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Citation	Journal of Asian Earth Sciences, 40(6), 1221-1229 https://doi.org/10.1016/j.jseaes.2010.09.013
Issue Date	2011-04-02
Doc URL	http://hdl.handle.net/2115/51239
Type	article (author version)
File Information	Shintani 2011 JAES.pdf

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Paleoenvironmental changes in the northern South China Sea over the past 28,000 years: a study of TEX₈₆-derived sea surface temperatures and terrestrial biomarkers

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Keywords: South China Sea, TEX₈₆, U_{37}^K , paleotemperature, biomarkers, terrestrial organic matter, Late Quaternary

Abstract: We have generated a record of TEX₈₆(TEX₈₆^H)-derived sea surface temperatures (SSTs) over the last 28 ka for core MD97-2146 from the northern South China Sea (SCS). The TEX₈₆^H-derived temperature of a core-top sample corresponds to the SSTs in warmer seasons. The SST record shows a drop during the Oldest Dryas period, an abrupt rise at the

onset of the Bølling-Allerød period, a plateau across the Younger Dryas period, and an abrupt rise at the beginning of the Holocene. The glacial–interglacial contrast in TEX₈₆^H-derived temperature is almost the same as that in foraminiferal Mg/Ca ratio-derived temperature, but it is larger than those in U_{37}^K and transfer function-derived temperatures. Possible interpretations are 1) the seasonal shift of glycerol dialkyl glycerol tetraether (GDGT) production, 2) the overestimation of temperature change by TEX₈₆^H, and 3) the underestimation of temperature change by U_{37}^K and transfer function approaches. The similar variation in TEX₈₆^H-derived temperature at the study site and Chinese stalagmite $\delta^{18}\text{O}$ during the last deglaciation suggests that changes in TEX₈₆^H-derived temperature in this period reflected atmospheric and oceanic reorganization on a millennial timescale. The long-chain n-alkanes are mainly of higher plant origin before ~14 ka and a mixture of higher plant and lithic origins after ~14 ka; the abundance ratio of long-chain to short-chain n-fatty acids decreases at ~15 ka, suggesting a drastic change in sediment sources at ~14–15 ka. We attribute the higher content of fresh higher plant n-alkanes and long-chain n-fatty acids before ~14–15 ka to enhanced aeolian transportation and/or arid environments. Increased precipitation likely due to intensified summer monsoon after ~14–15 ka enhanced the erosion of sedimentary rocks and increased the contribution of lithic n-alkanes.

1. Introduction

Numerous paleoceanographic studies of sea surface temperature (SST) have been undertaken in the South China Sea (SCS). Wang and Wang (1990) and Wang et al. (1995) generated summer and winter SST records for the SCS, based on foraminifer assemblages, and found that during the last glacial maximum (LGM) the SCS experienced larger

seasonal SST differences and a steeper latitudinal SST gradient than it does presently. Similar phenomena were reported using foraminifer- and alkenone-based SST records for the northern SCS (Huang et al., 1997a, b; Chen and Huang, 1998; Pelejero et al., 1999a; Chen et al., 2003). Kienast et al. (2001) identified a millennium-scale temperature variation that mimics Greenland ice core records. Recently, Oppo and Sun (2005) and Zhao et al. (2006) reported millennium-scale temperature records from the northern and southern SCS, respectively, for the time since the penultimate glacial interval. The glacial–interglacial changes of SST in the SCS have been attributed either to the inflow of cold water from the North Pacific (e.g., Wang and Wang, 1990; Wang et al., 1995) or to changes in winter monsoon intensity (e.g., Huang et al., 1997a, b). Disagreements of paleotemperatures in the SCS among different proxies such as alkenone U_{37}^K , the foraminiferal Mg/Ca ratio, and transfer function are potentially attributable to differences in the season and depth that each proxy reflects (e.g., Steinke et al., 2008). Alternative approaches are useful for better understanding paleotemperature changes in the SCS.

