Barium accumulation in the Atlantic sector of the Southern Ocean: Results from 190,000-year records

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Abstract. Extensive investigations of sedimentary barium were performed in the southern South Atlantic in order to assess the reliability of the barium signal in Antarctic sediments as a proxy for paleoproductivity. Maximum accumulation rates of excess barium were calculated for the Antarctic zone south of the polar front where silica accumulates at high rates. The correspondence between barium and opal supports the applicability of barium as a proxy for productivity. Within the Antarctic zone north of today´s average sea ice maximum, interglacial vertical rain rates of excess barium are high, with a maximum occurring during the last deglaciation and early Holocene and during oxygen isotope chronozone 5.5. During these periods, the maximum silica accumulation was supposedly located south of the polar front. Glacial paleoproductivity, instead, was low within the Antarctic zone. North of the polar front, significantly higher barium accumulation occurs during glacial times. The vertical rain rates, however, are as high as in the glacial Antarctic zone. Therefore there was no evidence for an increased productivity in the glacial Southern Ocean.

Introduction

During the last 15 years, the search for geochemical tracers which allow the reconstruction of the chemical characteristics of the oceans, past climates, and paleoproductivity was intensified [e.g., *Berger et al.*, 1983; *Prahl et al.*, 1989; *Boyle*, 1988, 1992; *Lea and Boyle*, 1989, 1990; *Elderfield*, 1991; *Rau et al.*, 1991]. It became apparent that marine sediments from upwelling areas show enhanced barite concentrations [e.g., *Revelle et al.*, 1955; *Goldberg and Arrhenius*, 1958; *Church*, 1976; *Brumsack*, 1989; *von Breymann et al.*, 1992]. The covariance between the barite concentration and an enhanced surface productivity [e.g., *Goldberg and Arrhenius*, 1958; *Dehairs et al.*, 1980; *Schmitz*, 1987; *Bishop*, 1988] lead us to assume that barium is a proxy for paleoproductivity [e.g., *Jumars et al.*, 1989; *von Breymann et al.*, 1992; *Dymond et al.*, 1992; *Shimmield et al.*, 1994].

Like other oceanographic parameters, dissolved barium shows drastic horizontal gradients at the oceanographic fronts within the Antarctic Circumpolar Current [*Chan et al.*, 1977; *Nürnberg*, 1995]. Furthermore, in the Southern Ocean, high concentrations of dissolved and particulate barium occur in the water column [*Chan et al.*, 1977; *Dehairs and Goeyens*, 1989] and within deep-sea deposits [*Turekian and Johnson*, 1966; *Shimmield et al.*, 1994].

Vertical profiles of dissolved barium are generally characterized by low concentrations in the surface water, which increase with water depth [e.g., *Wolgemuth and Broecker*, 1970; *Li et al.*, 1973; *Chan et al.*, 1977; *Broecker and Peng*, 1982]. The similarity of the barium profile to silica

and alkalinity profiles points to the involvement of barium in the biogenic cycle. The dissimilarity between barium profiles and those of nitrate and phosphate indicates the regeneration of barium with the less soluble skeletons of silica and/or carbonate [*Chan et al.*, 1977]. Apparently, barium is removed from surface waters by precipitation within sinking biogenic particles, which dissolve in the deeper water column and in the sediment. Most particulate barium is composed of barite crystals, which act as the main carrier for barium into the sediment [*Dehairs and Goeyens*, 1989; *Dehairs et al.*, 1991; *Bishop*, 1988]. A maximum of particulate barium commonly occurs between 200 and 500 m water depth [*Dehairs et al.*, 1990; *Stroobants et al.*, 1991].

Nevertheless, the process by which barite forms within the water column is still not known. According to several authors [*Chow and Goldberg*, 1960; *Dehairs et al.*, 1980; *Bishop*, 1988], barite formation takes place within microenvironments within the water column, where the organic matter of planktic cells or fecal pellets and aggregates decomposes. The excess sulfate results from the decay of labile sulfur in the organic matter [*Chow and Goldberg*, 1960; *Dehairs et al.*, 1980; *Bishop*, 1988]. Barite can be also formed during the dissolution of acantharian-derived celestite [*Bernstein et al.*, 1992]. An active intracellular formation of barite is observed in benthic xenophyophores [*Tendal*, 1972; *Gooday and Nott*, 1982]. Because these large protozoans rarely survive the sampling procedure and are difficult to identify, active intracellular formation was only rarely investigated, and its role in the barite budget is still not understood.

Additional sources of barite crystals are hydrothermal precipitates [*Boström et al.*, 1973]. It should be noticed, however, that hydrothermal sources are only of local significance [*Dymond et al.*, 1992]. In addition to barite crystals, particulate barium accumulates in seafloor deposits, by incorporation into or absorption by siliceous or

carbonaceous tests, in organic material, or in aluminosilicates [e.g., *Goldberg and Arrhenius*, 1958; *Chow and Goldberg*, 1960; *Dehairs et al.*, 1980; *Lea and Boyle*, 1989, 1990, 1991; *Lea et al.*, 1989].

The diagenetic mobilization of barium in sulfate-depleted sediments with often a subsequent reprecipitation in sulfate-bearing environments [*Brumsack*, 1989; *Torres et al.*, 1996] also contributes to the barite budget. However, the diagenetic mobilization in anoxic environments, in fact, restricts the application of barium as a paleoproductivity indicator to non-sulfate-depleted sediments [*Brumsack*, 1989; *von Breymann et al.*, 1992].

