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Major and trace element variations of the sediments at ODP Site 1144, South China Sea, during the last 230 ka and their paleoclimate implications

Gangjian Wei[a],*, Ying Liu[a], Xian-hua Li[a], Lei Shao[b], Dianyong Fang[b]

[a]*Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, State Key Lab. of Org. Geochemistry, Guangzhou, Wushan, GD 510640, China*
[b]*Laboratory of Marine Geology, Tongji University, Shanghai, 200092, China*

Abstract

We present here the major and trace element data of the sediments at ODP Site 1144 of the last 230 ka with time resolution about 1.5 kyr to investigate their relations to the climate changes. Estimated from TiO_2 and CaO contents, over 70% in weight of the sediments are terrestrial materials, and $CaCO_3$ abundance ranges between 7% and 19%. The variation patterns of some of the major elements, such as Al, Fe, K, Mg and Mn, and some of the trace elements, such as the alkali elements (such as Rb and Cs), the alkali earth elements (such as Ba) and most transition metals (such as Sc, V, Co, Cr, Zn), well match that of the oxygen isotopes of the planktonic foraminifer, after normalized with Ti, with higher values during interglacial periods and lower values during glacial periods. Whilst the Na abundance exhibits inverse variation patterns with lower values during interglacial periods and higher values during glacial periods. However, most refractory elements, such as Y, Zr, Nb, Hf, Ta, REEs, Th and U, do not show such patterns. These agree well with the behaviors of these elements during chemical weathering. Therefore, the changes of chemical weathering intensity in South China, the source area of these sediments may account for such variation patterns. During interglacials, wet and warm climate might occur at South China, which resulted in stronger chemical weathering, and dry climate might occur during glacials, which resulted in weaker chemical weathering. Such paleoclimate interpretation agrees with those from other paleoclimate proxies, such as pollen records, indicating that change of the East Asian monsoon, especially change of the winter monsoon is the key for such paleoclimate variation patterns.
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Keywords: South China Sea; Sediments; Major and trace elements; Paleoclimate

1. Introduction

Many paleoclimatic studies using chemical records in the marine sediments are concentrated

* Corresponding author. Tel.: +86 20 85290093; fax: +86 20 59290130.

E-mail address: gjwei@gig.ac.cn (G. Wei).

on the biogenic components, such as carbonate, opal, organic carbon, (Elderfield, 1990) and Ba (Dymond et al., 1992), and authigenic elements such as Mn (Mangini et al., 1990) and scavenged Al (Leinen and Pisias, 1984; Murray and Leinen, 1993). However, many of the major and trace elements are mainly associated with terrigenous materials in marine sediments (Goldberg and Arrhenius, 1958), especially for those sediments which are not dominated by biogenic components. Paleoclimatic records reconstructed on these elements are rare. Several studies on the variation of these elements in sedimentary rocks and marine sediments had revealed the change of the chemical weathering in source areas and shown the climate change in ancient time (Nesbitt and Young, 1982; Kronberg et al., 1986). However, in most of the paleoclimatic studies, especially for those studies concerning the climate change in orbital time scale, these element records in marine sediments are rarely included in the related discussion.

In the South China Sea, the Al/Ti, Sc/Ti and K/Ti ratios of the terrestrial components of the sediments from ODP Site 1144 exhibit very similar variation patterns with the oxygen isotopes of the planktonic foraminifer, indicating close relationship with climate change (Wei et al., 2003a). As all these four elements are associated with terrigenous materials in marine sediments, the well-presented climate-related patterns of these ratios indicate that the elements mostly associated with terrigenous materials are valuable proxies for paleoclimate. Former studies based on the records of Al, Sc, Ti and K indicate that changes of the chemical weathering in source areas, and the grain-size sorting during transportation may account for the climate related patterns (Wei et al., 2003a). The change of the chemical weathering may be associated with the climate changes in provenance areas. South China is believed to be the main source of the sediments in the northern part of the South China Sea since Miocene, as revealed by provenance studies on ODP Site 1144 and ODP Site 1148 sediment records (Shao et al., 2001; Li et al., 2003). If chemical weathering is the key role, the element records of the ODP 1144 sediments can be used as a proxy of climate changes in South China. If grain-size sorting is the key role, these element records may proxy the

changes of the hydraulic condition, which could be related to the changes of the sea level in the northern part of the South China Sea. Both of them are valuable climate/environment records. However, they have different paleoclimate implications.

The climate in the South China Sea and South China is largely controlled by East Asian Monsoon. Former studies on the pollen of the sediments in the northern South China Sea indicate warm and wet climate during interglacials and cold and dry climate during glacials in South China (Sun and Li, 1999; Sun et al., 2003). Also, studies on clay minerals reveal that chemical weathering in the land north of the South China Sea is strong during interglacials and weak during glacials (Tamburini et al., 2003). All they reach a conclusion that summer monsoon is strengthened during interglacials and winter monsoon is strengthened during glacials (Sun et al., 2003; Tamburini et al., 2003). On the other hand, sea-level changes within glacial/interglacial cycles can significantly change the landform at the margin of the South China Sea (Wang, 1999), resulting in the open/close of the gateway in northeast (Taiwan Strait) and south (Sunda shelf). Transportation of the sediments should be changed significantly as the sedimentation rates differ remarkably between glacials and interglacials in many parts of the South China Sea (Wang, 1999). These may possibly cause the change of the sources of the sediments and result in change of the chemical components. Seeking insight of the relationship between chemical components and the climate and environment change (change of the chemical weathering in source areas or transportation source/path) may reach a more definite conclusion. This may help to better understand the climate and environment changes in this area.