TEX₈₆ is a recently developed paleotemperature proxy (Schouten et al., 2002), which is based on glycerol dialkyl glycerol tetraethers (GDGTs). The TEX₈₆ paleothermometer has the advantage that it does not seem to be influenced by changes in salinity (Wuchter et al., 2004) and is more sensitive to temperature changes in tropical waters (Kim et al., 2010). However, caution is still required when applying TEX₈₆ because a water-column study suggested that TEX₈₆ recorded not only temperature changes, but also changes in archaeal ecology, nutrient concentrations, and possibly oceanographic conditions (Turich et al., 2007). More case studies are necessary to test the reliability of this proxy. Furthermore, TEX₈₆ has not been previously applied to SCS sediments.

Changes in terrestrial vegetation and sediment transport pathways have also been

investigated from the perspective of monsoon variation. Sun and Li (1999) reported a transition from a herb-dominated cool and dry climate during the last glacial to a warm and humid climate in the Holocene in south China, as shown by pollen and spore assemblages in the SONNE 17940 core from the northern SCS. Wang et al. (1999a) attributed the increase in clay content observed at ~14.5 ka in core 17940 to an increase in fluvial supply from the Pearl River due to the intensification of the summer monsoon. Pelejero (2003) revealed the parallel glacial–interglacial variability of terrestrial n-alkane concentration in four different cores retrieved from the northern, western and southern SCS, taking values linearly inversely correlated to the $U_{37}^{K'}$ -derived SST, with higher concentrations during glacials. This oscillation was attributed to the emergence and flooding of the shelves caused by sea level variations, together with SCS SSTs, have a clear dependency on the Northern Hemisphere climate evolution. Terrestrial biomarkers such as long-chain n-alkanes and long-chain n-fatty acids are useful for understanding the contribution and provenance of terrestrial material (e.g., Pelejero et al., 1999b; Pelejero, 2003; Yamamoto and Polyak, 2009).

This study presents records of TEX_{86}^H -derived SSTs and terrestrial biomarkers for the last 28,000 years from northern SCS core MD97-2146, located offshore from southern China. The objective of this work is to understand changes in SSTs derived from TEX_{86}^H as well as changes in sediment provenance. This is the first report of the application of TEX_{86}^H (TEX_{86}^H) paleothermometry in the SCS.

2. Oceanographic settings

The SCS is a marginal sea of the North Pacific with seven connections to surrounding seas and oceans (Fig. 1): the Taiwan Strait to the East China Sea (sill depth ~70 m), the

Bashi Strait to the North Pacific (sill depth ~2500 m), the Mindoro and Balabac Straits to the Sulu Sea (sill depths ~450 and ~100 m, respectively), the Malacca Strait to the Indian Ocean (sill depth ~30 m), and the Gaspar and Karimata Straits (~40-50 m) to the Java Sea (Wyrтки, 1961). Surface circulation in the SCS is driven by large-scale, seasonally-reversed monsoon winds (Wyrтки, 1961). In the boreal summer, southwesterly winds drive an inflow of Indian Ocean water through the Sunda Shelf and a clockwise surface circulation in the SCS. In the boreal winter, northeasterly winds drive an inflow of North Pacific and East China Sea waters through the Bashi and Taiwan Straits, and surface circulation in the SCS is counterclockwise.

3. Materials and Methods

3.1. Samples and age-depth model

During the IMAGES 1997 *Marion Dufresne* cruise, a giant piston core (MD97-2146; 38.69 m long) was collected from a water depth of 1720 m on the northern slope of the SCS at 20°07.08'N, 117°23.02'E (Fig. 1). The sediment retrieved consisted of dark gray nannofossil and foraminifer oozes with some radiolarians and diatoms (Chen et al., 1998).

