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지구화학적 추적자를 이용한 고생산성 연구

Paleoproductivity Reconstruction Using  
Geochemical Tracers

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한 국 해 양 연 구 소

## 제 출 문

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본 보고서를 “지구화학적 추적자를 이용한 고생산성 연구” 보고서로 제출합니다.

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# 요 약 문

## 1. 제목

지구화학적 추적자를 이용한 고생산성 연구

## 2. 연구개발의 목적 및 중요성

최근 지구환경 변화에 대한 문제가 국제적으로 심각하게 대두되고 있는데, 이것은 미래 인류의 생존이 지구환경 변화에 의해 좌우되기 때문이다. 인류의 생존에 직접적인 영향을 미치는 미래의 지구환경 변화를 정확히 예측하기 위해서는 과거동안에 일어났던 지구환경 변화를 명확히 알아야 한다. 미국을 비롯한 선진국에서는 많은 연구비를 투자하여 새로운 지구화학적 추적자를 이용하여 고생산성, 고기후 및 고해양 환경 변화를 연구하고 있다. 하지만 현재 우리나라에서는 지구화학적 추적자를 이용한 이런 연구는 거의 이루어지고 있지 않기 때문에 이분야에 대한 연구가 시급한 형편이다.

## 3. 연구개발의 내용 및 범위

- 가. 남극 맥스웰만에서 생물기원 원소들의 수직적 분포 변화와 홀로세 고기후 변화 연구
- 나. 남극 남 쉘트랜드 군도의 맥스웰만 퇴적물에서 다량, 미량, 희토류 원소들의 수직적 변화

다. 신생대 제4기동안 황해의 고환경 변화

#### 4. 연구개발 결과

가. 남극 맥스웰만 퇴적물에서 생물기원 원소, 다량, 미량, 회토류원소 들을 분석한 결과를 정리해 보면 세종 기지가 위치한 킹조지섬 주위 과거 6000년 동안의 기후변화는 다음과 같다;

6300 - 4000 년전 : 매우 추웠음

4000 - 1500 년전 : 점점 따뜻해짐

1500 - 현재 : 과거 6000년 동안 가장 따뜻함

나. 황해에서 유공충의 산소 동위원소를 분석한 결과에 의하면 해수면이 약 55 미터 낮았던 12,500에서 11,500 년전 사이에 황해해수의 염분은 7.6 ‰로 현재 황해해수의 염분(32 ‰)에 비해 상당히 낮은 값을 보인다. 그리고 이시기에 퇴적된 퇴적물의 유기탄소/총황 함량 비율이 일반 해양 퇴적물에서 조사된 비율보다 상당히 높아 그당시 황해의 염분이 상당히 낮았다는 것을 지시해 준다.

# SUMMARY

## 1. Title

Paleoproductivity reconstruction using geochemical tracers

## 2. Significance and Goal of the study

Recently many investigators have worked on the global environmental changes because in the future human life is considerably influenced by the environmental changes. In order to precisely predict the global environmental changes in the future which threaten the human life, we must know the global environmental changes occurred in the past. Many developed-countries have already invested a lot of money on the paleoproductivity, paleoclimatic and paleoceanographic studies using geochemical tracers. However, these kind studies have rarely done in our countries and thus it is urgent to work on the global environment changes.

## 3. Contents and Scope of the Study

- a. Vertical distribution of biogenic elements and its implication on Holocene paleoclimatic records in the Maxwell bay of the South Shetland Islands, West Antarctica
- b. Vertical variations of major, minor, and rare earth elements in the Maxwell

- bay sediments of the South Shetland Islands, West Antarctica
- c. Paleoenvironmental changes of the Yellow Sea during the late Quaternary

#### 4. Result of the Study

- a. On the basis of vertical distribution of biogenic, major, minor, and rare earth elements estimated in the Maxwell bay sediments, the paleoclimatic changes around the King George Island during the past 6000 years were followed;
- 6300 - 4000 BP : cold
  - 4000 - 1500 BP : gradual warm
  - 1500 - present : warmest
- b. The salinity in the Yellow Sea was reduced to about 7.6 ‰ from the present salinity (32 ‰) at the low sea level stand (12,500 - 11,500 yrs BP) when the sea level dropped by 56 m based on the oxygen stable isotopes measured at foraminifera. The high carbon/sulfur ratio during the low sea level is a strong evidence that the salinity of the Yellow Sea was extremely low at that time.

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## 제1장 서론

20세기 이후에 급속한 산업화로 인하여 석유, 석탄, 천연가스 등 화석 연료의 사용이 급격히 증가함으로써 엄청난 양의 이산화탄소가 대기 중으로 방출되어지고 있다. 대기 중 이산화탄소 농도 증가는 온실효과를 통해 대기 온도를 증가시키기 때문에 인류의 생존에 직접적으로 영향을 미치고 있다. 이산화탄소 농도가 현재와 같은 추세로 계속 증가한다면 2050년에는 그 농도가 현재의 2 배가 되고 지구 평균 온도는 2 - 3 °C 가량 증가한다고 예측하였다. 이런 온도 증가는 대규모 태풍의 발생, 지구의 사막화, 해빙에 따른 해수면 상승 등을 야기시켜 점점 인류의 생존을 어렵게 만들게 된다. 이런 까닭에 현재 미국을 비롯한 선진국들에서는 막대한 예산을 투자하여 대기에서 계속적인 이산화탄소 농도 변화를 관측하고 증가 양상을 분석, 예측을 하고 이에 따른 지구환경 변화를 연구하고 있다. 그리고 Past Global Changes (PAGE) 와 같은 공동연구 프로그램을 통하여 과거의 지구환경 변화를 연구함으로써 미래의 지구환경 변화를 예측하려는 연구가 지속적으로 진행되고 있다.

최근연구에 따르면 만년전 빙하기때 대기 중의 이산화탄소 농도가 현재의 농도에 비해 상당히 낮았던 것으로 추정되었다. 그리고 과거 이산화탄소 농도변화가 해양에서의 일차생산성 변화와 상당히 밀접한 관계를 보인다; 해양에서의 일차생산성이 많을때에는 이산화탄소 농도가 낮고 생산성이 작을때에는 이산화탄소 농도가 높았다. Broecker (1982)는 이런 상관성을 설명하기 위해 “biological pumping 이론”을 제시하였다. 해수표층에 존재하는 식물성 플랑크톤이 광합성을 통해 해수 중에 녹아있는 무기탄소를 고형유기탄소로 전화시키고 이 고형유기탄소는 자체무게때문에 해저면으로 가라앉게된다. 그러므로 해수표층에서는 용존 무기탄소 양이 상대적으로 작아지기 때문에 대기 중의 이산화탄소가 해수 중으로 유입되어져 대기 중의 이산화탄소 양이 감소하게된다. 결과적으로 식물성 플랑크톤이 많을수록, 즉 일차생산성이 많을수록 해수표층에 무기탄소 양이 많이 감소하여 보다 많은 양의 이산화탄소가 해수로 유입되어져 대기 중의 이산화탄소 농도가 감소하게된다.

그러므로 많은 사람들은 지질학적인 긴시간동안에 대기 중의 이산화탄소 농도가 해양에서 식물성 플랑크톤에 의한 일차생산성에 의해 조절되어진다고 생각하고 있다. 결과적으로 해양에서의 고생산성 변화연구는 과거 대기 중의 이산화탄소의 농도변화를 파악하는데 필수적이고 그것을 바탕으로하여 미래의 지구환경과 기후변동을 예측하는데 기본이되는 것이다.

이처럼 과거 수천년, 또는 수만년동안 고기후 및 고해양학적 연구는 미래의 기후 및 환경변화를 이해하는데 기본이 된다. 본연구에서는 지구화학적 추적자 즉, 유기탄소, 생물기원 규소, 무기인, 황, 다량원소, 미량원소, 회토류원소, 탄소와 산소 동위원소, 탄소 방사능 연대 측정 등을 이용하여 남극에 있는 킹조지섬 주위의 과거 6,000년 동안의 고기후변화와 황해에서 과거 12,500년 동안 해수면 변동에 따른 해수 염분변화를 연구하고자 한다.

## 제2장 남극 맥스웰만에서 생물기원 원소들의 수직적 분포 변화와 홀로세 고기후 변화 연구

### 2-1. ABSTRACT

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.

### 2-2. 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 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).

## 2-3. MATERIALS AND 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. 2-1). 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 10 % HCl. 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).

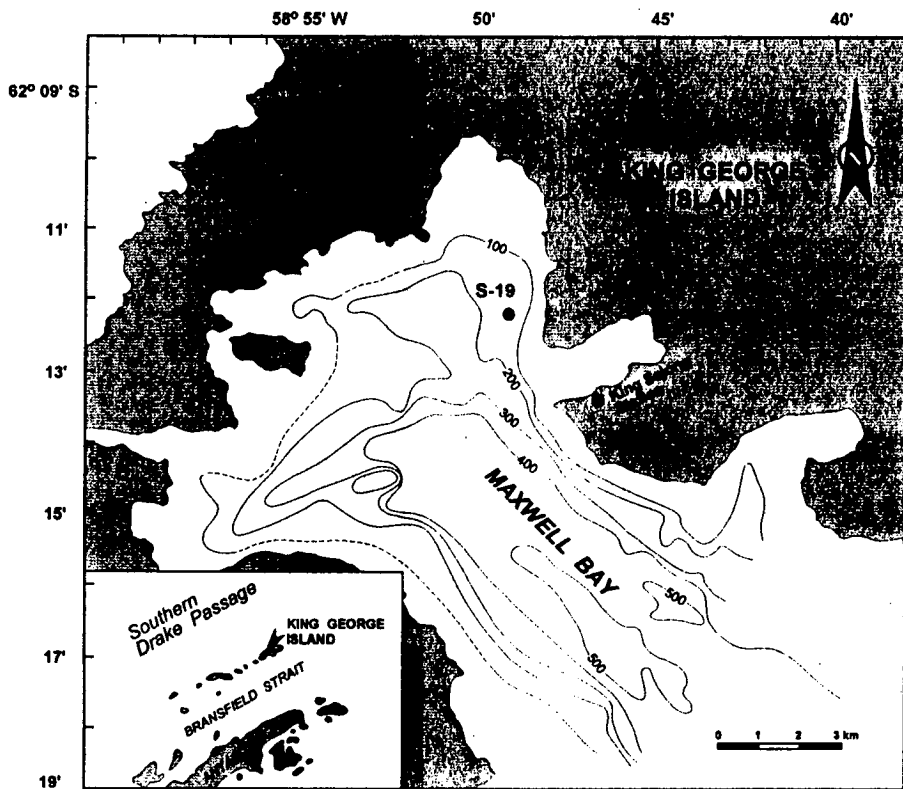


Figure 2-1. Map of the study area. Black circle indicates sediment core location.

