Transgressive Geochemical Records in the East China Sea: A Perspective with Holocene Paleoceanography

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Geochemical and sedimentological analyses of sediment piston core were used to trace paleoceanographic environmental changes in the East China Sea. The analytical results revealed three lithostratigraphic units (I, II, and III) corresponding to a highstand stage, a transgressive stage, and a lowstand stage, respectively. Accelerator mass spectrometry (AMS) 14C dated the boundaries between the units as 7 ka and 11 ka. That is, Unit I extended from the present to 7 ka, Unit II occupied a transitional episode from 7 to 11 ka, and Unit III was older than 11 ka. The transitional episode was characterized by sudden fluctuations in various geochemical proxies. Most strikingly, there was a gradual upward increase in both carbonate and total organic carbon (TOC) contents post-7 ka, during which time the δ13C values of organic material increased to a constant value. The gradual upward increase in the TOC and CaCO3 contents in Unit I were accompanied by slight variations in grain size that probably reflect a stable modern oceanographic environment. Within Unit II (7 to 11 ka), the geochemical signals were characterized by abrupt and steep fluctuations, typical of a transgressive stage. Vertical mixing may have provoked an increase in productivity during this interval, with large amounts of terrigenous organic matter and/or freshwater being supplied by neighboring rivers. The geochemical signals remained stable throughout Unit III but exhibited different patterns than signals in Unit I. The high terrigenous organic matter content of Unit III suggests correspondence to a lowstand stage.

Key words: East China Sea, paleoceanography, geochemical records, glacial and interglacial periods

1. Introduction

The East China Sea (ECS) is a typical shallow marine continental shelf, where large amounts of sediment supplied by numerous rivers have been deposited over pre-existing relict sediments (Beardsley et al., 1985; Milliman et al., 1985a; Alexander et al., 1991). Since the last glacial maximum (LGM), the sea level has gradually risen about 130 m to its present position (Emery and Aubrey, 1986; Fairbank et al., 1989). Given that the average depth of the East China Sea is generally less than 100 m, the present continental shelf was presumably exposed as a coastal or a tidal environment during the LGM. Consequently, enormous volume of terrigenous sediments supplied by regional rivers is an important source for the hemipelagic sediments of this study (Milliman et al., 1985a; Milliman et al., 1985b; Lee and Chough, 1989; Zhang, J., 1999).

Also, ECS has experienced a rapid retreat of coastline during the postglacial sea-level rise. Along with this paleoceanographic changes, a high-resolution study of the Holocene deposits should provide insight into Holocene paleoceanography. Relatively a lot of studies concerning the paleoenvironmental evolutions in ECS were conducted in terms of step-wise variation in paleoceanographic and stratigraphic variation (Yoo et al., 2002; Ijiri et al., 2005) and current-related environmental changes (Xu and Oda, 1999; Jine et al., 2000). Most significant environmental changes were caused by the changes in sea-level during transgressive period. However, there are very few high-resolution geochemical data from that period. Sediment piston cores were collected from the northeastern East China Sea to obtain a high-resolution record of any paleoenvironmental changes that accompanied the last sea level rise. The purpose of this research is to provide a detailed geochemical record of the transgressive period and

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to examine the data in relation to Holocene paleoceanographic changes.

2. Geological and oceanographic setting

The East China Sea (ECS) is a marginal sea basin of the West Pacific, considered to be an epicontinental area. The position of the ECS between the East Asia landmass and the western Pacific suggests sensitivity to both terrestrial and oceanic environmental changes. The shallow average water depth of less than 100 m means that much of the bottom topography of the ECS was subaerially exposed during glacial times when the sea level was approximately 120 m lower than today. Consequently, the paleoceanographic evolution of the ECS during the post-glacial transgression is likely expressed through both sedimentary and environmental changes.