Samples and Procedures

The area of investigation comprises the Atlantic sector of the Southern Ocean south of approximately 42°S (Figure 1). This area can be divided from north to south into the Subantarctic zone south of the Subtropical front, the polar frontal zone situated between the Subantarctic front and the polar front, and the Antarctic zone, which is covered by winter sea ice in the southernmost regions [*Peterson and Stramma*, 1991]. On the investigated transect south of Africa, the location of the polar front varies between 49°39'S and 50°47'S, and the location of the Subantarctic front varies between 45°15'S and 47°25'S [*Lutjeharms and Valentine*, 1984]. The surface waters are rich in nutrients and show significant gradients in concentration across the oceanographic fronts. For the investigation of the barium content, undisturbed surface sediments were sampled in the area from the southern Weddell Sea to the Subtropical front during several R/V *Polarstern* cruises from December 1986 to January 1994 (Figure 2). In addition, four sediment cores were recovered in the eastern Atlantic Ocean from each of the above mentioned zones on a transect between 43°S and 56°S

Figure 1. Shown are locations of sediment cores studied. Surface water circulation and oceanographic fronts are according to *Hellmer et al.* [1985], *Whitworth and Nowlin* [1987], and *Peterson and Stramma* [1991].

perpendicular to the oceanographic fronts (R/V *Polarstern* cruises ANT-VIII/3 and ANT-IX/4; Figure 1).

The lithology of the cores is dominated by diatomaceous muds (Figure 3). Core PS2082-1 from the Subantarctic zone shows a few intercalations of foraminiferal oozes at the top and calcareous muds beneath. The other cores also consist of diatomaceous oozes, which predominate in the cores of the Antarctic zone.

The age models of the surface sediments are based on diatom and radiolarian biofluctuation stratigraphies and biostratigraphies (A. Abelmann et al., unpublished report, 1992). For core PS2082-1, *Mackensen et al.* [1994] developed an age model by correlating the $d^{18}O$ records of the benthic foraminiferal species *Cibicidoides* spp. and *Fontbotia wuellerstorfi*, and the planktic species *Neogloboquadrina pachyderma* sin. and *Globigerina bulloides* to the SPECMAP stack. For core PS1756-5, an age model was constructed by combining the $d^{13}C$ profile of organic matter (G. Fischer et al., unpublished manuscript, 1997) and the siliceous microfossil biofluctuation measurements (A. Abelmann et al., unpublished report, 1992). The age model of core PS1768-8 is based on a $d^{18}O$ record of the planktic foraminiferal species *Neogloboquadrina pachyderma* sin. [*Niebler*, 1995], which is supported by three accelerator mass spectrometry (AMS) ^{14}C-dated samples in the upper section of that core (R. Gersonde et al., manuscript in preparation, 1997). For core PS1772-8, diatom and radiolarian biofluctuation stratigraphies and biostratigraphies were used to determine the stage boundaries (A. Abelmann et al., unpublished report, 1992). All the age models of the long sediment cores were combined with a $^{230}Th_{ex}$ constant flux model to evaluate sedimentation rates at high resolution [*Frank et al.*, 1996]. By normalization to $^{230}Th_{ex}$, the sediment accumulation rates were corrected for lateral sediment redistribution [*Frank et al.*, 1996] in order to estimate the vertical rain rates of excess barium (VRR Ba_{excess}) from the overlying water column.

For the determination of the barium content, the decarbonated sediment samples were dissolved by acid digestion. The sample material (100 mg) was weighed directly into Savillex Teflon cups. The digestion was performed by applying 3 mL HF (40%), 3 mL HNO_3 (65%), and 4 mL $HClO_4$ (60%) at 180°C for 10 hours. Subsequently, the acid was evaporated to dryness, and the residue was dissolved by 1 mL HCl (30%). Finally, the Teflon cups were filled to 50 mL with deionized water and stored in precleaned polyethylene bottles. The samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP AES). Accuracy was controlled by analyzing international reference material (MAG-1). Deduced from replicates, the precision of the method is about 2% for barium and 3% for aluminum. A detailed description of the method was reported by *Nürnberg* [1995].