In this paper, we present the major and trace element records of the bulk sediments from the top 163 mcd (meters composite depth) at ODP Site 1144. By comparing the similarities and differences of the behaviors of different elements within glacial/interglacial cycles, we can find more details about how these elements vary with climate changes. This may help to find the general control on these element records and further to better understand the climate changes in South China/the Northern part of the South China Sea.

2. Samples and analytical methods

The sediment cores were drilled at ODP Site 1144 (20°3.18′ N, 117°25.14′ E, at water depth of 2037 m, Fig. 1) during Leg 184. The length for hole A at ODP Site 1144 is up to 452.8 m, covering the last 1.1 Ma (Shipboard Scientific Party, 2000). Sedimentary rate of the top 220 mcd is 847.6 m/myr (Shipboard Scientific Party, 2000), which is significantly higher than most of the other sediment cores drilled at SCS (Wang, 1999). We focused on the top 163 mcd, which spans the last 230 ka, and covers a whole glacial/interglacial cycle. This enables us to investigate the relationship between the element records and climate changes.

All samples were supplied from Ocean Drilling Program (ODP). The analyzed sample was gathered one for every section from the top to core 17H of 1144A. Sampling interval was about 1.3 m on average, yielding a time resolution of about 1.5 ka. The bulk sediment samples were dried at 80 °C, ground to powder, then baked at 670 °C for 30 min to destroy organic matters. The sediment samples, together with a series of Chinese and USGS rock and sediment standards, were digested with $HF+HNO_3$ mix acid. Major elements were measured on a Varian Vista inductively coupled plasma atomic
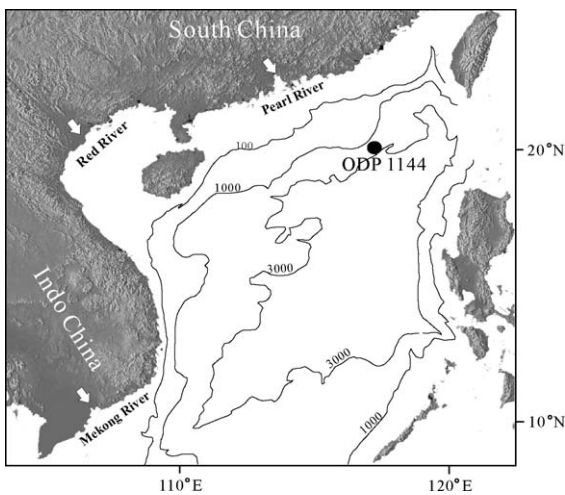

Fig. 1. Location of the ODP Site 1144. The image shows the continent and islands. The curves mark the 100-, 1000- and 3000-m isobaths. The arrows mark the mouth of the major river to the South China Sea: the Pearl River, the Mekong River and the Red River.

emission spectrometry (ICP-AES) in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, and trace elements were measured on a PE Elan 6000 inductively coupled plasma mass spectrometry (ICP-MS) in the same laboratory. Details of the chemical treatment and machine measurement refer to Liu et al. (1996), Li et al. (2002) and Wei et al. (2003a). Analytical precision is generally better than 1–2% for major elements and 1–3% for trace elements. Data of the samples including Al, Sc, Ti and K, which had been reported in Wei et al. (2003a), could be found in an attached Excel data sheet. The major elements are described as oxides, the total Fe denoted as FeO(T). SiO_2 was not measured, because our samples were digested with HF acid.

The preliminary age model constructed on the oxygen isotopes of G. ruber and some AMS ^{14}C dating for the sediments of ODP site 1144 is available from Buehring et al. (2003). According to this age model, the samples analyzed in this study date back to the last 230 ka. They cover the time period from prior to stage 7.4 (at 158.75 mcd) to the present and two entire glacial/interglacial cycles are involved. Linear sedimentary rates (LSRs) estimated from this age model are MIS 1: 0.69 m/kyr, MIS 2: 1.57 m/kyr, MIS 3: 1.14 m/kyr, MIS 4: 0.98 m/kyr, MIS 5: 0.56 m/kyr, MIS 6: 0.53 m/kyr, MIS 7: 0.38 m/kyr and the average of MIS 2–MIS 4 is 1.18 m/kyr. The maximum accumulation rate occurs in the last glacial, and the accumulation rates during glacials are generally larger than those during interglacials, which agree with many other areas in South China Sea (Wang, 1999).

3. Results

3.1. Major elements

Concentrations of some elements, such as Na, Mg, K, Ca and Sr, are high in the interstitial water of the ODP 1144 sediments, and the water content of these sediments is high too (Shipboard Scientific Party, 2000). Therefore, interstitial water may contribute significantly to the concentrations of these elements of the dry bulk sediments. The contributions of the interstitial water to the bulk dry

sediments for a single element can be estimated from the available shipboard MAD (moisture and density) data of mass of dry sediments (M_d), mass of pore water (M_{pw}) and concentrations of interstitial water (C_{iw}) as: $C_{iw} \times M_{pw}/M_d$. The sampling intervals of the shipboard MAD data are different from our sampling intervals for the element measurement (Shipboard Scientific Party, 2000). We calculate the corresponding M_d, M_{pw} and C_{iw} data of the element measurement samples using linear interpolate method from the available shipboard MAD data. The corrected concentrations of Na_2O, MgO, K_2O, CaO and Sr, together with the uncorrected results are shown in Fig. 2. The maximum correction occurs for Na because the Na^+ concentrations in the interstitial water are the highest, over 450 mM. The corrections for samples at the top 60 mcd are generally higher than those bellow due to their higher water contents. According to the corrections, the interstitial water contributes 30–70% of the total Na_2O concentrations of the dry bulk sediments at the top 60 mcd and 2–13% for MgO. In contrast, such contribution for K_2O, CaO and Sr are very small, only about 0.5–3.5%, 0.1–1.4% and 1–3%, respectively, which are mostly within the analytical errors of these elements.

