Article

A Geochemical Boundary in the East Sea (Sea of Japan): Implications for the Paleoclimatic Record

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Abstract : Sediment from six piston cores from the East Sea (Sea of Japan) was analyzed for evidence of paleoceanographic changes and paleoclimatic variation. A distinct geochemical boundary is evident in major element concentrations and organic carbon content of most cores near the 10-ka horizon. This distinctive basal Holocene change is interpreted to be largely the result of changing sediment sources, an interpretation supported by TiO_2/Al_2O_3 ratios. Organic carbon and carbonate contents also differ significantly between the Holocene and glacial intervals. The C/N ratio of organic matter is greater than 10 during the glacial period, but is less than 10 for the Holocene, suggesting that the influx of terrigenous organic matter was more volumetrically important than marine organic matter during glacial times. The chemical index of weathering (CIW) is higher for the Holocene than the glacial interval, and changes markedly at the basal Holocene geochemical boundary. Silt fractions are higher in the glacial interval, suggesting a strong effect of climate on silt particle transportation: terrigenous aluminosilicates and continental organic carbon transport were higher during glacial times than during the Holocene. Differences in sediment composition between the Holocene and glacial period are interpreted to have been climatically induced.

Key words : geochemical boundary, Holocene, climatic change, CIW.

1. Introduction

The East Sea (Sea of Japan), a typical inactive back-arc basin, is a semi-enclosed marginal sea with four shallow straits: the Korea (140 m deep), Tsugaru (130 m deep), Soya (55 m deep) and Tatarskiy (15 m deep). The Tsushima Current, a branch of the warm, saline Kuroshio Current, enters the East Sea through the Korea Strait. Shallow sills surround the East Sea (Fig. 1) limit its exposure to extraneous influences, such that vertical changes in East Sea sediment may provide a detailed record of paleoceanographic and/or paleoclimatic changes that took place in the vicinity as a result of geographic and eustatic factors during past glacial and interglacial periods (Oba *et al.* 1991; Keigwin and Gobarenko 1992; Tada *et al.* 1992; Tada 1997; Bahk *et al.* 2000). East Sea sediment

is known to contain clastic material sourced from neighboring continents, as well as aeolian dust transported by westerly winds.

Sediment in the East Sea consists of terrigenous, organic, and biogenic carbonate materials, which form a three-component system (TCS; Ricken 1993). The three-component system records both changes in sedimentation rates and variations in the relative contributions of each of the three components; these are functions of extrinsic factors such as current systems and climatic variation, and are critical to interpreting paleoceanographic and paleoclimatic changes.

For the last 10 years, the Korea Ocean Research and Development Institute (KORDI) has been examining the evolution of the East Sea, including paleoceanographic changes and their relation to climatic changes. Long-term studies of East Sea sediment show that sediment composition differs markedly between glacial, interglacial,

Fig. 1. Map of the core locations and bathymetry of the study area.

within 5% for MgO and 2% for other elements. All of the major elements have errors of < 3% for representative duplicate experimental results. The equation used to calculate the chemical index of weathering (CIW) is that of Harnouis (1988):

$$CIW=[Al_2O_3(\%)/Al_2O_3(\%) + CaO(\%) + Na_2O(\%)] \times 100$$

Carbonate and organic carbon contents were analyzed using a CHNS analyzer. Total carbon (TC) was measured directly from powdered dry sediment, and total organic carbon (TOC) content was determined after treatment with 1M hydrofluoric acid. Carbonate content was calculated as the mass difference between total and organic carbon. Grain size analysis was performed using standard sieve methods, and a Micromeritics Sedigraph 5100 (Micromeritics Instrument Corporation, GA, USA) was used for further analysis of sand and mud fractions.

3. Lithology and age controls

East Sea sediment consists of hemipelagic material and intercalated volcanic material (Fig. 2). The biogenic fraction, consisting of organic matter and carbonate, is relatively small. The total biogenic fraction rarely exceeds 30%, which is typical for hemipelagic sediment.