A branch of the Kuroshio Current flows over study area and enter the Yellow Sea and the East Sea through the Korea Strait. At present ECS is occupied by the open-sea water mass with high temperature and salinity due to the influence of the Kuroshio Current. It is well known that the present hydrographic condition is subdivided into three type; open ocean type with high temperature and high salinity, coastal water type of low temperature and low salinity. Between above two types, there is a mixing zone. The core site is just located under the pathway of the Kuroshio Current. Therefore, this core can provide detailed paleoenvironmental changes, which are closely related to sea-level changes.
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3. Materials and methods

A 560cm long core (EEZ02-PC20) was collected (31°55'020", 126°42'048") from the eastern China Sea (107 m water depth) during the cruise of EEZ 02 by Korea Ocean Research and Development Institute (KORDI) (Fig. 1 and Fig. 2). Core sediment was divided to provide aliquots for each of the required analyses: grain-size, organic carbon, carbonate, metal concentrations, and carbon and nitrogen isotopic ratios in organic matter. After the bulk sediments were separated into sand and mud fractions grain size analysis was conducted by the pipette methods and grain-size parameters were calculated following the method of Fork and Words (1957). Total organic carbon (TOC), total nitrogen (TN) and total sulfur (TS) were analyzed using a CHNS analyzer, (EA 1112) at the KORDI. Total carbon (TC) contents were determined using untreated powdered samples. TOC was measured after treatment with 1N hydrochloric acid. Carbonate contents were calculated using the weight difference between TC and TOC as follows: carbonate content (\%)=(TC (%)-TOC (%)) *8.33. TS contents were obtained directly from the CHNS results. Analyses of the elemental concentrations in the bulk sediments were undertaken using an inductively coupled plasma spectrometer (ICP) at the Korean Basic Science Institute (KBSI). Samples were digested with a mixture of hydrofluoric acid (HF), perchloric acid (HClO₄), and nitric acid (HNO₃) after drying at 105°C for 24 hr following grinding. The carbon and nitrogen isotope ratios of the organic matter were analyzed at the laboratory of Iso-Analytical Ltd, UK. The analytical results were referenced to standards. All analytical errors were less than 10% for CaCO₃, TOC, and TS, and less than 5% for major and minor elements. Five AMS ¹⁴C age dating were conducted using benthic foraminiferas and a peat fragment at the Beta Analytical Radiocarbon Dating Lab. of USA (Table 1).

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Materials</th>
<th>Ages (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>benthic foraminifera</td>
<td>2860±40</td>
</tr>
<tr>
<td>50</td>
<td>benthic foraminifera</td>
<td>4880±40</td>
</tr>
<tr>
<td>100</td>
<td>benthic foraminifera</td>
<td>7090±40</td>
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<tr>
<td>200</td>
<td>benthic foraminifera</td>
<td>7140±40</td>
</tr>
<tr>
<td>350</td>
<td>peat fragment</td>
<td>12650±40</td>
</tr>
</tbody>
</table>

4. Results and discussion

4.1. Grain size and sedimentological aspects, inorganic geochemistry

A visual examination of the core clearly showed lithographic changes at relatively sharp boundaries at 50 and 230 cm depths. Distinct differences in the sedimentological and geochemical characters at these horizons allowed the sedimentary sequence to be divided into lithostratigraphic units I, II, and III in descending order (Fig. 2).

As illustrated in Fig. 3 the mean grain size varied from 2.5 to about 8.5 phi corresponding to a range from medium sand to clay. A pronounced break occurred at 7 ka, after which time there was an upward fining in mean grain size pointing to oceanographic conditions remaining relatively constant over the last 7 ka. The upward fining grain size in Unit I implies a gradual change in the supply of fine sediment that has continued until present. The grain size of sediments is important in interpreting sedimentological environmental changes.
Fig. 3. Vertical variation in mean grain size (left) and mean grain-size vs. sorting coefficient, skewness and kurtosis of the cores. Sediments of the core 20 are composed of medium sand to clay size particles. Note the gradual upward fining in mean grain size since 7 ka (shaded zone).

Fig. 4. Vertical variation of Ti/Al, and other major and minor elements. Distinctive three layers are recognized. Shadow area indicates transgressive period.

Especially, the textural parameters show wide variation in the sorting coefficient, skewness, and kurtosis such that the distinctive upward fining in mean grain size is the most important characteristic of the
core sediments. In contrast, a large fluctuation in mean grain size occurred during the transgressive episode from 11 to 7 ka when large amounts of suspended material were transported by the Changjiang (Yangtze River). This suspended sediment load was discharged into the study area throughout the Holocene and the transgressive phase.

