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The use of inorganic chemistry in studying the palaeoceanography of the Weddell Sea

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Abstract: Changes in biological productivity over glacial to interglacial episodes within the world's oceans have been suggested to have a major impact on changes in atmospheric CO_2 content as recorded in long ice cores. In the last few years several studies have been undertaken in the Southern Ocean to validate this "glacial productivity hypothesis". These studies, and the work presented here, now demonstrate clearly that glacial productivity was *lower* south of the present-day Antarctic Polar Front. In order to establish palaeoceanographic and palaeoproductivity records for the Weddell Sea where an absence of foraminifera precludes the standard use of $\delta^{18}O$ stratigraphy and ^{14}C-dating, we have developed a method based on the synchronous removal of barium to the ocean floor by scavenging and formation of barite within the frustules of marine diatoms. The barium record is calibrated to the $\delta^{18}O$ timescale from a single core off Atka Bay on the eastern Weddell Sea continental margin at 70°S where foraminifera may be found. Using a barium-based chronology we demonstrate the major flux of both biogenic and lithogenic material to the seafloor in the northern Weddell Sea occurs during the last deglaciation (18–12 ky BP). Highest palaeoproductivity occurs in the vicinity of the Scotia Arc and decreases southwards due to increased seasonal sea ice cover. Increased Ti/Al ratios, a proxy of bottom water velocities, suggest increased flow of Antarctic Bottom Water during interglacial episodes. This work represents the first detailed study of geochemical palaeoceanographic indicators in the central and northern Weddell Sea area.

Key words: geochemistry, palaeoceanography, sediments

Introduction

The sediments of the Southern Ocean are known to contain a record of the changing biological productivity in surface waters, the supply of terrigenous material from glacial weathering of the Antarctic continent, and redistribution of the sediments by deep bottom currents. The open ocean waters surrounding the Antarctic continent are characterized by very high surface nutrient concentrations maintained by upwelling of the Circumpolar Deep Water (CDW). One result of this upwelling is a rain of diatoms to the sea floor that results in large accumulations (75% by weight) of opal in the so-called "diatom ooze belt" located just south of the present-day Antarctic Polar Front. Past estimates of opal production suggest that as much as 75% of the modern global accumulation may take place in this region (DeMaster 1981, Ledford-Hoffman *et al.* 1986), although these estimates were based on geographically restricted areas.

This high biological productivity and efficient use of upwelled nutrients has been suggested to vary through the late Pleistocene when the Earth has suffered major waxing and waning of the ice sheets resulting in a photosynthetic control on atmospheric carbon dioxide (Siegenthaler & Wenk 1984, Kier 1990) deduced from studies of ice cores (Barnola *et al.* 1987). In particular, a model of high glacial stage productivity which stimulates the "biological pump" to remove carbon to the deep sea, drawing down pCO_2 in the process, has been suggested (Martin 1990).

Part of the glacial productivity hypothesis for lowering atmospheric CO_2 also advocates reorganisation of the chemical circulation patterns within the oceans (Broecker & Peng 1989, Boyle 1988).

If such hypotheses are correct then the record of palaeoproductivity in the Southern Ocean should show enhanced productivity inversely correlated with changes in atmospheric CO_2. In the last few years geochemical and sedimentological data have been collected from Southern Ocean sediments which can be used to address these questions (Pudsey *et al.* 1988, Mackensen *et al.* 1989, Pudsey 1992). In particular the record of opal accumulation rate from sediments both north and south of the current Antarctic Polar Front (APF) has been studied in detail by Mortlock *et al.* (1991) and Charles *et al.* (1991). They have found that sediments to the north of the APF have high glacial productivity records (in agreement with the CO_2 record), but that south of the APF where present-day productivity reaches a maximum, the sedimentary record suggests *lower* glacial productivity. They conclude that the models of climate change and atmospheric CO_2 linked to an increase in glacial productivity in the Antarctic are not supported by the opal records from the Southern Ocean.

To date, most palaeoproductivity records for the world's oceans have been generated from organic carbon (C_{org}), $\delta^{13}C$ gradients in foraminifera, Cd/Ca and Ba/Ca ratios in benthic

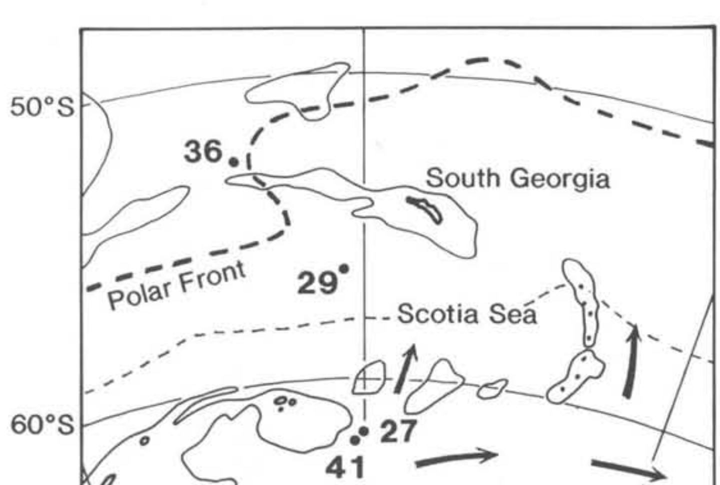

Fig. 1. Map of the Weddell Sea indicating the positions of cores 36, 29, 27, 41 and PS1506. The light dotted lines mark the winter and summer sea ice extents. The arrows indicate the clockwise circulation of the deep water within the Weddell gyre.

foraminifera, micropalaeontological species abundance and diversity measurements (e.g. Zahn *et al.* 1986, Sarnthein *et al.* 1988, Boyle 1988, Lea & Boyle 1989). Common to all these techniques is the establishment of an accurate chronology, usually obtained from matching the $\delta^{18}O$ of the foraminifera to the globally-averaged SPECMAP stack. Recently, other bulk sediment geochemical parameters have been shown to contain valuable indices of palaeoproductivity (reviewed in Shimmield 1992). Although calcite tests of foraminifera are recorded north of the APF, to the south the highly undersaturated waters result in almost total absence of foraminifera on which isotope measurements may be made. An exception to this occurs on the eastern Weddell Sea continental margin off Atka Bay (70°S, 10°W) where a local carbonate province has been sampled for $\delta^{18}O$ stratigraphy (Mackensen *et al.* 1988). The absence of a good chronology, particularly within the Weddell Sea and southern Scotia Sea, has hitherto made it difficult to examine the palaeoceanographic record of palaeoproductivity, Antarctic Bottom Water (AABW) formation and flow, and changes in terrigenous input.

In this paper we describe a novel technique for establishing an age model in the deep northern Weddell Sea and southern Scotia Sea based on the downcore distribution of barium, calibrated to a $\delta^{18}O$-dated core. Given this age model, the time- and spatially-dependent distribution of opal and organic carbon in the sediment has been studied, and estimates made of total mass accumulation rates over the last glacial-interglacial cycle. The results shown here suggest that glacial productivity was indeed lower during the last glacial maximum (LGM), but also provide, for the first time, detailed qualitative estimates for the biogenic and lithogenic fluxes associated with ice sheet melting following the LGM.