Lamination in mud results from glacial-interglacial variation in bottom and oceanographic conditions (Tada *et al.* 1992; Bahk *et al.* 2000). Sediment from near core tops consists of shelly or bioturbated mud, indicating an absence of glacial influence (Fig. 2).

AMS data and volcanic ash layers are used as age-control points in this study (Table 2). The Ulleung-II tephra layer was deposited about 93,000 yr BP (Chun *et al.* 1997), and the AT tephra dates to 24,000 BP (Murayama *et al.* 1993; Chun *et al.* 1997). AMS ages cited here come from previous studies (Chun *et al.* 1997; Bahk *et al.* 2000). Sedimentation rates vary from about 9 to 75 cm/kyr, suggesting that sedimentation rates were variable both geographically and temporally. A wide

and Holocene periods, and that this is related to oceanographic and paleoclimatic changes (Hyun *et al.* 1998; KORDI 1999, 2000).

This study examines paleoceanographic and paleoclimatic information obtained from East Sea sediment that was deposited during the transition interval between the last glacial period and the Holocene, and assesses paleoceanographic and paleoclimatic changes using the organic, carbonate and siliciclastic content of six sediment cores.

2. Materials and methods

Six piston cores (Table 1) were collected by the R/V *Onnuri*, of the KORDI. Cores were split, and the major and minor element concentrations from half of each core were analyzed using X-ray fluorescence (Philips/PW 1480) and ICP at the Korea Basic Science Institute (KBSI). Major element data are considered to be accurate

Table 1. Location, water depth and length of the cores used in this study.

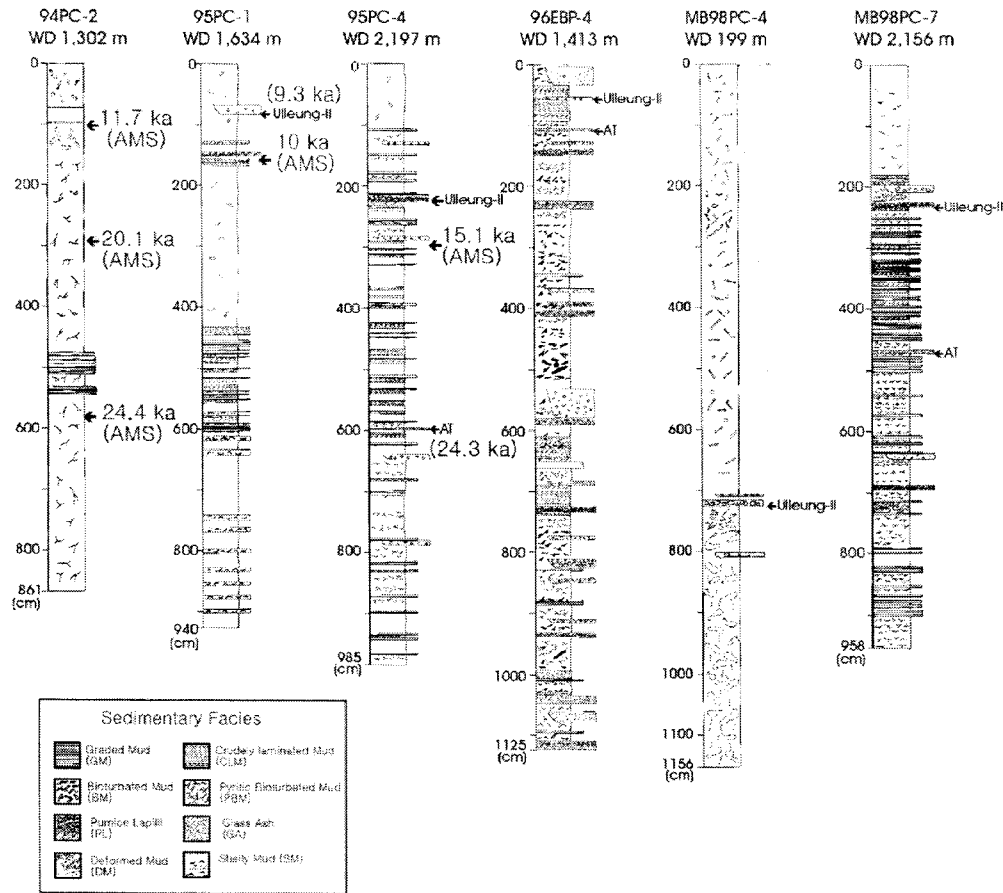| Core ID	Latitude (N)	Longitude (E)	Water depth (m)	Length (cm)	Physiography
94PC-2	37°50.8'	129°35.6'	1302	861	Lower slope
95PC-1	36°03.9'	130°59.4'	1634	940	Lower slope
95PC-4	37°15.2'	131°06.3'	2197	985	Basin plain
96EBP-4	37°46.1'	131°23.6'	1413	1110	Seamount slope
MB98PC-4	36°40.4'	129°39.6'	199	1156	Hupo Bank
MB98PC-7	36°40.8'	130°09.8'	2156	958	Slope

