that the relationship between organic carbon and biogenic barium fluxes in margin systems and open ocean systems differs markedly. Margin systems are characterized by a proportionally lower biogenic barium flux for a given organic carbon flux (Dymond et al., 1992; Francois et al., 1995; Dehairs et al., 2000; McManus et al., 2002). Dymond et al. (1992) suggested that low biogenic barium to organic carbon ratios (bio-Ba/Corg) in the Atlantic Ocean are a consequence of lower dissolved barium concentrations in seawater that reduce the effectiveness of barite formation. In contrast, Francois et al. (1995) proposed that it might result from the addition of refractory organic carbon from nearby continents, shelves or slopes rather than from a reduced barite formation. Recent works suggest that the processes controlling barite formation relate to changes in the ecosystem (Dymond and Collier, 1996) and to the kinetics of organic matter aggregates during settling and decomposition (Dymond and Collier, 1996; Dehairs et al., 2000; Jeandel et al., 2000). Overall, these issues have lead to serious questions about the quantitative use of biogenic barium to reconstruct present and past export production in margin environments (McManus et al., 2002).

In this paper we describe particulate biogenic barium fluxes in the deep Alboran Sea, SW

Mediterranean Sea, thus contributing to the understanding of the behavior and significance of this component in the ocean. The particle flux data were collected within the MTPII-MATER project (Mediterranean Targeted Project II-Mass Transfer and Ecosystem Response) funded by the European Commission, which main goal was to study and quantify mass transfer processes in contrasting trophic environments of the Mediterranean Sea (Monaco and Peruzzi, 2002). The reasons for choosing the Alboran Sea as a key area for this purpose were i) the well-known surface circulation dominated by the entrance through the Strait of Gibraltar of an Atlantic water jet forming two almost permanent anticyclonic gyres (the western and eastern Alboran gyres) and a geostrophic front (the Almeria-Oran front), and ii) the enhanced primary production associated to coastal upwelling to the north of the Alboran Sea, and to the edges of the gyres. The results obtained have provided important insights into the influence of these hydrological structures on the amount and character of the settling material at both the western (Fabres et al., 2002; 2004) and the eastern (Sanchez-Vidal et al., 2004a; b) Alboran Sea. The temporal evolution of particle fluxes in the western Alboran Sea is mostly controlled by intermittent fluvial discharge in autumn and winter, and by gyre-induced oscillations in primary production and coastal upwelling in spring and summer (Fabres et al., 2002). The spreading to the east and to the south of upwelled waters by the Atlantic jet drives the seasonal arrival of biogenic material to the eastern Alboran Sea (Sanchez-Vidal et al., 2004a). A deep advective input of mainly lithogenic and carbonate particles derived from intermediate and bottom nepheloid layers has been also observed throughout the Alboran Sea. Furthermore, Sanchez-Vidal et al. (2004b) have shown that less than 1% of the carbon fixed during photosynthesis in surface waters is transferred vertically and finally buried into the deep sediments, while a large portion is supplied by lateral advection and through the benthic nepheloid layer. The significance of all these processes is discussed in order to improve current knowledge on the formation of biogenic barium and its complex relationship with organic carbon in deep margin and basin systems.

5.2. MATERIAL AND METHODS

5.2.1. Moorings and sample collection

Data were obtained from three moorings, ALB1, ALB4 and ALB5, deployed from July 1997 to May 1998 in the Alboran Sea. The major constituent fluxes recorded by this experiment have been reported by Fabres et al. (2002; 2004) and Sanchez-Vidal et al. (2004a; b). Each mooring was equipped with two (ALB1) or three (ALB4 and ALB5) Technicap PPS3 sediment traps (Heussner et al., 1990) paired with current meters at 500-700 m depth (upper, U), 1000-1200 m depth (middle, M), and 30 m above bottom (lower, L) (Fig. 5.1, Table 5.1). Samples were collected over 11 months and consisted of three successive deployment periods: (I) July 1st 1997-October 31st 1997, (II) November 15th 1997-March 10th 1998, and (III) April 1st 1998-May 22nd 1998. Sampling intervals were 10-11 days except for the period from April 11th to May 16th 1998 when a 3-day interval was applied. The later and shorter sampling interval was implemented to carry out a High Frequency Flux Experiment (HFFE) in key transects from both the eastern and the western Alboran Sea (Fabres et al., 2004).

We also report data from six sediment cores obtained with an eight-tube multicorer system in October 1996, November 1997 and April 1998, which have been described in Masqué et al. (2003) (Fig. 5.1). Cores ALB1, ALB4 and ALB5 were collected below the moorings ALB1, ALB4 and ALB5. Core T1 was collected in the upper continental slope south of Malaga at a water depth of 654 m. Cores ALBD and ALBE were located near ALB1, following a west - east transect parallel to the continental slope south of Malaga. All cores recovered the sediment water interface and represent Holocene deposition.

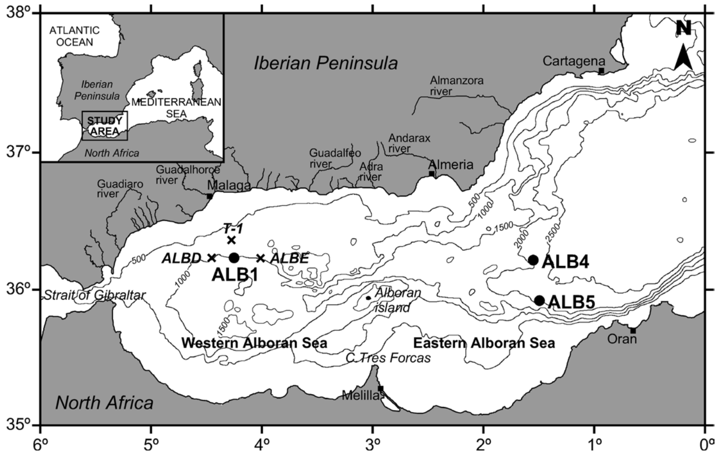

Figure 5.1. Location of mooring sites ALB1, ALB4 and ALB5 (black dots) and sediment cores T1, ALB1, ALBD, ALBE, ALB4 and ALB5 (crosses and black dots) within the Alboran Sea. Main river systems to the north of the Alboran Sea are also indicated. Bathymetric contours in meters.

Table 5.1. Location, water depth and trap depths levels of the mooring deployments in the Alboran Sea.