Materials and methods

For this study five cores have been investigated spanning a transect from just north of the APF (Core 36; Fig. 1), through the Scotia Sea (Cores 29, 27 and 41) to the eastern Weddell Sea continental margin (Core PS1506). Water depths for these cores are 3552, 3369, 3470, 3310 and 2550 m respectively. The latter core was collected by the Alfred Wegener Institute, Bremerhaven, Germany, whilst the four northerly cores were obtained by the British Antarctic Survey, Cambridge.

The cores have been subjected to discrete sample geochemical analysis at approximately 10 cm depth intervals. In the case of the BAS piston cores, the trigger core was also analysed in order to obtain the most recent sediment. Bulk sediment geochemistry was performed by X-ray fluorescence spectrometry on both pressed pellet discs for the minor elements and fused glass discs for the major elements. A rhodium target X-ray tube was used with mass adsorption coefficients described in detail in Shimmield (1985). For the elements presented here (Al, Ti, Ba, Ca) the analytical precision is better than 2%. The accuracy of the technique is constrained by running international certified reference materials to an r.m.s.d. of better than 5%. Organic carbon was determined by careful removal of any calcite and dolomite by hot sulphurous acid, and then freeze drying the sample prior to analysis using a Carlo-Erba NA1500 elemental analyser. Precision is estimated at 3% for low-carbonate (<30%) samples. Biogenic opal was obtained by leaching a dried sample with sodium carbonate solution which dissolves the hydrated silica dioxide. Small amounts of Si from clays may also be mobilized and thus Si and Al in the leachate are analysed following spectrophotometric methods developed at Edinburgh. A correction for Si leached from the clays is then applied, based on an average lithogenic Si/Al ratio.

The $\delta^{18}O$ data presented was measured on hand-picked samples of *Neoglobigerina pachyderma* at the Alfred Wegener

Institute. The ratio of ^{16}O to ^{18}O is given in standard δ notation with reference to the PDB standard. Average precision of the method was better than 0.05‰. The age model used in this study was derived from comparison of the obtained isotope records (for both planktonic and benthic species) against the SPECMAP stacked record.

Results and discussion

The development of a stratigraphy for the northern Weddell Sea

Fig. 2 presents the comparison of Ba, normalized to Al, against the $\delta^{18}O$ stratigraphy from core PS1506. As noted above, oxygen isotope stratigraphy is now recognised as being a key method for the reconstruction of Pleistocene sedimentation rates. Two major factors affect the $\delta^{18}O$ signature of planktonic foraminifera; global ice volume and temperature. Thus the downcore record of $\delta^{18}O$ may be interpreted as a record of glacial to interglacial change with light (more negative) foraminiferal calcite being secreted during interglacial periods when the ice sheets were smaller and the ocean water relatively enriched in ^{16}O. In the record shown here, the interglacial stages 1, 5 and 7 may be easily recognized at the surface, 180 and 325 cm depth, respectively.

The barium accumulating in the sediment has two main sources; a biogenic component produced by precipitation of barite ($BaSO_4$) within reducing microenvironments during the settling of diatom frustules through the water column (Dehairs *et al.* 1980, 1991, Bishop 1988, Dymond *et al.* 1992). The second, minor, component is Ba associated with the lithogenic mineral fraction (usually feldspars), with a typical Ba/Al weight ratio of 0.0075. Examination of Fig. 2 shows that most of the Ba is indeed of biogenic origin. The Ba is normalized to Al to remove the effects of dilution of Ba by calcite or opal (also of biogenic origin). The precise mechanism of the barite precipitation still requires further investigation, although Dymond *et al.* (1992) suggest that the depth increase of particulate Ba flux that they observed in sediment traps results from accumulation of dissolved Ba from seawater with a linear increase with depth. Dissolved barium is known to have a nutrient profile in the water column similar to silica and alkalinity (Lea & Boyle 1989). Dymond *et al.* (1992) argue that the observed depth increase in particulate Ba allows a function to be calculated for estimating palaeoproductivity. This is based on the observation that barite is very stable and slow to dissolve in deep-sea sediments so long as sulphate is present in the pore waters (Shimmield 1992). Other studies (Shimmield & Mowbray 1991, Shimmield *et al.* 1991, Clemens *et al.* 1991, Shimmield 1992) have shown that the close similarity between Ba/Al and $\delta^{18}O$ recorded in marginal mesotrophic areas of the ocean is a global phenomenon and probably reflects the standing stock of dissolved Ba in intermediate and deep water with a superimposed palaeoproductivity signal. As a consequence of the excellent preservation potential of barite, and the synchroneity of barite

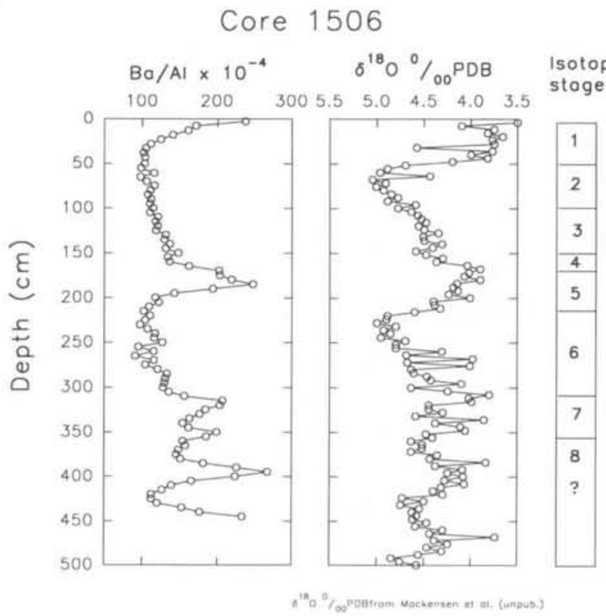

Fig. 2. The correlation between Ba/Al (weight ratio) and the $\delta^{18}O$ stratigraphy of core PS1506 measured on *N. pachyderma*. The isotope stage boundaries are given in the right hand column.

flux within any one ocean basin based on the chemistry of the overlying water column, we propose that the distribution of Ba/Al may be used to correlate the transect of cores studied here. By tying this correlation back to the oxygen isotope stratigraphy, it is possible to derive tentative age models for each of the cores and hence approximate sediment accumulation rates (see Fig. 3). However, it should be noted that this correlation is of a speculative nature, and that the mass accumulation rate parameters derived in this paper will be subject to later revision when independent age constraints become available.

