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Paleoproductivity at the Antarctic continental margin: opal and barium records for the last 400 ka

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Abstract

Records of biogenic opal and barium were measured in sediment cores at the Antarctic continental margin in the area of the Weddell, Lazarev and Cosmonaut seas. These records provide a qualitative and quantitative tool to estimate changes in paleoproductivity over the last 400 ka. The stratigraphy of the investigated cores is calibrated to a lithostratigraphy, adjusted to a stable isotope record from the eastern Weddell Sea, which is supported by a Th-dating method. We present evidence that interglacial productivity along the Antarctic continental margin is twice as high compared to subantarctic sites near South Orkney. A glacial/interglacial pattern with high productivity during peak warm stages can be observed back to 400 ka. High interglacial productivity is linked to a reduced sea ice coverage, which is regulated by the heat flux introduced by North Atlantic Deep Water (NADW) to the Antarctic Ocean. Generally, good correlations between the barium and opal records of the sediment cores indicate that dissolution of opal in the water column and the sediment does not obscure the surface productivity signal. Therefore, in this area biogenic opal in combination with other proxies, can be used for paleoproductivity estimates. Paleoproductivity is also assessed quantitatively from the barium record using the approaches of Dymond *et al*. (1992) and Francois et al. (1995). Paleoproductivity rates obtained by both methods show a good correspondence. In peak warm stages higher values are computed with the approach of Dymond et al. (1992). However, both methods provide values, which are representative of a high-productivity area. They are drastically reduced during glacial times. The extent and duration of sea ice coverage and the persistence of coastal polynyas is considered to be of primary importance in controlling the flux of biogenic material to sediments of the Antarctic continental margin.

Introduction

Today, variations in orbital parameters are known to induce cyclic climatic variations (Imbrie *et al*., 1984, 1989). They are the forcing mechanism for the complex interaction between oceanographic, glaciologic and productivity processes which control sedimentation and lead to specific sedimentation facies in the ocean. Gas inclusions in Antarctic and Greenland ice cores show that CO_2-variations in general correlate to the Late Quaternary climatic changes (Barnola *et al*., 1987; Lorius *et al*., 1990). It is assumed that the atmospheric CO_2-reduction during glacials is directly connected to an increase in ocean surface productivity (e.g. Lyle *et al.*, 1988; Sarnthein *et al*. 1988) and changes in ocean circulation. Productivity in polar regions, esp. in the Southern Ocean has been discussed controversially (Kumar et al., 1995; Mortlock *et al.*, 1991). Investigations in the Antarctic Ocean show that glacial productivity was lower than in interglacials (Charles and Fairbanks, 1990; Charles *et al.*, 1991; Mortlock *et al.*, 1991). There is evidence that changes in paleoproductivity south and north of the Polar Frontal Zone were contrary (e.g. Nürnberg, 1995). Also high northern latidudes show higher productivity in interglacials and lower productivity in glacials (Subba Rao and Platt, 1984; Stein and Stax, 1991; Schubert, 1995).

Marine productivity is in general dependant on light, temperature, nutrients and oceanographic circulation and is linked to variations in atmospheric CO_2. Production of organic matter in the ocean´s surface waters, the export to deeper water columns and the sedimentation on the seafloor (Broecker and Peng, 1982) removes CO_2 from surface waters. Due to equilibrium between the CO_2-content of the atmosphere and the CO_2-content of the oceans, a change in the oceans productivity forces a change in the atmospheric CO_2-concentration. Thus the marine paleoproductivity record provides a useful tool to reconstruct the Earth´s climate system.

The Southern Ocean is considered to be one of the highly productive areas of the world ocean (Van Bennekom *et al.*, 1988; Shimmield *et al*., 1994) and plays an important role for the silica cycle (Demaster, 1981; Ledfort-Hoffmann *et al*., 1986). Silica is a key nutrient in the marine environment and is utilized by diatoms, radiolaria, silicous sponges and silicoflagellates to build up frustules. Antarctic and subantarctic waters are enriched in dissolved silica and may support up to one third of the global biogenic production. As much as 75 % of the modern global accumulation of biogenic silica (opal) takes place in this region (Queguiner *et al.*, 1991), which is documented in the occurrence of a circumantarctic biosiliceous belt (Demaster, 1981) underlying the highly productive surface waters of the Polar Front between 50° - 55 °S. However, there is evidence that the Antarctic continental margin is also characterized by a high flux of organic material to the sea floor (Mackensen *et al*., 1990; Bathmann *et al.*, 1992; Wefer and Fischer, 1991). In contrast to the Polar Frontal Area, where biogenic sediments prevail, the sediments of the Antarctic continental margin receive a considerable amount of terrigenous material.

In this study we determined biogenic silica (opal) in 6 cores from the Antarctic continental margin (Fig. 1) as a qualitative proxy of ocean surface paleoproductivity. However, factors controlling biogenic silica preservation, such as dissolution of siliceous particles in the water column, at the sediment/water interface and within the sediment, make it very difficult to relate opal accumulation quantitatively to opal production in surface waters. Generally, opal preservation is influenced by the flux of opal to the sea floor, the mass accumulation rate of the sediment, the silica content of bottom waters, the structure of frustules (species selective dissolution) and the amount of trace elements in the opal (e.g. Al). Only few estimates of biogenic silica production rates have been made for the Southern Ocean, and these are restricted to the Pacific sector of the Antarctic Circumpolar Current (ACC) and the marginal ice zone of the Ross Sea (e.g. Nelson and Gordon, 1982; Nelson *et al*., 1991).

To cross-check the results from the opal analysis and support paleoceanographic interpretations, we used the biogenic barium record in deep sea sediments as another independant paleoproductivity proxy. The sedimentary barium content allows the calculation of absolute paleoproductivity rates (Dymond *et al*., 1992; Shimmield, 1992; Shimmield *et al*., 1994; Gingele and Dahmke, 1994; Bonn *et al*., 1994; Nürnberg, 1995; Bonn, 1995; Francois et al., 1995). Biogenic barium ($Ba_{(excess)}$) is a widely used tracer to estimate variations of paleoproductivity in marine sediments (Schmitz, 1987; Stroobants *et al*., 1991; Dymond *et al*., 1992; Gingele and Dahmke, 1994). It´s concentration can be assessed by applying normative techniques to total barium concentrations of the sediment (Fig. 2). The mechanism leading to the paleoproductivity signal is the precipitation of barite in reducing microenvironments within settling diatom frustules (Bishop, 1988). Nevertheless, barite is present in non-diatom dominated assemblages (Stroobants *et al*., 1991) although the contents are lower.

Organic carbon (TOC) and carbonate have also been used as proxies of past changes in ocean paleoproductivity (Müller and Suess, 1979; Sarnthein *et al*., 1988; Charles *et al*., 1991), although these parameters are prone to degradation and dissolution.