Generally, terrestrial materials and carbonate are the major components of the sediments from South China Sea. The terrigenous abundance can be estimated from the Ti concentration of the bulk sediments assuming that all Ti is of terrigenous origin (Schroeder et al., 1997). Similarly, the carbonate abundance can be estimated from the bulk CaO abundance by substracting the terrigenous CaO assuming that the CaO/TiO_2 ratios are constant in terrigenous matters (Murray et al., 2000).

$$\%\text{Terrigenous} = (\text{Ti}_{sample}/\text{Ti}_{Ter}) \times 100 \qquad (1)$$

$$\%\text{CaCO}_3 = 1.79 \times \%\text{CaO}_{bulk} - \%\text{TiO}_{2-bulk} \\ \times (\text{CaO}/\text{TiO}_2)_{Ter}] \qquad (2)$$

Where Ti_{Ter} and $(\text{CaO}/\text{TiO}_2)_{Ter}$ denote the Ti contents and CaO/TiO_2 ratios of the terrigeneous background of these sediments, respectively. The terrigeneous background of ODP 1144 sediments can be estimated from the compositions of their acid leached components, which provide an average

of 0.96 wt.% for TiO_2 abundance and 0.44 for CaO/TiO_2 ratios (Wei et al., 2003a).

Using these terrigeneous background data, the terrigenous abundance and $CaCO_3$ abundance of these sediments were calculated from their bulk TiO_2 and CaO abundance. The results indicate that over 70% of these sediments were made up of terrestrial materials. The terrigenous abundance generally ranges within 70 and 80 wt.% except for several spikes, giving an average of 77 wt.%. The $CaCO_3$ abundance ranges between 7 and 19 wt.% with an average of 11.4 wt.% (Fig. 3). The calculated $CaCO_3$ abundance was in good agreement with the shipboard $CaCO_3$ abundance data which are shown in Fig. 3 too (Shipboard Scientific Party, 2000), indicating that the calculations were reliable.

The oxygen isotope records of planktonic foraminifer G. ruber (Buehring et al., 2003) included in Fig. 3 shows the climate variation patterns. The $CaCO_3$ abundance shows higher values during interglacials and lower values during glacials in general, and is consistent with the general carbonate patterns in the South China Sea (Wang, 1999). However, the variations of the terrigenous abundance within glacial/interglacial cycles are very small. Generally, the relative variations of the terrigenous abundance are less than 10% and most of the significant changes of the terrigenous abundance do not occur at the main climatic change boundaries (Fig. 2). Also, the average of the terrigenous abundance during glacials (74%) does not differ much from that during the interglacials (75%). Therefore, the terrigenous abundance of the sediments from ODP Site 1144 seem not closely related to climate change.