## 2-4. 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. 2-2). 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  $^{14}\text{C}$  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. 2-2). Like organic C, therefore, the depth profile of biogenic Si contents appears to be controlled by the vertical flux of biogenic Si.

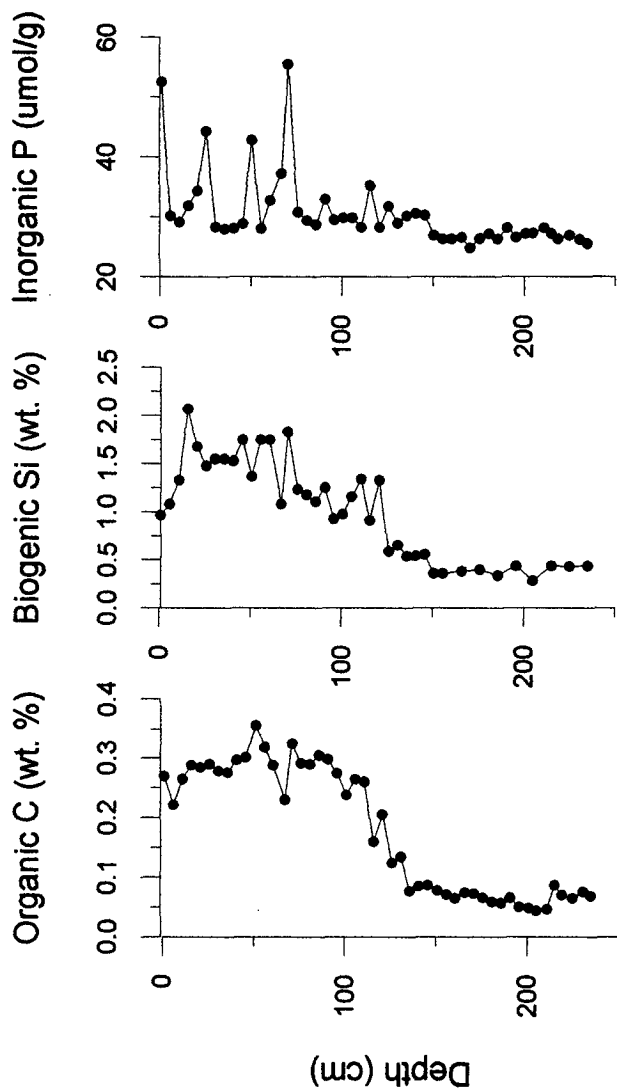


Figure 2-2. Depth profiles of organic C, biogenic Si, and inorganic P contents in core S-19 of the Maxwell bay.

Inorganic P contents, however, shows a quite different depth profile from those of organic C and biogenic Si (Fig. 2-2). 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 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. 2-2). The peak contents range from 43 to 56 mol/g, which are almost twice as much as the base-line values (about 30 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 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. 2-2). 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 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. 2-3). Based on the chronology in Figure 2-3, organic C and biogenic Si contents are plotted against the  $^{14}\text{C}$  ages (Fig. 2-4). 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 clay minerals when biogenic Si contents are below 10 wt. %. Thus it can be inferred that production of biogenic

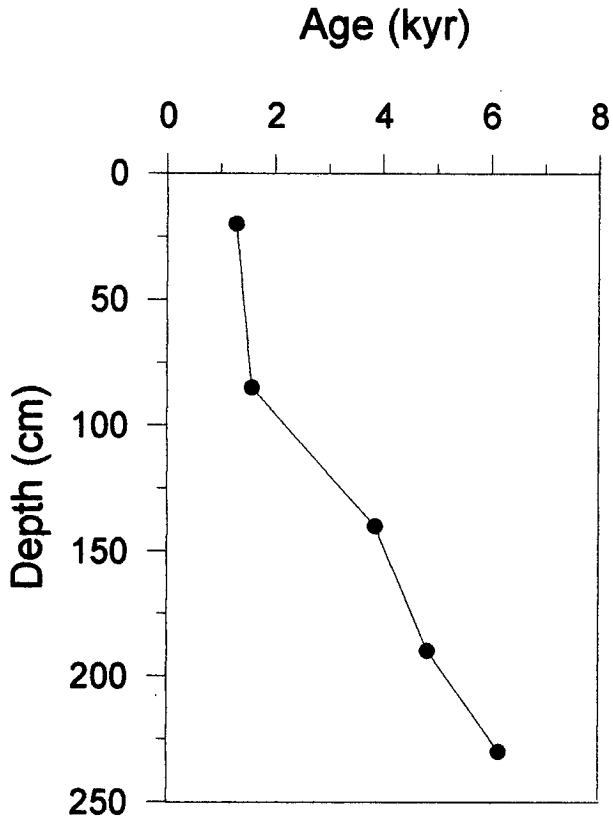


Figure 2-3.  $^{14}\text{C}$  age versus sediment depth in core S-19 of the Maxwell bay. A sedimentation rate above 85 cm is 0.23 cm/yr, and an average sedimentation rate is 0.032 cm/yr below 85 cm. (after Park et al., 1995).

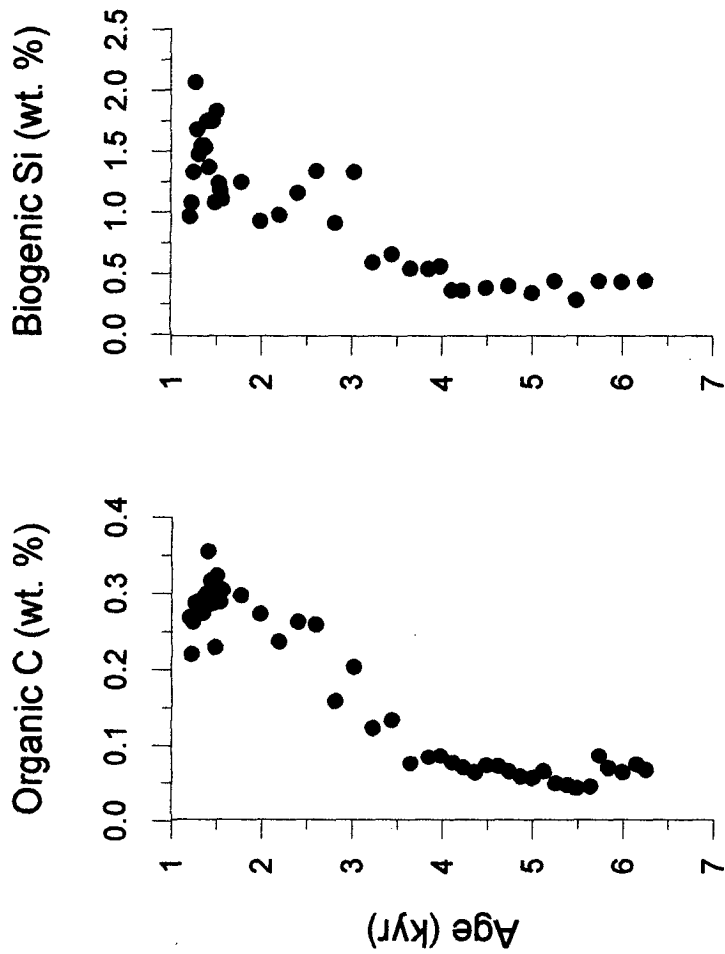


Figure 2-4. Organic C and biogenic Si contents versus  $^{14}\text{C}$  age in core S-19 of the Maxwell bay.



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 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. 2-3). 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 2-1), 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.

## 2-5. 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

Table 2-1. Comparison of records of Late Holocene paleoclimate change by Bjorck et al. (1996) to those in this study.

Bjorck et al. (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		

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.

### 제3장 남극 남 쉘트랜드 열도에 있는 맥스웰 만 퇴적물에서 다량, 미량, 희토류 원소들의 수직적 변화

#### 3-1. ABSTRACT

Vertical distribution of major, minor, and rare earth elements were determined to investigate the major factors controlling these element concentrations in Maxwell bay sediments. Na, Mg, K, Cr, and heavy rare earth element concentrations are mostly controlled by sediment texture. Meanwhile, Fe, Co, Cu, Mn, V, Cd, Zn, Pb and light rare earth element concentrations are mainly influenced by sulfide minerals. The negative Ce anomalies with no distinct vertical trend suggest that oxidizing conditions are dominant in the sediment column of the Maxwell bay, and the redox conditions have not significantly changed during the sediment deposition. The positive Eu anomalies and shale-normalized REE patterns which are similar to those of the hydrothermal solution indicate that the Maxwell bay sediments are significantly affected by the hydrothermal system. The rapid increase of total S contents in the Maxwell bay sediments indicates the *in situ* formation or existence of sulfide minerals. The sulfide minerals seem to be derived from the King George Island by the advance of sea ice before 4000 yr B.P.

