

## Vertical Distribution of Biogenic Elements and its Implication on Holocene Paleoclimatic Records in the Maxwell Bay of the South Shetland Islands, West Antarctica

DONGSEON KIM, BYONG-KWON PARK AND HO IL YOON

*Polar Research Center, Korea Ocean Research & Development Institute, Ansan P.O. Box 29,  
Ansan 425-600, Korea*

Depth profiles of organic carbon (C), biogenic silica (Si), and inorganic phosphorus (P) in Maxwell bay sediments were determined to investigate paleoclimatic changes during Holocene. Organic C and biogenic Si contents generally show a down-core decrease trend, which appears to be mostly controlled by their vertical fluxes through productivity in the surface waters, but it is uncertain that inorganic P contents are directly influenced by productivity changes with time. Before 4000 yr B.P. marine productivity seemed to be almost zero because ice permanently covered the surface waters of the study area. As the climate started to become relatively warm at 4000 yr B.P., ice was sporadically melted in the surface waters and thereby marine productivity gradually increased until 1500 yr B.P. For the last 1500 year, marine productivity must be high enough to overcome the dilution by high terrigenous sedimentation, thus that period was the warmest during the last 6000 year.

### INTRODUCTION

Recently there has been a great interest in the study of global climatic changes. Most studies on climatic changes has been conducted on ice and marine sediment cores to elucidate the long-term climatic variations associated with the transition from glacial to interglacial periods (Lorius *et al.*, 1985; Jouzel *et al.*, 1987; Prahl *et al.*, 1995; Singer and Shemesh, 1995). In order to precisely predict the near-future climatic changes that directly influence the existence of human life, however, it is essential to reconstruct climatic changes during the last several thousand years. Bay or fjord sediment cores around Antarctic continental shelf are appropriate for the study of relatively short- period climatic changes because high sedimentation makes it possible to record high resolution climatic changes over a short period, and Antarctic continental shelf is one of the most sensitive areas to climatic changes. Nevertheless, such studies are rare in Antarctic continental shelf because of the complexity of glacial-marine sedimentation and the limited availability of suitable core material (Domack *et al.*, 1991 and 1993).

In sediments, organic C and biogenic Si have been widely used as a proxy for reconstructing marine paleoproductivity because their contents are

directly related to their input fluxes from the surface water to sediments, even though they are altered by diagenetic processes in sediments (Muller *et al.*, 1983; Berger *et al.*, 1989; Domack *et al.*, 1993; Qiu *et al.*, 1993). Recently phosphorus has been recognized as a key factor for limiting oceanic productivity on the geologic time scale (Broecker and Peng, 1982; Codispoti, 1989; Compton *et al.*, 1993; Kump, 1993; Filippelli and Delaney, 1994; Van Cappellen and Ingall, 1994). In the ocean, dissolved P is mostly removed from the water column by transformation to or incorporation into a particulate form (Van Cappellen and Ingall, 1994). The burial of P into the sediments controls marine P concentration and thereby limits marine productivity. Therefore, the variation of P content in sediments, especially inorganic P content, may reflect the change of marine productivity.

In this paper, we describe depth profiles of biogenic elements (organic C, biogenic Si, and inorganic P) in a sediment core to investigate usefulness as a proxy for paleoproductivity in a sediment core from the Maxwell Bay of the South Shetland Island, Antarctica. Based on their depth profiles and the relation with productivity, we try to reconstruct climatic changes during the last 6000 years. Maxwell bay is a good site for the study of short period climatic changes because it is located in a subpolar