Variations in the concentrations of major and minor elements and their ratios can be expected given the compositional variations occurring in the large amount of suspended fine sediment transported to the site. The ratio of two typical conservative elements, Al and Ti, gradually decreased upwards from 7 ka (Fig. 4). Other elements also showed discontinuities at this point that presumably reflect differing sediment sources as well as changes in oceanic circulation. Along with the trend in Ti/Al, vertical excursions occurred in Fe, Mg, Ba, Mn, Cr, and V (Fig. 4) that allowed the entire sediment column to be divided into three units with distinctive boundaries at 7 ka and 11 or 12 ka, corresponding to highstand (post-7 ka), transgressive, and lowstand sedimentological environments.

Numerous attempts have been made to discriminate sediment sources in the East China Sea and Yellow Sea using geochemical parameters (Cho et al., 1999). Cho et al. (1999), for example, used elemental ratios including V/Al and Mn/Al. In this study geochemical proxies failed to indicate specific sources but did exhibit clear variations that could be used to subdivide the sediment column into three stages; highstand, transgressive, and lowstand stages (Fig. 4). Following the boundary at 7 ka, Fe, Mg, Mn, Cr, and V showed a gradual upward increase, whereas Ba and Ti/Al decreased. Between 7 and 11 ka there were insufficient data points, but this interval was considered a buffer or bridge zone between the upper and lower units.

Each unit was characterized by specific excursions of geochemical proxies reflecting a highstand stage, a transgressive stage, and a lowstand or exposed stage for units I, II, and III, respectively. Yoo et al. (2002) divided the sedimentary sequence deposited in this area after the last glacial maximum into five sedimentary units. They regarded these units as the products of a transgressive and a highstand system. Our study did not allow for any clear-cut correlations to be made.

4.2. Organic and carbonate content, C/N and C/S ratios

The total organic carbon content (TOC) of the cores were <1%, and the carbonate contents were <20%. The TOC contents were relatively low and varied proportionally with grain size; the coarser the grains, the lower the TOC. There was a gradual upward increase in TOC above 7 ka with marked fluctuations occurring during the transgressive and lowstand intervals. The carbonate contents remained relatively constant in units II and III but exhibited a significant upward increase above 7 ka. Both the C/N ratio and the $\Delta^{13}$C values of the organic matters displayed abrupt changes at 7 ka, which marked the divergence of two distinct compositional patterns. The abrupt changes in all these geochemical proxies above and below 7 ka imply that significant paleoceanographic changes occurred in the area coincident with the sedimentological changes.

The organic carbon content of sediments is controlled by surface biogenic productivity, changes in the extent of organic carbon preservation, and input from terrigenous organic sources (Stein, 1990). Also, the C/N ratio of organic matter can be used to identify different provenances (Stein, 1990; 1991; Muller, 1997; Muller and Suess, 1979). Sedimentary organic matters originating from marine sources typically have a C/N ratio of <10 in contrast to those from terrigenous sources that have a C/N ratio of >10. The C/N ratios of the organic content from the present cores fell into three distinct groups (Fig. 5 and 6). Below 11 ka the C/N ratio was always >10. After 7 ka the ratio was <10. Between 7 and 11 ka the ratio fluctuated from 7 to 12. Clearly, large amounts of terrigenous organic matter were initially supplied from the neighboring continent, but during the transgressive period increasing amounts of organic material came from highly productive marine sources, and the two contributions were admixed via active circulation.

The variation in biogenic carbonate contents of the sediment can be attributed to carbonate production or carbonate dissolution in significantly anoxic bottom conditions. The carbonate content of the present cores could be divided into two distinct horizons, although other geochemical and sedimentological proxies pointed to the presence of three units. There was an abrupt change above 7 ka marked by a sudden increase in carbonate
content. Below this level the carbonate content was very low and generally constant. Low carbonate contents in relatively shallow and rapidly accumulating sediments have been reported previously (Emerson and Berner, 1982; Berelson et al., 1990). The evolution of dissolved carbon dioxide from oxidation of organic material results in an increase in in situ dissolution of carbonate, i.e., relatively low carbonate contents in the sediment can arise where anoxic or hypoxic bottom water conditions prevail. However, the low carbonate content in the present cores is not believed to have resulted from such a diagenetic mechanism. If Unit III represents a lowstand episode during which the area was exposed subaerially, then the very low carbonate content may simply represent the extremely limited carbonate production during this time.