Figs 2 & 3 display pronounced maxima in Ba/Al in the Holocene sediment and in (suggested) isotope Stage 5. Such distributions are consistent with elevated concentrations of Ba in AABW and Antarctic Intermediate Water (AAIW) relative to NADW observed in today's ocean (the GEOSECS data set) together with the enhanced interglacial productivity described by Mortlock *et al.* (1991) and Charles *et al.* (1991) for the ocean south of the APF. Additional support for the proposed chronology comes from estimates of the abundance of the radiolarian *Cycladophora davisiana* (Jordan & Pudsey 1992). Hays *et al.* (1976) found that the first subsurface abundance peak of this radiolarian in the Southern Ocean may be correlated with the Last Glacial Maximum at 18 ky. Jordan & Pudsey (1992) identify this peak at 1.3 m depth in core 27 and 2.5 m in core 29 (Fig. 3). In addition, Jordan & Pudsey (1992) present evidence for two magnetic reversal events in core 41 that are suggested as being the Lake Mungo at 30 ky and the Laschamp at 40 ky. These events are indicated on Fig. 3. The time plane marking the end of the last deglaciation at 12 ky is correlated on the slight

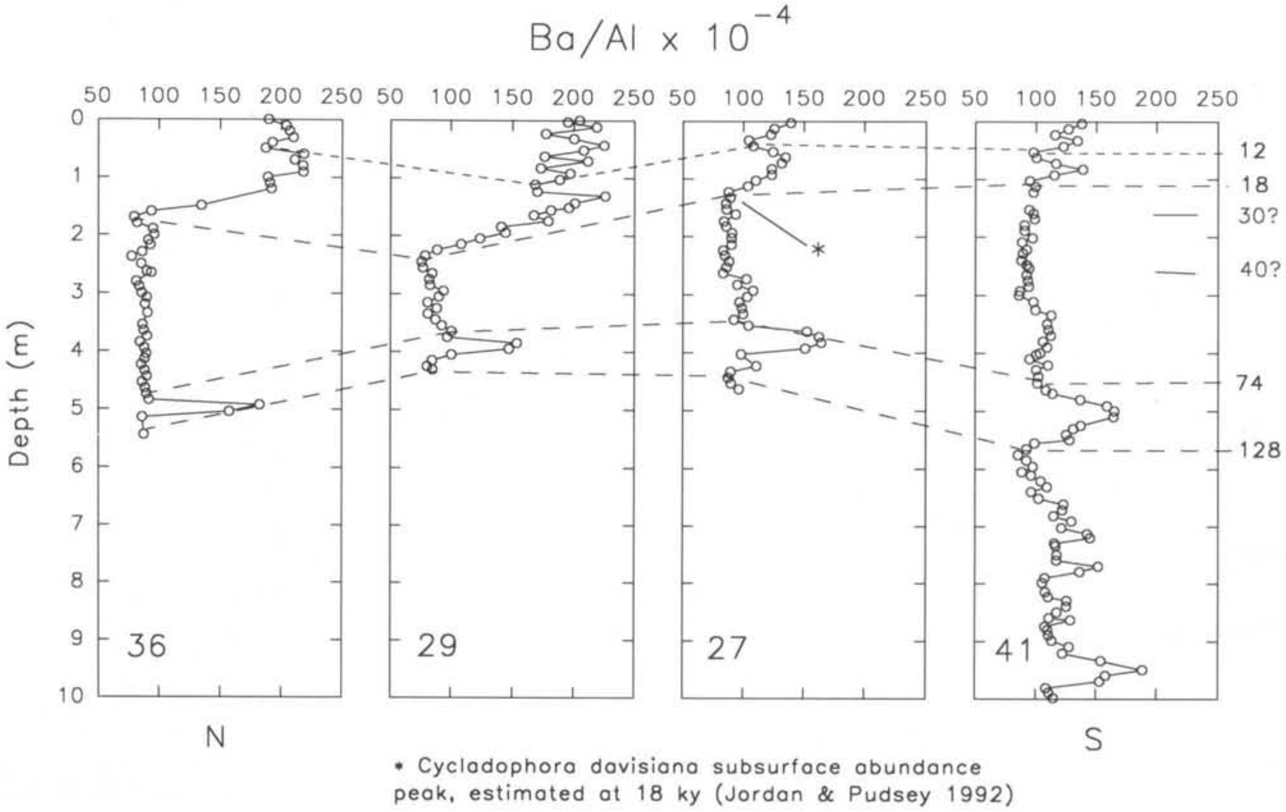

Fig. 3. Using the Ba/Al chronology from core PS1506, a correlation for cores 36, 29, 27 and 41 may be performed. The 18 ky BP time line is based on the first downcore abundance peak of *C. davisiana*. Magnetic events found in core 41 are assigned to the Lake Mungo (30 ky BP) and Laschamp (40 ky BP) (Pudsey 1992). Elevated Ba/Al in Stage 5 is characteristic of the Indian Ocean (Shimmield 1992). The light dashed line at 12 ky BP is uncertain.

decrease in Ba/Al that occurs in all cores. Such an event is marked by cooling over a 1000 year time span (at about 11 ky BP) in the northern hemisphere and is usually referred to as the Younger Dryas Event. This boundary is probably the most questionable within the stratigraphy presented here, but the Ba/Al records do appear to be responding consistently and further work using U-series isotopic disequilibrium methods may further constrain this horizon in time.

Using the preliminary age models deduced from the Ba/Al stratigraphy, and knowing the dry bulk density of the sediment samples, the variation of mass accumulation rate (MAR, in g cm^{-2} ky^{-1}) may be calculated. This is shown in Fig. 4 and indicates that the major accumulation rate of sedimentary material (comprising both lithogenic and biogenic material) occurs during the deglaciation between 12 and 18 ky. The lowest accumulation rates occur during interglacial isotope Stage 5 with high Holocene rates particularly in core 29. Despite the improvements in chronology for deep Weddell Sea sediments shown here, the MAR is poorly constrained and reflects the "coarseness" of the age model. Consequently, the summary diagram (Fig. 5a) indicates the mean and one standard deviation of the MAR for each major time stage to allow easier comparison between cores. Notice the lowest fluxes over the last 130 ky occur off the eastern Weddell Sea continental margin despite the closeness of this station to the Antarctic continent. Maximum deglaciation and Holocene fluxes occur in core 29 which is probably a result of maximum terrigenous input from melting of the LGM ice via calving icebergs and the high postglacial productivity. Subsequent focussing of sediment by AABW may have occurred.