Fig. 2. Columnar logs of cores with AMS and tephra age. Tephra ages are based on Chun *et al.* (1997).

Table 2. Age control points of each core.

Core ID	Depth (cm)	Ulleung-II	AT Ash	AMS Age (kyr)
94PC-2	110			1.75 ± 50
	250			20.1 ± 95
	570			24.4 ± 110
95PC-1		9.3		
	168			10.4 ± 60
95PC-4	225	9.3		
	250			14.86
	290			15.09
	590		24	
96EBP-4	50	9.3		
	100		24	
MB98PC-4	720	9.3		
MB98PC-7	240	9.3		
	480		24	

variation in sedimentation rates is characteristic of these cores.

4. Results and discussion

Major element contents and geochemical units

The three components (terrigenous clastic, organic, and biogenic carbonate) of each sediment aliquot provide information about sedimentation and paleoceanographic variation. It is well known that major element concentrations of sediment differ markedly between glacial and interglacial periods. Strong winds at intermediate latitudes during glacial intervals result in high terrigenous sediment flux to the ocean. The sources of this terrigenous sediment can be identified from geochemical signatures. Ti and Al are considered to be typical terrigenous elements, and can be used to discriminate the provenance of terrigenous material (Goldberg and Arrhenius 1958; Spears and Kanris-Sotirios 1976; Moorby 1983). Bhatt (1974) used the Ti/Al ratio as a climatic indicator. In a terrigenous clastic succession, the ratio is essentially a function of the quartz content, and thus of the energy of the depositional
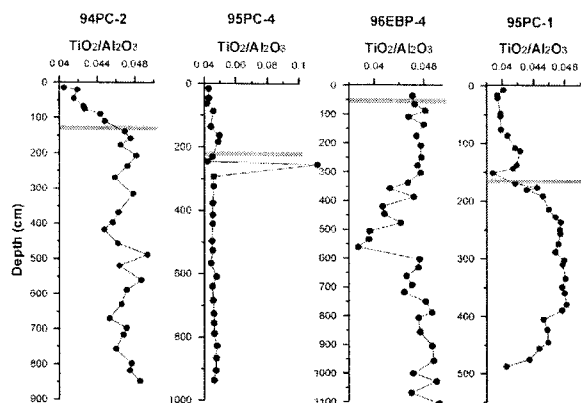
Fig. 3. The vertical variability of the TiO₂/Al₂O₃ ratio in four cores. Horizontal lines are the estimated Holocene boundary.

environment.

In East Sea sediment, the TiO_2/Al_2O_3 ratio varies significantly (from about 0.030 to 0.050) between the glacial period and the Holocene (Fig. 3). Comparatively low values during the Holocene contrast with high values in glacial-interval sediment from cores 94PC-2, 95PC-1 and 95PC-4 (Fig. 3) across a distinct compositional boundary. The sediments fall, therefore, into two geochemical groups that are also temporally delimited; their different compositions likely reflect variable source material and different depositional conditions, which might be the result of climatic variations.