The biogenic barium contents were assessed for three cores and used to compute paleoproductivity rates, which can be compared to the opal record and to measurements of productivity of the surface waters of the respective areas.

Our results are based on investigations of the late Quaternary deposits from the eastern Weddell, Lazarev and Cosmonaut seas. Similar records of opal and barium, measured on "Polarstern" cores (Shimmield *et al*., 1994; Frank *et al*., 1995) were found in sediments of the Antarctic continental margin between South Orkney and Gunnerus Ridge, covering nearly a third of the Antarctic coast line. Special emphasis in the interpretations is given to the environmental changes due to sea ice coverage and their influence on the paleoproductivity in response to the pronounced Quaternary climatic cycles covering the last 400 ka.

Oceanographic setting

The Weddell Gyre, a large, clockwise-rotating cyclone located south of the Antarctic

Circumpolar Current (ACC) is the most important oceanographic feature of the Weddell Sea region (Carmack and Foster, 1975, 1977; Deacon, 1979; Foldvik *et al.*, 1985; Gordon *et al.*, 1981). The gyre extends northeastward from the Antarctic Peninsula to 20 ˚E or 30 ˚E (Orsi *et al.*, 1993). The Weddell Gyre entrains heat and salt from the ACC and carries them to the Antarctic continental shelves, where highly saline deep and bottom waters are produced by freeze-out processes. The Weddell and Lazarev Seas are composed of the following major water masses: Cold Weddell Sea Bottom Water (WSBW) prevails near the bottom in the deep ocean and can be distinguished from the slightly warmer Antarctic Bottom Water (AABW). Above the bottom water resides the Weddell Deep Water (WDW). Overlying the WDW is the Winter Water (WW), which is modified in summer by heating and melting of sea ice. The mixing of warm WDW and WW produces the Modified Weddell Deep Water (MWDW) (Foldvik *et al.*, 1985; Foster and Carmack, 1976). Although North Atlantic Deep Water (NADW) only penetrates to the Polar Front at intermediate water depths, where it is incorporated into the ACC, it is a heat source for the Antarctic Ocean waters and consequently influences the formation of sea ice (HODDELL, 1993). Sea ice coverage in the Southern Ocean is crucial for a variety of physical and biological processes. Today an ice cover of 85 % or greater exist over a period of several month during the winter, thus effectively diminishing heat and gas exchange between the ocean and the atmosphere. Ice cover also reduces the amount of sunlight in the photic zone, which is believed to be the key factor for high latitude productivity (CLARKE and ACKLEY, 1984). However, polynyas exist during the winter as revealed by satellite images (GLOERSEN *et al.*, 1992). The annual Antarctic ice transgression is the largest of any region on Earth and has profound influence on the biological production and flux of particulate matter to the sea floor (FISCHER *et al.*, 1988).

Sample collection and analytical methods

Six gravity cores recovered during RV "Polarstern" expeditions at the Antarctic continental margin in the Weddell, Lazarev and Cosmonaut seas between 50 ˚W and 35 ˚E (Fig. 1) were used in this study (FÜTTERER, 1987); MILLER and OERTER, 1990; FÜTTERER, 1989; FÜTTERER and SCHREMS, 1991; BATHMANN *et al.*, 1992). The lithology, texture, amount of ice rafted debris (IRD), grain size distribution and the carbonate and the organic carbon contents were determined by using standard procedures described in GROBE (1986). The sediment cores consisted mainly of sandy or silty muds with varying amounts of opal, carbonate and terrigenous matter. In general grain sizes decrease with distance from the continent.

All six sediment cores along the Antarctic continental margin were analysed for opal to reveal qualitative changes in paleoproductivity during the last 400 ka. Geochemical analyses yielding downcore profiles of Ba, Al and Ti were performed on three of these cores. The stratigraphical approach and the analytical procedures for opal and barium are described in detail in the following section.

Stratigraphy

The stratigraphy of the cores discussed in this paper is based on the stable oxygen isotope record of two cores from Atka Bay, which was generated from benthic (*Epistominella exigua*) as well as planktonic foraminfera species (*Neogloboquadrina pachyderma*) (MACKENSEN *et al.*, 1989; GROBE *et al.*, 1990, GROBE and MACKENSEN, 1992). These are the only $\delta^{18}O$ records of the Antarctic continental margin which could be correlated with the global isotope stratigraphy so far.
The interpretation of the isotopic data in the other cores remains difficult because of strong diagenetic alterations (GROBE *et al.*, 1990) or low carbonate content. Because of these problems we used a lithostratigraphy as a tool for correlating the late Pleistocene sediments. The comparison of the isotopic record of PS1388-3 with the lithological parameters and biogenous components has shown, that significant changes occur at distinct times of global climatic change (GROBE and MACKENSEN, 1992). These prominent lithologic changes can be correlated with distinct isotopic events. The changes were found to be similar in all late Pleistocene sediments of the investigation area. In particular variations of the biogenic constituents can be correlated between cores and are synchronous within their resolution. In this way a lithostratigraphy was established for the cores, which is supported by the oxygen isotope record of PS1388-3. Additionally the record is supported by U/Th-dating. U/Th-dating was also supplied at core PS1575-1 (BREHME, 1992; FRANK *et al.*, 1995) and confirms the lithostratigraphic correlations.

Coarse fraction analysis.

The percentage of radiolarians in the sand fraction allows a first and easy estimation of opal contents of the sediment and was determined by counting and classifying at least 400-600 grains per sample. Investigations of smear slides have shown that the occurrence of radiolarians can be correlated with the siliceous microfossil content in the silt fraction in general, such as diatoms and silicoflagellates (GROBE and KUHN, 1987). Thus, the quantity of radiolaria could be used to predict the occurrence of silica in the sediments, because this parameter can easily be assessed and radiolaria are more resistant to dissolution.

Opal analysis

For the determination of the opal content we used an automated leaching method after DEMASTER (1981) and MÜLLER and SCHNEIDER (1993). This method involves the extraction of biogenic silica by concentrated 1M NaOH. The concentration of the dissolved silica is assessed by molybdate-blue spectrophotometry. The continuous absorbance versus time plot is evaluated according to the extrapolation procedure of DEMASTER (1981). The precision of this technique is better than 0.5 % based on replicate measurements of silicon standard solutions. The relative precision of the automated leaching method is better than 2 % for pure opal and opal-rich samples and 4-10 % for samples with less than 10 % biogenic opal, respectively (MÜLLER and SCHNEIDER, 1993). The threshold of 1-2 % in the cores is probably an artefact of a partial leaching of clay minerals.