Changes in palaeoproductivity of the northern Weddell Sea

The percentage of opal, C_{org} and Ba/Al have all been used as palaeoproductivity indicators within key areas of the world's oceans. In many areas opal is found to co-vary with Ba/Al and this observation is clearly supported by measurements from Core PS1506 (Fig. 6). (Note that opal is estimated from the total Si and Al contents with a correction for lithogenic silica at a ratio of 3.2 to 1, respectively; biogenic opal will be measured in the near future). However careful examination of the downcore record suggests that the phase coincidence of these two signals is not exact; this is particularly pronounced between 18 and 12 ky BP and 350–320 ky BP. Similarly, the Ba/Al versus opal records in cores 41 and 36 are not precisely in phase. In core 41 opal also leads Ba/Al at Stage 5 (128–72 ky BP) whereas in core

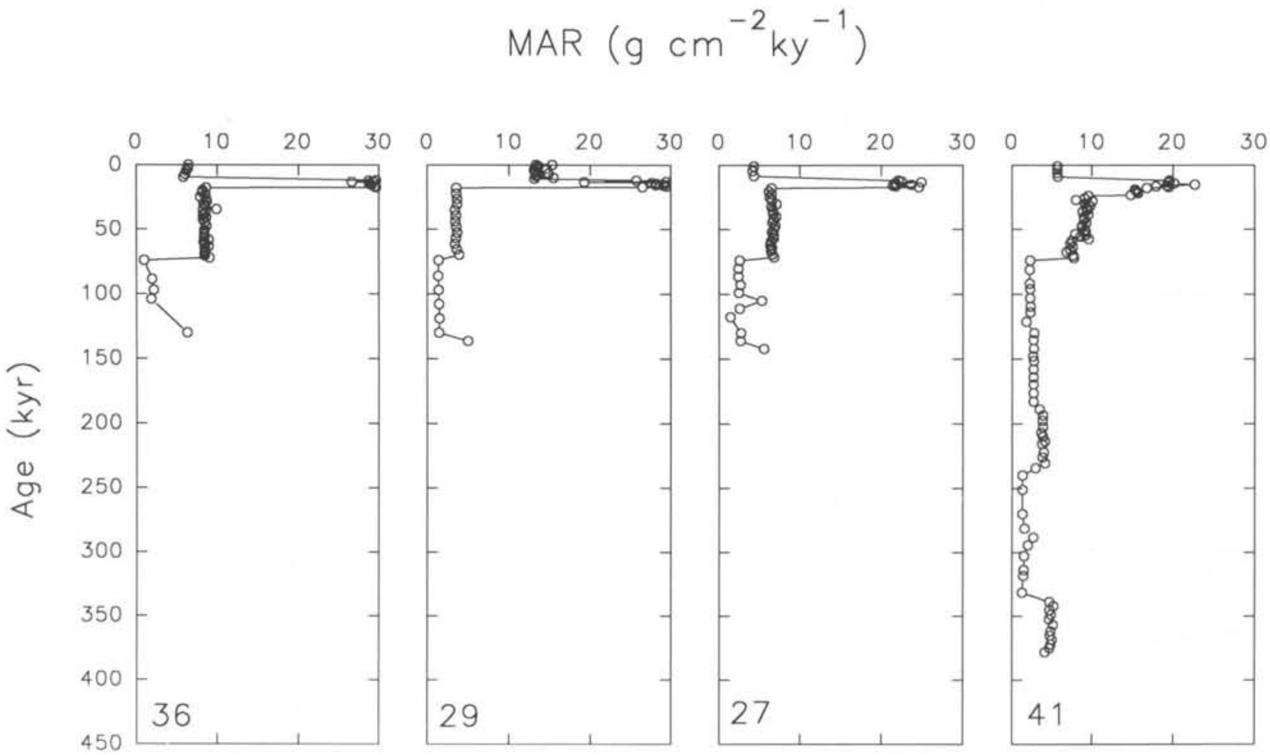

Fig. 4. The age distribution of mass accumulation rate (MAR) in g cm^{-2} ky^{-1}. Note the highest fluxes occur during the last deglaciation (12–18 ky BP).

36 the match of the records is rather poorer. Much of the discrepancy between these two proxy indicators may be attributed to preferential dissolution of opal relative to barite, and the increase in diatom productivity just south of the polar front. To examine changes in silica productivity, corrected for terrigenous dilution, the opal flux is calculated* (Fig. 5b). This shows the massive increase in opal flux just south of the APF (core 36 and 29) relative to sediments farther south in the Weddell Sea. In addition, major opal palaeoproductivity appears to occur during the last deglaciation. Given the similarity in water depth which, to a first approximation, controls the degree of opal dissolution, it appears that palaeoproductivity was highest during the change from glacial to interglacial conditions, a phenomenon also observed in core 41, albeit at much reduced amplitude. The high total mass accumulation rates during the deglaciation also probably helped in preserving the opal from further dissolution.

The total C_{org} profiles display some variation with age superimposed on an overall decrease with depth attributed to microbial remineralization (Fig. 7). Highest C_{org} contents are found near the APF (core 36) with an increase in the interglacial to glacial amplitude observed further south. At cores 27 and 41 interglacial Stage 5 (72 to 128 ky BP) C_{org} contents increase. When converted to C_{org} accumulation rates, the deglacial flux is again very high, but in this case the north-south gradient in opal is not reflected in C_{org}. At core PS1506 excess Ba (total Ba corrected for a lithogenic contribution), opal and C_{org} fluxes vary closely with the total MAR (Fig. 8). Such data are strongly determined by the age model used, however, it is clear that both total flux and the biogenic flux to the seafloor were significantly enhanced during interglacials when ice cover was at a minimum. In this scenario, the last deglaciation and present Holocene periods appear to be the most productive episodes in the late Quaternary history of the Weddell Sea.

* Opal flux (mg cm^{-2}ka^{-1}) = Opal concentration (wt.%x10) x linear sediment accumulation rate (cm ka^{-1}) x dry bulk density (g cm^{-3})

Bottom Water velocity and the formation of Antarctic Bottom Water

Previous work from BAS (Pudsey *et al.* 1988, Pudsey 1992) has provided sedimentological evidence for increased deep circulation during interglacials, near the major source of AABW in the Weddell Sea. Modern hemipelagic sediments become coarser grained from the centre to the edge of the Weddell gyre, reflecting an increase in marginal current velocities. These observations have been corroborated by data from current meter moorings (Pudsey 1992). Observed downcore cyclicity in the proportion of silt to clay is interpreted as reflecting a transport signal, with bottom current speeds during interglacials an order of magnitude higher than glacials. Other sedimentological and palaeontological criteria have been used to study bottom currents to the north in the Vema Channel (Ledbetter 1984, Johnson *et*