Before interpreting the barium signal as a paleoproductivity indicator, diagenetic redistribution has to be considered. In areas with high sediment accumulation and a high input of organic material, sulfate reduction could develop near the sediment surface due to the microbial degradation of organic carbon. A diagenetic mobilization of barite occurs in anoxic sediments, often exhibiting a subsequent reprecipitation in the sulfate-bearing environment [*Brumsack*,
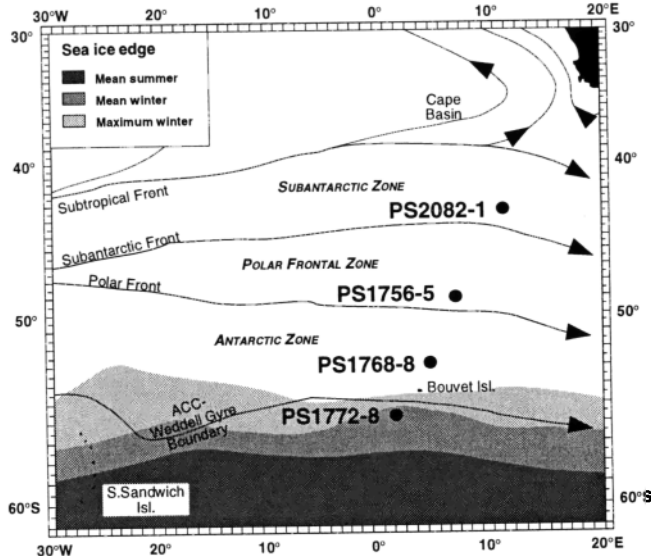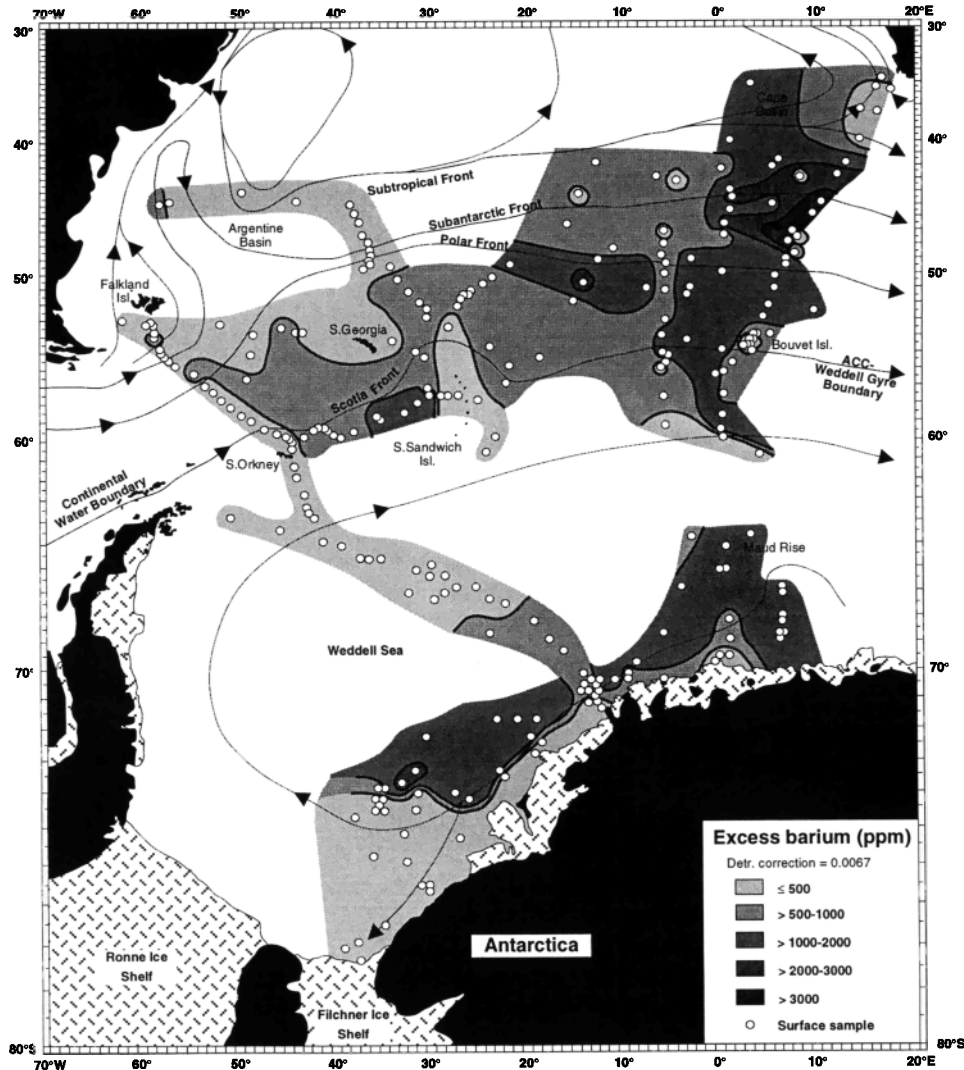
Figure 2. Concentrations of excess barium in surface samples from the southern South Atlantic. Surface water circulation and oceanographic fronts are according to *Hellmer et al.* [1985], *Whitworth and Nowlin* [1987], and *Peterson and Stramma* [1991].

1989; *Torres et al.*, 1996]. Within the Soctia Sea, *Nürnberg* [1995] measured pore water in a sediment core, which is built up of oxic to suboxic sediments as is indicated by pore water sulfate concentrations of 28-29 mmol/kg. Mobilization and redistribution of barium were not expected, because the pore water barium concentrations resemble those within the barite saturation zone published by *Church and Wolgemuth* [1972]. Although we have no pore water data for the investigated sediment cores, we assume that mobilization and redistribution of barium did not take place, because the cores have similar lithology, C_{org} accumulation rates, and linear sedimentation rates to the one in the Scotia Sea.