Barium analysis

Multielement analysis was performed with XRF technique including Ba, Al and Ti measurements with a Phillips PW1400-device. The analytical precision was 5 % rel. error margin for trace elements and 2 % rel. error margin for major elements. Since only biogenic barium, derived from discrete barite particles, which are associated with decaying organic matter (DEHAIRS *et al.*, 1980; DYMOND *et al.*, 1992) yields information on the flux of organic material to the seafloor, barium from other sources must be accounted for. Investigations in different sedimentary environments (e.g. DYMOND *et al.*, 1992; GINGELE and DAHMKE, 1994; SHIMMIELD *et al.*, 1994; STROOBANTS *et al.*, 1991) show that detrital barium from terrigenous matter is most important, while the input of barium as a constituent of carbonate or biogenic silica can be neglected. A normative approach is commonly used to distinguish between detrital barium and "bio"-barium (DYMOND *et al.*, 1992; GINGELE and DAHMKE, 1994). However, the barium content of terrigenous matter is highly variable, varying between 200 and 1000 ppm (DYMOND *et al.*, 1992). Three different approaches were tested in order to minimize the normative uncertainties. First the terrigenous fraction of the core was calculated by subtracting opal and carbonate and a trace amount of 400 ppm was assumed for this fraction (GINGELE and DAHMKE, 1994). The resulting concentration of detrital barium was subtracted from total barium concentrations (equation 1). Second a barium/aluminium-ratio of 0.0067, which was assessed for pure terrigenous sediments of the southern Weddell Sea (Nürnberg, 1995) was used for detrital correction, following the calculation of DYMOND *et al.* (1992) (equation 2). Recent investigations in the Pacific Ocean have shown that Al might also be of biogenic origin and that Ti is more appropriate to represent the terrigenous fraction of the sediment (MURRAY *et al.*, 1993). Even there is no indication for biogenic Al from Al/Ti-ratios in the sediments, which are well within a terrigenous range (MURRAY *et al.*, 1993) a normative approach with Ti was also carried out. A Ba/Ti-ratio of 0.126 (TUREKIAN and WEDEPOHL, 1961) was used to calculate a normative $Ba_{(excess)}$ content (equation 3).

(1) $Ba_{(excess)} = Ba_{(total)} - (400 \times TF/100)$

(2) $Ba_{(excess)} = Ba_{(total)} - (Al \times Ba/Al_{alusilicate})$

(3) $Ba_{(excess)} = Ba_{(total)} - (Ti \times Ba/Ti_{alusilicate})$

The calculations of a normative $Ba_{(excess)}$ content are based on the assumption that the composition of the terrigenous material in respect to the barium content remained constant in time and space.
$Ba_{(excess)}$ contents obtained by all three approaches vary within a narrow margin (Fig. 2), with the exception of core PS1648-1. In this core Ti-values are extremely high, due to a titanomagnetite source rock in the hinterland (TESSENSOHN, 1979) which subdues $Ba_{(excess)}$ below zero. Therefore Ti should not be used for normative purposes in this case. This example shows that normative approaches have to be applied carefully, where the provenance of the detrital source changes. For further calculations Al was used to obtain $Ba_{(excess)}$ contents (equation 2).

Accumulation rates

Accumulation rates were computed for opal and $Ba_{(excess)}$ following the calculations of VAN ANDEL *et al.* (1975), THIEDE *et al.* (1982) and MÜLLER and SUESS (1979), based on integrated sedimentation rates and dry bulk density measurements.
Accumulation rates for $Ba_{(excess)}$ were derived from normative $Ba_{(excess)}$ concentrations obtained by equation 2. The calculation of accumulation rates is a prerequisite for the estimation of absolute paleoproductivity rates following the approach of DYMOND *et al.* (1992). Although accumulation rates provide an import time and dilution control, they are also a source of possible artefacts, which may lead to misinterpretations of records. The key factors in the computation of accumulation rates are the linear sedimentation rates. Depending on the available stratigraphy they may be integrated over highly variable time intervals like a complete isotope stage, several stages or a substage, thus leading to accumulation rates, which resemble mainly the sedimentation rate pattern. It has been shown that sequences

deeper than 5 m below the surface are increasingly compressed by the coring procedure (MELLES, 1991). Therefore an apparent reduction of sedimentation rates is most likely artificial.

Results and Discussion

Biogenic sediment constituents and productivity proxies

In general, opal concentrations measured by the leaching method mirror the downcore record of radiolarians in the coarse fraction of all six cores (Fig. 3). Biogenic opal is enriched in five horizons, which correspond to the peak warm events of the interglacial stages 1, 5, 7, 9, 11, (Fig. 3). Concentrations rarely drop below a threshold of 2 % in glacial stages and reach 5 to 45 % in peak warm times, thus producing a distinct glacial/interglacial pattern. The highest interglacial values of 20-45 % are found in core PS1821-6 from the Cosmonaut Sea followed by the cores from the continental slope of the Lazarev Sea (PS2038-2) and Weddell Sea (PS1375-3, PS1648-1). At site PS1575-1 near South Orkney interglacial opal values only reach 5-8 %. The flux of biogenic silica to the seafloor and the preservation, which is a function of the sedimentation rate, are believed to be responsible for the observed differences in interglacial maxima. In cores with comparable sedimentation rates like PS1821-6, PS2038-2 and PS1375-3 interglacial opal values are controlled by the flux of biogenic silica produced in the photic zone. However, the influence of the sedimentation rate on opal contents is visible in cores from a confined area, underlying surface waters of the same productivity regime, but with different sedimentation rates like PS1506-1 and PS1648-1. Situated only about 110 km further southwest at the same water depth on the continental slope PS1648-1 receives approximately twice as much terrigenous matter compared to PS1506-1, which results in a better preservation and a doubling of the interglacial opal maxima (Fig. 3).
The low level of opal contents in glacial stages reflects both, terrigenous dilution and enhanced silica dissolution combined with a substantial decrease in siliceous primary productivity. We assume that although opal is susceptible to dissolution the downcore records represent siliceous primary productivity (MORTLOCK *et al*., 1991; SCHLÜTER, 1990). The opal records show enhanced biological productivity in the interglacials, indicating largely ice-free conditions during the summer month. The lack of opal in glacial stages is interpreted as a response to permanent sea ice coverage. As mentioned in the methods section the 2 % threshold is probably an artefact of the leaching method. Comparing the absolute opal values of the different sites and considering the preservation effect exerted by different sedimentation rates