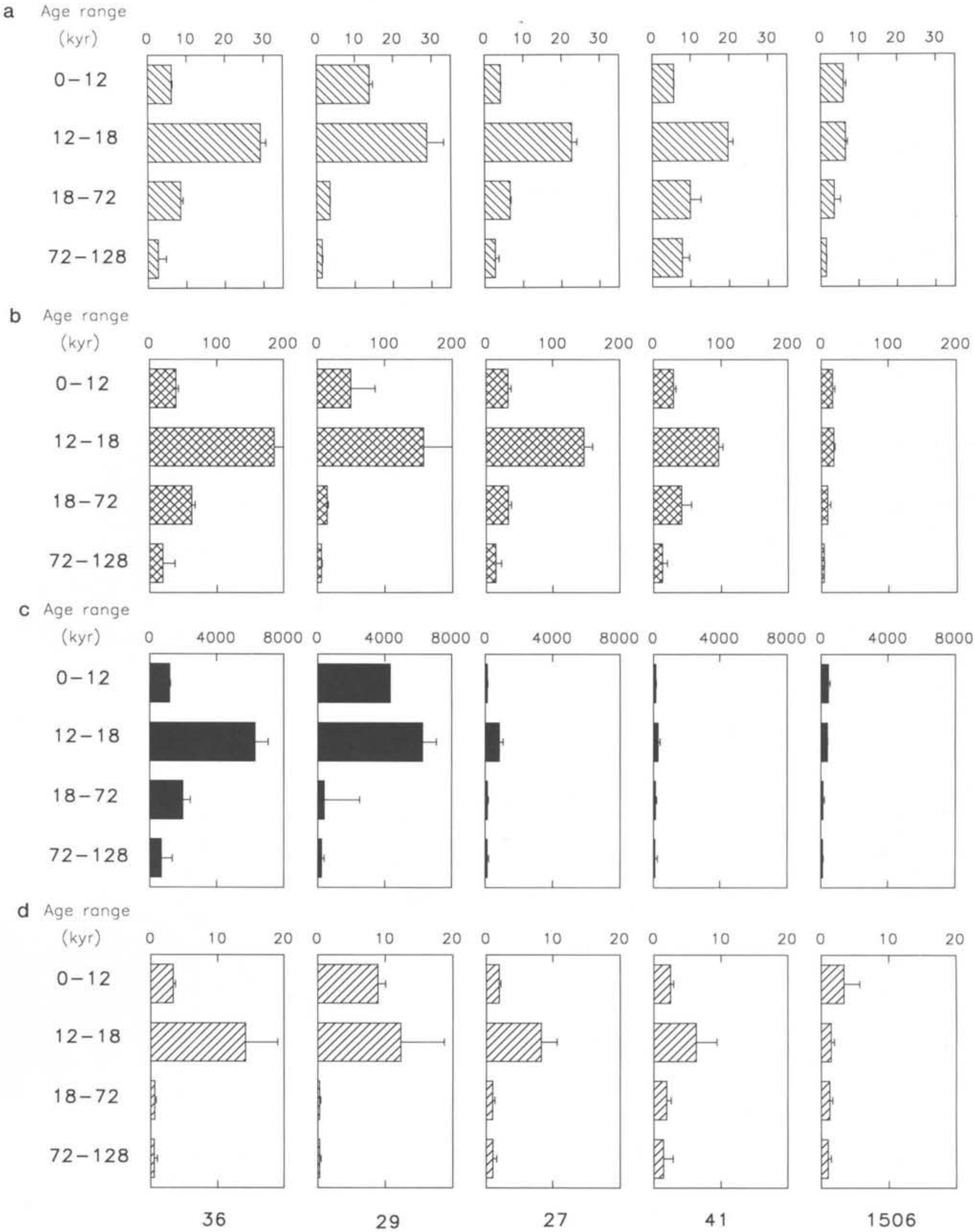

Fig. 5. Summary diagram illustrating the change in flux of **a.** MAR, **b.** biogenic silica (opal), **c.** C_{org} and **d.** excess Ba (corrected for a lithogenic ratio of Ba/Al =0.0075). The age ranges correspond to Stage 1 (0–12 ky), the last deglaciation (12–18 ky), Stages 2, 3 and 4 (18–72 ky) and Stage 5 (72–128 ky). Note the biogenic silica fluxes are restricted to the region of the APF; farther south sea ice cover and dissolution reduce the fluxes considerably.

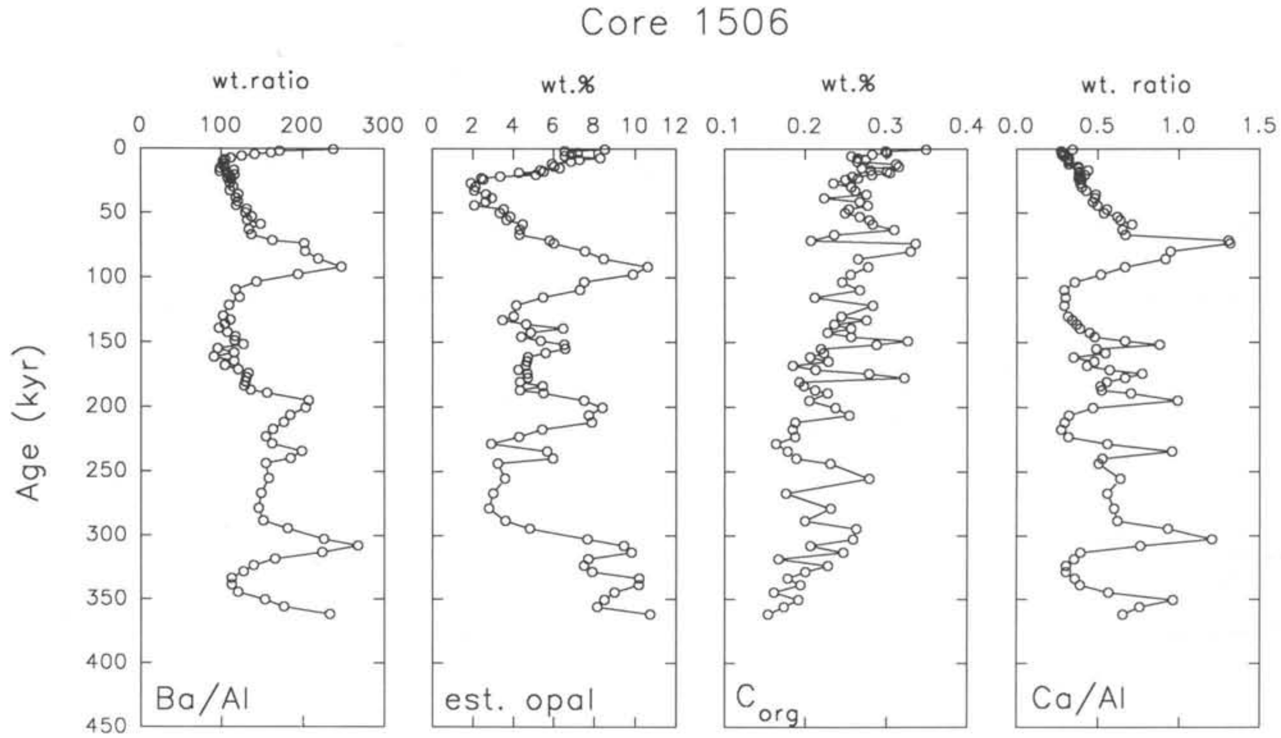

Fig. 6. The chronology of Ba/Al, opal (estimated from total Si minus an average lithogenic component), C_{org} and Ca/Al in core PS1506. Note the close correspondence of Ba/Al and opal, but Ca/Al (an indicator of the amount of calcite present) is out of phase due to selective modification by dissolution. C_{org} decreases with depth due to microbial degradation.