Station	Latitude	Longitude	Water depth	Trap code	Trap depth
Western Alboran Sea					
ALB1	36º 14.39' N	04º 15.41' W	1000 m	ALB1-U	470 m
				ALB1-L	975 m
Eastern Alboran Sea					
ALB4	36º 13.06' N	01º 33.53' W	2240 m	ALB4-U	645 m
				ALB4-M	1170 m
				ALB4-L	2210 m
ALB5	35º 55.47' N	01º 30.77' W	2100 m	ALB5-U	510 m
				ALB5-M	1050 m
				ALB5-L	2070 m

5.2.2. Analytical methods

Sediment trap sample processing and analytical procedures are described in Fabres et al. (2002), while sediment core processing is described in Masqué et al. (2003). Trace element determination was performed on ~20 mg splits of sediment trap and sediment core samples. Complete digestion of the sample was accomplished through hot (~80°C) sequential HNO_3, HCl, and HF dissolution in Teflon vials. Ba, Al, Ti and Mn were analysed on a Liberty 150 ICP-AES in the W.M. Keck Collaboratory for Plasma Spectrometry at Oregon State University (Dymond and Collier, 1996).

By convention, particulate barium in excess of that associated with crustal phases is operationally defined as "Biogenic Barium" (bio-Ba) and calculated as:

$$\text{bio-Ba} = \text{total-Ba} - \text{Al}(\text{Ba}/\text{Al})_c \qquad (5.1)$$

where total-Ba and Al are measured concentrations, and $(\text{Ba}/\text{Al})_c$ is the crustal ratio for these elements. Dymond et al. (1992) proposed Ba/Al_c ratio ranges between 0.005 and 0.010. Since using a value within this range was too high for our lithogenic-dominated samples we chose a Ba/Al_c of 0.0033 to represent the regional crustal ratio (Fig. 5.2), which is discussed in detail below.

5.3. RESULTS

5.3.1. Terrigenous Ba input and Ba/Al ratio

Much of the discussion of bio-Ba as a productivity proxy has been developed in pelagic environments where the crustal fraction within particle fluxes is extremely low. In particulate matter with a large terrigenous fraction, such as that collected in the Alboran Sea, errors in the estimation of the lithogenic Ba/Al ratio can introduce errors in the estimation of the bio-Ba flux (Dymond and Collier, 1996). The knowledge of the regional Ba/Al ratio of aluminosilicates is essential for a reliable determination of bio-Ba in sediments (Klump et al., 2000).

To calculate bio-Ba we need to know the lithogenic Ba/Al ratio (Ba/Al_c) relevant to our samples. Assuming that the crustal barium is refractory and that all the aluminium is detrital, then the lowest Ba/Al ratio observed in the traps and sediments should represent a maximum value for the Ba/Al_c. The correlations between aluminium, titanium, iron and other common lithogenous elements in our traps are all greater than 0.99 and the calculated lithogenic flux is always a major fraction of the total particulate flux. Accordingly, it is safe to assume that all the aluminium is lithogenic (Dymond et al., 1997).

The lowest Ba/Al ratio found in the Alboran Sea trap samples is 0.00388, (Fig. 5.2), which is observed throughout the water column at all three moorings during late autumn. The lowest Ba/Al ratio found in the sediments is 0.00335, recorded in sediments from station ALB5. Fabres et al. (2002) identified intermittent local fluvial discharge as the responsible for the supply of lithogenic particles to mid-water depths in the western Alboran in autumn and winter 1997-1998. Accordingly, Masqué et al. (2003) demonstrated the influence of the western fluvial sources and a marked physiographic control over the distribution of lithogenic material in the bottom sediments of the Alboran Sea. Furthermore no important Saharan dust intrusions affected the southern Iberian Peninsula during late autumn 1997 (Rodriguez et al., 2001). Also, the present day Saharan dust deposition described by Guerzoni et al. (1997) represents 7-9% of the annual lithogenic flux in our upper traps. Therefore, on an annual basis we can expect that eolian inputs from southern sources to contribute less than 10% of the total lithogenic flux.

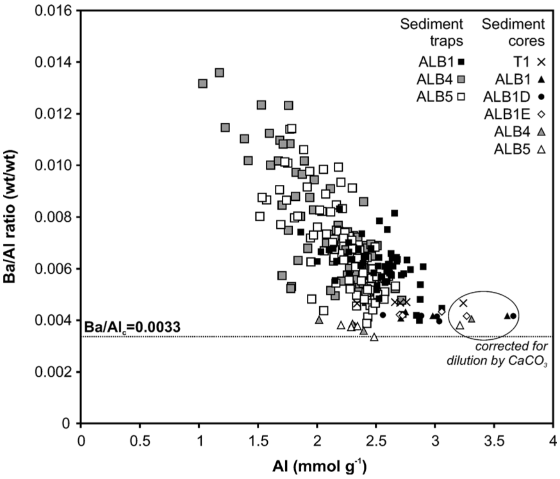

Figure 5.2. Ba/Al wt. ratio as related to Al (mmol g^{-1}) for all sediment trap and sediment core data in this study. Four subsample points are plotted for each sediment core: 0.25 (core top), 1.25, 2.25 and 13.5-22.5 cm below bottom. The Ba/Al ratio versus Al corrected for dilution by CaCO3 of the core top samples (encircled) highlights the two end-members (crustal and biogenic barium).

Although the apparent Ba/Al$_c$ ratio is lower than the average shale value, such low ratios have been reported in the eastern Mediterranean Sea (Wehausen and Brumsack, 1999; Weldeab et al., 2003), the Chilean margin (Klump et al., 2000) and the eastern Arabian Sea (Prakash Babu et al., 2002; Schenau et al., 2001). Recently, Reitz et al. (2004) reported a regional average ratio of 0.0031 for the eastern Atlantic surface sediments and a ‘global’ average ratio of 0.0037 based on sequential extraction procedures. Our results are also in good agreement with a detailed study of the Ba/Al ratio in the clay mineral fraction of eastern Mediterranean sediments (Rutten and De Lange, 2002), where a Ba/Al ratio of 0.0030-0.0036 was reported. Consequently, we considered a value of 0.0033 to represent the regional lithogenic ratio in the Alboran area and we use this ratio for calculating the bio-Ba in our trap and sediment samples.