a decrease from East to West can be observed. As a first approximation this is attributed to a decreasing surface productivity. However, this has to be tested on a second independant productivity proxy. Therefore three cores were chosen for barium analysis.
Total barium contents in the cores vary from 600 ppm in the glacial sections to 2400 ppm in the peak warm events of the interglacial stages. Since the terrigenous fraction of the cores with an average of 95 % and consequently the Al-concentration is rather constant the detrital correction subtracts a constant amount of 400-600 ppm from total barium contents. Therefore the resulting $Ba_{(excess)}$ downcore records mirror total barium contents on a lower level (Fig. 2). $Ba_{(excess)}$ contents closely resemble the opal records with constant low levels in glacial stages and sharp maxima in interglacial stages (Fig. 4). The highest values are again found at site PS1821-6 in the Cosmonaut Sea with 1500-2000 ppm followed by 1000-1500 ppm at site PS1648-1 in the Weddell Sea. Site PS1575-1 near South Orkney is characterized by 400-800 ppm $Ba_{(excess)}$ in interglacial stages (Fig. 4). This decrease in $Ba_{(excess)}$-values from East to West is consistent with the observed trend in opal contents. However, inconsistencies exist in the downcore record of both paleoproductivity proxies. The interglacial $Ba_{(excess)}$-peaks of stage 9 (PS1575-1, PS1648-1), substage 7.3 and stage 11 (PS1821-6) are not adequately represented by opal maxima (Fig. 4), which is attributed to opal dissolution events in the sediment.
Since barite is a highly refractive species it is regarded as more reliable than opal. In contrast to other common productivity proxies like organic carbon, carbonate and opal, which are greatly reduced in the water column and at the sediment/water interface by dissolution and degradation an average of 30 % of the $Ba_{(excess)}$ (dependant on the mass accumulation rate (MAR)) survives burial in the sediment (DYMOND *et al.*, 1992; SHIMMIELD *et al.*, 1994; STROOBANTS *et al.*, 1991). However, barite can be mobilized in a highly anoxic environment, where sufficient organic matter leads to sulphate reduction in interstitial waters and destruction of the productivity signal (BRUMSACK, 1989; FALKNER *et al.*, 1993; VON BREYMANN *et al.*, 1992). This can be ruled out in the cores because barite is very stable and hard to dissolve in deep sea sediments as long as sulphate is present in the pore waters (SHIMMIELD, 1992). TOC-contents are uniformly low and sulphate reduction detectable by the smell of H_2S, is neglectable.
Although the opal records suggest a reasonable correspondance with the $Ba_{(excess)}$-signal, a close comparison reveals that the phasing of the two parameters is different, with opal leading the $Ba_{(excess)}$ during deglaciation periods. This phenomenon, also observed in other cores from the Southern Ocean (SHIMMIELD *et al.*, 1994), is particularly obvious in core PS1821-6 (Cosmonaut Sea) and little less obvious in core PS1648-1 (Weddell Sea). No phase lag between opal and barium values exists in core

PS1575-1 (South Orkney). The phase lag seems to be correlated with the intensity of the opal and barium signals. Since barium is regarded as more resistant to dissolution than opal, it is difficult to explain the lack of a barium peak, when opal values are already high at an initial deglaciation step. Three explanations for the observed phasing, are possible:

(1) Firstly, a drastic increase in the input of organic matter during the onset of deglaciation could lead to a pore water profile, where sulphate is exhausted at a shallow depth and the barium peak moves upward by early diagenetic mobilization and precipitation while opal peaks remain at the same depth. However, to our knowledge no pore water profiles have been measured, where sulphate is depleted at less than one meter core depth, thus making this approach highly unlikely. It is also not supported by organic carbon contents, which are uniformly low.

(2) Secondly, meltwater input during deglaciation phases reduces dissolved barium in surface waters and it´s incorporation into organic matter to such an extent, that the formation of barite particles is severely impeded thus leading to a lack of biogenic barium at an initial stage. This could explain the stronger phase lag in the southern cores compared to that from South Orkney.

(3) However, we favour a third possibility, that explains the observed phasing of both proxies with the dilution of biogenic barium by rapid accumulation of siliceous matter. This also explains, why the strongest phasing is observed in PS1821-6, the core with the highest opal content.

In the investigation area carbonate records exhibit characteristic downcore patterns, which are used to support the lithostratigraphic correlation. Values are generally below 10 %, with minima in glacial stages, rising in interglacials and dropping to near zero in peak warm times. The lack of carbonate in peak warm times is due to dissolution by increased levels of carbon dioxide, which results from the degradation of organic matter at the sediment water interface and within the sediment (EMERSON and BENDER, 1981; BROECKER and PENG, 1982). Thus, carbonate lows coincide with high productivity events indicated by opal and barium records.

TOC-contents in the cores are uniformly low. TOC-values drop from a maximum of 0.2-0.4 % to a residual level of 0.1-0.2 %, which stays constant throughout the rest of the core. Only site PS1821-6 shows a glacial-interglacial pattern, though on a very low level (0.1-0.2 %), which resembles the fluctuations observed in the opal and $Ba_{(excess)}$ record (Fig. 4).

Accumulation rates of $Ba_{(excess)}$ and opal were computed from concentrations. Downcore records of both proxies clearly indicate a glacial-interglacial pattern with peaks in interglacial sections and lows in the glacial parts (Fig. 5).

Paleoproductivity calculations

Recently DYMOND *et al*. (1992) developed an algorithm to recalculate new production (p_{new} = export production) from the accumulation of biogenic barium (equation 4). This algorithm connects new production (P_{new}), dissolved barium content of the water column (Ba), water depth (z) and particulate barium flux (F_{Ba}). The rain of biogenic barium or particulate barium flux was estimated from the mass accumulation rate of the sediment (MAR) and the $Ba_{(excess)}$ accumulation rate using the tentative relation found by DYMOND *et al.* (1992), (equation 5). The resulting preservation factors slightly exceed an average of 30 %, which was found to be the mean percentage of the $Ba_{(excess)}$-flux surviving burial in the sediment (DYMOND *et al*., 1992). Based on these values, rates of new production were computed for the studied sites and paleoproductivity (PP) was estimated using the relation from BERGER *et al*. (1989), (equation 7). Dissolved barium in the water column increases from North to South in the South Atlantic from 50 nmol/kg near the equator to 100-106 nmol/kg at the southernmost available GEOSECS-station at 60°S (CHAN *et al*., 1977; BROECKER and PENG, 1982). Situated up to 10 degrees further south the calculations for the studied sites were carried out with 110 nmol/kg thus accounting for possibly slightly higher barium contents at intermediate water depths. The same value was used for interglacial as well as glacial sections of the core. Though there are changes in NADW input to the Southern Ocean, there are no significant differences in Ba/Ca-ratios of benthic foraminifera (LEA and BOYLE, 1990), indicating a rather constant value of dissolved barium. The evaluation of additional sediment trap data enabled Francois et al. (1995) to simplify the quantitative approach of Dymond et al. (1992). They postulated that the flux of biogenic barium is rather independant from dissolved barium in the water column. The relationship between export production and flux of biogenic barium is thus described by a simplified power function (equation 6).