## 3-2.. INTRODUCTION

The chemical composition of marine sediments is controlled by the relative contributions of particulate materials derived from different sources, by the uptake or fixation of elements during sedimentation and by post-depositional changes brought about by diagenetic reactions in the sediments (Calvert, 1976). The chemical elements are initially supplied to the site of deposition from terrestrial sources via rivers or the atmosphere and from biological activity within the ocean. The concentrations of major, minor, and rare earth elements (REE) in marine sediments reflect the range of chemical, oceanographic and sedimentary controls on their supply to, distribution in and removal from the ocean. Many minor elements typically have different solubility in oxygenated or oxygen deficient sea water and are partitioned between the solid and solution phases to different extents under different redox conditions (Dyrssen and Kremling, 1990). Hence, examination of the chemical behavior of the minor elements in the sediment column could potentially provide valuable information on the chemical state of the environment of deposition of ancient sediments (Piper and Issacs, 1996). The chemistry of the REE, especially their similar chemical properties and low solubility that allow only limited elemental fractionation during weathering and diagenesis, makes these elements useful as geochemical indicators in sediment and in sedimentary rocks ( Fleet, 1984; McLennan, 1989).

Maxwell bay is a deep and glacially influenced U-shaped fjord bounded by King George Island on the northeast and by Nelson Islands on the southwest in the South Shetland, Antarctica. This region belongs to a temperate to sub-polar setting with warm and humid weather. Sedimentary processes in the Maxwell bay are significantly influenced by glacial processes, and glaciomarine sediments are

entirely covered in the bottom of the Maxwell bay. The sediment column are clearly distinguished by several sediment layers with different sediment texture and properties (Yoon et al, 1997). The aims of this study are to describe the vertical distribution of major, minor, and REE concentrations in the Maxwell bay sediments and to determine major factors controlling their vertical distribution. We also try to elucidate the sedimentary conditions of the Maxwell bay based on the vertical variations of these elements

### 3-3. MATERIALS AND METHODS

Sediment core S-19 was collected with a gravity corer at a water depth of 110 m from the Maxwell bay of the South Shetland Island, West Antarctica (Fig. 3-1). 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. Sediment size analysis was conducted by the Sedigraph after removing organic C and calcium carbonate. Organic C contents were determined by a Carlo-Erba CNS analyzer after eliminating inorganic C by 10 % HCl. Total C and S contents were also analyzed by a Carlo-Erba CNS analyzer. Calcium carbonate contents were calculated by subtracting organic C contents from total C contents. Major and minor elements were measured by the Induced Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) in the Korea Basic Science Center. Rare earth element concentrations were determined by the Induced Coupled Plasma - Mass Spectroscopy (ICP-MS) in the Korea Basic Science Center. Complete sample dissolution prior to introduction into the ICP-AES and ICP-MS was achieved by HNO<sub>3</sub>-HF-HClO<sub>4</sub>

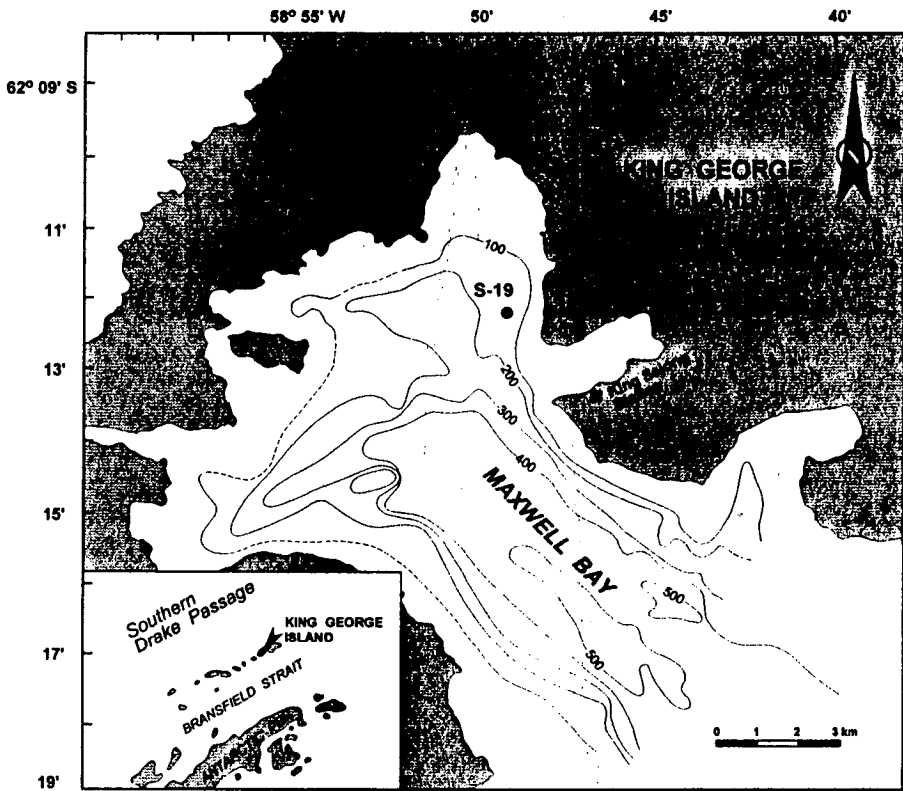


Figure 3-1. Map of the study area. Black circle indicates sediment core S-19 location.



total digestion in Teflon beaker (Park and Yoon, 1994).

### 3-4. RESULTS AND DISCUSSION

#### **Major elements**

Major elements show rather different depth distribution patterns at core S-19. Na, Mg, and K generally decrease with sediment depth, while Ca and Fe increase (Fig. 3-2). Al and Ti do not display any distinct vertical distribution trend, with large fluctuation with depth (Fig. 3-2). Depth profiles of Na, Mg, K are similar to that of clay (Fig. 3-3), and their concentrations are well correlated with clay contents (Fig. 3-4), suggesting that their concentrations are mostly controlled by sediment texture. In general, Al and Ti are incorporated in detrital components of marine sediments which consist of rock fragments and mineral derived from the continents by weathering (Calvert, 1976). Also their concentrations are significantly influenced by sediment texture; high concentrations are observed in fine grain sediments since they are well incorporated into clay minerals. At core S-19, however, Al and Ti concentrations do not exhibit any correlation with clay contents (Fig. 3-4), reflecting that their concentrations are not much influenced by sediment texture. Depth profile of Ca is similar to that of CaCO<sub>3</sub> (Fig. 3-3), thus Ca exist mainly in CaCO<sub>3</sub>. Fe concentrations are negatively correlated with clay contents (Fig. 3-4), even though they usually have a positive relationship with clay contents. Thus they are significantly affected by other processes, besides sediment texture. Depth profile of Fe is rather similar to that of total S (Fig. 3-3), which suggests that Fe concentrations are mostly influenced by sulfide minerals.

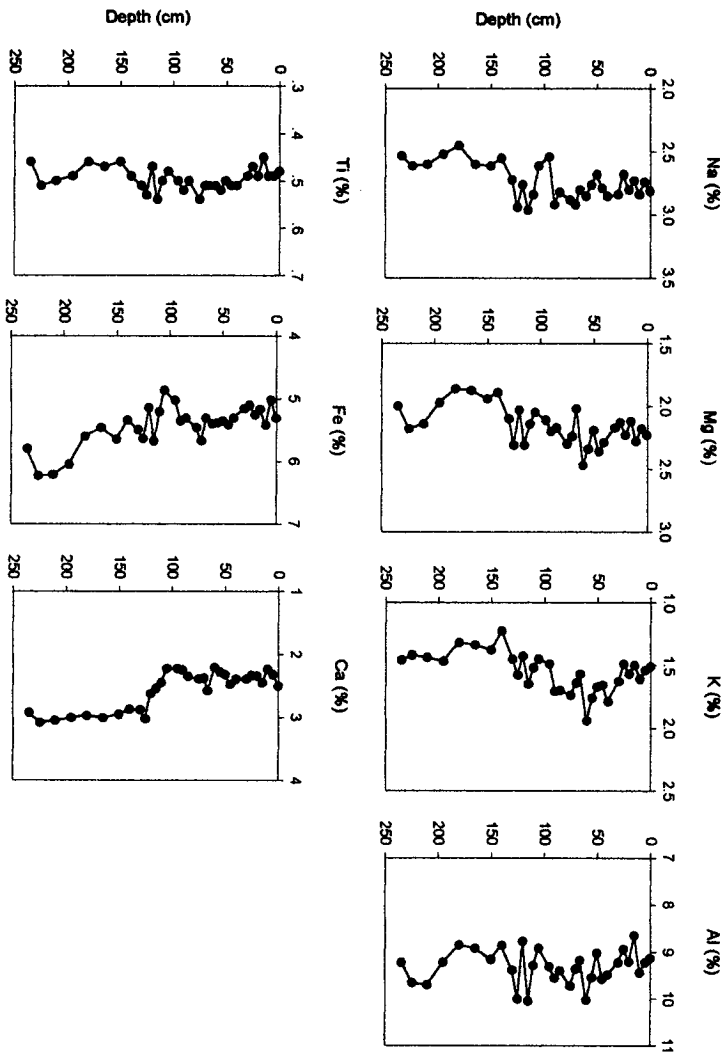


Figure 3-2. Vertical profiles of major element concentrations in core S-19 of the Maxwell bay.