5.3.2. Fluxes of bio-Ba through the water column

The time-weighted fluxes and concentrations of the total Ba, bio-Ba and total Al are given in Table 5.2. Total mass flux and fluxes of major constituents including Corg, biogenic silica (bio-Si, taken as SiO_2. $0.4H_2O$ following Mortlock and Froelich, 1989), and $CaCO_3$ are also shown for comparison. The annual bio-Ba fluxes range between 0.39-1.07 µmol m^{-2} d^{-1}, or 15-76% of the total-Ba content in the individual samples, with average annual values of 53% (ALB4), 49% (ALB5), and 44% (ALB1). In the western Alboran Sea, bio-Ba flux increases considerably between 500 m and the near-bottom trap (ALB1 in Fig. 5.3). In contrast, the bio-Ba flux decreases with depth at both stations of the eastern Alboran Sea (ALB4 and ALB5 in Fig. 5.3). The depth decrease in bio-Ba flux at ALB5 is small in comparison with the decrease at ALB4. However we may have underestimated the time-weighed fluxes of bio-Ba in the near bottom ALB4 trap due to the gap of bio-Ba data in periods I and III, during which high bio-Ba fluxes were recorded at all other traps.

Table 5.2. Time weighed fluxes, mass accumulation rates (core top) and concentrations of trace elements and major constituents in the Alboran Sea.

	Water depth	Ba	bio-Ba	bio-Ba flux	bio-Ba/ Corg x100	Al flux	Corg flux[1]	bio-Si flux[1,2]	$CaCO_3$ flux[1]	Mass flux[1]	Mn/Al x100
	(m)	*(μmol g^{-1})*	*(μmol g^{-1})*	*(μmol $m^{-2}d^{-1}$)*	*(wt. ratio)*	*(mmol $m^{-2}d^{-1}$)*				*(mg $m^{-2}d^{-1}$)*	*(molar ratio)*
Sediment traps											
ALB1	470	2.77	1.18	0.70	0.31	1.45	2.60	0.53	0.83	594	0.43
	970	3.18	1.47	1.07	0.55	1.91	2.24	0.58	1.37	727	0.81
ALB4	645	2.97	1.62	0.83	0.41	1.06	2.31	0.49	1.14	502	0.48
	1170	2.91	1.69	0.59	0.48	0.66	1.42	0.31	0.79	350	0.51
	2210	2.75	1.24	0.39	0.52	0.74	0.86	0.16	0.87	318	0.57
ALB5	510	2.75	1.35	0.92	0.37	1.47	2.84	0.57	1.56	682	0.45
	1050	2.77	1.37	0.89	0.38	1.41	2.70	0.59	1.32	652	0.41
	2070	2.73	1.31	0.88	0.50	1.46	2.03	0.53	1.68	670	0.66
Sediment cores											
T1	654	2.47	0.72	3.59	0.85	13.50	4.84	0.46	8.00	4995	1.86
ALB1	962	2.44	0.51	1.10	0.68	6.44	1.85	0.04	3.91	2162	1.03
ALBD	946	2.46	0.50	1.40	0.63	8.38	2.52	0.10	4.95	2778	1.42
ALBE	1011	2.24	0.48	0.57	0.67	3.24	0.98	0.11	2.03	1190	1.12
ALB4	2065	1.60	0.29	0.41	0.55	2.86	0.85	0.06	5.50	1417	2.22
ALB5	1993	1.65	0.22	0.38	0.33	3.78	1.35	0.06	5.36	1718	1.66

[1] Time weighed flux of major constituents has been calculated using only the samples in which bio-Ba was analyzed

[2] bio-Si (biogenic silica) is taken as $SiO_2 \cdot 0.4\ H_2O$ following Mortlock and Froelich (1989)

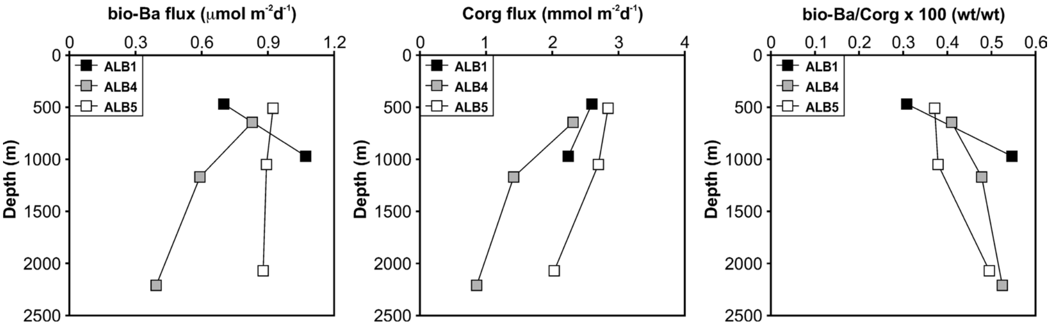

Figure 5.3. Depth profiles of time-weighed annual mean bio-Ba flux (μmol m^{-2} d^{-1}), Corg flux (mmol $m^{-2}d^{-1}$), and bio-Ba/Corg x100 wt. ratio at ALB1, ALB4 and ALB5 mooring stations.

The annual bio-Ba to organic carbon ratio (bio-Ba/Corg) increases with depth at all stations, which is a common observation in most oceanic sediment traps (Fig. 5.3). The increase in bio-Ba/Corg ratio results from a preferential loss of Corg relative to bio-Ba, although both components decrease down the water column, except at ALB1 where almost all near-bottom fluxes increase relative to the upper trap (Table 5.2). There is a linear relationship between the flux of bio-Ba (μmol m^{-2} d^{-1}) and Corg (mmol m^{-2} d^{-1}) of all samples (r^2=0.73, intercept = 0.23, slope of 0.27 ± 0.02 at the 95% confidence interval). The flux of bio-Ba (μmol m^{-2} d^{-1}) also correlates with that of bio-Si (mmol m^{-2} d^{-1}) (r^2=0.80, intercept = 0.38, slope of 0.87 ± 0.06 at the 95% confidence interval) in the pooled dataset (Fig. 5.4).

The temporal record of bio-Ba flux is characterized by two peaks occurring at all three stations in July 1997 and May 1998 (Fig. 5.4). Throughout the record, the bio-Ba fluxes at each mooring follow a similar pattern at all depths in the water column. Some minor peaks are observed in October 1997, December 1997 and January 1998. The bio-Ba concentration (μmol g^{-1}) in the settling particles begins to increase during the spring-summer blooms and remains relatively high later in the summer. This is followed by a period of very low values in the late fall, and a gradual increase towards the spring peak (Fig. 5.4). The bio-Ba/Corg ratio follows the same pattern during the monitored year.