Comparatively uniform major element concentrations in 95PC-1 and 95PC-4 throughout the Holocene suggest that climatic and oceanographic conditions were stable throughout this time. Like the Ti/Al ratio, this suggests that sediment composition in the East Sea cores is strongly associated with climatic variation.

Organic matter and calcium carbonate records

The amount of organic matter in sediment is dependent not only on productivity at the ocean surface but also on its origin, preservation, and diagenetic history (Muller and Suess 1979; Stein 1990, 1991). The TC and TOC curves for the six cores are all characterized by an inflection point at base of the Holocene, but exhibit contrasting patterns at the beginning of the Holocene that suggest abrupt and geographically variable oceanographic changes (Fig. 4). In 95PC-1 and 98PC-7, TC and TOC increase abruptly at the beginning of the Holocene, and then remain comparatively constant throughout the rest of the Holocene. Distinct drops of TC and TOC around the Holocene boundary are evident in 98PC-4, 95PC-4 and 95PC-1 (Fig. 4). The ratio of total organic carbon to total nitrogen (C/N ratio) is commonly used to determine the origin of organic matter (Fig. 5; Muller 1977; Muller and Suess 1979; Stein 1990, 1991): high C/N ratios are characteristic of continental organic matter, as opposed to marine organic matter. In 95PC-1 and 98PC-4, the C/N ratio is high (>10) throughout the glacial interval,
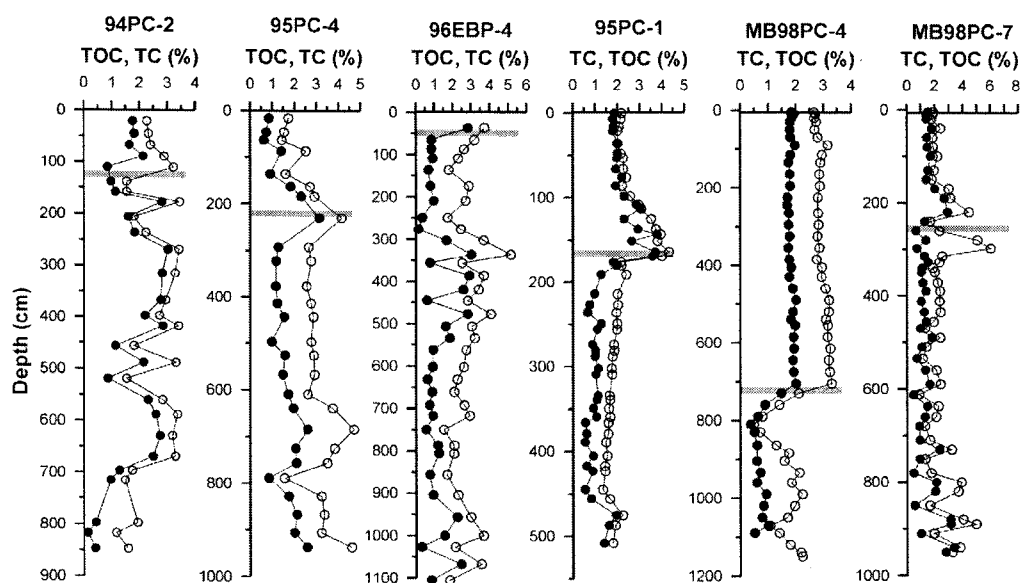

Fig. 4. Variability in the total organic carbon and total carbon in the six cores. Open circle and black circles indicate TC and TOC, respectively. Horizontal lines are the Holocene boundary.