However, when we transfer the major element records to Ti-normalized ratios (g/g, the same for all the major and trace elements in the following discussion), many of them, such as Al_2O_3/TiO_2, K_2O/TiO_2, MgO/TiO_2, $FeO(T)/TiO_2$ and MnO/TiO_2 ratios, exhibit similar patterns with that of the planktonic foraminifer oxygen isotopes (Fig. 4). Generally, these ratios exhibit higher values during interglacials and lower values during glacials. In contrast, the Na_2O/TiO_2 ratio exhibits inverse variation patterns, with lower values during the last interglacial periods. The variations of $P_2O_5/$
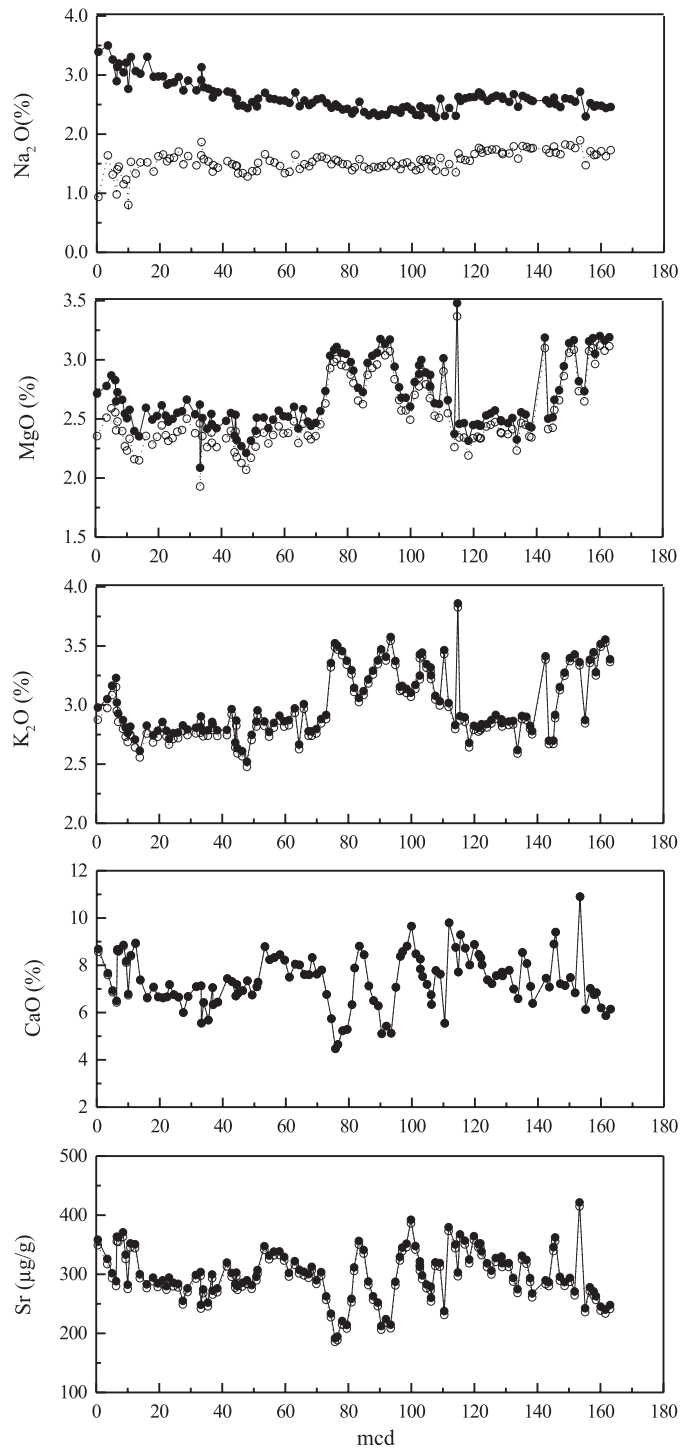
Fig. 2. Sea-salt corrections of the Na_2O, MgO, K_2O, CaO and Sr concentrations of the bulk sediments. The solid circles represent the measured concentrations of the bulk sediments and the open circles represent the corrected concentrations. Noted that the sea-salt corrections for CaO concentrations are very small, the corrected and uncorrected data are overlapped.
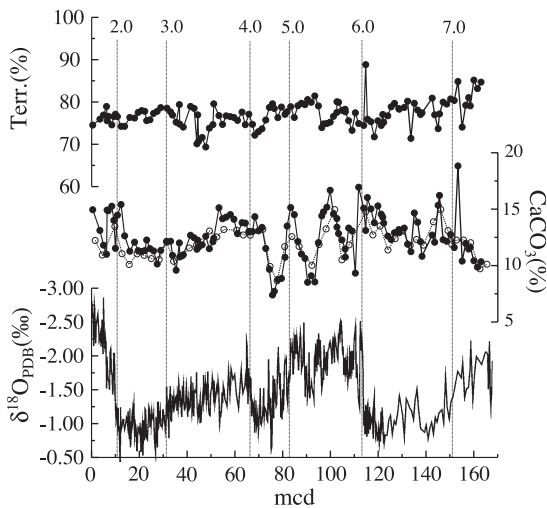
Fig. 3. Variations of the terrigenous abundance and CaCO$_3$ abundance of the sediments at ODP Site 1144. The oxygen isotopes of planktonic foraminifer *G. ruber* are included to show the time scale of the sediments. The oxygen isotope data are from Buehring et al. (2003). The dash line and open circles represent the ship-board data of the carbonate concentrations. The calculated CaCO$_3$ concentrations agree well with the ship-board data. The vertical dash lines mark the boundaries of the climate stages and the numbers mark the identities of the climate boundaries.

TiO$_2$ ratios are very small and they show no glacial/ interglacial cycles. There are some time lags between the element ratios and the oxygen isotopes and the high element ratios keep for several thousand years more when interglacial turns to glacial (Fig. 5a). However, the variations of the element ratios are nearly in pace with the oxygen isotopes at the boundaries from glacials to interglacials.

3.2. Trace elements

The Ti-normalized ratios of the trace elements of ODP 1144 sediments basically exhibit two kinds of variation patterns, matching the oxygen isotopic patterns or not. The alkali elements and alkali earth elements (such as Rb, Cs and Ba), and most of the transition metals (such as Sc, V, Cr, Co, Zn), and Ga as well, exhibit the patterns well matching the patterns of foraminifer oxygen isotopes as those for most major elements (Fig. 5a). The relative variation of the Ti-normalized ratios of these elements are usually over 20–30% within glacial/interglacial cycles, with the maximum of over 50% for Rb, Cs and Co. As for most of the other elements, such as Ge, Zr, Hf, Nb, Ta, Y and rare earth elements (REEs), Th and U, the relative variations of the Ti-normalized ratios range from 10% to 30%, with the least variation occurring in Hf, Ta, Y and REEs, less than 15%. Furthermore, the variation patterns of these elements do not match the oxygen isotopes and exhibit no glacial/
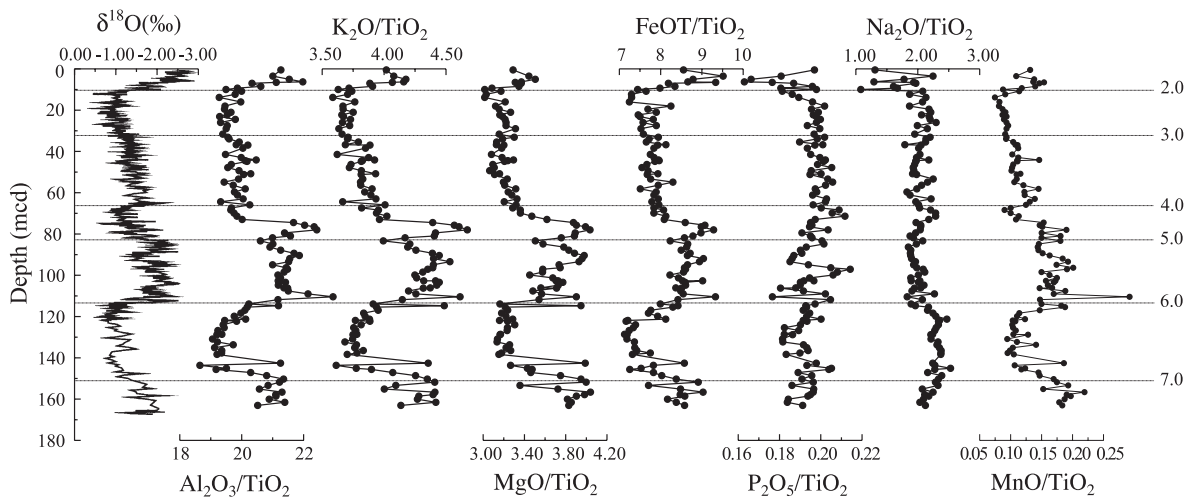