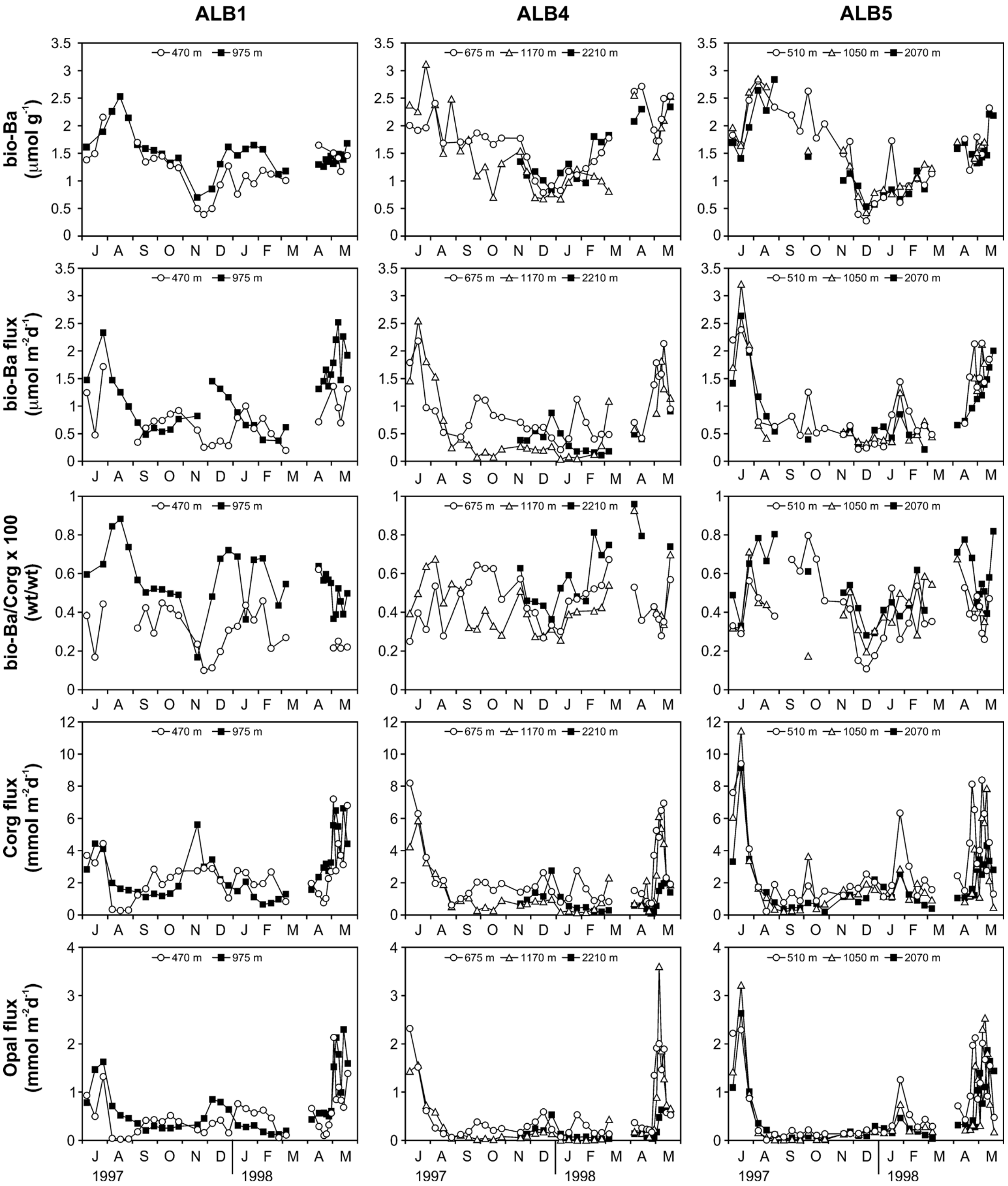

Figure 5.4. Time series plots of bio-Ba concentration (μmol g^{-1}), bio-Ba flux (μmol m^{-2} d^{-1}), Corg flux (mmol m^{-2} d^{-1}), and bio-Ba/Corg x100 wt. ratio at ALB1, ALB4 and ALB5 mooring stations.

5.3.3. The composition and accumulation rate of surface sediments

The accumulation rates and concentrations of the total Ba, bio-Ba and total Al in surface sediments (0.25 cm below bottom, core top) are also shown in Table 5.2 along with total mass and the major constituent fractions including Corg, bio-Si and $CaCO_3$. Bio-Ba is calculated the same way as in sediment traps using the same crustal Ba/Al ratio discussed above (0.0033). Both bio-Ba concentration and accumulation rates were the highest in station T1 located on the upper slope above the western basin and reached minimum values in the deep eastern basin station ALB5.

The oxygen concentrations in the core tops were near seawater values at all the stations as reported by Bianchi et al. (2003), with oxygen penetration depths from 2.2 cm at T1 to 4.1 cm at ALB4. Therefore, no dissolution and mobilization of bio-Ba is likely to take place in these sediments (McManus et al., 2002).

5.4. DISCUSSION

5.4.1. Spatial distribution of bio-Ba fluxes over the Alboran Sea

The annual averaged bio-Ba fluxes measured in the Alboran Sea are similar to those observed in other marine systems including the Equatorial Pacific (Dymond et al., 1992, 1996), the tropical NE Atlantic (François et al., 1995; Jeandel et al., 2000), and the Ross Sea (McManus et al., 2002). The bio-Ba fluxes are higher than in the Bay of Biscay (Dehairs et al., 2000) or in the western Atlantic Ocean (Dymond et al., 1992). The Corg fluxes in the Alboran Sea are very high such that the bio-Ba/Corg ratios of the settling material are low. Recent studies have revealed that the variation of bio-Ba versus Corg with depth in many ocean margin systems differs from that of the open ocean (Francois et al., 1995; Dehairs et al., 2000), with a lower bio-Ba flux relative to the Corg flux. The ratios recorded in the Alboran Sea are amongst the lowest reported (Fig. 5.5) and are similar to the Ross Sea and the Bay of Biscay. Francois et al. (1995) proposed that the low bio-Ba/Corg ratios in these regions results from the addition of refractory Corg resuspended from the shelf or from terrigenous sources. Dehairs et al. (2000) also recognized the difference between margin and open ocean systems and hypothesized that water column formation processes could contribute to these differences. In spite of the relatively high bio-Ba/Corg ratios in the Equatorial Pacific, Dymond and Collier (1996) observed a significant range in the bio-Ba/Corg during the annual cycle, which they attributed to changes in the ecosystem and export efficiency. In order to consider the systematics of bio-Ba and Corg in the Alboran Sea we must first consider the effect of horizontal transport of benthic material on the bio-Ba/Corg ratio and the composition of sediments in the basin.