(4) $P_{new} = (F_{Ba}\ 0.171\ Ba^{2.218}\ z^{0.476-0.00478\ Ba}/2056)^{1.504}$

(5) $Ba_{(excess\ flux)} = Ba_{(acc.)}/0.209 \log MAR-0.213$

(6) $P_{new} = 1.95\ (Ba_{(excess\ flux)})^{1.41}$

(7) $P_{new} = PP^2/400 - PP^3/340.000$

In this study we used both approaches to compare the effects on paleoproductivity rates. Generally downcore records of P_{new}- and paleoproductivity-values correlate nicely. However, in peak warm stages the approach of Dymond et al. (1992) yields 30-40% higher values. Paleoproductivity rates calculated according to Dymond et al.,

(1992) varied between 200-350 g C m^{-2} a^{-1} at site PS1821-6 and 150-230 g C m^{-2} a^{-1} at site PS1648-1 in interglacial stages. These values are comparable to rates from high productivity areas, e.g. upwelling systems off the west coasts of South America or Southwest Africa (BERGER *et al*., 1989). Site PS1575-1 near South Orkney only reached 100-200 g C m^{-2} a^{-1} and is roughly consistent with estimations of global ocean surface productivity (BERGER *et al*., 1989). Direct measurements of primary production are scarce and highly variable in the investigation area. They are mostly determined during plankton blooms in the short Antarctic summer and the figures are difficult to extrapolate to a yearly production. Nevertheless, values of 400-1000 mg C m^{-2} d^{-1} were measured at the continental margin of the Weddell Sea (GLEITZ *et al*., 1994), reaching 1500 mg C m^{-2} d^{-1} in ice-free areas. To compare these measurements, which were taken during a period from January to March with our estimations, we have to consider the time, which is available for production. Productivity from January to March was found to decrease towards March, when sea ice starts to form in the area (GLEITZ *et al*., 1994). Considering the data on sea ice coverage provided by satellite images (GLOERSEN *et al*., 1992), we assume an ice-free period of six month for the sites at the continental margin, which can be used for biological productivity. However, recent information from the Weddell Sea suggests that the incorporated phytoplankton acclimatizes well to the sea ice environment and primary production is sustained to some extent (GLEITZ and THOMAS, 1993). As suggested by satellite images (GLOERSEN *et al*., 1992) the productivity may be linked to the development and persistence of coastal polynyas, which do not close completely in winter (EICKEN and LANGE, 1989; SCHAREK, 1991). Proceeding on the assumption of a six month production period, we get a rough estimate of 80-230 g C m^{-2} a^{-1} for the Weddell Sea margin. On an average this is consistent with our calculations from the barium record at site PS1648-1 and confirms the rating of the Antarctic margin as a highly productive area.

Paleoproductivity rates exceeding 250 g C m^{-2} a^{-1} are rarely found in the present ocean (Berger 1989). In our core material they occur in substage 5.5 of cores PS1575-1 and PS1821-6. The extremely high rates may be an effect of integrating linear sedimentation rates over a substage and not an entire isotope stage. Integrating over the whole stage 5 would reduce paleoproductivity rates to the level of those in the other interglacial stages.

Paleoceanographic implications

The Southern Ocean today is a mixing reservoir for incoming NADW and recirculated water from the Pacific and Indian Oceans. The contribution of the NADW to the CDW has changed during the climatic cycles, particularly when production of bottom water in the North Atlantic nearly ceased due to sea ice coverage (OPPO and FAIRBANKS, 1987). NADW is largely composed of upper ocean waters and thus in the North Atlantic is the most nutrient depleted deep water mass formed in the oceans today. In the South Atlantic it has still high $\delta^{13}C$ values (KROOPNICK, 1985), therefore, up to 50 % of the glacial/interglacial $\delta^{13}C$ amplitude in the Southern Ocean is due to changes in the contribution of NADW (OPPO *et al.*, 1990). Together with climate-controlled global changes between carbon reservoirs, changes in NADW input into the Southern Ocean are the most important reasons for the changes in $\delta^{13}C$ observed in high southern latitude cores.
Variations in the relative flux of NADW to the Southern Ocean influence the properties of the CDW and surface water (CORLISS, 1982; CHARLES and FAIRBANKS, 1990; HODDELL, 1993). Because NADW is a heat source for the Atlantic sector of the Antarctic Ocean waters, it consequently influences the formation of sea ice (HOWARD and PRELL, 1994). The amount of sea ice and additional snow coverage is crucial to the availability of light in surface waters, and hence is a main factor in controlling primary productivity. This is particularly important, because in Southern Ocean surface waters no nutrient limitation occurs between the Polar Front and the Antarctic Divergence (DEFELICE and WISE, 1981). Variations in productivity during climatic cycles correspond to the extent of sea ice in a similar way as during the recent seasonal processes, in which seasonal changes in sea ice coverage control productivity and thus biogenic silica flux. We infer this from sediment trap studies in the Antarctic Ocean (DUNBAR, 1984; WEFER *et al.*, 1990).
Our productivity calculations from the core top samples suggest that at least parts of the Antarctic continental margin today are areas of high productivity and must be accounted for estimations of mass balances of silica and barium. However, this does not seem to have any implications on the accumulation of organic carbon and carbonate. Carbon is effectively recycled prior to burial and remineralized in the water and at the sediment/water interface.
The opal and barium records indicate that the cyclicity of primary production varies in response to the glacial/interglacial changes. The events of higher productivity during peak warm times, indicated by maxima in silica and biogenic barium content and intense bioturbation, and the variations of carbonate can be explained in terms of interaction of sea ice coverage, deep water convection and water masses. On the

Weddell Sea continental margin, the WDW appears to influence the depth range of lysocline and CCD (ANDERSON, 1975; MACKENSEN *et al*., 1990). However, the depth of the CCD depends on the properties of water masses and the productivity in surface waters as well. A high flux of organic matter increases the CO_2 content in the interstitial waters and thus the solution of carbonate. During a climatic cycle the CCD oscillates between 4000 m and 2000 m. It reaches the shallowest water depth during the most intense productivity.

Variations of atmospheric CO_2 during Pleistocene climatic cycles were supposed to be controlled by Southern Ocean productivity, such that a more effective "biological pump mechanisms" during glacial times causes the Southern Ocean to be a sink for atmospheric CO_2 (KEIR, 1988). Enhanced productivity during glacials should be caused by higher solar radiation and reduced circulation of surface waters (SUNDQUIST and BROECKER, 1985), or by increased atmospheric dust fallout which supplies iron to an iron-limited Antarctic surface water (MARTIN, 1990). On the other hand, a reduced consumption of nutrients was postulated because of the extensive sea ice coverage during glaciations (MIX and FAIRBANKS, 1985). This may result in an increasing amount of preformed nutrients in low latitudes which may enhance productivity there (SARNTHEIN *et al*., 1988).

The glacial sediments analyzed in this study clearly indicate strongly reduced productivity and sedimentation rates during glaciations in high southern latitudes around the Antarctic continent. This evidence is consistent with other recent studies, indicating low productivity in the Southern Ocean during glacial times (LABEYRIE and DUPLESSY, 1985; MACKENSEN *et al*., 1989; GROBE *et al*., 1990; MORTLOCK *et al*., 1991; GROBE and MACKENSEN, 1992). Estimates of sea ice distribution during the last glacial maximum show continuous ice coverage south of 60 °S (HAYS, 1978; COOKE and HAYS, 1982). During these times the availability of light in surface waters was strictly reduced by a snow covered sea ice, which will have been the most significant factor limiting productivity in the Antarctic Ocean.