In order to apply the barium signal as a proxy for paleoproductivity, the total barium had to be corrected for the nonbiogenic portion. Aluminum, the most characteristic element of aluminosilicates, is assumed to represent the terrigeneous portion of clay minerals [*Shimmield et al.*, 1990]. *Murray et al.* [1993] proposed that a portion of dissolved aluminum is scavenged by biogenic particles within

the water column. Such scavenging is not expected in the Weddell Sea sediments, because the Al/Ti ratios in sediment cores show no downcore variation and therefore are indeed of crustal origin [*Bonn*, 1995]. South of South Orkney Island, the Al/Ti ratios vary considerably (W. Bonn, personal communication, 1996), thus pointing to a significant scavenging of aluminum. Nevertheless, the differences between the barium data corrected by Ti and Al are minor (108 ± 33 ppm; n = 123). There are no titanium data for the investigated sediment cores to get the scavenged portion of aluminum. *Nürnberg* [1995] compared the Ba/Al ratios in sediment cores with the accumulation rates of excess barium, which were both used to derive information about the productivity. Both parameters correlate well in core sections with high terrigenous input. In core sections with aluminum concentrations less than 2%, however, no correlation is observed. We therefore conclude that 2% of the aluminum is presumably scavenged by biogenic particles. Assuming a consistently lowered aluminum content by 2%, the excess
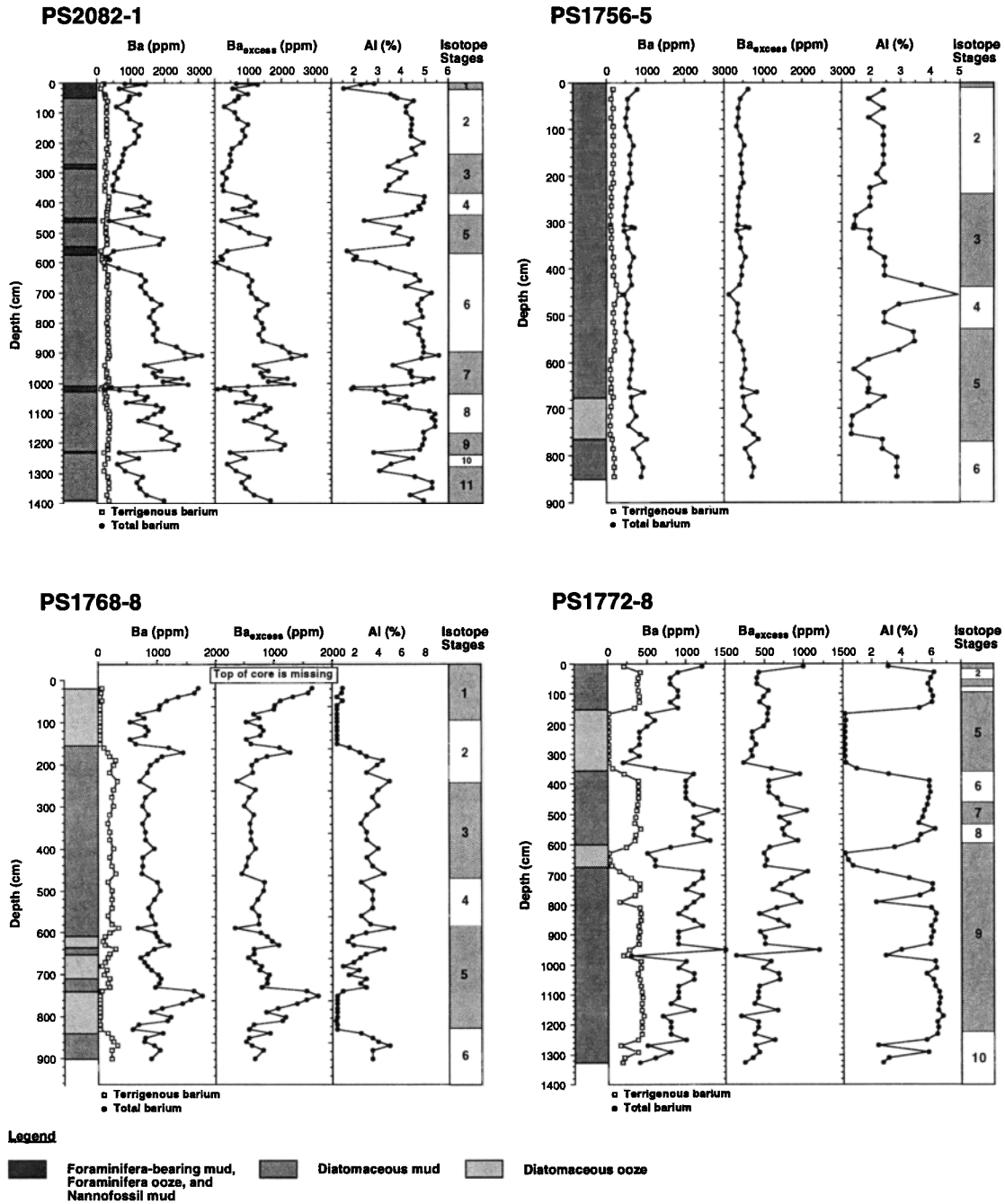
Figure 3. Barium and aluminum concentrations in sediment cores. Stratigraphy is according to *Mackensen et al.* [1994], *Niebler* [1995], *Frank et al.* [1996], G. Fischer et al. (unpublished manuscript, 1997), and A. Abelmann et al. (unpublished report, 1992).

barium would be enhanced by approximately 134 ppm. Such error is, to our mind, negligible in view of the up to 4700 ppm high excess barium concentrations.

Owing to lack of titanium data, we normalized the total barium by aluminum and applied the following calculation:

$$Ba_{terr} = Al_{sample} \times (Ba/Al)_{crust} \qquad (1)$$

where Ba_{terr} is the terrigenous barium, Al_{sample} is the aluminum content in the sample, and $(Ba/Al)_{crust}$ is the barium to aluminum ratio of the crust.