The total organic carbon to total sulfur ratio (C/S ratio) of organic matter also provides valuable information as to the sedimentary and paleoceanographic environments (Leventhal, 1983; Berner, 1984; Kim et al., 1999). The C/S ratio of sediments in most marine environments is about 2.8, with a positive correlation between TC and TS (Berner and Raiswell, 1983). Figures 5 and 6 show that the C/S ratios of the cores varied between 1 and 12 and probably reflect a rapid accumulation of non-marine sediments prior to early diagenetic processes (Raiswell and Berner, 1986). The mixing of sediments from diverse sources could also have contributed to the disparity. Compared with the average C/S average ratio in marine sediments of 2.8, the ratio from fresh water environments is much higher as a result of a lower level of pyrite formation and the lower content of dissolved sulfate compared to seawater (Berner and Raiswell, 1984). Hence, the high C/S values recorded in this study may point to a freshwater supply of sediments or the rapid accumulation of non-marine
In particular, the carbon isotopic ratios of organic matter have been used as a proxy for paleoproductivity and atmospheric carbon dioxide levels, while nitrogen isotopic ratios have provided valuable data related to changes in the degree of nitrate utilization (Calvert et al., 1992; Fontugne and Calvert, 1992; Holmes et al., 1997). Consequently, the carbon and nitrogen isotopic ratio of the organic matter present in the East China Sea cores are expected to reflect environmental changes that occurred during the transgressive, low stand episodes and the Holocene.

As shown in Fig. 5, relatively high values of stable carbon isotopes and accompanying excursions have occurred since 7 ka, with smaller variations in isotopic ratios lower in the sediment cores. The δ¹³C values showed a gradual increase upwards in the cores, following a similar pattern to that of the TOC and carbonate contents. The two distinct patterns are most apparent in Fig. 7 and distinguish
two groups of sediments separated by approximately a 4 per mil difference in carbon isotopes and a 1.5 per mil difference in nitrogen isotopic values. The carbon isotope ratio displayed lower values during the Holocene but somewhat higher values during the transgressive episode. As with organic carbon, carbon isotope values have been used to determine the provenance of organic matter as well as to detect changes in productivity (Lehmann et al., 2002). Terrigenous sources exhibit lower values (-26 per mil) and consequently ten of the samples analyzed here are thought to derive from a terrigenous environment which is consistent with high C/N ratios >8 (Fig. 7). The higher values near -21 per mil, accompanied by low (<10) C/N ratio, are thought to have arisen from in situ productivity during the Holocene.

Alternations in carbon and nitrogen isotopic compositions of organic matter have been examined previously. In particular, it has been demonstrated that nitrogen isotope values change in accordance with sedimentary environments (Lehmann et al., 2002). A previous research has found that during anoxic conditions in the Holocene, nitrogen isotope values could decrease to about 3 per mil below initial values, while in oxic conditions these values could increase by 3 per mil (Emmer and Thunell, 2000). This dissimilarity between oxic and anoxic responses may be attributed to variations in the type, timing, and degree of microbial activity. In the present cores there was approximately a 1.5 per mil difference between values determined during the transgressive episode and those from the Holocene. This result may reflect differences in the type and degree of prevailing microbial activity, perhaps as a response to sea level rise since the LGM. Modern paleoceanographic conditions were established about 7 ka, after that time most geochemical signals used in this study were stable.

5. Conclusions

The sedimentology and geochemistry of the sediment cores showed clear compositional differences between the Holocene and the preceding transgressive episode that arose from changes in the sedimentary depositional environments following a gradual sea level rise since the LGM. The grain size characteristics were consistent with this interpretation. There was a distinct boundary between the upper and lower portions of the sedimentary sequence. The organic carbon content and C/N and C/S ratios of the core revealed marked variations throughout the sequence. During the transgressive episode, a large part of the organic content was derived from terrigenous sources, whereas organic matter was largely produced in situ by marine biota during the Holocene highstand. The carbon isotopic ratio of the organic matter confirmed the terrigenous provenance of these materials during the transgressive phase. The variations in carbon and nitrogen isotopes between the Holocene highstand and transgressive sediments also suggest that oceanographic evolution accompanied sea level rise. Stable and modern oceanographic conditions were established approximately 7 ka. The most important conclusion of this study is that geochemical data can provide valuable insight into a sequence of transgressive and Holocene paleoceanography.

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