Conclusions

These investigations of the productivity proxies biogenic silica and barium suggest, that the Antarctic continental margin is an area of high surface productivity. In spite of a seasonal ice cover productivity rates approach those known from upwelling areas off the west coasts of South America and South Africa.

High paleoproductivity rates, comparable to recent ones were also computed for the previous interglacials 5, 7, 9 and 11. It can be concluded that the sea ice coverage, which is the limiting factor for the biological production today, was likewise reduced during those periods. The sea ice coverage today is largely dependant on the heat transfer from NADW to subantarctic waters.

Our results imply that this heat transfer was active during the interglacials 5, 7, 9 and 11. Paleoproductivity was strongly reduced during glacials due to a permanent sea ice coverage. However, measurable quantities of opal and biogenic barium suggest that productivity did not cease completely.

The comparison of the paleoproductivity proxies opal and biogenic barium shows that generally both - in contrast to carbonate and organic carbon - give qualitative evidence of glacial/interglacial productivity changes. However, minor differences occur. Opal is susceptible to dissolution in the water column, at the sediment/water interface and in the sediment. It´s preservation is supported by high opal fluxes and high sedimentation rates in general. Dissolution of opal may explain the lack of peaks of biogenic silica, where a high productivity is indicated by the barium record. Biogenic barium shows maxima in all interglacials throughout the cores investigated and is regarded as a reliable paleoproductivity proxy, also allowing the assessment of absolute paleoproductivity rates. We believe that the observed phasing between opal and barium records during deglaciation phases is an effect of dilution of the barium signal by rapid accumulation of biogenic silica. We suggest that it is neccessary in high latitudes to have a minimum of two independant paleoproductivity parameters in order to make reliable paleoenvironmental interpretations.

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Table 1. Position and water depth of gravity cores.

Core	Tool	Latitude (°)	Longitude (°)	Depth (m)
PS1375-3	SL	72° 09,000 S	17° 06,000 W	1750
PS1506-1	SL	68° 43,095 S	05° 50,098 W	2426
PS1575-1	SL	62° 50,097 S	43° 20,013 W	3461
PS1648-1	SL	69° 44,040 S	06° 31,048 W	2529
PS1821-6	SL	67° 03,092 S	37° 28,083 E	4027
PS2038-2	SL	69° 21,179 S	06° 17,101 E	1630

Figures

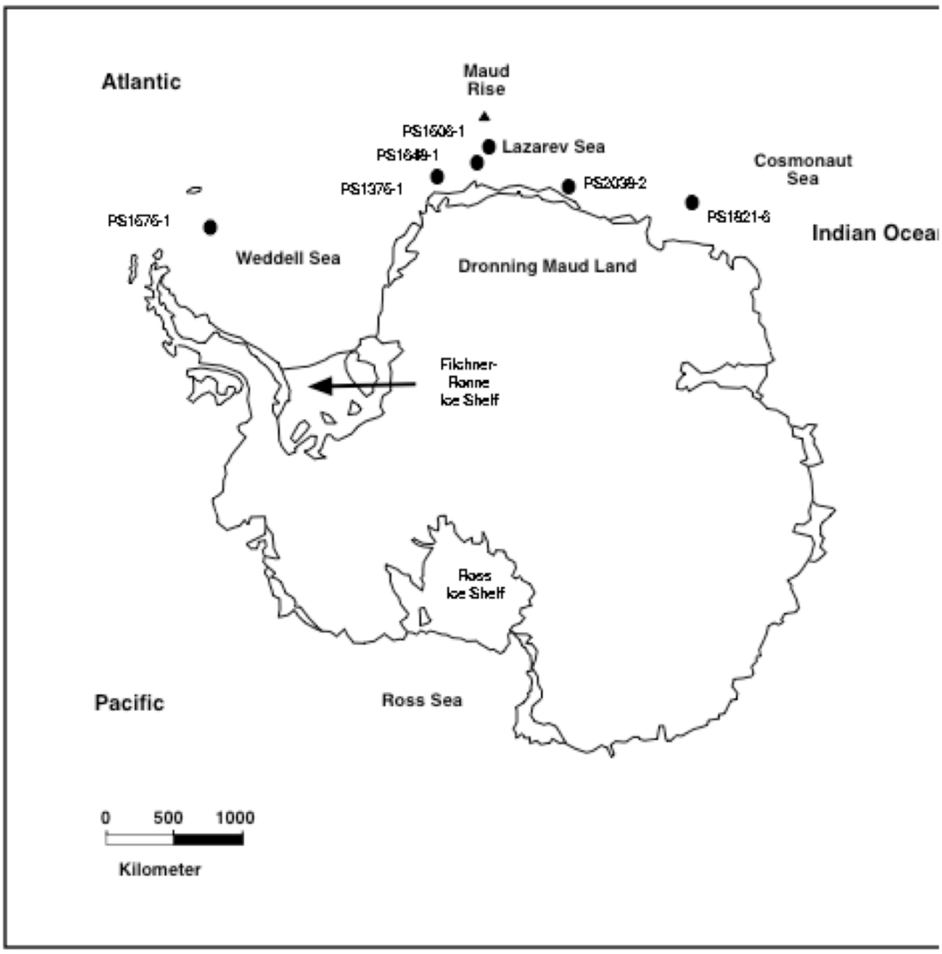

Figure 1: Area of investigation with positions of the studied sites.