An age model in calendar years was created from the AMS ^{14}C ages of seven samples of the planktonic foraminiferan *Globigerinoides sacculifer* (Lin et al., 2006) and six samples of mixed planktonic foraminifera *Globigerinoides ruber* and *G. sacculifer* (Shintani et al., 2008). The calendar age was converted using the CALIB5.0 program and marine04.14C dataset (Reimer et al., 2004) with a 400-year global reservoir correction (Shintani et al., 2008). Lin et al. (2006) created an age model using a combination of ^{14}C ages and stratigraphic correlation with nearby core 17940 (Wang et al., 1999b). The present work does not use any stratigraphic correlation, however, because the assumption that

temperatures in core 17940 changed synchronously with Greenland temperatures (Wang et al., 1999b) is not necessary.

A total of 76 samples were collected every 20 cm on average (equivalent to approximately 300-year intervals) down to a depth of 19 m (0-28 ka).

3.2 Hydrocarbon analysis

Lipids were extracted (x 2) from 1 g of dried sediment using a DIONEX Accelerated Solvent Extractor ASE-200 at 100°C and 1000 psi for 10 min with 11 ml of CH₂Cl₂–CH₃OH (6:4) and then concentrated. The lipid extract was separated into four fractions using column chromatography (SiO₂ with 5% distilled water; i.d., 5.5 mm; length, 45 mm): F1 (hydrocarbons), 3ml hexane; F2 (aromatic hydrocarbons), 3 ml hexane-toluene (3:1); F3 (ketones), 4 ml toluene; F4 (polar compounds), 3 ml toluene–CH₃OH (3:1); *n*-C₂₄D₅₀ and *n*-C₃₆H₇₄ were added as internal standards to F1 and F3, respectively.

An aliquot of F4 was trans-esterified with 1 ml 5% HCl–CH₃OH at 60°C for 12 h under N₂. The esterified lipids were supplemented with 2 ml distilled water and extracted (x 3) with toluene. The extract was back-washed (x 3) with distilled water, passed through a short bed of Na₂SO₄, and separated into two fractions with SiO₂ column chromatography: F4-1 (acids), 4 ml toluene; F4-2 (alcohols), 3 ml toluene-CH₃OH (3:1); *n*-C₂₄D₅₀ was added as an internal standard to F4-1.

Gas chromatography (GC) was conducted using a Hewlett Packard 5890 series II gas chromatograph with on-column injection and electronic pressure control systems, and a flame ionization detector (FID). Samples were dissolved in hexane. Helium was the carrier gas and the flow velocity was maintained at 30 cm/s. A Chrompack CP-Sil5CB column was used (length, 60 m; i.d., 0.25 mm; thickness, 0.25 µm). The oven temperature was

programmed to rise from 70 to 130°C at 20°C/min, from 130 to 310°C at 4°C/min, and to hold at 310°C for > 30 min. The standard deviations of five duplicate analyses averaged 7.5% of the concentration for each compound.

Gas chromatography-mass spectrometry (GC-MS) of F1, F3 and F4-1 was conducted using a Hewlett Packard 5973 GC-mass selective detector with on-column injection and electronic pressure control systems, and a quadrupole mass spectrometer. The GC column and oven temperature and carrier pressure programs were as described above. The mass spectrometer was run in full scan mode (m/z 50–650). Electron ionization (EI) spectra were obtained at 70 eV. Compound identification was achieved by comparing mass spectra and retention times with those of standards and published data.

3.3 Glycerol dialkyl glycerol tetraether (GDGT) analysis

An aliquot of F4-2 was dissolved in hexane–2-propanol (99:1) and filtered. Glycerol dialkyl glycerol tetraethers (GDGTs) were analyzed using high performance liquid chromatography-mass spectrometry (HPLC-MS) with an Agilent 1100 HPLC system connected to a Bruker Daltonics micrOTOF-HS time-of-flight mass spectrometer. Separation was conducted using a Prevail Cyano column (2.1 x 150 mm, 3µm; Alltech) and maintained at 30°C following the method of Hopmans et al. (2000) and Schouten et al. (2007). Conditions were: flow rate 0.2 ml/min, isocratic with 99% hexane and 1% 2-propanol for the first 5 min followed by a linear gradient to 1.8% 2-propanol over 45 min. Detection was achieved using atmospheric pressure, positive ion chemical ionization-mass spectrometry (APCI-MS). The spectrometer was run in full scan mode (m/z 500–1500). Compounds were identified by comparing mass spectra and retention times with those of GDGT standards (formed from the main phospholipids of *Thermoplasma acidophilum* via

acid hydrolysis) and those in the literature (Hopmans et al., 2000). Quantification was achieved by integrating the summed peak areas in the (M+H)⁺ and the isotopic (M+H+1)⁺ ion traces.