For the Atlantic sector of the Southern Ocean, a regional $(Ba/Al)_{crust}$ ratio is developed from three core-top samples, which were situated beneath the Filchner Ice Shelf and thus were characterized by a negligible biogenic input for a long time period [*Schlüter*, 1991]. The barium content in these samples is therefore of terrigenous origin. The corresponding $(Ba/Al)_{crust}$ ratio is 0.0067, which is applied to calculate the excess barium:

$$Ba_{excess} = Ba_{tot} - (Al \times 0.0067) \qquad (2)$$

Table 1. Surface Sediment Sampling Positions

Sample	LSR cm kyr^{-1}	MAR g cm^{-2} kyr^{-1}	AR Ba$_{excess}$ μg cm^{-2} yr^{-1}
PS1654-1	60.0	36.0	71.68
PS1751-2	0.5	0.3	1.04
PS1752-5	0.5	0.3	1.17
PS1754-2	1.5	0.9	2.79
PS1755-1	2.0	1.2	5.63
PS1756-6	7.0	1.9	4.36
PS1764-2	41.0	24.6	46.56
PS1765-1	25.0	5.5	5.15
PS1768-1	15.0	7.0	7.81
PS1651-2	19.0	11.4	8.48
PS1652-2	55.0	33.0	20.99
PS1771-4	25.0	15.0	10.53
PS1649-1	0.8	0.5	0.56
PS1772-6	0.5	0.4	0.25
PS1773-2	0.3	0.2	0.30

Abbreviations are LSR, linear sedimetation rate; MAR, mass accumulation rate; and AR Ba$_{excess}$ accumulation rate of Ba$_{excess}$

where Ba$_{excess}$ is the excess barium, Ba$_{tot}$ is the total (measured) barium, and Al is the aluminum content of the sample. The calculated (Ba/Al)$_{crust}$ ratio matches the global (Ba/Al)$_{aluminosilicate}$ ratio of 0.0065 given by *Wedepohl* [1991].

Results

In surface sediments, the excess barium concentrations range from a few ppm to about 4700 ppm in this study (Figure 2 and Table A1; the data of Table A1 have been archived, and are available in a digital form, at the World Data Center-A for Paleoclimatology, NOAA/NGDC 325 Broadway, Boulder, CO, 80303, phone 303 497 6280, fax 303 497 6513, Internet e-mail: paleo@mail.ngdc.noaa.gov). Within the Antarctic Circumpolar Current, the excess barium contents west of the Greenwich meridian are lower than 2000 ppm. The highest excess barium concentrations (>3000 ppm) occur in the polar frontal zone of the eastern South Atlantic. Sediments along the coastal area west of 10°W, near islands (Falkland, South Orkney, South Sandwich, South Georgia, and Bouvet), in the Weddell Basin, and in the Argentine Basin show very low values (<500 ppm).

The regionally varying accumulation of biogenic sediment components has to be considered when interpreting their distribution patterns. Recent accumulation rates of excess barium (AR Ba$_{excess}$) were determined for sites lying on a NE-SW trending transect that crosses the oceanographic fronts at 12°E to 0° in the eastern South Atlantic (Figure 4 and Table 1). The dominant portion of excess barium is accumulated within the Antarctic zone just south of the polar front, whereas areas commonly covered by winter sea ice and areas north of the polar front exhibit very low accumulation rates of excess barium.

The downcore records in cores PS2082-1, PS1756-5, PS1768-8, and PS1772-8 reveal excess barium concentrations up to 2700 ppm (Figure 3 and Table A2; the data of Table A2 have been archived, and are available in a digital form, at the World Data Center-A for Paleoclimatology, NOAA/NGDC 325

Broadway, Boulder, CO, 80303, phone 303 497 6280, fax 303 497 6513, Internet e-mail: paleo@mail.ngdc.noaa.gov). Within the polar frontal zone (PS1756-5) the excess barium concentrations are around 500 ppm and do not vary significantly with depth, whereas excess barium exhibits drastic downcore variations in all other cores. Within the core sections characterized by diatomaceous ooze, the aluminum concentrations are significantly lowered (<1 %). All other sections exhibit aluminum concentrations up to 7%.

On the basis of the ^{230}Th$_{ex}$ normalization approach to correct for focusing and winnowing [*Frank et al.*, 1996], excess barium accumulation rates were converted to vertical rain rates (Figure 5 and Table A2). Downcore vertical rain rates of excess barium vary between 0.1 and 4.8 μg cm^{-2} yr^{-1}. Core PS1768-8, located north of today's average sea ice maximum within the Antarctic zone, shows the highest vertical rain rates of 4.2 and 4.8 μg cm^{-2} yr^{-1} at the termination oxygen isotope chronozone 2 to 1 and during oxygen isotope chronozone 5.5, respectively. In the Antarctic zone with winter sea ice (PS1772-8), high vertical rain rates of excess barium exclusively occur during oxygen isotope chronozone 5.5 (3.9 μg cm^{-2} yr^{-1}). Core PS1756-5, located in the polar frontal zone, shows maximum rates during oxygen isotope chronozone 2, 3 and 5.5 of about 2.6 μg cm^{-2} yr^{-1}. North of the Subantarctic front (PS2082-1), the pattern of excess barium accumulation changes substantially. The highest vertical rain rates occur during glacials (1.0 to 1.3 μg cm^{-2} yr^{-1}).