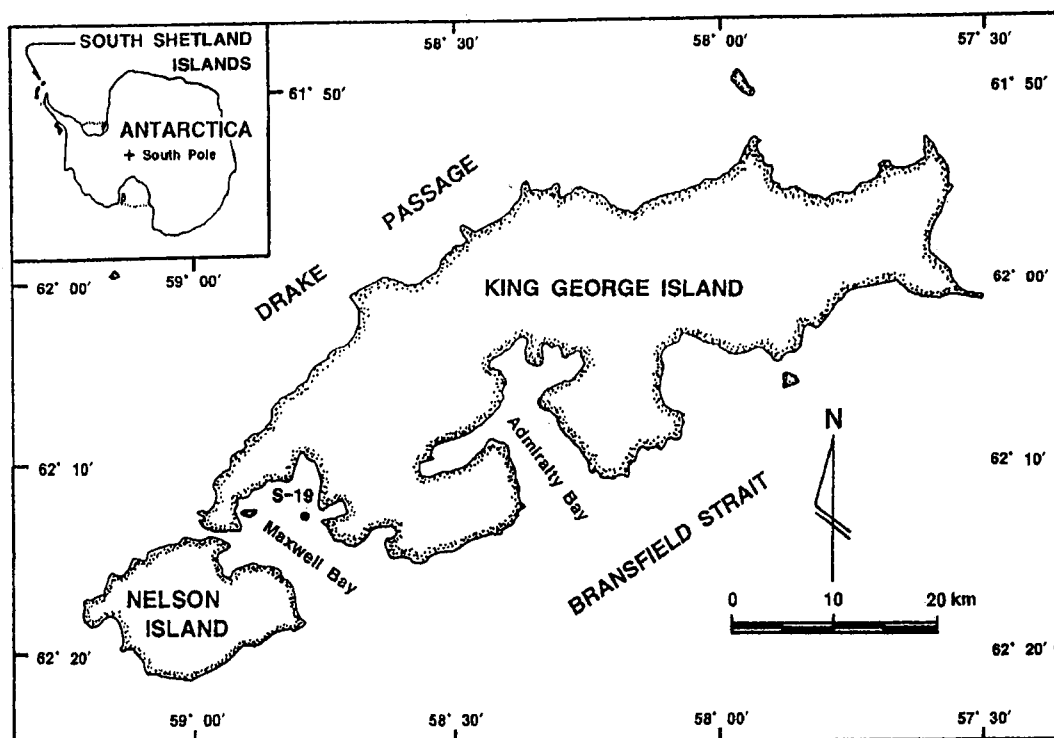


Fig. 1. Map of the study area. Black circle indicates sediment core location.

region where annual climatic changes are large and high sedimentation can provide the record of high resolution climatic changes over short period (Yoon *et al.*, 1997).

## METHODS

Sediment core S-19 was collected with a piston corer at a water depth of 110 m from the Maxwell bay of the South Shetland Island, West Antarctica (Fig. 1). Geologic setting of the Maxwell bay was well described by Yoon *et al.* (1997). A sediment core was sectioned by the 5 cm interval, and each sediment sample was dried at 80°C for 4 days and then grounded. Organic C contents were determined by a Carlo-Erba CNS analyzer after eliminating inorganic C by 8% H<sub>2</sub>SO<sub>4</sub>. Biogenic Si contents were estimated by a time-series dissolution experiment in 1.0 M NaOH at 85°C following the procedure of Muller and Schneider (1993). Inorganic P contents were determined after continuous shaking for 16 hours in 1.0 N HCl at a room temperature (Aspila *et al.*, 1976).

## RESULTS AND DISCUSSION

### *Vertical distribution of biogenic elements*

Organic C contents show relatively constant values (about 0.4 wt.%) in the upper 90 cm of the core, with a small fluctuation with depth (Fig. 2). Over the 90–140 cm interval, they decrease rapidly from 0.3 to 0.08 wt.% and then remain constantly below 140 cm. The rapid decrease of organic C contents does not seem to be the result of organic matter remineralization by bacteria because organic matter remineralization usually occurs intensively within the upper 10–30 cm of sediment depth in coastal environments (Bernier, 1980). Thus, the rapid decrease of organic C contents reflects a significant environmental change at this interval. In bay or fjord sediments, organic C content is mainly controlled by the dilution due to terrigenous sedimentation as from river or melt-water and the vertical flux of organic C through productivity in the surface water (Syvitski *et al.*, 1990; Domack *et al.*, 1993). The much lower organic C contents in the lower part of the core is the result of either the lower vertical flux of organic C due to low productivity in the surface water or the more dilution by high input flux of terrestrial material as from melt-water. Park *et al.* (1995) estimated sedimentation rates using <sup>14</sup>C age dating in this core and found that sedimentation rates are almost an order of magnitude higher in the upper part than in the lower