TEX_{86}^H was calculated from the concentrations of GDGT-1, GDGT-2, GDGT-3 and a regioisomer of crenarchaeol using the following expression (Schouten et al., 2002; Kim et al., 2010):

$$TEX_{86}^H = \log TEX_{86} = \log ([GDGT-2] + [GDGT-3] + [Crenarchaeol\ regioisomer]) / ([GDGT-1] + [GDGT-2] + [GDGT-3] + [Crenarchaeol\ regioisomer])$$

TEX_{86}^H is defined as the logarithmic function of TEX_{86} and yields the best correlation with SST when the data from polar and subpolar oceans are removed (Kim et al., 2010). Temperature was calculated according to the following equation based on a global core-top calibration (Kim et al., 2010):

$$T = 68.4 \times TEX_{86}^H + 38.6$$

where T = temperature [°C]; analytical accuracy was 0.45°C in our laboratory.

4. Results

4.1. TEX_{86}^H

The TEX_{86}^H -derived temperature profile indicates that between 18 and 28 ka SSTs were nearly constant at 23.3°C, decreased to 20.8°C at 16.7 ka, and then increased abruptly to 25.8°C by 14.5 ka. After 14.5 ka SSTs increased gradually to 26.3°C by 12.9 ka, and then

decreased to 25.4°C at 12.3 ka, before increasing abruptly to 28.0°C by 11.0 ka. After 11.0 ka SSTs increased gradually to 28.7°C by 5.3 ka and remained constant thereafter (Fig. 3A). The core-top temperature was 28.1°C. This temperature is higher than the mean annual SST (26.6°C; NOAA, 1998) and agrees with the SST in May and September-October at this site (~28.0°C and ~27.7-28.6°C, respectively; NOAA, 1998).

The Branched and Isoprenoid Tetraether (BIT) index, a proxy for soil versus marine organic matter input to sediments (Hopamans et al, 2004), was constantly low (< 0.03).

4.2. Normal alkanes

Normal alkanes (n-alkanes) occur as a major component of the F1 (hydrocarbon) fraction and show a unimodal distribution with a maximum at C₃₁. The total concentration of long-chain C₂₅-C₃₃ n-alkanes varies between 0.41 and 1.66 µg/g in sediment, with an average of 0.86 µg/g (Fig. 4A). The odd carbon number preference index (CPI) values of C₂₄-C₃₄ homologues (Bray and Evans, 1961) vary between 2.0 and 6.2, with an average of 3.4. The average chain length (ACL) values of C₂₇-C₃₃ homologues (Bray and Evans, 1961) vary between 29.1 and 30.3, with an average of 29.7.

Most samples showed the n-alkane distribution as a mixture of a pattern with high odd carbon number preference (CPI > ~5; Fig. 4A) and a pattern heavily influenced by mature (thermally altered) n-alkane with low CPI values (~2.5; Fig. 4A). The former is typical of terrestrial higher plant waxes (Eglinton and Hamilton, 1967). This pattern indicates that the OM was derived from fresh higher plant material. The latter is typical of coal and coaly shale (Bray and Evans, 1961), indicating an influx of mature (lithic) OM.