Fig. 4. Ti-normalized ratios of the major elements, Al$_2$O$_3$, Na$_2$O, K$_2$O, FeO(T), MgO, P$_2$O$_5$ and MnO of the sediments at ODP Site 1144. For sake of comparison, the oxygen isotopes of *G. ruber* are also displayed. Oxygen isotope data are from Buehring et al. (2003). The variations of Ti-normalized Al$_2$O$_3$, Na$_2$O, K$_2$O, FeO(T), MgO and MnO ratios exhibit significant climatic controlled patterns. The horizontal dash lines mark the boundaries of the climate stages, and the numbers mark the identities of the climate boundaries.
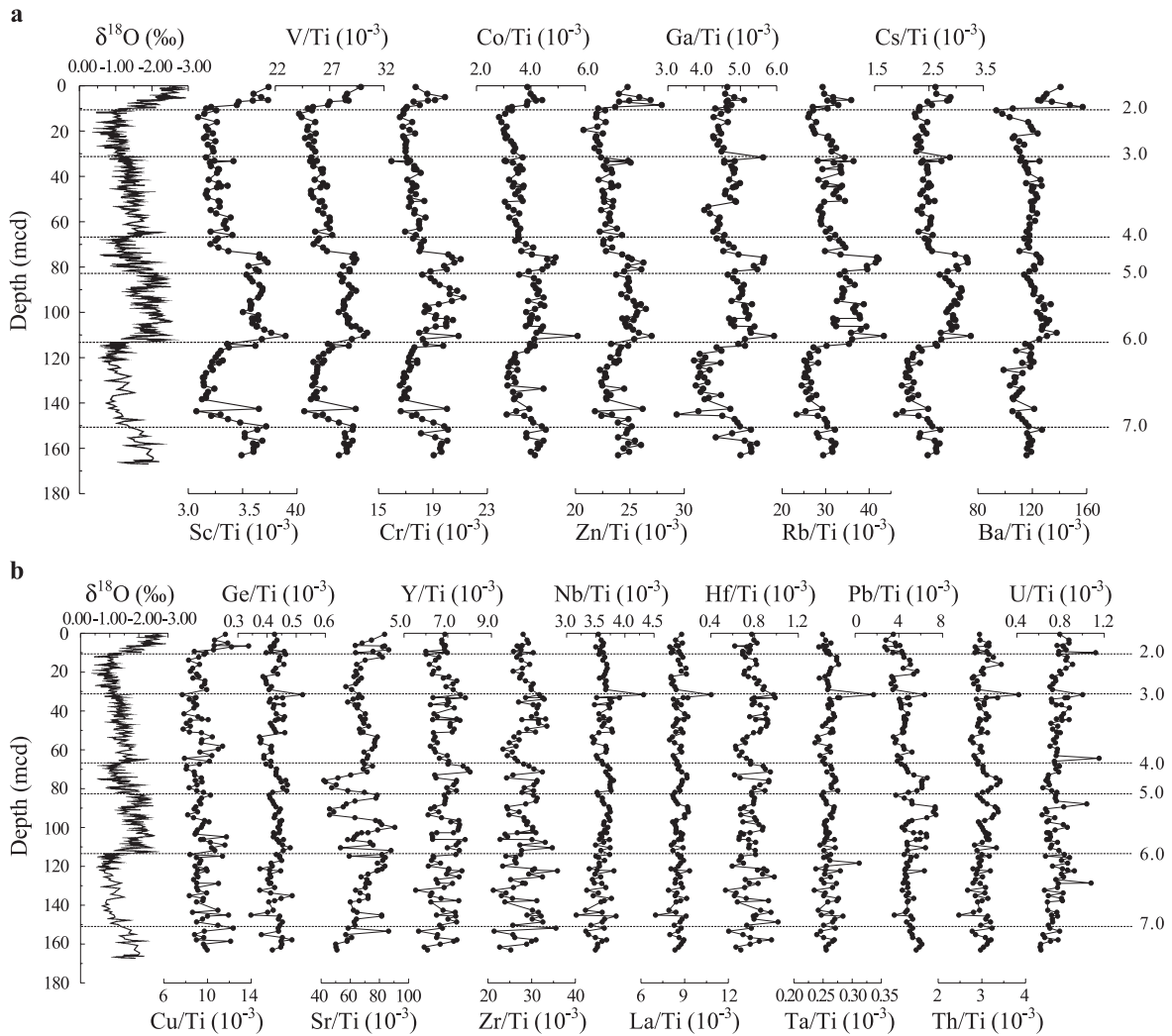
Fig. 5. (a) Variations of Ti-normalized ratios of some trace elements that exhibit SPECMAP-like variation patterns. The oxygen isotopes of *G. ruber* from Buehring et al. (2003) are included to show the climate variations. The horizontal dash lines mark the boundaries of the climate stages and the numbers mark the identities of the climate boundaries. (b) Variations of Ti-normalized ratios of some trace elements that exhibit no SPECMAP-like variation patterns. The oxygen isotopes of *G. ruber* from Buehring et al. (2003) are included to show the climate variations. The horizontal dash lines mark the boundaries of the climate stages and the numbers mark the identities of the climate boundaries.

interglacial cycles (Fig. 5b). The Cu/Ti and Pb/Ti show weak glacial/interglacial cycles. However, they do not match the oxygen isotopes as well as those for alkali elements and other transition elements. The variations for Sr/Ti ratios are different from the above two kinds of patterns, but closely match those for carbonate abundance as most of the Sr is bonded in carbonate.