part. The lower organic C contents in the lower part, therefore, are attributed to lower vertical flux of organic C due to low productivity, not to more dilution by high terrigenous sedimentation. Biogenic Si contents display a similar depth profiles with organic C contents with a few minor exception, ranging from 0.4 to 2.1 wt.% (Fig. 2). Like organic C, therefore, the depth profile of biogenic Si contents appears to be controlled by the vertical flux of biogenic Si.

Inorganic P contents, however, shows a quite different depth profile from those of organic C and biogenic Si (Fig. 2). Inorganic P contents are relatively low and constant below the 150 cm of sediment depth, while above 150 cm, they display a large variation with depth. In marine sediments, inorganic P has been used for as a proxy for paleoproductivity on a geologic time scales because phosphorus acts as a limiting nutrient for marine productivity (Compton *et al.*, 1993; Kump, 1993; Filippelli and Delaney, 1994; Van Cappellen and Ingall, 1994). In sediments, organic P is transformed to inorganic P in sediments by diagenetic processes (Ruttenberg and Berner, 1993, Kim, 1996). Thus inorganic P is enriched in sediments when input flux of organic P is high. Inorganic P contents are also relatively low below the 150 cm of sediment depth compared to above 150 cm, even though they do not exhibit big difference as much as organic C and biogenic Si contents. Inorganic P contents increase by about 3  $\mu\text{mol/g}$  over the 145~150 cm interval. Assuming that inorganic P contents below 150 cm are the background level which is not related to the organic P diagenesis, the increased amount in inorganic P is derived from organic P as input flux of organic P increases.

Inorganic P contents display several cyclical peaks by the 25 cm interval in the upper 100 cm of the core (Fig. 2). The peak contents range from 43 to 56  $\mu\text{mol/g}$ , which are almost twice as much as the base-line values (about 30  $\mu\text{mol/g}$ ). These cyclic variations seem to be related to the P diagenesis. High input fluxes of organic P cause enrichment of organic P in sediments where organic P is subsequently decomposed by bacteria metabolism. Phosphate, the by-product of organic P remineralization, is released and accumulated in pore water and thereby, the phosphate concentrations in pore water become high enough to form authigenic P minerals. Some of phosphate is also removed from pore water by the adsorption on Fe