Excess Barium Distribution in Surface Sediments

The modern Southern Ocean is a high-nutrient low-chlorophyll (HNLC) area, where iron limitation may cause the incomplete consumption of the nutrients [*Martin et*
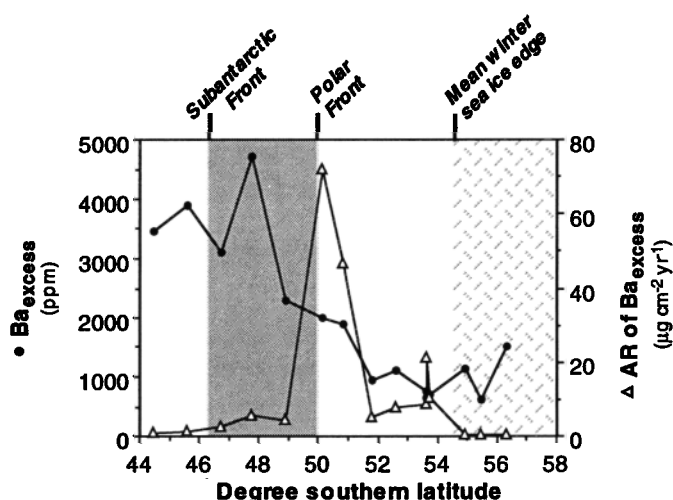

Figure 4. Concentrations of excess barium and accumulation rates of excess barium in surface sediments from a NE-SW trending transect crossing the oceanographic fronts at 12°E to 0° in the eastern South Atlantic. The polar frontal zone and the mean winter sea ice are shaded. Stratigraphical data are according to A. Abelmann et al. (unpublished report, 1992).
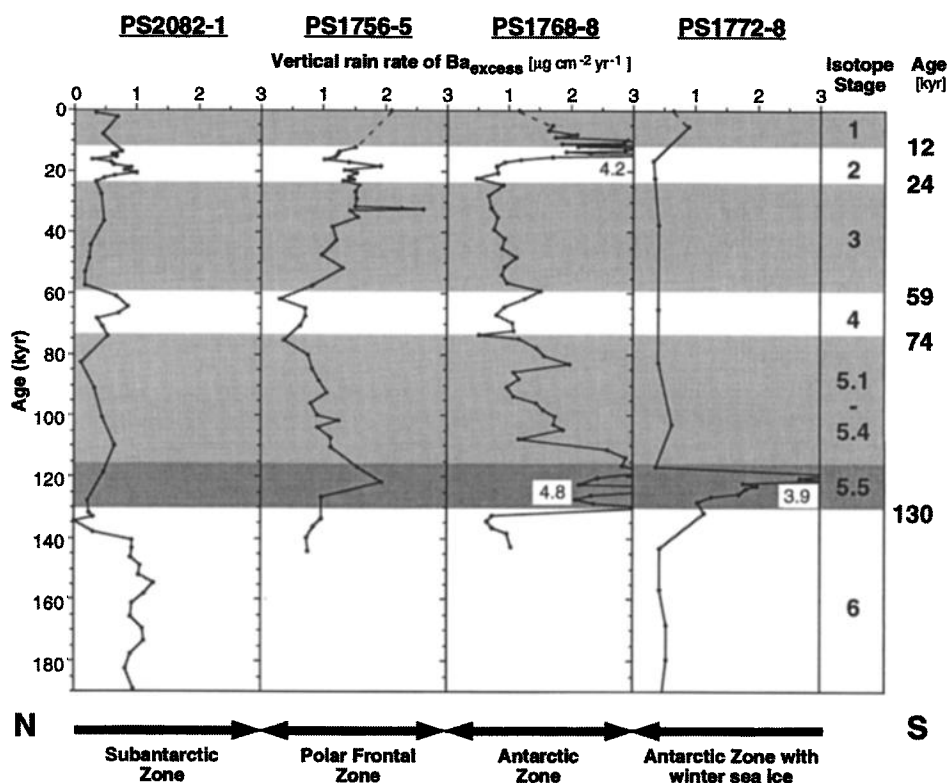
Figure 5. Vertical rain rates of excess barium (VRR Ba_{excess}) down to oxygen isotope chronozone 6 in cores of the southern South Atlantic. The interglacial isotope stages are shaded. The dashed line connects the first core sample with the corresponding surface sample. Stratigraphy is according to *Mackensen et al.* [1994], *Niebler* [1995], *Frank et al.* [1996], G. Fischer et al. (unpublished manuscript, 1997), and A. Abelmann et al. (unpublished report, 1992).

al., 1990; *Kumar et al.*, 1995]. The Antarctic surface water is enriched in inorganic nutrients, especially in the area south of the polar front. Owing to upwelling at the Antarctic divergence, a continous supply of nutrients occurs.