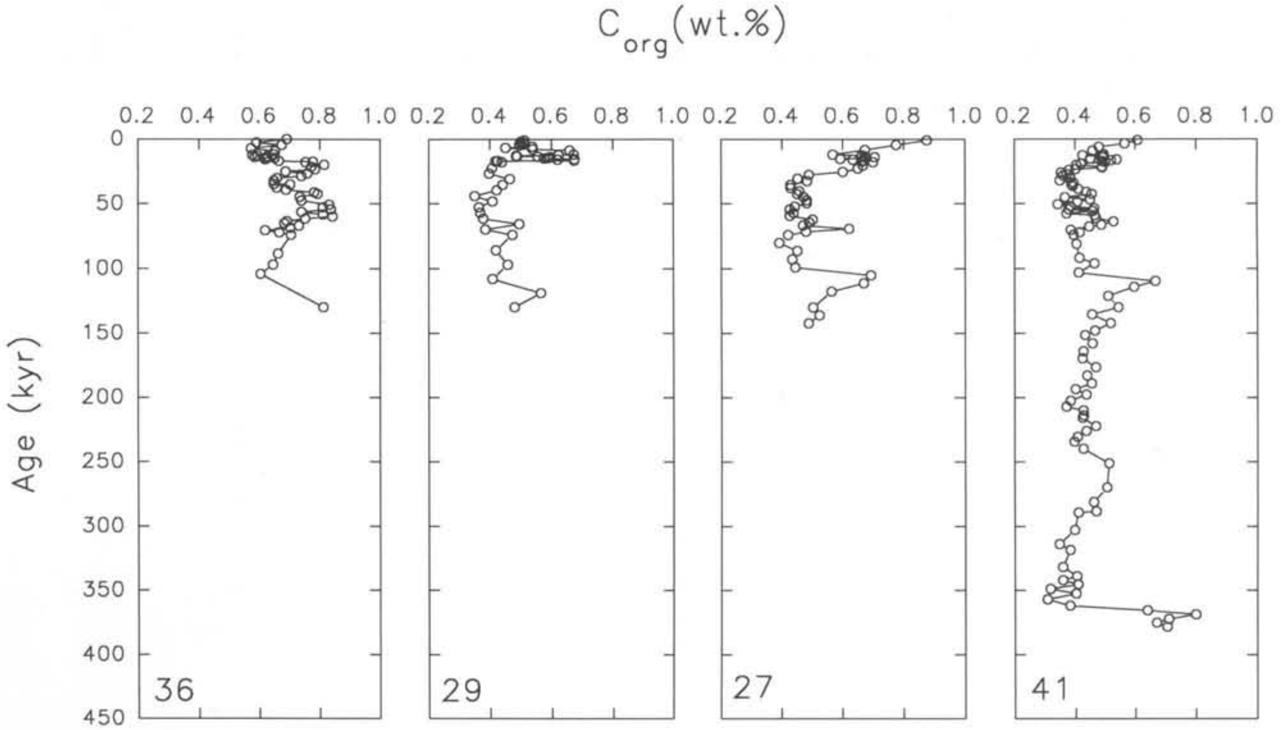

Fig. 7. The chronology of C_{org} (weight %) in cores 36, 29, 27 and 41. Note the changes induced by palaeoproductivity and accumulation rate on the overall depth decrease due to microbial degradation.

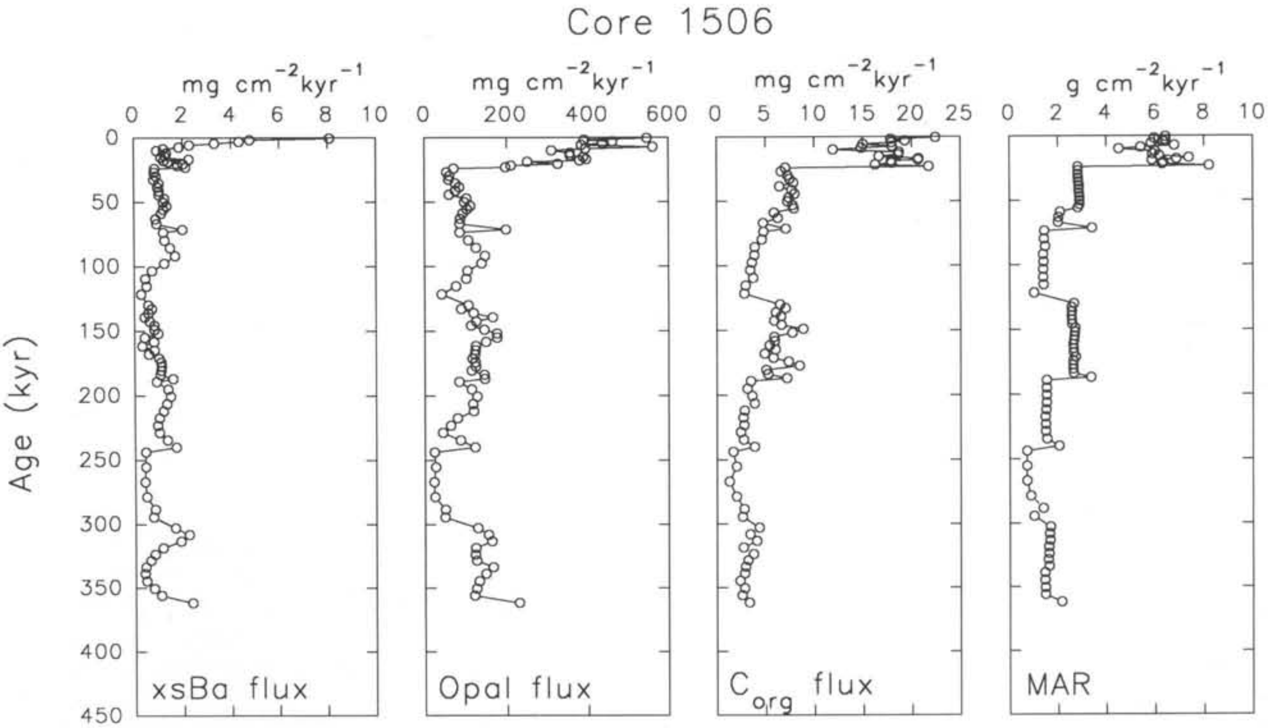

Fig. 8. Fluxes of excess Ba, opal (estimated), C_{org}, and total mass accumulation rate in core PS1506. Note the high post-glacial fluxes and the low accumulation rates in isotope Stage 5 (72–128 ky BP) unlike the Holocene.