4. Discussion

4.1. Factors controlling the variation of Ti-normalized ratios

Generally, titanium is the best proxy for terrigenous component in marine sediments, especially for the sediments from the South China Sea (Wei et al.,

2003b). The Ti-normalized ratios eliminate the effect of dilution by biogenic and authigenic elements on the variation patterns of the element records. Thereby, they are helpful to identify whether there is any authigenic enrichment of these elements in marine sediments (Murray et al., 2000). During chemical weathering, titanium is released from primary minerals but precipitated before it is carried out of the sample mass (Nesbitt and Markovics, 1997). As a result, Ti usually behaves as a conservative element in a weathering profile. Therefore, Ti-normalized ratios help to track the behavior of the elements during chemical weathering (Nesbitt and Markovics, 1997). The following factors may cause the changes of the Ti-normalized ratios in marine sediments: (1) change of the quantity of biogenic/authigenic matters, (2) change of the source areas of the sediments, (3) change of chemical weathering in the source areas of the sediments and (4) grain-size sorting during the transportation of the sediments.

Change of the biogenic/authigenic materials seem not contribute to the SPECMAP-like patterns of these elements because such patterns are also exhibited in the element records of the detrital components of the ODP 1144 sediments (Wei et al., 2003a). In addition, most of the elements with their variation patterns matching that of the oxygen isotopes, such as K, Sc, V, Rb, Cs, etc., are not likely to enrich in authigenic materials in marine sediments (Goldberg and Arrhenius, 1958).

Previous studies indicate that no change of the provenance of sediments of the ODP Site 1144 had been found during the last 1 Ma (Shao et al., 2001). Several Nd isotopes of the detrital components of these sediments also support this conclusion. The $^{143}Nd/^{144}Nd$ ratios of the detrital sediments at 38.37 mcd (MIS 3), 81.27 mcd (MIS 5) and 143.54 mcd (MIS 6) are 0.512049 ± 7 (2σ), 0.512055 ± 7 (2σ) and 0.512067 ± 8 (2σ), respectively, showing no difference within glacial/interglacial cycles. Furthermore, the La–Th–Sc and Th–Sc–Zr/10 discrimination diagrams of these sediments also exhibit no change within glacial/interglacial cycles (Fig. 6). As these elements are usually believed to be conservative and suitable index for provenance of the sediments (Bhatia and Crook, 1986). Therefore, change of the source areas within glacial/interglacial cycle is not expected for the sediments at ODP Site 1144 and it sounds not contribute to such variation patterns of the elemental records of these sediments.
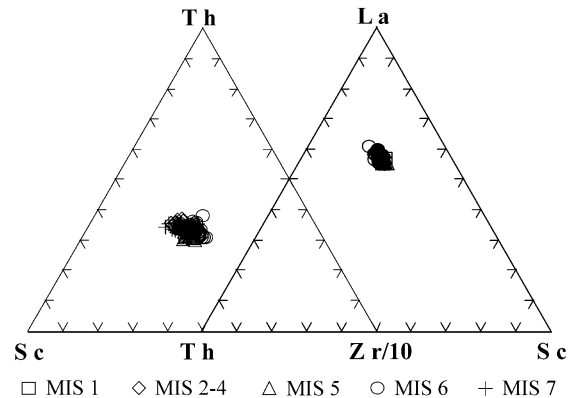

Fig. 6. La–Th–Sc and Th–Sc–Zr/10 discrimination diagrams of the ODP Site 1144 sediments. The squares indicate those of MIS 1, the diamonds indicate those of MIS 2–MIS 4, the triangles indicate those of MIS 5, the circles indicate those of MIS 6 and the crosses indicate those of MIS 7. All these are overlapped and can not be distinguished in the diagrams.

Previous studies on the Al/Ti, K/Ti and Sc/Ti ratios, both of the bulk and terrestrial components of the 1144 sediments, indicate that these variation patterns of the element ratios are mainly controlled by the change of the chemical weathering degree in their source areas (Wei et al., 2003a). In addition, the hydraulic sorting of the sediments may also influence their patterns (Wei et al., 2003a). Considering the whole records of the major and trace elements presented above, the chemical weathering mechanism could be re-confirmed.

Looking insight the major element records, the SPECMAP-like patterns of the Al/Ti, Fe/Ti, K/Ti, and Mg/Ti ratios and the inverse patterns of Na/Ti ratios agree well with their behavior during chemical weathering. In weathering profiles, Al is resistant to leaching during chemical weathering and enriches in weathering products (Nesbitt and Young, 1982; Nesbitt and Markovics, 1997). The behavior of Fe is believed to be similar to Ti during chemical weathering and Fe/Ti ratios should keep constant in weathering profiles (Nesbitt and Markovics, 1997). However, Fe tends to be enriched in some weathering profiles (Peuraniemi and Pulkkinen, 1993). Also, the variations of the Fe/Ti ratios are well correlated with that of Al/Ti ratios in marine sediments, with higher values in the sediments from intense chemical weathering sources (Kronberg et al., 1986). Therefore, Fe could be enriched in weathering product relative to Ti