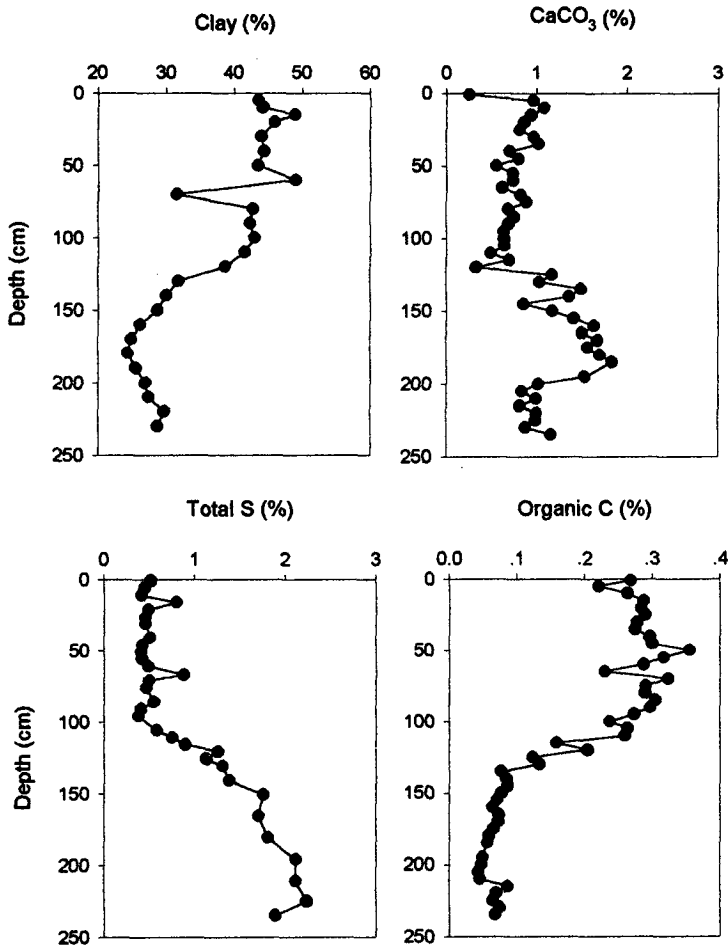


Figure 3-3. Vertical profiles of clay, calcium carbonate, total S, and organic C contents in core S-19 of the Maxwell bay.

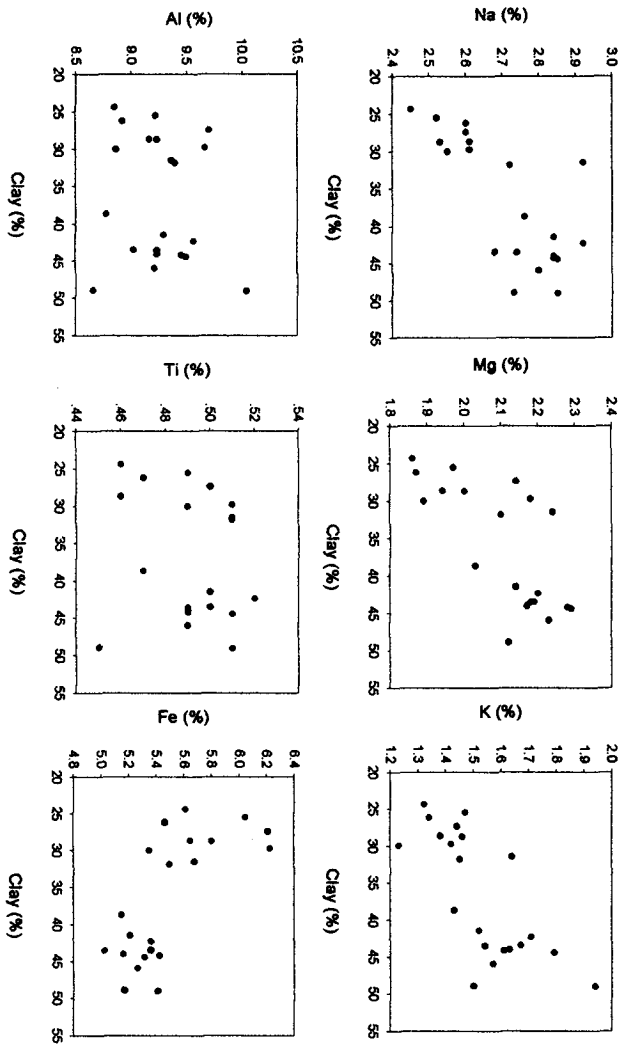


Figure 3-4. Plots of major element concentrations vs. clay contents.

## Minor elements

Minor elements also show different vertical distribution patterns at core S-19 (Fig. 3-5). Cu, Co, and Pb increase with sediment depth, meanwhile Cr exhibits a downcore decrease trend. Sc, V, Mn, Zn, Ni, and Cd display large variations with sediment depth without any vertical trend. The depth profile of Cr is similar to that of clay (Fig. 3-3). Hence the Cr concentration is predominantly affected by sediment texture. Like Fe, the vertical increases of Cu, Co, and Pb are mainly due to the formation of sulfide minerals below 100 cm at core S-19 because these minor elements are well incorporated into sulfide minerals. The formation of sulfide mineral in the lower part of core S-19 is supported by the increase of total S contents at these depths (Fig. 3-3). In general, many minor elements are associated with sulfide minerals, especially Cu, Zn, Co, Cd, and Pd (Oudin, 1987; Hannington et al., 1991). Thus these minor elements are usually enriched in sulfide mineral deposits. At core S-19, however, Zn and Cd do not have relative high concentrations below 100 cm where sulfide minerals seem to form.

In order to determine whether minor elements are enriched below 100 cm, minor elements are normalized by Sc which is an inert element, not involved in diagenetic reaction occurred in marine sediments. Co/Sc and Cu/Sc ratios are relatively constant at the top 100 - 120 cm and then rapidly increase below those depths, reaching maximum values at 200 cm (Fig. 3-6), of which depth profiles are rather similar to that of total S. Therefore, Co and Cu concentrations at core S-19 are mostly controlled by sulfide minerals. Mn/Sc, V/Sc, Pb/Sc, Cd/Sc, and Zn/Sc ratios show relatively high values at the top 10 - 30 cm (Fig. 3-6), which is not related to the sulfide minerals because total S contents are relatively low at those depths. However, these ratios also relatively increase with sediment depth below 100 cm where total S contents increase, implying that Mn, V, Pb, Cd, and Zn concentrations are also influenced by sulfide minerals. Consequently, these

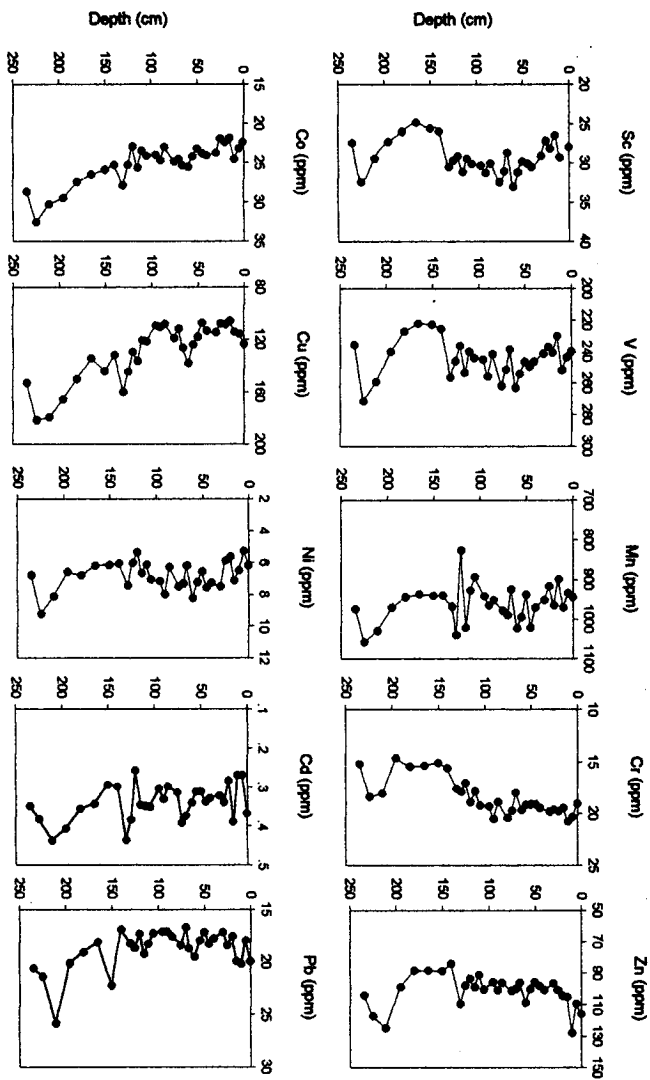


Figure 3-5. Vertical profiles of minor element concentrations in core S-19 of the Maxwell bay.