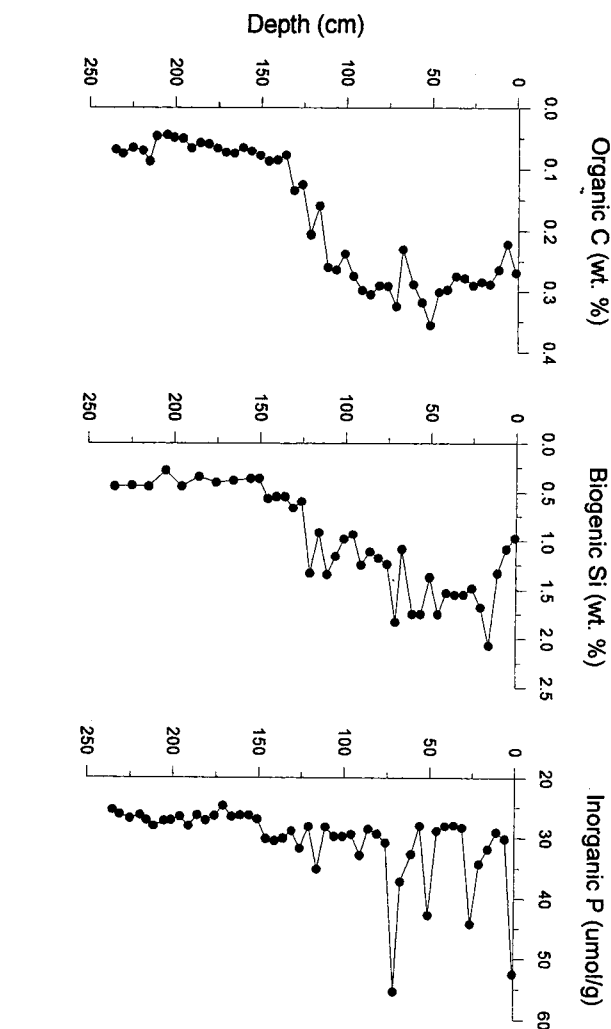
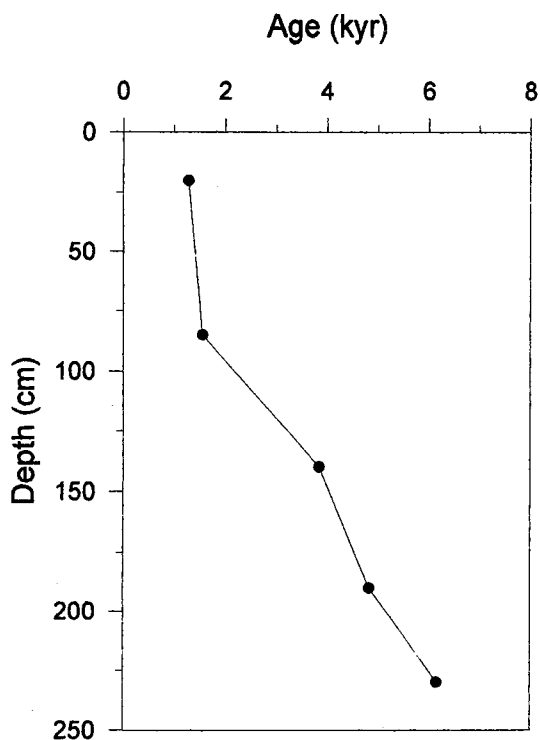


Fig. 2. Depth profiles of organic C, biogenic Si, and inorganic P contents in core S-19 of the Maxwell bay.

oxyhydroxides. The cyclic peaks of inorganic P contents, therefore, may reflect high input fluxes of organic P at those depths derived from high productivity in surface water. If the cyclic peaks are closely related to the changes of productivity with times, organic C and biogenic Si contents would show the similar vertical distribution pattern. However, the cyclic peaks are not observed in the depth profiles of organic C and biogenic Si contents (Fig. 2). It is uncertain, therefore, that the cyclic variations of inorganic P contents are attributed to the changes of productivity in surface water.

#### *A paleoclimatic synthesis*

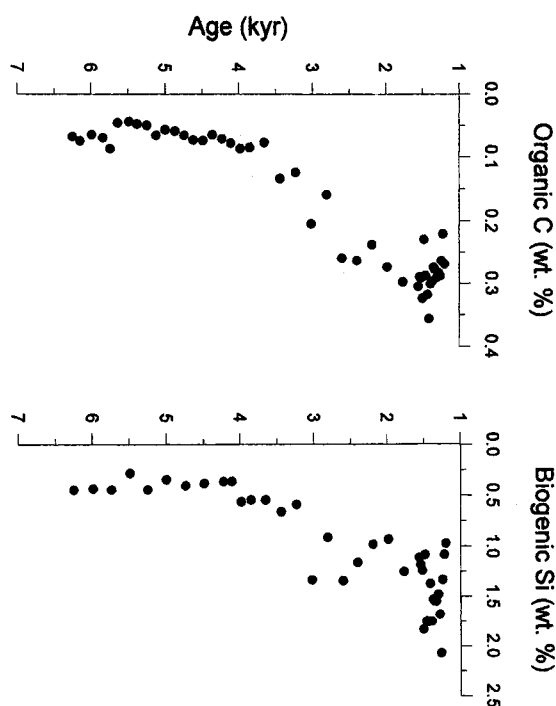
In the previous section, it was suggested that organic C and biogenic Si contents are generally controlled by their vertical fluxes which are mainly