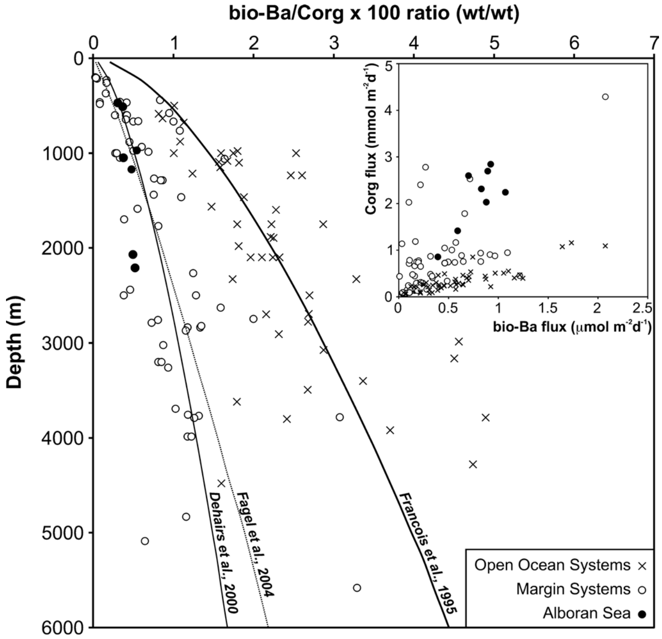

Figure 5.5. Depth distribution of bio-Ba/Corg x100 wt. ratios in the Alboran Sea and other areas reported in the literature. Crosses are open ocean systems as identified by Francois et al. (1995): Equatorial Pacific and California current stations from Dymond et al. (1992), and Pacific and Atlantic stations from Francois et al. (1995). Open circles are margin systems as identified by Francois et al. (1995): Bering Sea, Okhtosk, Panama Basin, Demamara, Sargasso, Sohm, Bear Island, Fram Strait, Greenland Basin, Aegir Ridge, Barents shelf, Barents Sea, Arabian Sea, adding the Atlantic stations from Dymond et al. (1992), Jeandel et al. (2000), Dehairs et al. (2000) and Fagel et al. (2004), and the Ross Sea stations from McManus et al. (2002). Closed circles are Alboran Sea stations (this study). The inset shows the relationship between bio-Ba and Corg fluxes at the same stations.

As in most continental margin areas, in the Alboran Sea there is strong lateral transport of particulate material. Recent publications on the major constituents and the Corg dynamics in our Alboran Sea sediment traps have revealed a down-slope transport of organic matter from the shelf (Fabres et al., 2002; Sanchez-Vidal et al., 2004b). In the two stations closest to the continental margin, ALB1 and ALB5, up to 44% of the Corg flux collected by the middle and lower sediment traps is supplied by lateral advection. In contrast, vertical settling appears to dominate the Corg fluxes at ALB4. Sediment mass balance modeling suggests that a large fraction of Corg (up to 62%) in the sediments is supplied laterally presumably by a benthic nepheloid layer below 30 m above the bottom. All fluxes at ALB1 increase dramatically with water depth, including bio-Ba and the bio-Ba/Corg ratio. The increase in bio-Ba with depth at ALB1 results from lateral input. If this is indeed the case then the additional flux should have some of the characteristic composition of up-slope sources such as the sediment in core T1 (Fig. 5.1). Fabres et al. (2002) argue that the development of a nepheloid layer detaching from the margin where the T1 sediment core is located (see Fig. 5.4 in Fabres et al., 2002) is responsible for the higher fluxes in the lower trap. The sediment core T1 has the highest bio-Ba content of any of the sediments we sampled (0.72 μmol g^{-1}), and could contribute to the increase of bio-Ba flux in ALB1. This high bio-Ba may be due to higher primary production and bio-Ba fluxes in the northern part of the western Alboran Sea and/or a higher preservation of bio-Ba under conditions of high mass accumulation rates.

Additional support for the hypothesis of lateral transport of sediment comes from the significant increase of lithogenic, calcium carbonate and bio-Si annual fluxes towards the bottom trap. This lateral input includes particles resuspended from upslope areas as suggested by the two-fold increase of the Mn/Al molar ratio in the bottom trap (Table 5.2). This enrichment is generated by the benthic redox cycling and enrichment of particulate Mn in the bottom boundary layer (Heggie et al., 1987; Price et al., 1999). Based on this evidence we hypothesize that the bottom trap at ALB1 is recording near bottom transfer of biological-rich sediment, including higher bio-Ba. The influence of such lateral advection has been observed also in the OMEX traps off the mid-European margin by Dehairs et al. (2000).

In contrast, at the eastern Alboran Sea station ALB4 neither increases in lithogenic, bio-Si nor in Mn/Al molar ratio are observed. The bio-Ba/Corg ratio remains close to the same value at all three depths, ranging 0.41-0.52 (wt/wt). The absence of lateral input of Corg at this station has been also reported by Sanchez-Vidal et al. (2004a). Thus, and as seen on Figure 5.3, in absence of lateral input of material, a loss of up to 53% of the bio-Ba flux occurs between the upper trap and the seafloor.

At station ALB5 lateral transport into the bottom trap is evident by the increase in calcium carbonate and lithogenic fluxes, together with an increase of the Mn/Al molar ratio (Table 5.2). This non-vertical flux of Corg represents 44% of the total Corg flux at 2000 m of water depth (Sanchez-Vidal et al., 2004b). The bio-Ba fluxes and concentration however do not increase with depth indicating minimal input of Ba by lateral transport at this site. The difference between stations ALB1 and ALB5 is the lower primary production in the North-African shelf near ALB5 in comparison with the Iberian shelf near ALB1, as observed from SeaWiFS images by Garcia-Gorriz and Carr (2001). This would affect the composition of the nepheloid layer particles, which would be more enriched in lithogenic and calcium carbonate components. Indeed, the sediment cores at this site display very low bio-Ba concentrations (0.22-0.29 μmol g^{-1}) and bio-Ba/Corg ratio (0.33-0.55 wt/wt), thus resuspended material that feeds the nepheloid layer in this area is not enriched in bio-Ba.