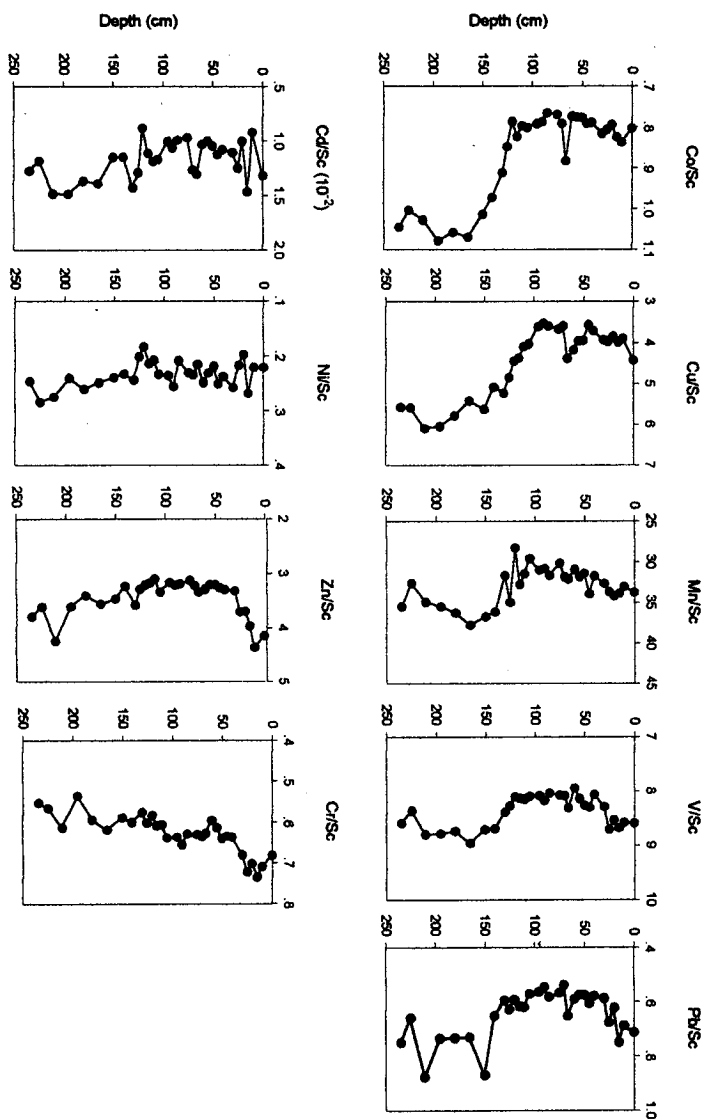


Figure 3-6. Vertical profiles of minor elements/Sc ratios in core S-19 of the Maxwell bay.

minor element concentrations at core S-19 are controlled not only by sulfide minerals, but also by other processes, such as sediment texture. Ni/Sc and Cr/Sc ratios do not increase below 100 cm (Fig. 3-6), suggesting that Ni and Cr are not associated with sulfide minerals.

### **Rare earth elements (REEs)**

Light rare earth elements (LREEs) have relatively high concentrations below 100 cm sediment depth, meanwhile heavy rare earth elements (HREEs) are relatively enriched in the top 100 cm. The vertical profiles of HREEs display similarities to that of clay contents. Thus their concentrations seem to be fairly influenced by sediment texture, and HREEs are not well associated with sulfide minerals. However, LREEs show similar vertical profiles with total S contents, implying that LREEs are well associated with sulfide minerals.

The  $La_N/Yb_N$   $\{(La_{sample}/La_{NASC})/(Yb_{sample}/Yb_{NASC})\}$ , which defines relative behavior of LREEs to HREEs ranges from 0.84 to 1.06 (Fig. 3-7a). The  $La_N/Yb_N$  values are close to 1 below 140 cm, but they are less than 1 at the top 140 cm. Thus LREEs are relatively depleted compared to HREEs at the top 140 cm. In seawater, HREEs are significantly enriched relative to LREEs, which is due to the relatively greater stability of HREE complexes in seawater (Brookins, 1989). Hence the REE compositions at the top 140 cm are more influenced by seawater than those below 140 cm.

The Ce anomaly ( $Ce/Ce^*$ ), which indicates the degree of Ce enrichment or depletion with respect to adjacent REE ranges between 0.84 to 0.89 (Fig 3-7b). The  $Ce/Ce^* > 0.9$ ,  $< 1.1$ , and  $0.9-1.1$  indicates negative, positive, and no anomaly, respectively.  $Ce^{3+}$  is oxidized in the oceans to  $Ce^{4+}$  which is highly insoluble under oxidizing conditions and is preferentially incorporated or adsorbed in octahedral sites of precipitates or as  $CeO_2$  on the surfaces of grains in bottom



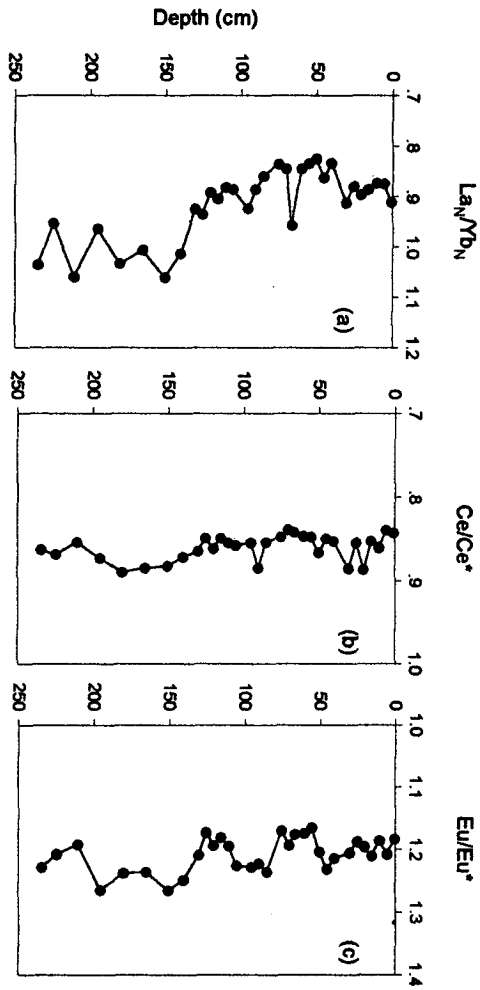


Figure 3-7. Vertical profiles of (a)  $La_n/Yb_n$ , (b)  $Ce/Ce^*$ , and (c)  $Eu/Eu^*$  in core S-19 of the Maxwell bay.

sediments (Elderfield and Greaves, 1982; Koeppenkastrop and De Carlo, 1992). Thus the Ce anomaly has been used to identify the redox conditions in ancient environments; the Ce/Ce\* values are negative under oxidizing conditions (Grandjean et al., 1988; Liu and Schmitt, 1990). The Ce/Ce\* values at core S-19 are negative in the entire sediment column and do not show any distinct vertical trend, with small fluctuation with depth (Fig. 3-7b). Hence oxidizing conditions are dominant in the entire sediment column, and the redox conditions have not significantly changed during the sediment deposition.

The Eu anomalies represented by Eu/Eu\* shows positive values in the entire sediment column, with no distinct vertical trend (Fig. 3-7c). The positive Eu anomaly is found either in water affected by eolian input or in the hydrothermal solutions and the sediments resulting from high T-basalt alternation along mid-ocean ridges and back-arc spreading centers (Michard et al., 1983; Elderfield, 1988; German et al., 1993). The positive Eu anomalies observed at core S-19 appear to be effects of the hydrothermal system because the hydrothermal system is located near the Maxwell Bay (Suess et al., 1988; Lawver et al., 1995).

Shale (NASC)-normalized REE patterns are shown in Figure 3-8. Most of LREEs and HREEs are considerably depleted, but Eu is exclusively enriched in the entire sediment column. These shale-normalized REE patterns are rather similar to those observed in the hydrothermal solutions in which Eu is greatly enriched (McLennan, 1989). Therefore, the REE compositions at core S-19 are significantly influenced by the hydrothermal system.

### **Origin of sulfide minerals**

In marine sediments, the increase of total S contents indicates *in situ* formation of sulfide mineral by the reaction of dissolved Fe and sulfide which is produced by sulfate reduction through sulfate reducing bacteria (Berner, 1980).

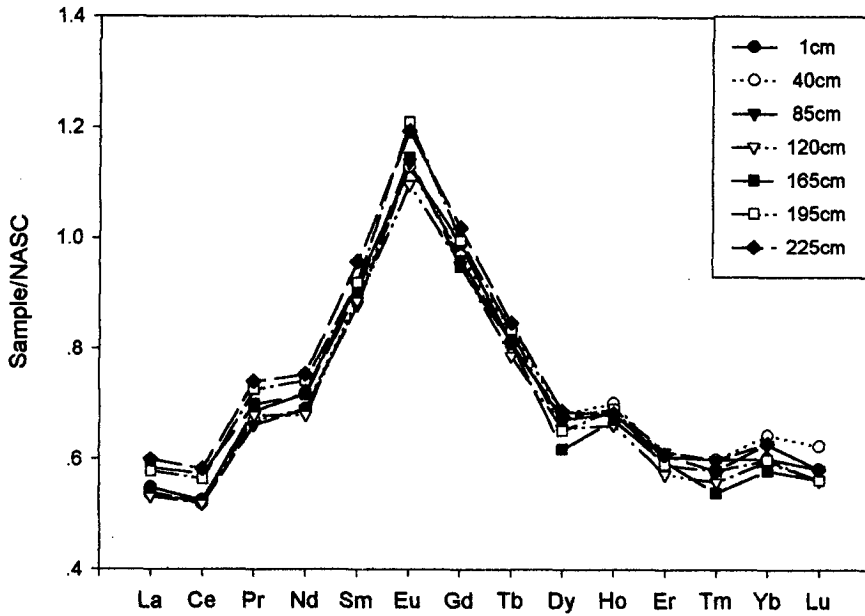


Figure 3-8. Shale (NASC)-normalized REE patterns in core S-19 of the Maxwell bay.