indicating a terrigenous origin. In 95PC-1, the C/N ratio in glacial-age sediment below the base of the Holocene fluctuates between 7 and 15, and generally exceeds 10, but remains below 10 above the base of the Holocene. This suggests that larger amounts of continental organic material reached the area during glacial times than during the Holocene. The sharpest upward decrease in the C/N ratio is at the boundary of the Holocene in 98PC-4; the ratio is consistently below 10 in 98PC-7, although it fluctuates considerably. The generally higher continental organic contribution in glacial-age sediment supports the interpretation of greater allochthonous (terrigenous clastic) influx during glacial and transitional times, and implies that autochthonous material must form a comparatively
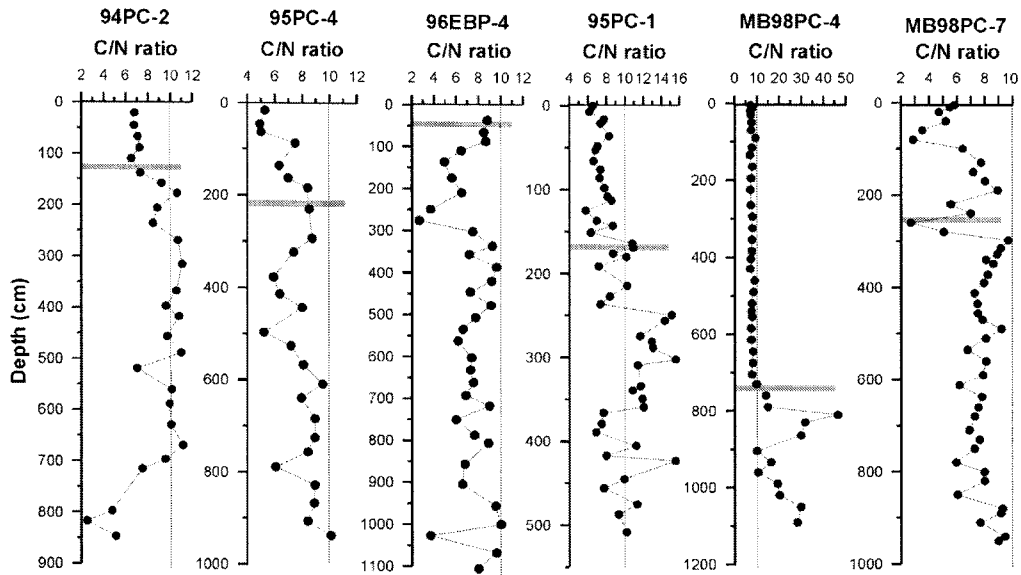

Fig. 5. C/N ratio variation in the core. Vertical lines indicate a C/N ratio of 10. The C/N ratio was greater than 10 during the glacial periods in 94PC-2, 95PC-1, and 98PC-4. Horizontal lines are the Holocene boundary.
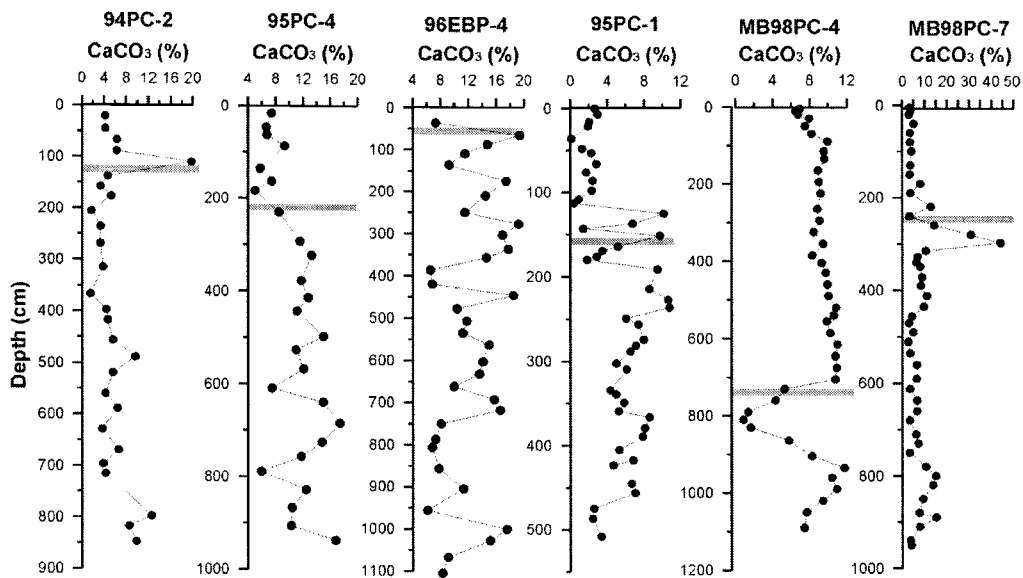