5.4.2. Mechanisms of bio-Ba formation

A complete interpretation of bio-Ba as a proxy related to organic matter export requires an understanding of the mechanisms of barite formation. These mechanisms have been explored for over 30 years and the community is only marginally closer to a clear answer. Because surface seawaters in non-polar regions are generally undersaturated with respect to barite (Church and Wolgemuth, 1972; Monnin et al., 1999), barite crystals are assumed to precipitate within supersaturated microenvironments of settling particles (Dehairs, 1980) such as recently dead siliceous plankton and large aggregates particles (Collier and Edmond, 1984; Dymond and Collier, 1996 and references therein). The sources of barium and sulfate in these microenvironments could originate from the oxidation of organic sulfur to sulfate (Chow and Goldberg, 1960; Dehairs et al., 1980; Bishop, 1988), the release of barium during plankton decomposition (Ganeshram et al., 2003), or the release of both barium and sulfur from the dissolution of acantharian-derived celestite (Bernstein et al., 1992). Many investigators have noted that barium is associated with many other biogenic phases beyond barite (Collier and Edmond, 1984; Paytan et al., 1993). In particular, leaching experiments (Ganeshram et al., 2003; Eagle et al. 2003) have shown that the barium identified as biogenic (non-detrital) includes associations with carbonate, organic matter, opal, Fe-Mn oxyhydroxides as well as mineral barite.

Although recent reports of dissolved Ba concentrations in the western Mediterranean are not available, Bernat et al. (1972) report concentrations of 80 nmol Kg^{-1}, nearly constant throughout the water column and almost two times higher than dissolved barium in Atlantic surface waters (Monnin et al., 1999). In spite of the higher dissolved concentrations, the trap data clearly do not suggest higher bio-Ba/Corg ratios in upper waters of the Alboran Sea compared to other sites (Fig. 5.5). Accordingly it seems that chemical equilibria responding to upper ocean dissolved Ba concentrations play a relatively minor role in biogenic barite formation. Rather, it is clear that the kinetics of barite precipitation in association with settling particles, including such variables as water column transit times of exported organic matter and maturation time for barite synthesis, must play the dominant role (Dehairs et al., 2000).

To constrain the processes that control bio-Ba formation and fate in the Alboran Sea, we will examine the temporal variability of the bio-Ba flux and bio-Ba/Corg ratio throughout the monitoring period. The seasonal variation in bio-Ba flux is characterized by two periods of high flux near the beginning and the end of the monitoring period (July 1997 and April-May 1998). These correspond with peaks in bio-Si and Corg fluxes which reflect the seasonality in surface primary productivity (Fig. 5.4). The upwelling off the Spanish coast in

June 1997 and April 1998 has been detected by satellite imagery (Garcia-Gorriz and Carr, 2001), and the related high biogenic fluxes throughout the Alboran Sea have been reported by Fabres et al. (2002) and Sanchez-Vidal et al. (2004b). These studies document the bio-Si and Corg flux peaks which follow the development of diatom-rich phytoplankton communities, which contribute with up to 84% of the carbon biomass in the 100 m surface layer (Arin et al., 2002). The high bio-Ba during this period therefore supports the notion that bio-Ba is related to export production. We note however, that at the end of the spring bloom, while other major constituent, including Corg flux decline rapidly bio-Ba remain high (e.g. through August 1997; Fig. 5.4).

Low bio-Ba/Corg ratios are found in the second cup at the three stations where the highest bio-Ba and Corg fluxes are recorded. This, as noticed by Dymond and Collier (1996), may result from the fast sinking velocities at the beginning of the bloom which prevent barite precipitation. Fabres et al. (2004) reported settling speeds fluctuating between 80 and more than 500 m d^{-1} in the April-May 1998 bloom event. Towards the end of the bloom, in August 1997, settling speeds become lower and the bio-Ba/Corg ratio increases significantly. The time available for bio-Ba formation is longer and its formation is more efficient. Our results suggest that the bio-Ba/Corg ratio in sediment traps may be strongly related to ecosystem dynamics which in turn control settling rates (Dymond and Collier, 1996). Specifically we hypothesize that the formation of bio-Ba during organic matter degradation in this environment, in part, depends on the ballasting effect of the lithogenic, carbonate and/or bio-Si particles. The massive aggregation processes during the early phase of the spring bloom is characterized by low remineralization of organic matter and a low bio-Ba formation, and a high flux of particles, including Corg, to the sea floor but low bio-Ba/Corg ratio. As suggested by Francois et al. (2002), the ballasting effect of carbonate minerals is an important factor promoting the transfer of organic carbon to the deep sea. During the decreasing phase of the bloom in July 1997 the ballasting effect is reduced, because the earlier event has removed much of the lithogenic and carbonate particles, allowing remaining organic-rich particles to settle more slowly (Fabres et al., 2004) with more significant barite precipitation.

Towards the end of November at station ALB1 and by mid-December at stations ALB4 and ALB5 bio-Ba/Corg ratios are low. The decrease in this ratio is not driven by a significant increase of Corg flux but rather by a decrease of the total Ba concentration (Fig. 5.4). This period is also associated with a large increase of lithogenic fluxes. The total Ba/Al ratio drops down to 0.0039, close to the value we have chosen to represent the regional detrital ratio (0.0033). Indeed, a massive input of continental sediments carried by fluvial discharge from southern Iberian Peninsula rivers has been recorded by Fabres et al. (2002).

5.4.3. Bio-Ba and export production

Although we have added even more caution to the application of bio-Ba/Corg relationships as quantitative productivity or carbon export proxies in margin environments, we will discuss how our Alboran Sea data compare with the significant body of published proxy calibrations. Using our bio-Ba data and the equation proposed by Francois et al., (1995) we calculate a new production (P_{new}) of 32-56 mg C m^{-2} d^{-1} (2.16-5.35 mmol m^{-2} d^{-1}). This is much lower than the range reported by Sanchez-Vidal et al. (2004b) based on a modified version of the C-flux vs. depth relationship published by Martin et al. (1987) (88-110 mg C m^{-2} d^{-1} or 7.33-9.17 mmol m^{-2} d^{-1}) or the P_{new} reported by L'Helguen et al. (2002) using ^{15}N uptake rates. This difference could indicate that the bio-Ba P_{new} equation reported by Francois et al. (1995) does not apply to coastal settings or that previous reports overestimated P_{new}. If we use the power function of Dehairs et al. (2000) characteristic for margin systems for calculating P_{new} from bio-Ba, our results for the sites where bio-Ba is not laterally advected (i.e. all except the bottom trap of ALB1) are in better agreement with expected P_{new} (Table 5.3).

Table 5.3. Calculated new production based on bio-Ba fluxes.