Organic matter deposited in marine sediments is sequentially oxidized by oxygen, nitrate, and Mn and Fe oxides, and sulfate (Froelich et al., 1979; Berner, 1980). As a result, sulfate reduction usually occurs in organic-rich coastal sediments or upwelling areas (Berner, 1980; Rowe and Howarth, 1985; Edenborn et al., 1987; Thamdrup et al., 1994). At core S-19, however, organic C contents are relatively low especially below 100 cm where total S contents rapidly increase (Fig. 3-3). Kim et al. (1997) suggested that the organic matter deposited below 100 cm at core S-19 was mainly derived from continents through rivers. In these organic-poor sediments, sulfate reduction rarely occurs. Also in the previous section, the negative Ce anomalies suggest that the oxidizing conditions are dominant in the entire sediment column of core S-19 and the redox conditions have not significantly changed during the sediment deposition. Therefore, sulfate reduction has not occurred at core S-19 and thereby, the increase of total S are not due to *in situ* formation of sulfide minerals.

It was suggested that in the Maxwell Bay, sea ice advanced to the core S-19 site before 4000 yr B.P. and then gradually retreated to the present location by becoming warm climate after 4000 yr B.P. (Kim et al., 1997; Yoon in preparation). Thus the sediments below 100 cm with low organic C and high total S contents would be deposited when the sea ice advanced to the core S-19 site. The sea ice entrains terrestrial materials during its formation in land and delivers them to marine sediments by advance into ocean. Also the sea ice dredges the bottom sediments or rocks and carries terrestrial sediments or rock fragments during the movement from land to ocean. Hence diamitons are well developed in front of the sea ice (Domack, 1990). The sediments below 100 cm at core S-19 appear to be diamitons because they contain large gravel and show very bad sorting (Yoon in preparation). The sulfide mineral enriched in the sediment below 100 cm are mainly derived by the advance of sea ice before 4000 yr B.P. from

King George Island where the hydrothermal origin quartz-pyrite rocks have been well recognized and described by many investigators (Littlefair, 1978; Park, 1991; So et al., 1995). The positive Eu anomalies and shale-normalized REE patterns which are similar to those of the hydrothermal solution support the suggestion that the sulfide minerals found at core S-19 are the hydrothermal origin.

### 3-5. CONCLUSIONS

The major, minor and rare earth elements measured in the Maxwell Bay display different chemical behaviors in the sediment column. The sediment texture is a major factor controlling the vertical distribution of Na, Mg, K, Cr, and HREEs. Meanwhile, Fe, Co, Cu, Mn, V, Cd, Zn, Pb and LREE concentrations are mainly influenced by sulfide minerals. The negative Ce anomalies with no distinct vertical trend suggest that oxidizing conditions are dominant in the entire sediment column, and the redox conditions have not significantly changed during the sediment deposition. The positive Eu anomalies and shale-normalized REE patterns which are similar to those of the hydrothermal solution indicate that the sediments deposited in the Maxwell bay are significantly influenced by the hydrothermal system.

The rapid increase of total S contents below 100 cm sediment depth indicate the *in situ* formation or existence of sulfide minerals at these depths. The *in situ* formation of sulfide minerals does not seem to occur at core S-19 because organic C contents are extremely low, and the Ce anomalies are negative in the entire sediment core. The sulfide minerals appear to be derived from the King George Island by the advance of sea ice before 4000 yr B.P. which is supported by the positive Eu anomalies and shale-normalized REE patterns.

## 제4장 신생대 제4기동안 황해의 고환경 변화

### 4-1. ABSTRACT

Based on the stable isotopes and geochemical analyses, the sedimentary environment of the Yellow sea was significantly influenced by the sea level changes during the late Quaternary. At the low sea level stand (12,500 - 11,500 yrs B.P.) when the sea level dropped by 56 m, the salinity of seawater was reduced to about 7.6 ‰, and the sedimentation rate in the central part of the Yellow Sea was three times higher than the present one. The high C/S ratio during the low sea level is a strong evidence that sedimentation took place in much freshwater environment than the present.

### 4-2. INTRODUCTION

The Yellow Sea is a typical epicontinental sea, characterized by a flat and broad sea floor with an average water depth of 55 m. It serves as the important depocenter of clastic sediments derived through the Huanghe (Yellow) River which is one of the largest sediment discharges in the world (Milliman and Meade, 1983). The Yellow Sea was subaerially exposed by the sea level drop during the late Pleistocene and subsequently inundated during the Holocene transgression (Park et al., 1994). As a result, sedimentary structure and surface sediment distribution are predominantly influenced by the sea level changes (Lee and Yoon, 1997). Large mud deposits have been well developed in the central part of the

Yellow Sea and sand sheets extensively cover the eastern part with abundant tidal sand ridges (Lee and Chough, 1989). Previous investigations have shown that the sea level changes are the major factor in controlling the sedimentary processes in the Yellow Sea during the late Quaternary (Lee et al, 1988; Milliman et al., 1989; Yang, 1989; Lee, 1991; Lee and Yoon, 1997).

Foraminifera assemblages have been analyzed to elucidate the paleoenvironmental changes associated with the sea level changes in the Yellow Sea (Kim et al., 1970; Chang and Lee, 1984; Wang et al., 1985; Cheong, 1991; Zheng and Fu, 1994; Woo et al., 1995). However, there are only few studies on paleoenvironmental changes of the Yellow Sea using stable isotopes and geochemical data (Kim and Kennett, 1997). The salinity of the Yellow Sea has probably changed by the sea level oscillation during the late Quaternary because the water volume of the Yellow Sea was fairly reduced by the sea level drop, but freshwater discharges of the Huanghe River would not significantly change. Oxygen isotope is a powerful tool for assessing the salinity changes caused by the sea level changes (Craig, 1965), especially in the Yellow Sea where salinity is linearly well correlated with the  $\delta^{18}O$  of seawater (Kang et al., 1994). In addition, the C/S ratio was useful to distinguish freshwater from marine sedimentary rock (Berner and Raiswell, 1984). The C/S ratio of the sediments under freshwater or brackish environments is much higher than that in the marine sediments. In this paper we assess the paleoenvironmental changes of the Yellow Sea associated with the sea level changes during the late Quaternary using the stable isotopes and geochemical data.

### 4-3. MATERIALS AND METHODS

Core CC02 was collected by a piston corer in the central part of the Yellow Sea where water depth is 78 m (Fig. 4-1). The core CC02 (278 cm in length) is clearly divided into two distinct layers at a core depth of 115 cm; the upper layer is mostly composed of silt and clay, and the lower layer is sandy mud. Water contents are much higher in the upper layer (>50 %) than in the lower layer (<30 %) (Lee and Yoon, 1997). Primary sedimentary structure was not observed in both layers and intense bioturbation with vertical and horizontal burrows characterizes the entire core (Lee and Yoon, 1997).

The core CC02 was sectioned by the 5 cm interval, and each sample was dried at 80 °C for 4 days. Organic C contents were determined by a Carlo-Erba CNS analyzer after eliminating inorganic C using 1 N HCl. Total S contents were also measured by a Carlo-Erba CNS analyzer. Ten individuals of benthic foraminifera, *Ammonia beccarii* (150 - 250 m) were used for the analyses of oxygen and carbon isotopes. The isotope measurements were carried out at the Korea Basic Science Institute using a PRISM II mass spectrometer (VG Isotech company), which is linked on-line to a fully automated carbonate preparation device. The analytical reproducibility of oxygen and carbon isotopes was 0.1 ‰. All isotope values are referred to Peedee belemnite (PDB) scale. Accelerator mass spectrometer (AMS) radiocarbon determinations on benthic foraminifera were made at the Lawrence Livermore National Laboratory, USA.



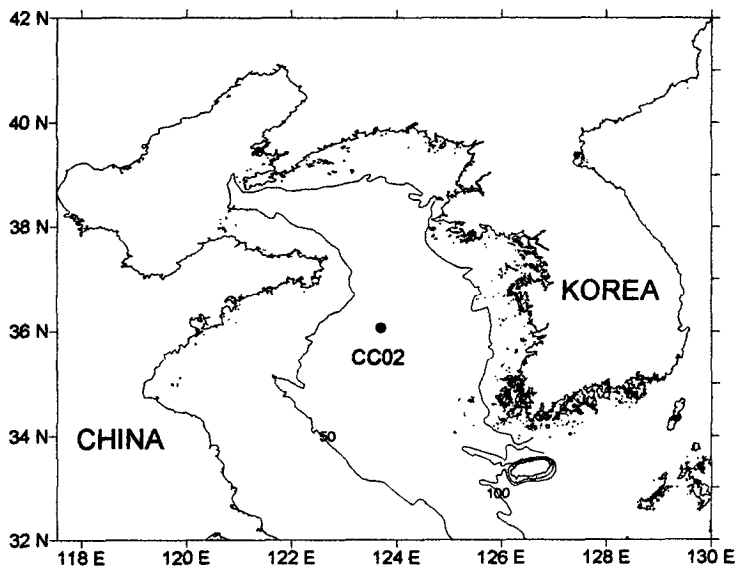


Figure 4-1. Location map of core CC02 in the Yellow Sea.