Fig. 6. Vertical fluctuations in $CaCO_3$ (%) in the core. Large variation in the carbonate contents is seen at the boundary of the Holocene. Horizontal lines are the Holocene boundary.

greater proportion of Holocene sediment. The carbonate content curves are similar to those for organic matter and also serve to distinguish Holocene from glacial-age sediment. Holocene carbonate contents are roughly constant: they are less than 3% in 95PC-1, fluctuate between 5 and 9% in 98PC-4, and are about 4% in 98PC-7 (Fig. 6). Carbonate contents are significantly higher during the glacial interval in 95PC-1, exhibit a striking contrast with constant Holocene values in 98PC-4, and increase abruptly at the base of the Holocene in 98PC-7 (Fig. 6).

The carbonate content of sediment is controlled by factors such as surface production, dissolution, and dilution by terrigenous material. Biogenic carbonates are easily dissolved as they fall through the water column, and can be diluted by fine terrigenous material carried by bottom currents or supplied by aeolian dust. In a pelagic setting, carbonate production is proportional to total organic carbon, and carbonate content can be used as an indicator of surface carbonate production (Broecker and Peng 1982). In East Sea sediment, carbonate is not likely to have been affected by dissolution, because the water is not very deep: the carbonate compensation depth (CCD)
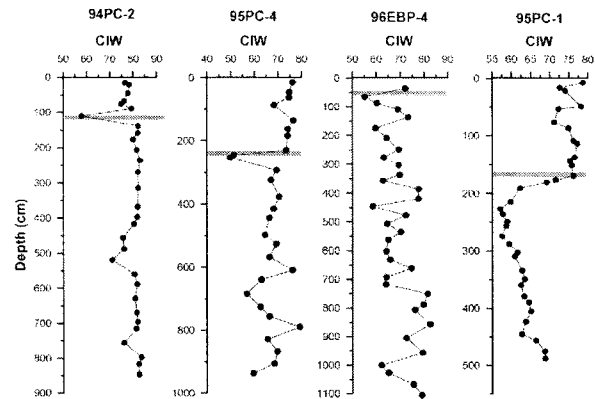

Fig. 7. Vertical variation in the chemical index of weathering (CIW) of the four cores. The horizontal bars indicate the Holocene boundary.