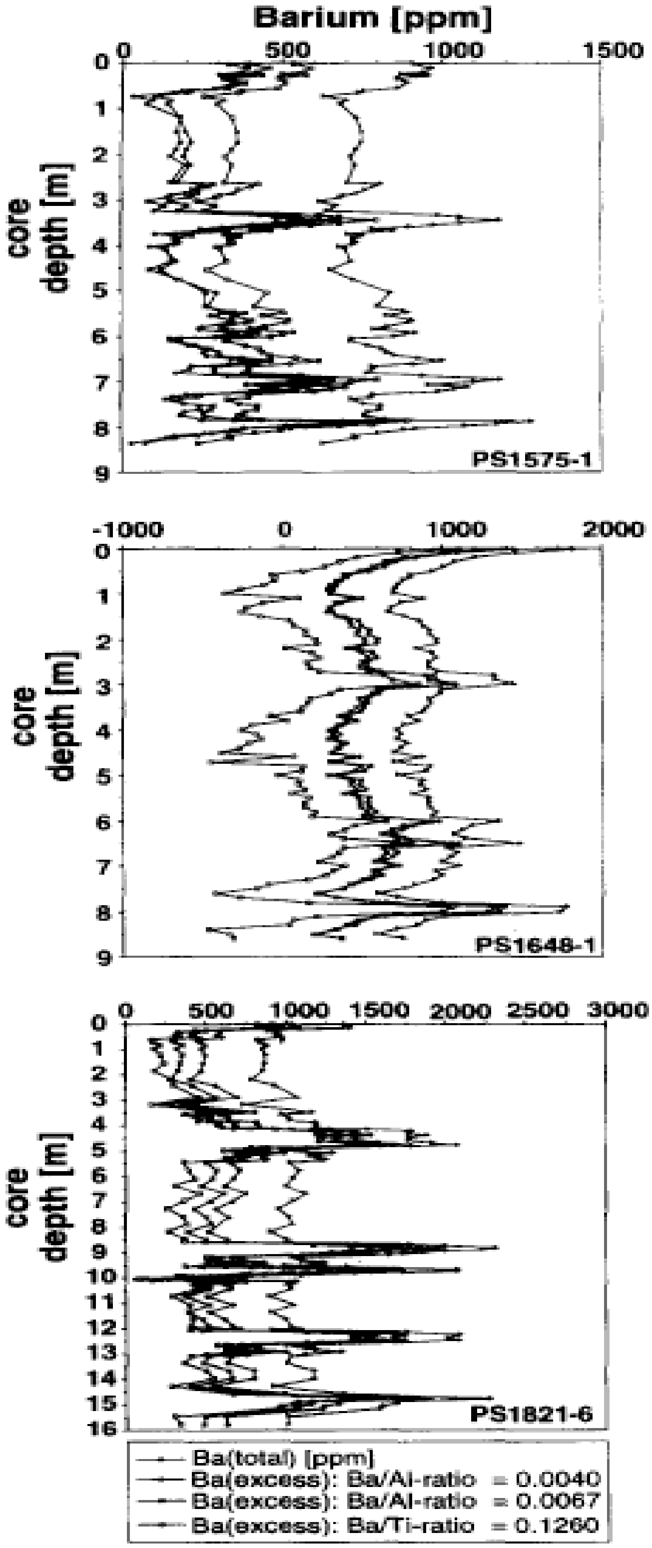

Figure 2: The effects of different Ba/Al - and Ba/Ti-values on computing the detrital barium background (equation 1, 2, 3) from Ba $_{(total)}$-values.

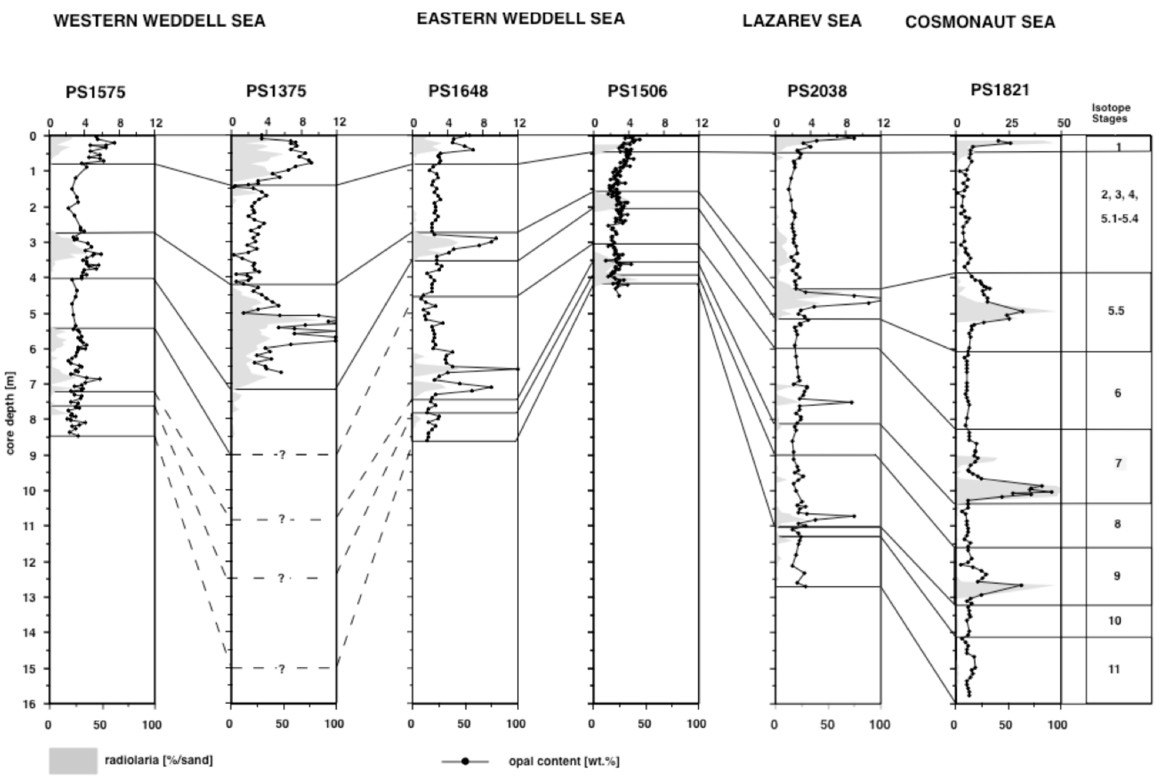

Figure 3: Downcore distributions of opal and radiolaria (shaded) can be correlated from core to core.