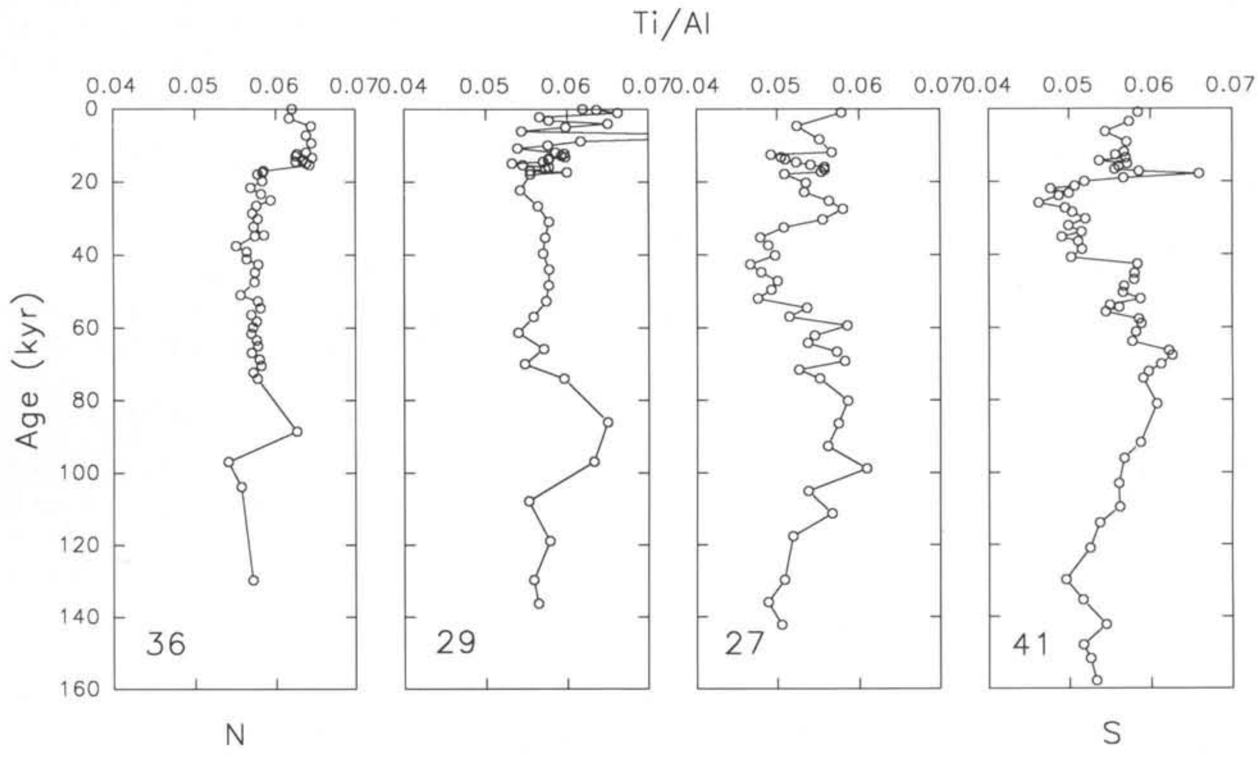

Fig. 9. The chronology of Ti/Al (weight ratio) in cores 36, 29, 27 and 41. High Ti/Al, indicative of increased bottom currents and greater sediment winnowing (Schmitz 1987), occurs during the interglacial episodes.

al. 1984) but no clear relationship between bottom current strength and glacial/interlacial cycles was found in this work. The motivation for detailed knowledge of deep circulation comes from modelling studies which have demonstrated that a knowledge of the ratio NADW to AABW is important for CO_2 budgets (e.g. Kier 1990).

Several papers over the last decade have suggested that geochemical parameters may be used to infer changes in grain size of the lithogenic fraction (Boyle 1983, Schmitz 1987, Shimmield 1992). In these cases, the principal application concerned identification of aeolian material and the impact of climate change on wind velocities. Such changes can be inferred from changes in the Ti/Al ratio when Ti is thought to incorporate preferentially into the heavier mineral fraction (ilmenite, rutile, magnetite), whereas Al is a common element in the lithogenic mineral and clay fraction. Schmitz's study on the Bengal fan, and associated laboratory studies, demonstrated that Ti/Al ratios faithfully record changes in the bottom current velocity, with higher ratios indicating increased currents allowing the heavy minerals to become proportionately more concentrated.

Fig. 9 displays the down core records for Ti/Al for the BAS cores. Overall, there is a clear trend towards increased Ti/Al ratios during the interglacial periods, which is particularly evident in cores 36 and 29 just to the south of the APF. Farther south, the Ti/Al record suggests that bottom water flow was enhanced for longer durations than recorded by the palaeoproductivity proxies, particularly Ba/Al. This increased bottom water flow relative to a minimum at 40 ky BP continued after Stage 5 and commenced prior to Stage 2. Note also that Holocene Ti/Al ratios also decrease in a southerly direction, consistent with the maximum velocities probably occurring through the Scotia Sea (if small changes in the overall bulk lithogenic composition of the sediment can be assumed). These findings agree with the study of Pudsey (1992) who also found that LGM sediments were deficient in silt and fine sand. She suggested that present-day bottom current velocities (at 10 cm s^{-1}) are some 10x faster than during the last glacial maximum. Here, we clearly demonstrate that palaeoproductivity indices and proxies for palaeocurrent velocity are coherent on a glacial to interglacial time frame. Near the APF, there is a very strong co-variance suggesting sea ice extent was a dominant control on both bottom water formation during the processes of salt expulsion and cooling, and on primary productivity identified from opal and Ba/Al.

Summary and conclusions

Through the use of inorganic geochemical tracers and measurements of the content of opal and organic carbon in piston cores it has been possible to examine the palaeoceanography of the northern Weddell Sea over the last 160 ky. This study confirms previously published work (Mackensen *et al.* 1988, Mortlock *et al.* 1991, Charles *et al.* 1992) that interglacial productivity was higher immediately south of the present-day Antarctic Polar Front and contrasts with current hypotheses suggesting that increased palaeoproductivity in the mesotrophic areas of the ocean may have been responsible for the reduced atmospheric CO_2 (measured in ice cores).

By using the content of barium in the sediments, not only as a palaeoproductivity proxy, but also as a chronostratigraphic tracer, we have reconstructed the past history of sediment accumulation and biogenic fluxes to the northern Weddell Sea. Due to the heavily undersaturated (with respect to calcite) waters within the deep Weddell Sea, the preservation of calcareous foraminifera is virtually nil, preventing the usual $\delta^{18}O$ isotope stratigraphy approach from being applied. Establishing the barium-based chronology has been made possible by correlation with a core from a unique carbonate province occurring off the eastern Weddell Sea continental margin where $\delta^{18}O$ measurements have been made. However, until corroborative age information becomes available, this age model and the conclusions drawn from its use must be considered speculative.

We have found that the highest biogenic fluxes of opal and organic carbon occur at, and just south of, the APF. Throughout the Weddell Sea there is a consistent picture of highest biogenic and lithogenic fluxes occurring during the deglaciation period (12–18 ky BP) following the Last Glacial Maximum. During isotope Stage 5e, thought to represent global environmental conditions similar to the Holocene climatic optimum, biogenic fluxes were surprisingly low using the age model derived here.

Highest sedimentary fluxes of biogenic opal occur just to the south of the APF. Within the Weddell gyre fluxes decrease, presumably due to the combined effect of a decrease in primary productivity (due to increased seasonal sea ice cover) and an increase in opal dissolution within the water column and at the sediment-water interface. A proxy for sediment grain size, Ti/Al ratios, suggests increased bottom water flow during the interglacials, corroborating previous sedimentological data.