## 4-4. RESULTS AND DISCUSSION

### **Radiocarbon chronology and sedimentation rate**

The AMS radiocarbon measurement was conducted for four depths of core CC02 (Table 4-1 and Fig. 4-2). Reservoir correction was not made on the measured radiocarbon ages due to insufficient information on core-top radiocarbon measurements in the central part of the Yellow Sea. The reservoir effect on radiocarbon age dates does not seem to be significant in the Yellow Sea because radiocarbon age measured on core-top benthic foraminifera is only 4 year in the tidal flat of the Yellow Sea (Kim and Kennett, unpublished data). The measured radiocarbon ages were converted to calendar ages (Cal B.P.) by using the calibration curve of Stuiver et al. (1991) and Stuiver and Braziunas (1993). Sedimentation rates were calculated from the slopes of the calendar ages and sediment depths (Fig. 4-2). Sedimentation rates are estimated to be 17.6 cm/kyr in the upper 175 cm and 60.3 cm/kyr below 175 cm. The sedimentation rate estimated in the upper 175 cm represents the modern sedimentation rate of the Holocene deposits. This sedimentation rate is much lower than those (40 - 170 cm/kyr) estimated in the nearby mud deposits by Alexander et al. (1991), who have used  $^{210}\text{Pb}$  method for sedimentation rate estimation. Harden et al. (1992) suggested that radiocarbon measurements are a better approach for determining accurate sedimentation rates than  $^{210}\text{Pb}$  method because the  $^{210}\text{Pb}$  method is influenced predominantly by biological deep mixing. Therefore, the sedimentation rates estimated in the central mud belt of the Yellow Sea by Alexander et al. (1991) are thought to be overestimated.

The sedimentation rate rapidly increases from 17.6 to 60.3 cm/kyr

Table 4-1. Radiocarbon dates of core CC02

Sediment depth (cm)	Materials	<sup>14</sup> C ages* (yrs)	Calendar ages** (yrs B.P.)
20	Foraminifera	2,200	1,800
95	Foraminifera	5,370***	5,720
175	Foraminifera	9,840	10,600
278	Foraminifera	11,020	12,300

\* Reservoir correction was not made.

\*\* Calendar ages were obtained from <sup>14</sup>C ages using the calibration curves of Stuiver et al. (1991) and Stuiver and Braziunas (1993).

\*\*\* Data from Kim and Kennett (1997).

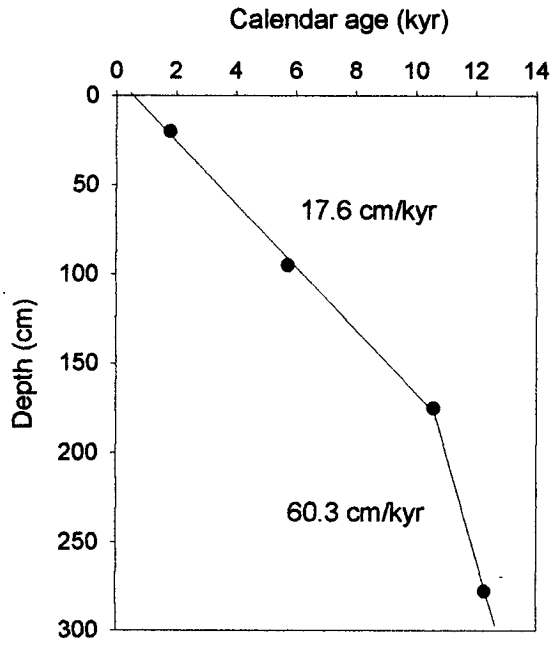


Figure 4-2. Calendar age vs. sediment depth. Sedimentation rates were calculated from the slopes.

below 175 cm (Fig. 4-2). This rapid increase in sedimentation rates seems to be related to the Holocene sea level change in the Yellow Sea. Geng et al. (1987) proposed that at about 11,500 yrs B.P. the sea level reached - 56 m when the North Yellow Sea shelf was transgressed by the sea and abruptly rose to the present sea level from 11,500 to 7,000 yrs B.P. Based on the sea level oscillation curve by Geng et al. (1987), before 11,500 yrs B.P. the water depth of core CC02 site was about 20 m and the North Yellow Sea was subaerially exposed or was a fresh water environment. The drainage basin of the Huanghe River had extended to the central part of the Yellow Sea where core CC02 was collected, and terrestrial materials were directly transported to the central part. Therefore, the sedimentation rate at the central part was high during the low sea level stand. As the sea level rapidly rose to the present sea level, the drainage basin of the Huanghe River had retreated from the central part of the Yellow Sea, and less terrestrial materials were supplied to the core CC02 site. The bottom sediments in the central part of the Yellow Sea may be reworked and redistributed by the marine transgression. As a result, the sedimentation rate decreased during the sea level rise.

### **Oxygen and carbon isotopes**

Results of stable isotopic analyses conducted on a benthic foraminifera, *Ammonia beccarii* are shown in Figure 3. *Ammonia beccarii* precipitates its test in almost isotopic equilibrium with the seawater (Grossman, 1987). At core depths of 115 -160 cm, no benthic foraminifera were available for stable isotopic analyses. The benthic  $^{18}\text{O}$  and  $^{13}\text{C}$  show a downcore decrease trend (Fig. 4-3). At the top 115 cm,  $^{18}\text{O}$  and  $^{13}\text{C}$  values range from 0.87 to 1.86 ‰ and from -1.15 to -0.18 ‰, respectively. Below 160 cm, on the other hand, they are much lighter (-0.64 - -4.29 ‰ for  $^{18}\text{O}$  and -1.59 - -4.10 ‰ for  $^{13}\text{C}$ ), with a large fluctuation. The shift

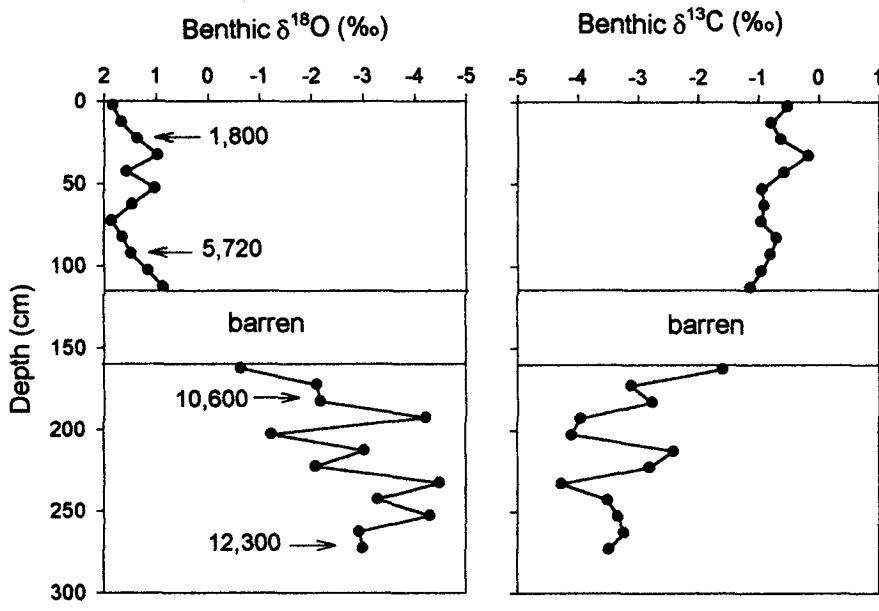


Figure 4-3. Benthic (*Ammonia beccarii*) oxygen and carbon isotope records of core CC02. Numbers along the oxygen isotope record indicate calendar ages. At core depths of 115 -160 cm, no benthic foraminifera were available for stable isotopic analyses.

to lighter  $^{18}\text{O}$  value during the late Pleistocene has been rarely observed in marine environments. In general, the  $^{18}\text{O}$  shifts to heavier values during the late Pleistocene due to the decrease in temperature and the increase in global ice volume (Anderson and Arthur, 1982). As a consequence, the vertical variation of  $^{18}\text{O}$  must be ascribed to the salinity change in seawater derived by the sea level oscillation in the Yellow Sea. During the low sea level stand, salinity in the Yellow Sea might be low compared to the present Yellow Sea Cold Water (32 - 33 ‰) because the water volume of the Yellow Sea had significantly reduced by the sea level drop, but river discharges from the continents would not considerably change. Before 11,500 yrs B.P. when the sea level dropped by 56 m from the present level, oxygen isotope was extremely light, with a range of -2.09 - -4.29 ‰ (Fig. 4-3). During the late Pleistocene and early Holocene (11,500 - 7,000 yrs B.P.) when the sea level abruptly rose from -56 m to the present level, the oxygen isotope had largely increased from -4.21 to 0.87 ‰ (Fig. 4-3), which can be explained by the increased input of seawater having heavy oxygen isotope into the Yellow Sea from the East China Sea by the sea level rise. Oxygen isotope composition (0.87 - 1.86 ‰) remained high after 7,000 yrs B.P. when the sea level was stable at the present sea level. The depth profile of  $^{18}\text{O}$  is quite similar to that of  $^{13}\text{C}$  (Fig. 4-3). The  $^{18}\text{O}$  values are linearly well corrected with the  $^{13}\text{C}$  values (Fig. 4-4), which suggests that the vertical distributions of the  $^{18}\text{O}$  and  $^{13}\text{C}$  signal are controlled by the same process that must be the salinity change in seawater

In the Yellow Sea, the  $^{18}\text{O}$  values of seawater show a linear relationship with salinity (Kang et al., 1994);  $\text{salinity (\%)} = 4.35 \text{ }^{18}\text{O (\%)} + 34.0$ . Following this equation, the salinity of seawater in the Yellow Sea changes by 4.35 ‰ for each 1‰ changes in oxygen isotope. Using this slope, we have calculated the salinity of seawater at the low sea level stand in the Yellow Sea. The average

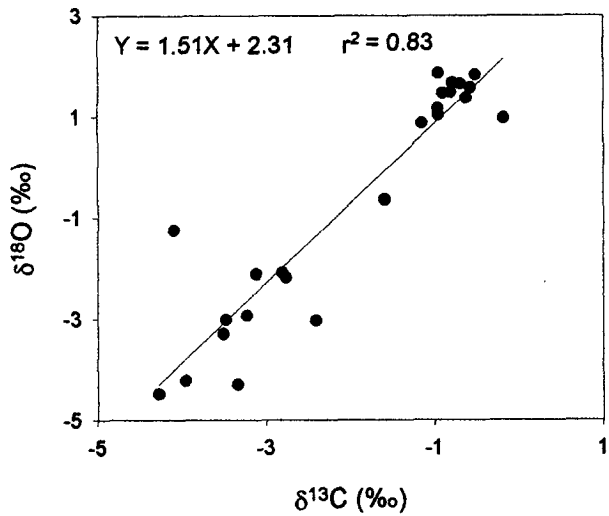


Figure 4-4. The benthic  $^{18}\text{O}$  vs.  $^{13}\text{C}$  values at core CC02.