in the East Sea is between 1,500 and 2,000 meters depth (Ichikura and Ujiie 1976). The changes in carbonate content evident at the Holocene boundary in 95PC-1 and 98PC-7 are probably the result of variable surface production or supply from neighboring continents. The low carbonate content at the Holocene boundary in 98PC-
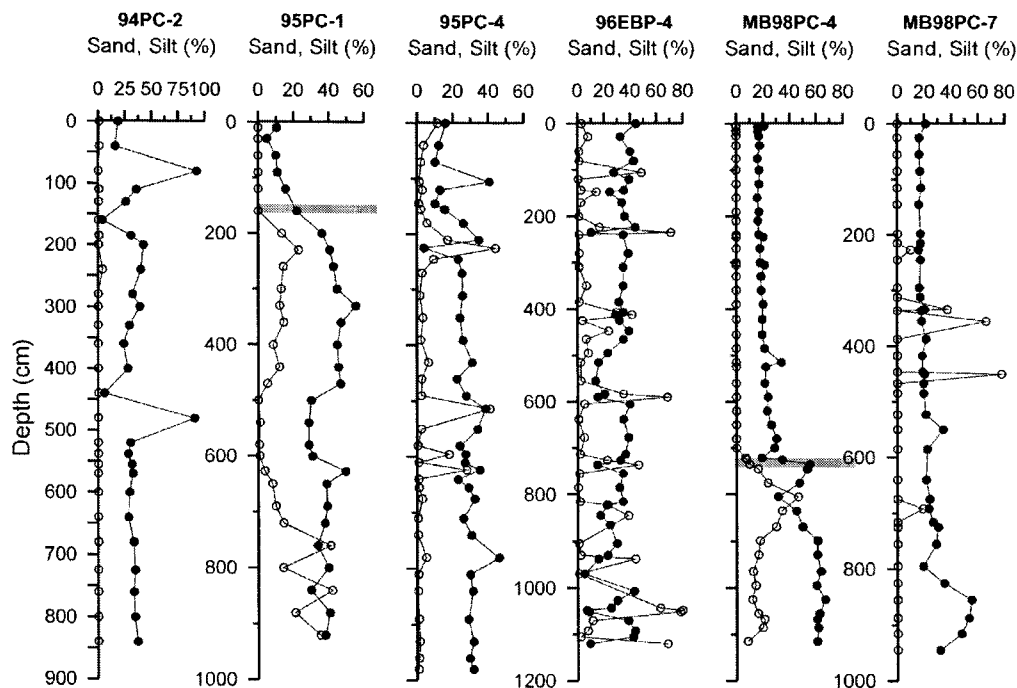

Fig. 8. The results of grain size analysis. Open circles and solid circles indicate sand and silt fractions, respectively. There is a slight increase in the silt fraction during the glacial period in 98PC-4 and 95PC-1. The horizontal lines are the Holocene boundary.

4 is probably because of dilution by terrigenous clastic material or reduced carbonate production.

Chemical index of weathering (CIW)

The terrigenous fraction of bulk sediments commonly has several sources, including aeolian dust and volcanic material. Sediment composition is, therefore, very useful for determining both source area and paleoclimatic parameters. To evaluate these, the chemical index of weathering (CIW; Harnouis 1988) and grain size are used. The CIW is calculated from major element concentrations, and indicates the degree of weathering in the source area. In the formula for the CIW, sodium and calcium are considered typical mobile elements in weathering; thus, these elements are the most useful for characterizing the provenance of sediment (Nesbitt and Young 1982; Harnouis 1988). Lower CIW values of sediment indicate a well-weathered sediment source. Differences in CIW are considered to reflect different sediment sources or climatic change.

As shown in Fig. 7, the CIW varies with depth in the four selected cores. The most significant aspect of the CIW is the difference in values for Holocene and glacial interval sediment. Distinct changes in CIW are seen in cores 95PC-1 and 95PC-4, whereas the patterns in the others are obscure. In 95PC-1, the CIW curve is characterized by constant values during the Holocene, and a steep downward decrease near the base of the Holocene. A distinctly lower CIW at a depth of 220 cm (probably the last glacial maximum, as deduced from the mean sedimentation rate) indicates that well-weathered siliciclastic material was supplied, probably by intense winds, and that relatively large amounts of mobile elements, such as Na and Ca, were supplied from the neighboring continent. In 95PC-4, the CIW gradually decreases down-core until approximately 24 kyr (about 600 cm depth). The silt fraction is higher during the glacial period in 95PC-1 and 95PC-4 (Fig. 8). Grain size variations in 95PC-1 clearly indicate that a large amount of silt-sized sediment was supplied during the glacial period (Fig. 9). Large amounts of aeolian quartz and carbonate are known to have been supplied to the East Sea during the last glacial period (Dersch and Stein 1994; Oba and Pedersen 1999).