The recent distribution of excess barium in the sediments (Figure 2) is also reflected by the biogenic silica content [*DeMaster*, 1981; M.Schlüter et al., Silica cycle in surface sediments of the South Atlantic, submitted to *Deep Sea Research*, 1996] with maxima on the Weddell Sea shelf, in the Scotia Sea, and in the eastern Atlantic sector of the Antarctic Circumpolar Current. High excess barium concentrations in the Weddell shelf deposits are reflected by high production of biogenic silica [*Schlüter*, 1991]. In the deep central Weddell Sea, instead, very low excess barium concentrations were observed. This is in accordance with low benthic fluxes of biogenic silica [*Schlüter*, 1991] and with the smallest annual particle flux in that region yet observed in the world ocean [*Wefer and Fischer*, 1991]. In the Scotia Sea, the high excess barium concentrations correlate with high integrated production rates of biogenic silica, whereas south of that region within the marginal ice zone of the northern Weddell Sea, lower biogenic silica values are determined [*Quéguiner et al.*, 1991]. The maximum excess barium accumulation within the Antarctic Circumpolar Current occurs in the Antarctic zone between the polar front and the winter sea ice boundary (Figure 4). North of the polar front and within the ice covered Antarctic zone, excess barium accumulation decreases

rapidly. This pattern is also reflected by the accumulation of opal [*DeMaster*, 1981; *Charles et al.*, 1991; *Mortlock et al.*, 1991]. Investigations of *Tréguer and Van Bennekom* [1991] show that the highest production of biogenic silica occurs within the surface layer of the ice free and seasonally ice covered Antarctic zone, whereas within the polar frontal zone, low biogenic silica values are found. Suggested by remote sensing data, the primary production rate within the Antarctic Circumpolar Current is no more than 40-50 g C m^{-2} yr $^{-1}$ [*Antoine et al.*, 1996]. Nevertheless, the high opal accumulation occurs south of the polar front, probably due to a low dissolution rate of siliceous material in that region [*Nelson et al.*, 1995]. North of the polar front and within seasonally ice covered areas, only low amounts of siliceous material are apparently exported, mainly due to a high dissolution rate of silicate in surface waters.

Barium as a Paleoproductivity Indicator

Within the northern Antarctic zone south of the polar front, peak vertical rain rates of excess barium were reached during the last deglaciation and the following Holocene climatic optimum (circa 14 - 8 ka B.P.) and oxygen isotope chronozone 5.5 (Figure 5). The high productivity interval during oxygen isotope chronozone 5.5 is also documented at sites PS1756-5 and PS1772-8. Core PS1772-8 was recovered from the southern Antarctic zone where productivity is

Table 2. Average Vertical Rain Rates of Excess Barium in the Eastern South Atlantic

	Average Vertical Rain Rate Ba_{excess}, $\mu g\ cm^{-2}\ yr^{-1}$			
	Core PS2082-1	Core PS1756-5	Core PS1768-8	Core PS1772-8
Holocene (0-10 kyr)	0.5 ± 0.1	2.1	1.9 ± 0.5	0.8 ± 0.1
Last glacial maximum (16-26 kyr)	0.6 ± 0.2	1.4 ± 0.2	0.9 ± 0.2	0.3 ± 0.01

recently low due to annual sea ice cover (Figure 4). Since sea ice cover leads to diminished new productivity, the high excess barium vertical rain rates of up to 3.9 $\mu g\ cm^{-2}\ yr^{-1}$ during interglacial oxygen isotope chronozone 5.5 can only be explained by a retreat of the sea ice edge during this climatic optimum. Sea ice cover, instead, expanded significantly during glacial periods [e.g., Cooke and Hays, 1982; Olaussen, 1988] as deduced from the lower vertical rain rates at site PS1768-8 during oxygen isotope chronozone 2-4 (Figure 5). During glacial periods north of the polar frontal zone (PS2082-1), vertical rain rates of excess barium were considerably higher than during interglacials, pointing to an enhanced new production. However, the glacial vertical rain rates of the Subantarctic zone are not comparable to interglacial rates south of the polar front.

To explain regional patterns during glacial/interglacial changes in the Atlantic sector of the Southern Ocean, we averaged vertical rain rates of excess barium for the Holocene (0-10 ka) and the last glacial maximum ((LGM) 16-26 ka; Table 2). Significant variations between 0.3 and 2.1 $\mu g\ cm^{-2}\ yr^{-1}$ are apparent during glacial/interglacial

periods. During the Holocene, high average vertical rain rates of excess barium of about 2.1 and 1.9 $\mu g\ cm^{-2}\ yr^{-1}$ occur in cores PS1756-5 and PS1768-8, respectively (Table 2). Farther north, the average vertical rain rates decrease, resulting in a very low value of 0.5 $\mu g\ cm^{-2}\ yr^{-1}$ in the Subantarctic zone (43°S; PS2082-1).

During the LGM, the highest vertical rain rates of excess barium are found at 49°S in core PS1756-5 (1.4 $\mu g\ cm^{-2}\ yr^{-1}$). The vertical rain rates in core PS2082-1 are somewhat higher during the LGM than during the Holocene. Summer sea surface temperature estimates based on radiolarian transfer functions in core PS2082-1 were 4°-5°C lower than today [Brathauer, 1996], indicating conditions similar to the recent southern Subantarctic zone, i.e., a northward migration of the Subantarctic front. The vertical rain rates of excess barium in core PS1768-8 are similar to the Holocene rates in core PS1772-8 (0.9 $\mu g\ cm^{-2}\ yr^{-1}$), indicating that this site location was densely covered by winter sea ice during the LGM. According to Gersonde et al. [1994], the mean winter sea ice boundary was located near 50°S. Summer sea surface temperatures of -1.3°C based on
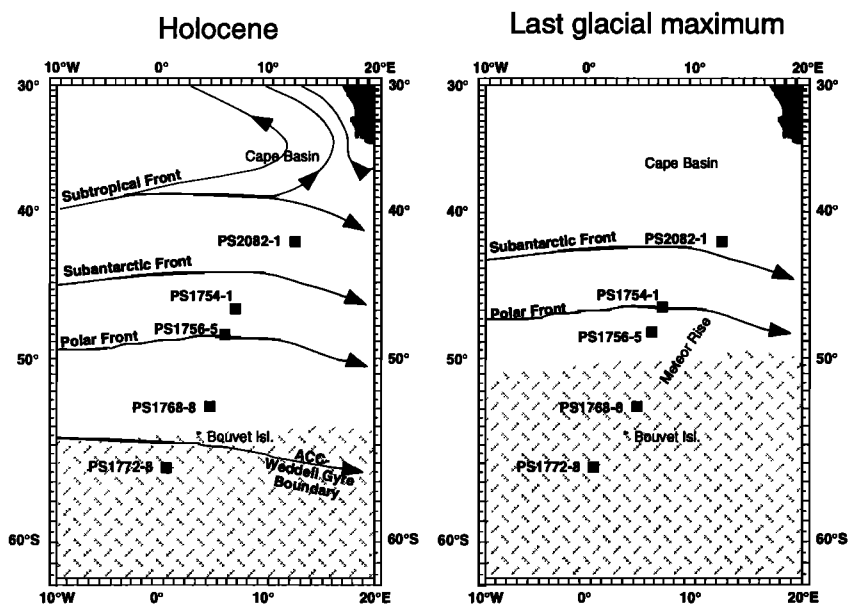