**Fig. 3.**  $^{14}\text{C}$  age versus sediment depth in core S-19 of the Maxwell bay. A sedimentation rate above 85 cm is 0.23 cm/yr, and an average sedimentation rate is 0.032 cm/yr below 85 cm. (after Park *et al.*, 1995).

dependent on productivity in the surface waters. The down-core decrease trend in organic C and biogenic Si contents reflects that marine productivity increases as time passes. In order to construct a chronology at this core, the  $^{14}\text{C}$  dates determined by Park *et al.* (1995) are used. Stuiver *et al.* (1981) suggested that  $^{14}\text{C}$  reservoir corrections of 1200~1300 years are typical for most Antarctic biota. Thus the  $^{14}\text{C}$  ages are revised for a reservoir correction of 1300 years (Fig. 3). Based on the chronology in Fig. 3, organic C and biogenic Si contents are plotted against the  $^{14}\text{C}$  ages (Fig. 4). During the period between 6300 to 4000 yr B.P., organic C and biogenic Si contents were relatively very low, which suggests low productivity in the surface waters during that period. At 4000 yr B.P. organic C and biogenic Si contents started to increase as productivity became relatively high and continued to increase until 1500 yr B.P. after which they showed a large fluctuation.

Biogenic Si contents were about 0.4 wt.% before 4000 yr B.P. Muller and Schneider (1993) found that in the alkaline leaching method for biogenic Si analysis, 0.4 wt.% Si is consistently derived from



**Fig. 4.** Organic C and biogenic Si contents versus  $^{14}\text{C}$  age in core S-19 of the Maxwell bay.

clay minerals when biogenic Si contents are below 10 wt.%. Thus it can be inferred that production of biogenic Si in the surface waters did not occur before 4000 yr B.P. Organic C contents were also extremely low, less than 0.1 wt.% before 4000 yr B.P. Considering that near-shore sediments usually contain terrestrial organic matter, < 0.1 wt.% of organic C appears to be mostly derived from lands through melt-waters. Syvitski *et al.* (1990) assumed that Baffin Island fjord sediments contained 0.1 wt.% of terrigenous organic C to investigate a sedimentation effect on organic C contents. Marine productivity, therefore, seemed to be almost zero before 4000 yr B.P. which occurred only when ice permanently covered the surface waters of the study area. Thus the study area was entirely covered by ice even in summer time before 4000 yr B.P. As the climate started to become relatively warm at 4000 yr B.P., ice was sporadically melted in the surface waters and thereby marine productivity increased. Judging on the basis of the steady increase in organic C and biogenic Si contents from 4000 to 1500 yr B.P., the climate had become gradually warm during that period. After 1500 yr B.P. the climate seemed to be stabilized and were still warm, thus ice covered seasonally the surface waters because organic C and biogenic Si contents were

**Table 1.** Comparison of records of Late Holocen paleoclimate change by Bjorck *et al.* (1996) to those in this study

Bjorck <i>et al.</i> (1996)		This study	
Age (yr B.P.)	Climate	Age (yr B.P.)	Climate
5000-4200	cold	6300-4000	cold
4200-3000	warm	4000-1500	gradual warm
3000-1200	cold	1500-present	warmest
1200-present	warm		

still high and did not show a distinct trend, just fluctuating with time.

As the surface waters were periodically uncovered by ice after 1500 yr B.P., inputs of terrestrial material from melt-waters should increase and thereby sedimentation rates was high. The sedimentation rates estimated by the  $^{14}\text{C}$  age dating were almost an order of magnitude higher after 1500 yr B.P. than before (Fig. 3). The high sedimentation would influence considerably organic C and biogenic Si contents. Organic C and biogenic Si contents after 1500 yr B.P. were controlled not only by their vertical fluxes through productivity in the surface waters, but also by the dilution due to terrigenous sedimentation as from melt-waters. Thus the large variation in organic C and biogenic Si contents cannot be directly correlated to the productivity changes in the surface waters, i.e., the climate changes with times. The important thing is that marine productivity after 1500 yr B.P. must be high enough to overcome the dilution by high terrigenous sedimentation because organic C and biogenic Si contents were still higher after 1500 yr B.P. than before, in spite of an order of magnitude higher sedimentation rate.