	Water depth *(m)*	P_{new} ^{1} *(mg C $m^{-2}d^{-1}$)*	P_{new} ^{2} *(mg C $m^{-2}d^{-1}$)*	P_{new} ^{3} *(mg C $m^{-2}d^{-1}$)*
ALB1	0-100	**88.25**		
	470		33.36	94.78
	970		56.36	156.69
ALB4	0-100	**107.59**		
	645		41.24	116.07
	1170		31.95	88.35
	2210		*23.17**	*62.84**
ALB5	0-100	**110.10**		
	510		54.60	126.06
	1050		48.59	131.83
	2070		44.44	139.36

[1] From Sanchez-Vidal et al. (2004b). [2] Obtained through the equations of Francois et al. (1995) (Corg/bio-Ba = 4787 $Z^{0.616}$) and Martin et al.'s (1987) modified ($P_{new} = Corg_z (Z/100)^{-0.753}$), where $Corg_z$ is Corg flux at depth *Z*. [3] Obtained through the equations of Dehairs et al. (2000) (Corg/bio-Ba = 16360 $Z^{0.646}$) and Martin et al.'s (1987) modified. * Underestimated due to the gap in bio-Ba data.

It must be emphasized however that caution must be used when applying this (or other) paleoproductivity proxy in margin environments where strong hydrological dynamics, that redistribution the vertical and horizontal particles, and heterogeneous sedimentation patterns can affect the observed bio-Ba/P_{new} relation.

5.5. CONCLUSIONS

We have expanded the particulate bio-Ba data from the Alboran Sea to further assess the processes controlling the flux of bio-Ba to the seafloor and evaluate its potential use as a proxy for modern and past productivity in continental margins. The relationship between particulate bio-Ba and Corg found throughout the water column and in the sediments of the Alboran Sea supports the recent findings that the ratio of bio-Ba relative to Corg in sinking particulate matter in margin regions is much lower than in the open ocean. The higher ratios at the end of enhanced productivity events suggest that the processes controlling bio-Ba formation might depend on the ballasting effect of the lithogenic, carbonate or bio-Si particles. Ballasting and rapid sinking of particulate matter promote the transfer of Corg to the sediment and reduce the time needed for bio-Ba to form in the particles.

Lateral transport of sediments has been observed in the station located at the lower slope in the western Alboran Sea. This advected material includes freshly sedimented biogenic material, such as bio-Si, Corg and bio-Ba. Such particle transport is common in margins and may complicate the use of bio-Ba and other paleoproductivity proxies in such settings. The bio-Ba as a proxy of productivity must be used cautiously and requires a careful consideration of the dynamics of particle fluxes for any given location, in order to discriminate the influence of vertical and horizontal inputs to the sediments.

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This paper is dedicated to the memory of Jack Dymond who once said, "Most proxies have great potential ... until you look closely."

5.6. REFERENCES

Arin, L., Moran, X.A., Estrada, M., 2002. Phytoplankton size distribution and growth rates in the Alboran Sea (SW Mediterranean): Short term variability related to mesoscale hydrodynamics. Journal of Plankton Research, 24 (10):1019-1033.

Bernat, M., Church, T., Allegre, J., 1972. Barium and strontium concentrations in Pacific and Mediterranean sea water profiles by direct isotope dilution mass spectrometry. Earth and Planetary Science Letters, 16: 75-80.

Bernstein, R.E., Byrne, R.H, Betzer, P.R., Greco, A.M., 1992. Morphologies and transformations of celestite in seawater: the role of acantharians in strontium and barium geochemistry. Geochimica et Cosmochimica Acta, 56: 3273-3279.

Bianchi, A., Calafat, A., De Wit, R., Garcin, J., Tholosan, O., Cacho, I., Canals, M., Fabres, Grout, H., Masque, P., Sanchez-Cabeza, J., Sempere, R., 2003. Microbial activity at the deep water sediment boundary layer in two highly productive systems in the Western Mediterranean: The Almeria-Oran front and the Malaga upwelling. Oceanologica Acta, 25: 315-324.

Bishop, J.K.B., 1988 The barite-opal-organic carbon association in oceanic particulate matter. Nature, 331: 341–343.

Chow, T.J., Goldberg, E.D., 1960. On the marine geochemistry of barium. Geochimica et Cosmochimica Acta, 20: 192-198.

Church, T.M., Wolgemuth, K., 1972. Marine barite saturation. Earth and Planetary Sciences. Letters, 15: 35-44.

Collier, R., Edmond, J., 1984. The trace element geochemistry of marine biogenic particulate matter. Progress in Oceanography, 13: 113-199.

Dehairs, F., Chesselet, R., Jedwab, J., 1980. Discrete suspended particles of barite and the barium cycle in the open ocean. Earth and planetary Science letters, 49: 528-550.

Dehairs, F., Fagel, N., Antia, A.N., Peinert, R., Elskens, M., Goeyens, L., 2000. Export production in the Bay of Biscay as estimated from barium -barite in settling material: a comparison with new production. Deep-Sea Research I, 47: 583–601.

Dymond, J., Suess, E., Lyle, M., 1992. Barium in deep-sea sediment: A geochemical proxy for paleoproductivity. Paleoceanography, 7: 163–181.

Dymond, J., Collier, R., 1996. Particulate barium fluxes and their relationships to biological productivity. Deep-Sea Research, 43: 1283–1308.

Dymond, J., Collier, R., McManus, J., Honjo, S., Manganini, S., 1997. Can the aluminium and titanium contents of ocean sediments be used to determine the paleoproductivity of the oceans?. Paleoceanography, 12: 586-593.

Eagle, M., Paytan, A., Arrigo, K.R., van Dijken, G., Murray, R.W., 2003. A comparison between excess barium and barite as indicators of carbon export. Paleoceanography, 18: 1021.

Fabres, J., Calafat, A., Sanchez-Vidal, A., Canals, M., Heussner, S., 2002. Composition and spatio-temporal variability of particle fluxes in the Western Alboran Gyre, Mediterranean Sea. Journal of Marine Systems, 33-34: 431-456.

Fabres, J., Sanchez-Vidal, A., Calafat, A., Canals, M., Heussner, S., and Delsaut, N., 2004. Biological and physical control on particle transfer to mesopelagic depths: Results of a High Frequency Flux Experiment in the Western Alboran Sea (Western Mediterranean). Deep-Sea Research I. (Submitted)

Fagel, N., Dehairs, F., Peinert, R., Antia, A., André, L., 2004. Reconstructing export production at the NE Atlantic margin: potential and limits of the Ba proxy. Marine Geology, 204 (1-2): 11-25.