Figure 6. Schematic diagram showing the sea ice distribution and the location of the oceanographic fronts in the eastern sector of the South Atlantic during the Holocene and the last glacial maximum according to our interpretation. The zone of maximum export production is between the polar front and the sea ice which is shaded.

diatom transfer functions further indicate that the summer sea ice boundary was situated south of the site location of PS1768-8 [*Zielinski*, 1993]. *Frank* [1996] investigated a sediment core on the same transect (PS1754-1; 46°46'S, 007°37'E; Figure 6) and observed high vertical rain rates of excess barium during the LGM (1.9 µg cm^{-2} yr^{-1}), which were as high as during the Holocene at the polar front. *Niebler* [1995] reconstructed temperatures based on oxygen isotope records of planktic foraminifers for this core, which provided evidence for temperature conditions in the modern southern polar frontal zone. We therefore suspect that the polar front migrated by about 3° latitude northward during the LGM. Consequently, core PS1756-5 was located south of the polar front. This pattern is in accordance with observations of *Morley and Hays* [1979], who postulated a northward shift of the polar front during the LGM by about 3°-5° latitude in the western Atlantic and 1°-3° latitude in the eastern Atlantic.

Figure 6 illustrates the sea ice distribution and the location of the oceanographic fronts in the eastern Atlantic sector of the Southern Ocean during the Holocene and the LGM. Recent oceanographic investigations by *Lutjeharms and Valentine* [1984] deduced that the polar front varies between 49°39'S and 50°47'S due to a recent location of core PS1756-5 within the polar frontal zone. However, the extremely high vertical rain rates of excess barium in the surface sediment of core PS1756-5 (48°54'S) dated to 0.5 ka B.P. point to a location at the polar front. Therefore it is apparent that the front was mainly located 1°-2° farther north during the entire Holocene time span (Figure 6). The export production was probably not higher in the glacial Southern Ocean, because during the LGM the vertical rain rates of excess barium are as high as in the modern zone of maximum export production. Also, the zone of maximum export production expanded by about 6° during the Holocene and by about 4° during the LGM, pointing to a less extended high-productivity belt. This interpretation is in accordance with biogenic silica productivity estimates of *Mortlock et al.* [1991] and *Charles et al.* [1991]. *Charles et al.* [1991] explain the higher opal burial rates in the southern Subantarctic zone (46°-49°S) with a northward shift of the "silica front." Also, *Bareille et al.* [1997] and *Francois et al.* [1995] do not observe any increase in export production during glacial times in the Indian sector of the Southern Ocean. In contrast, *Kumar et al.* [1995] postulated a Fe-based enhanced glacial productivity north of the present polar front in the Atlantic sector of the Southern Ocean. This is supported by more recent investigations at the Antarctic polar front of the Atlantic sector showing that higher values of dissolved iron significantly increase primary production north of the Antarctic zone [*De Baar et al.*, 1995; *Löscher et al.*, 1997].

Conclusion

The investigations of excess barium and the subsequent estimation of vertical rain rates support previous descriptions of the Quaternary depositional environment in this area. The sedimentary signals can be summarized as follows:

1. The distribution of excess barium in the Weddell Sea and the Antarctic Circumpolar Current reflects the distribution of the production of biogenic silica. Maximum accumulation rates of excess barium occur within the Antarctic zone. This

region is also characterized by high opal accumulation rates. In conclusion, our investigations support the applicability of barium as a productivity indicator within the Southern Ocean.

2. During the interglacial oxygen isotope chronozones 1 and 5, the area south of the Subantarctic zone was characterized by high excess barium vertical rain rates. Especially within the Antarctic zone, maximum vertical rain rates of excess barium were observed during the last deglaciation and following climatic optimum and the oxygen isotope chronozone 5.5, pointing to a more expanded zone with maximum export to the south than today. During glacials, within the Subantarctic zone, enhanced excess barium accumulation is observed, but the vertical rain rates of excess barium are as high as south of the Subantarctic front. Therefore export production was not higher in the glacial Southern Ocean. In conclusion, changes in productivity seem to be controlled by sea ice fluctuations within the Antarctic zone and expansions to the north.

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