Bjorck *et al.* (1996) provided a fairly detailed picture of climate change during the last 5000 years on the basis of the results obtained from lithological, geomagnetic, geochemical, and diatom analyses in lake sediments on James Ross Island, Antarctica. In general, their records are well matched with ours (Table 1), except a cold period of 3000 - 1200 yr B.P. at which our records show that climate was getting relatively warm. It is difficult to explain the reason for this disagreement, but regional differences may attribute the disagreement.

## CONCLUSIONS

In the sediment core collected in the Maxwell Bay, Organic C and biogenic Si contents generally decrease with sediment depth. Considering that

sedimentation rates are much higher in the upper part of the core than in the lower part, the depth profiles of organic C and biogenic Si contents appear to be controlled by their vertical fluxes from surface waters. Thus the down-core decrease trend in organic C and biogenic Si contents reflects that marine productivity increases as time passes. Inorganic P contents shows a quite different depth profile from those of organic C and biogenic Si. Thus inorganic P does not seem to be a good proxy for tracing paleoproductivity at this study area. Before 4000 yr B.P. marine productivity seemed to be almost zero and then gradually increased from 4000 to 1500 yr B.P. Since 1500 yr B.P. marine productivity must be high enough to overcome the dilution by high terrigenous sedimentation. Assuming that climate is the most important factor controlling marine productivity in Antarctic continental shelf on geologic time scales, it was very cold before 4000 yr B.P. when the study area was permanently covered by ice. Climate was gradually getting warm from 4000 to 1500 yr B.P. and after then it was the warmest during the last 6000 years. Bjorck *et al.*'s (1996) records of climatic changes during the last 5000 years are well matched with ours, except a cold period of 3000~1200 yr B.P. at which our records show that climate was getting relatively warm.

In this paper, we show the preliminary results of our paleoclimatic study in Antarctica. For more detail and concrete paleoclimatic records in Antarctica, we will continue to conduct this kind of work in the Bransfield Strait and other bay sediments.

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## REFERENCES

- Aspila, K.I., H. Agemian and A.S.Y. Chau., 1976. A semi-automatic method for the determination of inorganic, organic, and total phosphate in sediments. *Analyst*, **101**: 187-197.
- Berner, R.A., 1980. *Early Diagenesis: A Theoretical Approach*. Princeton Univ. Press, 241 pp.
- Berger, W.H., V.S. Smetacek and G. Wefer, 1989. Ocean productivity and paleoproductivity- An overview. In: *Productivity of the Ocean: Present and Past*, edited by W.H. Berger, V.S. Smetacek, and G. Wefer, John Wiley & Sons,