when chemical weathering is enhanced. K and Mg are easily removed from primary minerals during chemical weathering. However, they tend to be combined into the weathering products and generally enrich in weathering profiles (Weaver, 1967; Nesbitt et al., 1980). As for Na, it is very easily removed from the primary minerals during chemical weathering and has, generally, low contents in weathering profile (Nesbitt et al., 1980). Therefore, enhanced chemical weathering may result in higher Al, Fe, K and Mg contents but lower Na contents in weathering products if the chemical weathering degree is not extremely high. As the terrestrial materials in marine sediments are made up of the weathering products from continents (Windom, 1976), changes of chemical weathering in source areas might be recorded in the marine sediments. The variation patterns of the major elements of the ODP 1144 sediments show high Al/Ti, Fe/Ti, K/Ti and Mg/Ti and low Na/Ti ratios during interglacials, and low Al/Ti, Fe/Ti, K/Ti and Mg/Ti and high Na/Ti ratios during glacials. These patterns may indicate that chemical weathering was stronger during interglacials than during glacials.

The pattern of Ca/Ti can not be used to extract such information even though Ca is similar to Na during chemical weathering (Nesbitt et al., 1980). About 80–90% of the total CaO of these sediments are contributed from biogenic carbonate, thereby the patterns of Ca/Ti ratios are controlled by the accumulation of biogenic carbonate. While P and Mn have similar chemical behaviors to Ti during chemical weathering, their concentration change is insignificant (Peuraniemi and Pulkkinen, 1993; Nesbitt and Markovics, 1997). The variations of the P/Ti ratios of these sediments show no significant glacial/interglacial cycles, which agrees with such characteristics. However, the variations of the Mn/Ti ratios exhibit strong glacial/interglacial cycles, indicating the behavior of Mn during chemical weathering process may be similar to that of Al, and Fe, or K and Mg in the source areas.

Among the trace elements which exhibit glacial/interglacial cycles in the records of ODP 1144 sediments, the behavior of Rb and Cs are similar to that of K during chemical weathering, Ba similar to Mg (Nesbitt et al., 1980; Nesbitt and Markovics, 1997) and Ga similar to Al in sedimentary rocks (Taylor and McLennan, 1985). The well presented glacial/interglacial cycles of Rb/Ti, Cs/Ti, Ba/Ti and Ga/Ti are in

agreement with the chemical weathering mechanism, which indicates that the changes of chemical weathering at the source areas play an important role on the variation patterns of these elements. The behaviors of the transition metals during chemical weathering are not well known. According to Nesbitt and Markovics (1997), Sc is conserved on weathering profile, and V/Ti, Cr/Ti and Zn/Ti ratios tend to increase when chemical weathering is enhanced. The well presented glacial/interglacial cycles for V/Ti, Cr/Ti, Zn/Ti and Sc/Ti ratios of the ODP 1144 sediments are agreeable with their results.

As for the trace elements showing no glacial/interglacial cycles, Zr and Hf are believed to be bonded primarily in zircon, and they are resistant to chemical weathering (Nesbitt and Markovics, 1997). Similarly, Nb and Ta are mostly concentrated on some accessory heavy minerals, and also supposed to be resistant to chemical weathering in sedimentary rocks (Taylor and McLennan, 1985). Both heavy minerals and clays are important hosts for REEs in sedimentary rocks (Condie, 1991). Under extreme chemical weathering, REEs, Y and Th are mobile (Nebstitt, 1979; Nesbitt et al., 1980; Nesbitt and Markovics, 1997). The Nb/Ti, Ta/Ti, REEs/Ti and Y/Ti ratios are nearly constant in the records of the ODP Site 1144 sediments, with the relative variability generally less than 15% except for several spikes. In contrast, the relative variability for Zr/Ti, Hf/Ti and Th/Ti ratios are larger (up to 30%). These ratios do not display glacial/interglacial variation patterns. Such patterns may again indicate that chemical weathering should be the main control on the element records, as these elements were co-varied with Ti during the chemical weathering, thereby the Ti-normalized ratios of these elements would not display the glacial/interglacial variation.

Hydraulic sorting affects the grain size of the detrital sediments, and may partially account for such variation patterns, as most elements tend to enrich in fine grain fractions in sediments (Zhang et al., 2002). However, considering the behaviors of the above-mentioned elements, the effect of hydraulic sorting on these variation patterns is very limited. The reasons are: (1) most of the elements tend to be concentrated in fine grain size fractions, including those exhibiting significant glacial/interglacial cycles (such as Al, K, Mg, Mn, V, Cr, Rb, Cs) and those showing no glacial/interglacial cycles (such as P, Nb, Ta, Y and Th)

(Zhang et al., 2002). However, the variation patterns of the Ti-normalized ratios of these two groups of elements are significantly different. (2) The patterns for Ba, which tends to enrich in coarse grain fractions (Zhang et al., 2002), are similar to those concentrated in fine grain fractions. Whilst, the concentrations of Na, showing inverse variation patterns, is not affected by grain size (Zhang et al., 2002). (3) The variation of the grain sizes of the ODP 1144 sediments is limited, with medium sizes mostly ranging within 2–10 μm, and their variation patterns do not match that of the oxygen isotopes (Wei et al., 2003a). Therefore, the hydraulic sorting is not considered as the main controlling factor of the elemental variation patterns. The change of chemical weathering at their source areas should act as the key role.