Francois, R., Honjo, S., Manganini, S.J., Ravizza, G.E., 1995. Biogenic barium fluxes to the deep sea: Implications for paleoproductivity reconstruction. Global Biogeochemical Cycles, 9: 289–303.

Francois, R., Honjo, S., Krishfield, R., Manganini, S., 2002. Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean. Global Biogeochemical Cycles, 16 (4): 1087.

Ganeshram, R.J., Francois, R., Commeau, J., Brown-Leger, S.L., 2003. An experimental investigation of barite formation in sea-water. Geochimica and Cosmochimica Acta, 67: 2599-2605.

Garcia-Gorriz, E., Carr, M.E., 2001. Physical control of phytoplankton distributions in the Alboran Sea: A numerical and satellite approach. Journal of Geophysical Research, 106: 16795-16805.

Gingele, F., Dahmke, A., 1994. Discrete barite particles and barium as tracers of paleoproductivity in South Atlantic sediments. Paleoceanography, 9: 151-168.

Guerzoni, S., Molinaroli, E., Chester, R., 1997. Saharan dust inputs to the Western Mediterranean Sea: Depositional patterns, geochemistry and sedimentological implications. Deep-Sea Research II, 44: 631-645.

Heggie, D., Klinkhammer, G., Cullen, D., 1987. Manganese and copper fluxes from continental margin sediments. Geochimica et Cosmochimica Acta, 51:1059-1070.

Heussner, S., Ratti, C., Carbonne, J., 1990. The PPS 3 time-series sediment trap and the trap sample processing techniques used during the ECOMARGE experiment. Continental Shelf Research, 10: 943-958.

Jeandel, C., Tachikawa, K., Bory, A., Dehairs, F., 2000. Biogenic barium in suspended and trapped material as a tracer of export production in the tropical NE Atlantic (EUMELI sites). Marine Chemistry, 71: 125–142.

Klump, J., Hebbeln, D., Wefer, G., 2000. The impact of sediment provenance on barium-based productivity estimates. Marine Geology, 169: 259-271.

L'Helguen, S., Le Corre, P., Madec, C., Morin, P., 2002. New and regenerated production in the Almeria-Oran Front area, Eastern Alboran Sea. Deep-Sea Research, 49: 83-99.

Martin, J.H., Knauer, G., Karl, D.M., Broenkow, W.W., 1987. VERTEX: carbon cycling in the northeast Pacific. Deep-Sea Research, 34 (2): 267-285.

Masqué, P., Fabres, J., Canals, M., Sanchez-Cabeza, J.A., Sanchez-Vidal, A., Cacho, I., Calafat, A., Bruach, J.M., 2003. Accumulation rates of major constituents of hemipelagic sediments in the deep Alboran Sea: a centennial perspective of sedimentary dynamics. Marine Geology, 193: 207-233.

McManus, J., Dymond, J., Dunbar, R.B., Collier, R., 2002. Particulate barium fluxes in the Ross Sea. Marine Geology, 184: 1-15.

Monaco, A., Peruzzi, S., 2002. The Mediterranean Targeted Project MATER - a multiscale approach of the variability of a marine system -overview. Journal of Marine Systems, 33-34: 3-21.

Monnin, C., Jeandel., C., Cattaldo, T., Dehairs, F., 1999. The marine barite saturation state of the world oceans. Marine Chemistry, 65: 253-261.

Mortlock, R.A., Froelich, P.N., 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. Deep-Sea Research, 36: 1415-1426.

Paytan, A., Kastner M., Martin E.E., Macdougall J.D., Herbert T., 1993. Marine barite as a monitor of seawater strontium isotope composition. Nature, 366: 445–449.

Paytan, A., Kastner, M., Chavez, F., 1996. Glacial to interglacial fluctuations in productivity in the Equatorial Pacific as indicated by marine barite. Science, 274: 1355-1357.

Prakash Babu, C., Brumsack, H.J., Schnetger, B., Böttcher, M.E., 2002. Barium as a productivity proxy in continental margin sediments: a study from the eastern Arabian Sea. Marine Geology, 184: 189-206.

Price, N.B., Brand, T., Pates, J.M., Mowbray, S., Theocharis, A., Civitarese, G., Miserocchi, S., Heussner, S., Lindsay, F., 1999. Horizontal distributions of biogenic and lithogenic elements of suspended particulate matter in the Mediterranean Sea. Progress in Oceanography, 44: 191-218.

Reitz, A., Pfeifer, K., De Lange, G.J., Klump, J., 2004. Biogenic barium and the detrital Ba/Al ratio: a comparison of their direct and indirect determination. Marine Geology, 204 (3-4): 289-300.

Rodríguez S., Querol, X., Alastuey, A., Kallos, G., Kakaliagou, O., 2001. Saharan dust contributions to PM10 and TSP levels in Southern and Eastern Spain. Atmospheric Environment, 35: 2433-2447.

Rutten, A., De Lange, G.J., 2002. A novel selective extraction of barite, and its application to eastern Mediterranean sediments. Earth and Planetary Science Letters, 198: 11-24.

Sanchez-Vidal, A., Calafat, A., Canals, M., Fabres, J., 2004a. Particle fluxes in the Almeria-Oran front: control by coastal upwelling and sea surface circulation. Journal of Marine Systems,.52: 89-106.

Sanchez-Vidal, A., Calafat, A., Canals, M., Frigola, J., Fabres, J., 2004b. Particle fluxes and organic carbon budget across the Eastern Alboran Sea (SW Mediterranean Sea). Continental Shelf Research. (Submitted).

Schenau, S.J., Prins, M.A., DeLange, G.J., Monnin, C., 2001. Barium accumulation in the Arabian Sea: Controls on barite preservation in marine sediments. Geochimica et Cosmochimica Acta, 65: 1545-1556.

Schmitz, B., 1987. Barium, equatorial high productivity and the northward wandering of the Indian continent. Paleoceanography, 2: 63-77.

Wehausen R., Brumsack H.-J., 1999. Cyclic variations in the chemical composition of eastern Mediterranean Pliocene sediments: A key for understanding sapropel formation. Marine Geology, 153: 161-176.

Weldeab, S., Emeis, K.-C., Hemleben, C., Schmiedl, G., Schulz, H., 2003. Spatial productivity variations during formation of sapropel S5 and S6 in the Mediterranean Sea: Evidence from Ba contents. Palaeogeography, Palaeoclimatology, Palaeoecology, 191: 169-190.