- New York.
- Bjorck, S., S. Olsson, C. Ellis-Evans, H. Hakansson, O. Humlum and J.M. Lirio, 1996. Late Holocene paleoclimatic records from lake sediments on James Ross Island, Antarctica. *Palaeogeogr. Palaeoclimat. Palaeoecol.*, **121**: 195-220.
- Broecker, W.S. and T.-H. Peng, 1982. Tracers in the Sea. Eldigio, Palisades, New York.
- Codispoti, L.A., 1989. Phosphorus vs. nitrogen limitation of new and export production. In: Productivity of the Ocean: Present and Past, edited by W.H. Berger, V.S. Smetacek, and G. Wefer, John Wiley & Sons, New York.
- Compton, J.S., D.A. Hodell, J.R. Garrido and D.J. Mallinson, 1993. Origin and age of phosphorite from the south-central Florida Platform: Relation of phosphogenesis to sea-level fluctuations and  $\delta^{13}\text{C}$  excursions. *Geochim. Cosmochim. Acta*, **57**: 131-146.
- Domack, E.W., A.J.T. Jull and S. Nakao, 1991. Advance of East Antarctic outlet glaciers during the Hypsithermal: Implications for the volume state of the Antarctic ice sheet under global warming. *Geology*, **19**: 1059-1062.
- Domack, E.W., T.A. Mashiotta and L.A. Burkely, 1993. 300-year cyclicity in organic matter preservation in Antarctic fjord sediments. In: The Antarctic Paleoenvironment, A Perspective on Global Change Antarctic Research Series. **60**: 265-272.
- Filippelli, G.M. and M.L. Delaney, 1994. The oceanic phosphorus cycle and continental weathering during the Neogene. *Paleoceanography*, **9**: 643-652.
- Jouzel, J., C. Lorius, J.R. Petit, C. Genthon, N.I. Barkov, K.M. Kotlyakov and V.M. Petrov, 1987. Vostok ice core: A continuous isotope temperature record over the last climatic cycle (160,000 years). *Nature*, **329**: 403-408.
- Kim, D. 1996. Biogeochemical cycling of carbon, phosphorus, and silica in California continental slope sediments. Ph.D. Diss., University of California, San Diego.
- Kump, L.R., 1993. The coupling of the carbon and sulfur biogeochemical cycles over Phanerozoic time. In: Interactions of C, N, P, and S Biogeochemical Cycles and Global Change., edited by R. Wollast, F.T. Mackenzie, and L. Chou, NATO ASI Ser. I, **4**: 475-490.
- Lorius, C., J. Jouzel, C. Ritz, L. Merlivat, N.I. Barkov, Y.S. Korotkevich and V.M. Kotlyakov, 1985. A 150,000-year climatic record from Antarctic ice. *Nature*, **316**: 591-596.
- Muller, P.J., H. Erlenkeuser and R. Von Grasfenstein, 1983. Glacial-interglacial cycles in oceanic productivity inferred from organic carbon contents in eastern North Atlantic sediment cores. In: Coastal Upwelling, Part B, edited by J. Thiede and E. Suess, Plenum, New York.
- Muller, P.J. and R. Schneider, 1993. An automated leaching method for the determination of opal in sediments and particulate matter. *Deep-Sea Res.*, **40**: 425-444.
- Park, B.-K., H.I. Yoon, H.J. Woo, K.S. Lee, E.-J. Barg and J. Southon, 1995. Late Holocene paleoceanography from core sediments in the Admiralty Bay and Maxwell Bay, King George Island, Antarctica. *J. Korean Soc. Oceanogr.*, **30**: 302-319.
- Prahl, F.G., N. Piasias, M.A. Sparrow and A. Sabin, 1995. Assessment of sea-surface temperature at 42 °N in the California Current over the last 30,000 years. *Paleoceanography*, **10**: 763-773.
- Qiu, L., D.F. Williams, A. Gvozdkov, E. Karabanov and M. Shimarova, 1993. Biogenic silica accumulation and paleoproductivity in the northern basin of lake Baikal during the Holocene. *Geology*, **21**: 25-28.
- Ruttenberg, K.C. and R.A. Berner, 1993. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. *Geochim. Cosmochim. Acta*, **57**: 991-1007.
- Singer, A.J. and A. Shemesh, 1995. Climatically linked carbon isotope variation during the past 430,000 years in Southern Ocean sediments. *Paleoceanography*, **10**: 171-177.
- Stuiver, M., G.H. Denton, T.J. Hughes and J.L. Fastook, 1981. History of the marine ice sheet in west Antarctica during the last glaciation: A working hypothesis. In: The Last Great Ice Sheets, edited by G. Denton and T. Hughes, Wiley, New York.
- Syvitski, J.P.M., K. William, G. LeBalnce and R.E. Cranston, 1990. The flux and preservation of organic carbon in Baffin Island fjord. In: Glacimarine Environments: Processes and Sediments, edited by J.A. Downdeswell and J.D. Scourse, Geol. Soc. Spec. Pub. No. 53.
- Van Cappellen, P.V. and E.D. Ingall, 1994. Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus. *Paleoceanography*, **9**: 677-692.
- Yoon, H.I., M.W. Han, B.-K. Park, J.-K. Oh and S.-K. Chang, 1997. Glaciomarine sedimentation and paleo-glacial setting of Maxwell Bay and its tributary embayment, Marian Cove, South Shetland Islands, West Antarctica. *Mar. Geol.*, in press.