4.2. Paleoclimate implications

The reconfirming of the chemical weathering mechanism indicates that element records of the ODP Site 1144 sediments can proxy the change of the chemical weathering degree at their source areas, the South China. As chemical weathering on continents is largely controlled by moisture and temperature, and wet and warm climate may enhance the chemical weathering (Nesbitt and Young, 1982). The variation patterns of the element records of the ODP Site 1144 sediments indicate that wet and warm climate occurs in South China, which results in enhanced chemical weathering during interglacials, and that dry climate accompanies with relatively weak chemical weathering during glacials. This paleoclimate interpretation agrees well with the new pollen records from the ODP 1144 sediments (Luo et al., in press; Sun et al., 2003) and clay mineral records (Tamburini et al., 2003). The climate in South China is largely controlled by East Asia Monsoon and the precipitation in South China is mainly supplied from summer monsoon (Ding, 1994). In general, during interglacials the summer monsoon is enhanced, and the winter monsoon is strengthen during glacials (Wang, 1999). The variations of the chemical weathering degree as revealed by the element records of the ODP Site 1144 sediments agree with the variations of the monsoon climate in South China, indicating that they may act as proxy for monsoon climate.

We perform harmonic analysis of the Al/Ti ratios, which well show the chemical weathering controlling patterns using the SPECTRUM software (Schulz and Stattegger, 1997). The results indicate that the Al/Ti ratios exhibit significant eccentricity cycle (100 kyr) and the obliquity cycle and precession cycle are not evident (Fig. 7). In contrast, eccentricity cycle is not evident in the spectra of $CaCO_3$ abundance, but obliquity cycle (41 kyr) and precession cycle (23 kyr) are significant (Fig. 7). Generally, the 100-kyr eccentricity cycle is believed to be related to the variation of the ice volume in the Northern Hemisphere, and the 41-kyr obliquity cycle and 23-kyr precession cycle are believed to be associated with variations of the summer insolation at high northern latitude (Imbrie et al., 1993). In South China Sea, the enhance of summer monsoon is closely related to the 41-kyr obliquity cycle and the 23-kyr precession cycle, and the 100-kyr eccentricity cycle is less important (Jian et al., 2001). However, the strengthening of the winter monsoon is mostly related to the 100-kyr eccentricity cycle, and the 41-kyr obliquity cycle and the 23-kyr precession cycle are less important (Jian et al., 2001). The spectra of the Al/ Ti ratios indicate change of the chemical weathering
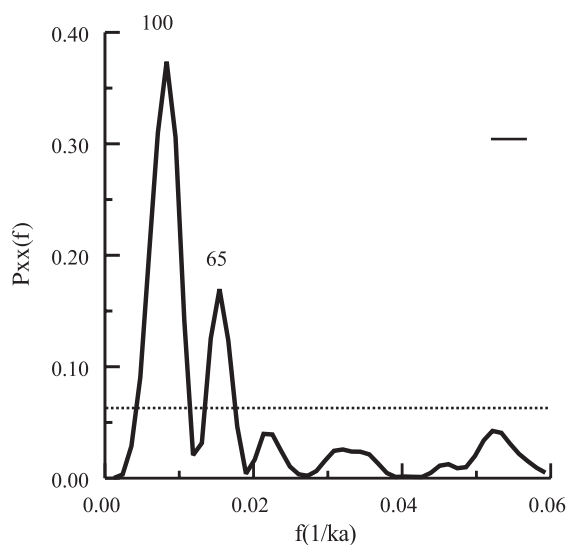

Fig. 7. Harmonic analysis (Siegel's test) of the Al/Ti ratios using SPECTRUM (Schulz and Stattegger, 1997). Setting: OFAC=4, HIFAC=1, α=0.05, λ=0.4; horizontal bar marks 6-dB bandwidth; dashed line indicates false alarm level of 95% confidence intervals. Numbers represent the respective cycles of the peaks.

degree in South China may relate to the variations of ice volume and possibly controlled by the variations of winter monsoon. Therefore, even though the precipitation in South China is mostly supplied by summer monsoon (Ding, 1994), and precipitation is very important for chemical weathering, the change of the chemical weathering in South China sounds largely controlled by the variation of winter monsoon, and the variation of summer monsoon sounds less important.

5. Summary

The major and trace element records of the bulk sediments from ODP Site 1144 exhibit significant climate controlled patterns during the last 210 ka. Many of the elements show the variation patterns well matching that of the planktonic foraminifer oxygen isotopes.

The Ti-normalized ratios of most of the major elements, such as Al, K, Mg, Fe and Mn, the alkali elements, such as Rb and Cs, the alkali earth elements, such as Ba, and most of the transition metals, such as Sc, V, Co, Cr, Zn, exhibit significant SPECMAP-like patterns, with higher values during interglacials and lower values during glacials. However, the Na/Ti ratios show inverse variation patterns, with lower values during interglacials and higher values during glacials. Whilst many of the refractory elements, such as Y, Zr, Nb, Hf, Ta, REEs, Th and U show no SPECMAP-like patterns. Furthermore, some of them (Nb, Ta, REEs) show near constant Ti-normalized ratios during the last 210 ka in ODP 1144 sediments. These agree with the behaviors of the these elements during chemical weathering process, indicating that change of chemical weathering degree at their source areas of these sediments is the key for such variation patterns.

As South China is the main provenance of the ODP 1144 sediments, these elemental variation patterns indicate the climate in South China was wet and warm during interglacials , resulting in enhanced chemical weathering, and dry during glacials, resulting in weakened chemical weathering. Such climate change may be associated with the change of the East Asian monsoon. During interglacials, summer monsoon was enhanced, which result in wet and warm climate in South China, and during glacials, winter monsoon was strengthened, which result in dry climate in South China. Spectra analysis shows significant 100-kyr eccentricity cycle but lack of 41-kyr obliquity cycle and 21-kyr precession cycle for the change of chemical weathering degree, indicating that the variation of winter monsoon, rather than summer monsoon is the key for the change of chemical weathering degree.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.palaeo.2004.06.011.

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