$^{18}\text{O}$  at the high sea level stand is 1.41 ‰ and - 3.30 ‰ at the low sea level stand. The  $^{18}\text{O}$  difference between the two stages is 4.71 ‰ which corresponds to 20.5 ‰ difference in salinity, assuming that the  $^{18}\text{O}$  difference is derived only by the salinity change. As the present salinity of the Yellow Sea bottom water is about 32.5 ‰ (Youn et al., 1991), the salinity of the Yellow Sea was 12.0 ‰ at the low sea level stand. Oxygen isotope composition is also influenced by the changes of seawater temperature and global ice volume (Anderson and Arthur, 1982, references therein). If we allow for a glacial temperature decrease of 2 °C (CLIMAP project member, 1981; Thunell et al., 1988), the  $^{18}\text{O}$  signal would increase by 0.5 ‰. During the Last Glacial Maximum when the sea level reached -130 m, the  $^{18}\text{O}$  signal increased by 1.0 ‰ due to the increase in global ice volume (Berger, 1979; Savin and Yeh, 1981). Considering that the sea level was -56 m in the Yellow Sea at the 11,500 yrs B.P., the increase of the  $^{18}\text{O}$  signal by the global ice volume change would be 0.5 ‰. The increase in the  $^{18}\text{O}$  signal by changes of both seawater temperature and the global ice volume would be 1.0 ‰ at the low sea level stand. Therefore, the salinity (12.0 ‰) inferred from  $^{18}\text{O}$  signal by counting only the salinity effect would be reduced by 4.4 ‰ if the  $^{18}\text{O}$  signal change derived by the seawater temperature and global ice volume changes is considered. Consequently the salinity of seawater in the Yellow Sea was 7.6 ‰ at the low sea level stand. The low salinity of surface waters was also found during the last glaciation in the northern East China Sea which is connected with the Yellow Sea (Xu and Oda, 1994). They suggested that the salinity of surface waters was severely low in the northern East China Sea between 16 to 10 Ka due to huge amount of discharge from the Huanghe River system, and the low salinity surface water was gradually replaced by open seawater between 10 and 6 Ka, which is in good agreement with our results. About half of sea floor in the Yellow Sea was subaerially exposed at the low sea level stand because an

average water depth of the Yellow Sea is 55 m. The water volume of the Yellow Sea would be reduced to much less than half of the present one by the sea level drop. Assuming that the river discharges from the continents did not significantly change, the water volume at the low sea level stand would be reduced to about a fourth of the present one because the salinity of seawater decreased to a fourth of the present one.

### **Organic C and total S**

Organic C contents generally decrease with depth (Fig. 4-5). Organic C contents are relatively constant (about 1.0 wt. %) in the upper 115 cm. Over the 115 - 178 cm interval, they distinctly decrease from 0.88 to 0.26 wt. % and then remain constantly below 178 cm. The vertical distribution of organic C contents appears to be closely related to the sea level changes. The sediments with very low organic C contents below 178 cm were deposited before 11,500 yrs B.P. when the sea level dropped by 56 m. During the low sea level stand, the sedimentation rate was almost three times higher than that of the high sea level stand (Fig. 4-2), and thereby, organic C was diluted with increased amounts of terrestrial materials. The vertical profile of total S contents shows the same trend as that of organic C (Fig. 4-5). In marine sediments C/S ratio averages about 2.8 in weight (Berner, 1982; Berner and Raiswell, 1983). In the sediments of freshwater or brackish environments (salinity less than 18 ‰), the C/S ratio is much higher than in the marine sediments because of much less diagenetic pyrite formation in the sediments laid down in freshwater which contains much less dissolved sulfate compared to seawater (Berner and Raiswell, 1984). At the core CC02, C/S ratios in the upper 178 cm are relatively constant and low (1.0 - 2.5) and then increase rapidly up to 5.2 below 178 cm (Fig. 4-5). The high C/S ratios below 178 cm indicate that the sediments were deposited at the low sea level stand when the

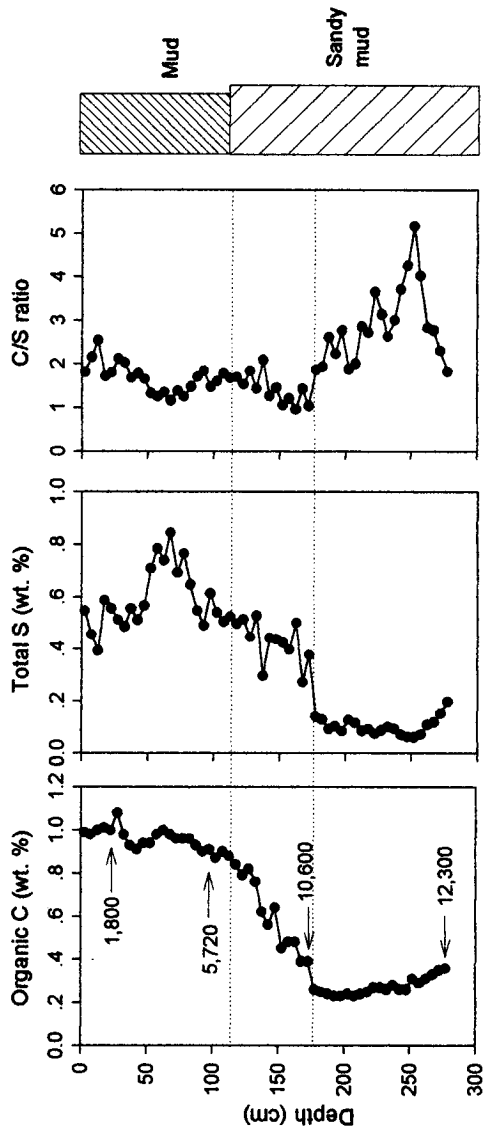


Figure 4-5. Vertical profiles of organic C, total S, and C/S ratio at core CC02. Numbers along the vertical profile of organic C indicate calendar ages.

salinity of the Yellow Sea was very low (7.6 ‰).

The both of organic C and total S contents increased rapidly over the interval from 10,700 to 7,000 yrs B.P. (core depths of 115 - 178 cm) (Fig. 4-5), of which increase is probably derived by the sea level rise. During the sea level rise, the sedimentation rate was lower as much as a factor of three than at the low sea level stand (Fig. 4-2), and thereby organic C contents increased due to less dilution by the reduced supply of terrestrial materials. Total S contents also increased because of the increased input of seawater with high dissolved sulfate concentration to the Yellow Sea from the East China Sea by sea level rise, which is supported by the benthic  $^{18}\text{O}$  signal (Fig. 4-3). After 7,000 yrs B.P. when the sea level was stable at the present level, organic C contents are relatively high and constant, and total S contents are also relatively high, with a small fluctuation (Fig. 4-5). The high organic C and total S contents are ascribed to deposition of the Holocene mud after the sea level was high. In lithology, the core CC02 is clearly divided into two distinct layers at the core depth of 115 cm based on sediment texture (Fig. 4-5). The upper layer is composed of mostly silt and clay, with an average grain size of 9.5  $\mu$ . In the lower layer, meanwhile, sediments contain 25 - 30 % sand, with an average grain size of 7.0. The upper mud layer was deposited after 7,000 yrs B.P., and the lower sandy mud layer was deposited during the Holocene transgression and the late Pleistocene low sea level stand (12,500 - 7,000 yrs B.P.).

#### 4-5. CONCLUSIONS

In the Yellow Sea, the sea level changes during the late Quaternary are well

characterized by three periods; low sea level stand from 12,500 to 11,500 yrs B.P., sea level rise from 11,500 to 7,000 yrs B.P., and high sea level stand from 7,000 yrs B.P. to present. Each period is well characterized sedimentologically and geochemically. At the low sea level stand, the sedimentation rate was relatively high (60.3 cm/kyr) in the central part of the Yellow Sea due to the increased supply of terrestrial materials by the extension of the Huanghe River drainage basin into the central part. Salinity inferred from the benthic  $^{18}\text{O}$  signal was very low, about 7.6 ‰, of which low salinity suggests that the water volume of the Yellow Sea was reduced to a fourth of the present one by the sea level drop. Organic C contents are relatively low (0.23 - 0.36 wt. %) due to dilution by the increased supply of terrestrial materials. The high C/S ratios during the low sea level stand indicate that the sediments were deposited under freshwater or brackish environments. As the sea level rose, the sedimentation rate considerably decreased from 60.3 to 17.6 cm/kyr due to reduced terrestrial supply by the retreat of the Huanghe River drainage basin from the central part of the Yellow Sea. Salinity had increased from 7.6 to 32.5 ‰ by intrusion of seawater from the South China Sea. Organic C and total S contents also increased due to less dilution and an increase in the salinity of seawater, respectively. During the high sea level stand, the sedimentation rate was the same as that during the sea level rise, and the Holocene mud has deposited in the central part of the Yellow Sea. Organic C and total S contents were relatively high, which is ascribed to the deposition of the Holocene mud. The relatively constant stable isotope and geochemical data suggest that the sedimentary environment has been stable during the high sea level stage.



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