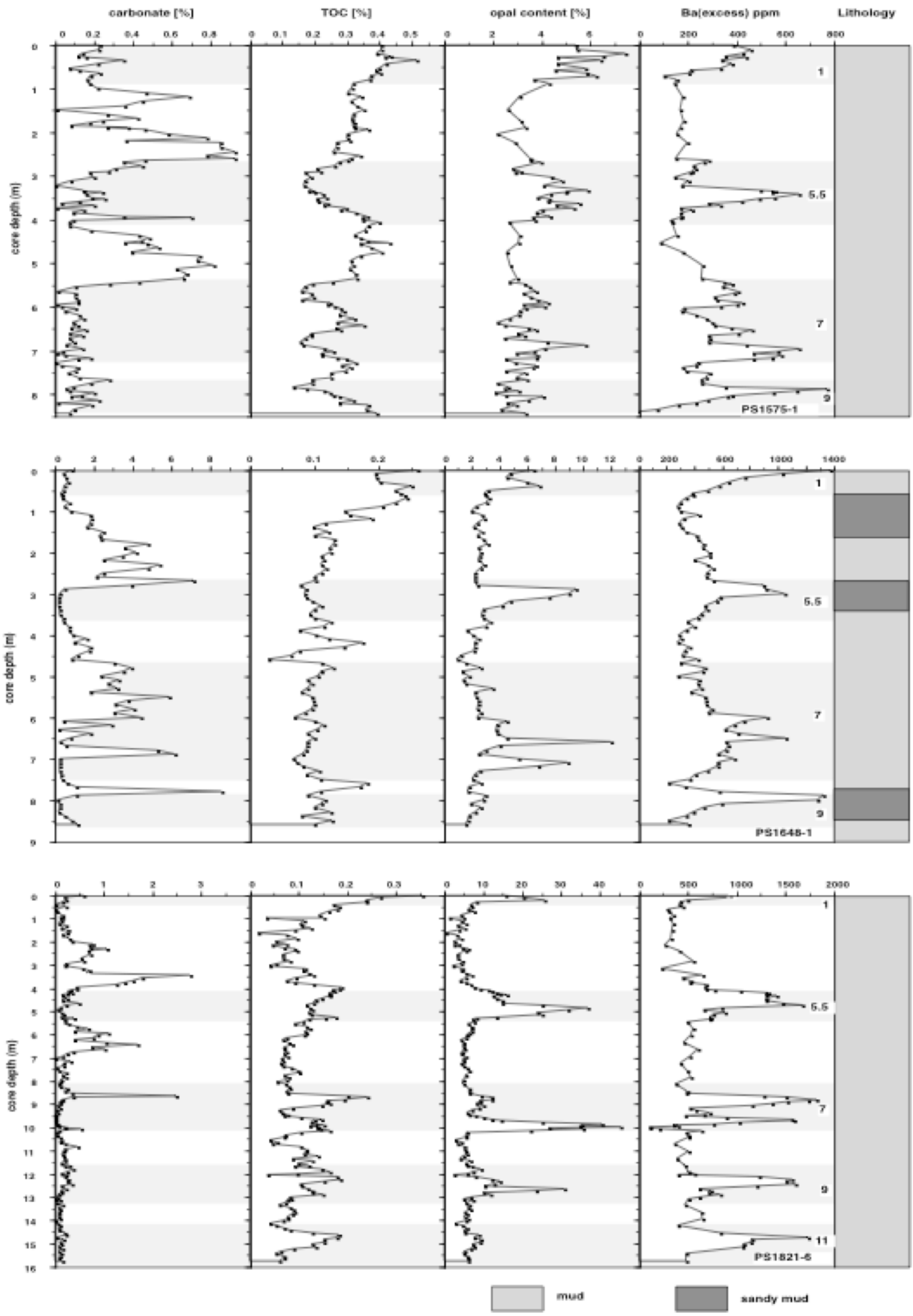

Figure 4: Lithology, downcore distribution of carbonate, organic carbon (TOC), opal and biogenic (excess) barium of cores PS1575-1, PS1648-1 and PS1821-6.

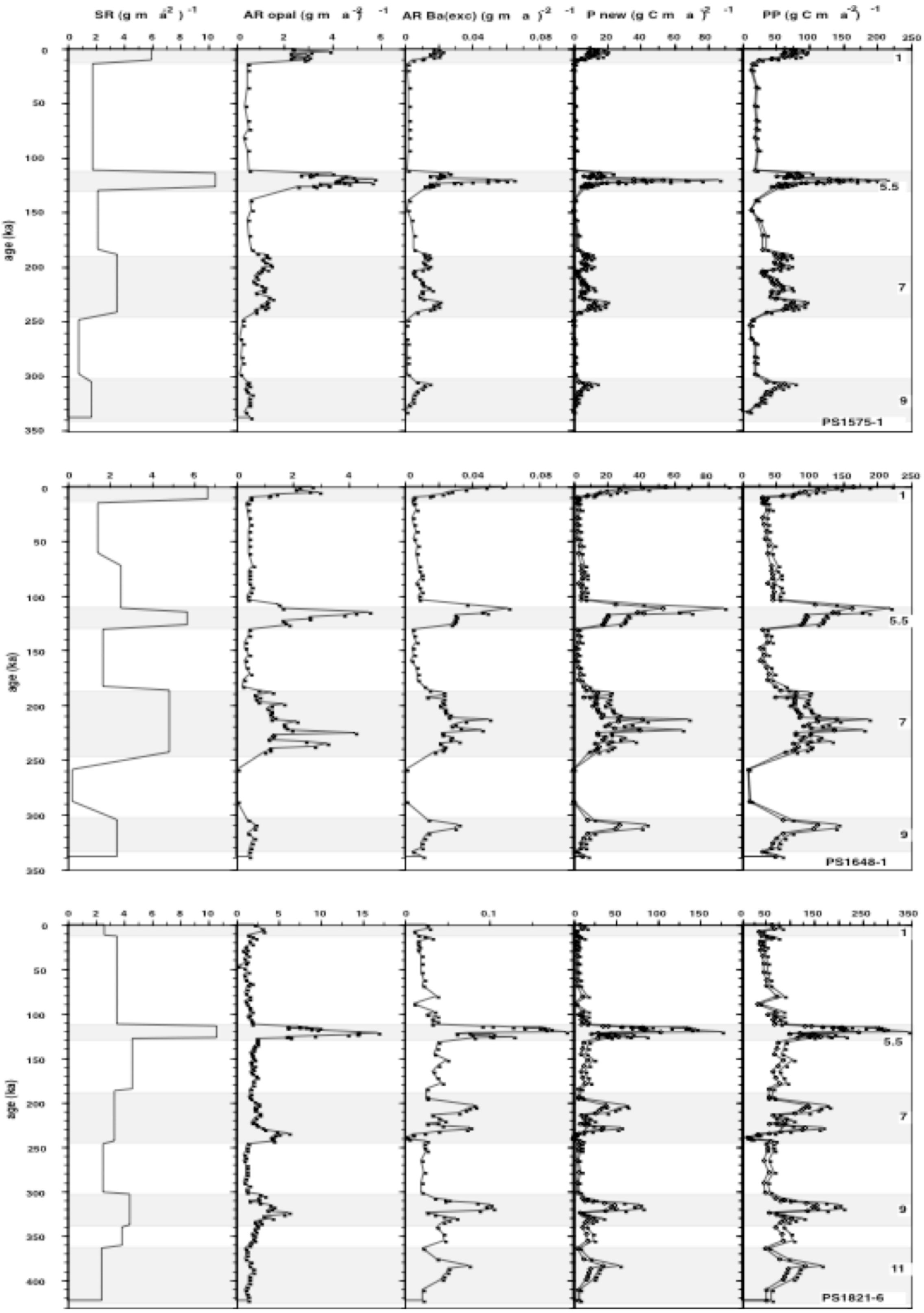

Figure 5: Sedimentation rate, accumulation rates of opal and barium$_{(excess)}$, export production (P_{new}) and paleoproductivity (PP) of cores PS1575-1, PS1648-1 and PS1821-6. Mean sedimentation rates were calculated for the isotope stages and substages. Export production and paleoproductivity were computed according to Dymond et al. 1992 (squares) and Francois et al. 1995 (circles).