Climatic and paleoceanographic variation inferred from chemical data

Sediment from the East Sea contains unique information on paleoceanographic and paleoclimatic history, which can be deciphered by analysis of sediment composition,
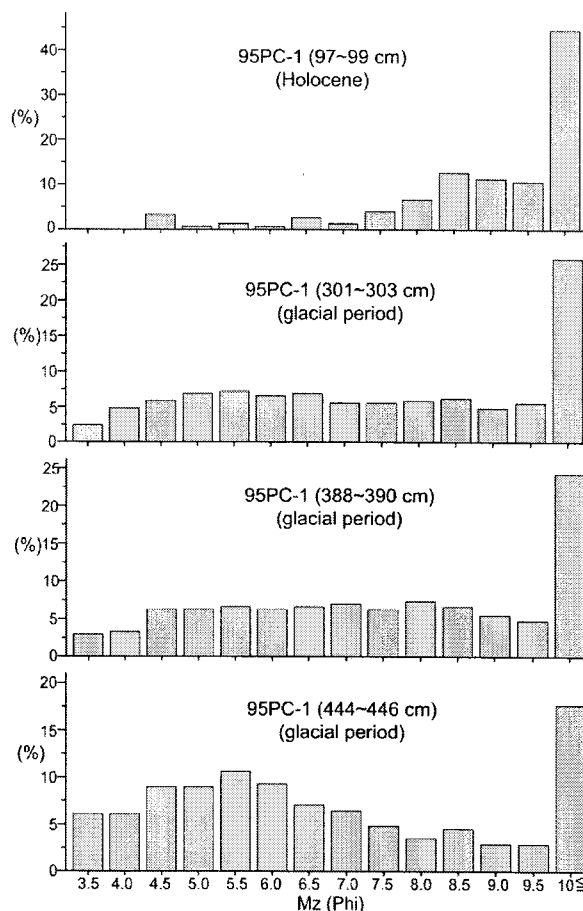

Fig. 9. Histograms of grain size analysis in 95PC-1. The silt fraction is significantly higher (4.5 – 8.5 phi) in the lower layer compared to the upper layer (97 – 99 cm), which corresponds to the Holocene interval.

particularly of the terrigenous fraction.

The chemical composition of aeolian dust supplied from the Asian landmass has been characterized (e.g., Windom 1975; Rea and Janecek 1982; Taylor *et al.* 1983; Rea 1990), and the flux of loess from China has been demonstrated to be directly linked to climatic variation, based on the marine planktonic oxygen-isotope record and quartz content of the North Pacific (Hoven *et al.* 1989). Dramatic shifts in the supply of aeolian sediment to the East Sea (Dersch and Stein 1994) reflect glacial-interglacial climate cycles.

The CIW of sediment in the four cores shows quite different patterns for glacial and Holocene periods. During the glacial interval, large volumes of well-weathered mobile elements, such as potassium and calcium, contained in siliciclastic materials, were supplied from inland China.

A pronounced geochemical boundary in East Sea sediment cores marks the end of this episode. Sediment composition in the East Sea reflects paleoclimatological and paleoceanographic variations, both of which are to some extent controlled by eustatic sea-level changes.

5. Summary

Geochemical data lead to the following conclusions regarding paleoceanographic changes and their relation to paleoclimate during the last glacial and interglacial periods.

1. Changes in the concentrations of most major elements are clear evident at the Holocene boundary, indicating that Holocene and glacial-age sediment composition differed. This suggests that the source of terrigenous material was different in the Holocene than in the last glacial maximum.

2. Variations in organic carbon content, carbonate content, and C/N ratio support the interpretation of changing sediment sources, and suggest that paleoceanographic changes took place during the transition between the last glacial period and the Holocene.

3. The chemical index of weathering (CIW) also supports the interpretation of different terrigenous sediment sources during the glacial and Holocene. Considerable paleoclimatic variation is evident at the base of the Holocene.

Acknowledgments

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