This study has shown that modern techniques of inorganic geochemistry may be used in the Southern Ocean to establish both a chronostratigraphic framework within which to study past palaeoceanographic changes, and to examine the change in the flux of biogenic and lithogenic constituents with time.

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References

BARNOLA, J.M., RAYNAUD, D., KOROTKEVITCH, Y.S. & LORIUS, C. 1987. Vostok ice core provides 160,000-year record of atmospheric CO_2. *Nature*, **329**, 408-414.

BOYLE, E.A. 1983. Chemical accumulation variations under the Peru Current during the past 130,000 years. *Journal of Geophysical Research*, **88**, 7667-7680.

BOYLE, E.A. 1988. Cadmium: Chemical tracer of deepwater palaeoceanography. *Paleoceanography*, **3**, 471-489.

BROECKER, W.S. & PENG, T.-H. 1989. The cause of glacial to interglacial atmospheric CO_2 change: A polar alkalinity hypothesis. *Global Biogeochemical Cycles*, **3**, 215-239.

CHARLES, C.D., FROELICH, P.N., ZIBELLO, M.A., MORTLOCK, R.A., & MORLEY, J.J. 1991. Biogenic opal in Southern Ocean sediments over the last 450,000 years: Implications for surface water chemistry and circulation. *Paleoceanography*, **6**, 697-728.

CLEMENS, S., PRELL, W., MURRAY, D., SHIMMIELD, G.B. & WEEDON, G.P. 1991. Forcing mechanisms of the Indian Ocean monsoon. *Nature*, **353**, 720-725.

DEHAIRS, F., STROOBANTS, N. & GOEYENS, L. 1991. Suspended barite as a tracer of biological activity in the Southern Ocean. *Marine Chemistry*, **35**, 399-410.

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.

DeMASTER, D.J. 1981. The supply and accumulation of silica in the marine environment. *Geochimica et Cosmochimica Acta*, **45**, 1715-1732.

DYMOND, J., SUESS, E. & LYLE, M. 1992. Barium in deep-sea sediment: a geochemical proxy for paleoproductivity. *Paleoceanography*, **7**, 163-181

HAYS, J.D., LOZANO, J.A., SHACKLETON, N.J. & IRVING, G. 1976. Reconstruction of the Atlantic and western Indian Ocean sectors of the 18,000 B.P. Antarctic Ocean. *In* CLINE, R.M. & HAYS, J.D. *eds*. Investigation of Late Quaternary Paleoceanography and Paleoclimatology. *Geological Society of America Memoir*, No. 145, 337-372.

JOHNSON, D.A., LEDBETTER, M.T., TAPPA, E. & THUNELL, R. 1984. Late Tertiary/Quaternary magnetostratigraphy and biostratigraphy of Vema Channel sediments. *Marine Geology*, **58**, 89-100.

JORDAN, R.W. & PUDSEY, C.J. 1992. High-resolution diatom stratigraphy of Quaternary sediments from the Scotia Sea. *Marine Micropalaeontology*, **19**, 201-237.

KIER, R.S. 1990. Reconstructing the ocean carbon system variation during the last 150,000 years according to the Antarctic nutrient hypothesis. *Paleoceanography*, **5**, 253-276.

LEA, D. & BOYLE, E.A. 1989. Barium content of benthic foraminifera controlled by bottom water composition. *Nature*, **338**, 751-753.

LEDBETTER, M.T. 1984. Bottom-current speed in the Vema Channel during the last 160,000 years. *Marine Geology*, **33**, 71-89.

LEDFORD-HOFFMAN, P.A., DeMASTER, D.J. & NITTROUER, C.C. 1986. Biogenic silica accumulation in the Ross Sea and the importance of the Antarctic continental shelf deposits in the marine silica budget. *Geochimica et Cosmochimica Acta*, **50**, 2099-2110.

MACKENSEN, A., GROBE, H., HUBBERTEN, H.-W., SPIESS, V. & FUTTERER, D.K. 1989. Stable isotope stratigraphy from the Antarctic continental margin during the last one million years. *Marine Geology*, **87**, 315-321,

MARTIN, J.H. 1990. Glacial-interglacial CO_2 change: the iron hypothesis. *Paleoceanography*, **5**, 1-13.

MORTLOCK, R.A., CHARLES, C.D., FROELICH, P.N., ZIBELLO, M.A., SALTZMAN, J., HAYS, J.D., & BURCKLE, L.H. 1991. Evidence for lower productivity in the Antarctic Ocean during the last glaciation. *Nature*, **351**, 220-222.

PUDSEY, C.J., BARKER, P.F. & HAMILTON, N. 1988. Weddell Sea abyssal sediments: A record of Antarctic Bottom Water flow. *Marine Geology*, **81**, 289-314.

PUDSEY, C.J. 1992. Late Quaternary changes in Antarctic Bottom Water velocity inferred from sediment grain size in the northern Weddell Sea. *Marine Geology*, **107**, 9-33.

SARNTHEIN, M.A., WINN, K., DUPLESSY, J.-C. & FONTUGNE, M.R. 1988. Global variations of surface ocean productivity in low and mid latitudes: Influence on CO_2 reservoirs of the deep ocean and atmosphere during the last 21,000 years. *Paleoceanography*, **3**, 361-399.

SCHMITZ, B. 1987. The TiO_2/Al_2O_3 ratio in the Cenozoic Bengal abyssal fan sediments and its use as a paleostream energy indicator. *Marine Geology*, **76**, 195-206.

SHIMMIELD, G.B. 1992. Can sediment geochemistry record changes in coastal upwelling palaeoproductivity? Evidence from northwest Africa and the Arabian Sea. *In* SUMMERHAYES, C., PRELL, W. & EMEIS, K., *Upwelling Systems Since the Early Miocene. Geological Society Special Publication*, **64**, 29-46.

SHIMMIELD, G.B. 1985. *The geochemistry and mineralogy of East Pacific sediments, Baja California, Mexico*, Ph.D. Thesis, University of Edinburgh. (Unpublished).

SHIMMIELD, G.B. & MOWBRAY, S. 1991. The inorganic geochemical record of the northwest Arabian Sea: A history of productivity variation over the last 400 k.y. from Sites 722 and 724. *In* PRELL, W.L. & NIITSUMA, N., *et al. eds. Proceedings of the ODP, Scientific Results*, **117**, College Station, TX (Ocean Drilling Program), 409-429.

SHIMMIELD, G.B., MOWBRAY, S. & WEEDON, G.P. 1991. A 350 ka history of the Indian Southwest Monsoon- evidence from deep-sea cores, northwest Arabian Sea. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **81**, 289-299.

SIEGENTHALER, U. & WENK, T. 1984. Rapid atmospheric CO_2 variations and ocean circulation. *Nature*, **308**, 624-626.

ZAHN, R., WINN, K. & SARNTHEIN, M. 1986. Benthic foraminiferal $\delta^{13}C$ and accumulation of organic carbon: *Uvigerina peregrina* group and *Cibicidoides wuellerstorfi*. *Paleoceanography*, **1**, 27-42.