If we assess the end-member CPI values of higher plant and mature OM, we can estimate the concentrations of n-alkanes of both origins. Assuming that the long-chain

n-alkanes derived from higher plant waxes have CPI values of 6.2 (maximal value for samples in the study core), and that those derived from mature rocks have CPI values of 1 (typical values of OM in catagenesis and metagenesis stages; Tissot and Welte, 1984), we calculated concentrations of “higher plant” and “lithic” C₂₅-C₃₃ n-alkanes from the total C₂₅-C₃₃ n-alkane concentration and the CPI value using the following formulae (Yamamoto and Polyak, 2009):

Higher plant C₂₅-C₃₃ n-alkane

$$= \text{total C}_{25}\text{-C}_{33} \text{ n-alkane} \times \{(6.2+1) (\text{CPI}-1)\} / \{(6.2-1) (\text{CPI}+1)\}$$

Lithic C₂₅-C₃₃ n-alkane = total C₂₅-C₃₃ n-alkane – higher plant C₂₅-C₃₃ n-alkane

The concentration of higher plant long-chain n-alkanes varies between 0.29 and 1.33 µg/g with an average of 0.64 µg/g. The concentration of lithic long-chain n-alkanes varies between 0 and 0.55 µg/g with an average of 0.23 µg/g. Both total and higher plant n-alkanes show a similar pattern over the last 30 kyr: they are higher between 14 and 30 ka than between 2 and 14 ka, and increase to present-day values at around 2 ka (Fig. 4A). In contrast, lithic n-alkanes remain low until 15 ka, increased at 15 ka, and then increase gradually thereafter (Fig. 4A).

4.3. Normal fatty acids

Normal fatty acids (n-fatty acids) occur as a major component of the F4-1 (acid) fraction and show a bimodal distribution with a maximum at C₁₆ and C₂₆ or C₂₈. Short-chain n-fatty acids are ubiquitous in eukaryotes and bacteria, while long-chain n-fatty acids are specific to higher plants (Kvenvolden et al., 1967). The even CPI values of

C₂₅-C₃₃ homologues (Kvenvolden et al., 1967) were nearly constant with a range of between 3.6 and 4.8 and an average of 4.2 (Fig. 4B).

The total concentration of n-fatty acids (C₁₄-C₃₄) varies between 5.9 and 34.5 µg/g, with an average of 10.7 µg/g (Fig. 4B). The concentration of short-chain n-fatty acids (C₁₄-C₁₈) varies between 1.3 and 12.1 µg/g, with an average of 3.6 µg/g (Fig. 4B). The concentration of long-chain n-fatty acids (C₂₆-C₃₄) varies between 2.3 and 13.4 µg/g, with an average of 4.7 µg/g. The concentration of short-chain n-fatty acids was constant with the exception of a peak at 17.3 ka, while the concentration of long-chain n-fatty acids shows several peaks prior to 15 ka (Fig. 4B).

5. Discussion

5.1. SST changes

The U_{37}^K -derived temperature in this core was reported by Shintani et al. (2008). Temperature records were calculated using the equations of Prah et al. (1988). The SSTs fluctuated slightly between 28–16 ka but maintained an average of 24.0°C. By 14.8 ka, SSTs increased to 24.7°C, whereupon they remained constant until 10.7 ka. After 10.7 ka SSTs increased to 26.5°C by 6.1 ka and then increased more gradually to reach 27°C at present (Fig. 3B). This variation is similar to that recorded in nearby core 17940 (Pelejero et al., 1999a). Present-day SST at the study site shows a seasonal variation between 23.7°C in January and 28.9°C in July, with a mean annual value of 26.6°C (Fig. 2; NOAA, 1998). The U_{37}^K -derived core-top temperature is 26.0°C. This temperature is slightly lower than the mean annual SST at this site (26.6°C; NOAA, 1998). As indicated from satellite observations, chlorophyll concentrations do not display large seasonal variations, with only a moderate maximum in the winter season in the study area (Zhang et al., 2006). The

weighted-average SST (0–30 m) based on chlorophyll concentration is 25.7°C, which is only 0.6°C lower than the mean annual temperature at 0–30 m (26.3°C). These observations suggest that the U_{37}^K -derived temperature reflects the mean annual SST at the study site.

The core-top temperature based on TEX_{86}^H is 28.1°C. This temperature is 1.5°C higher than the mean annual SST (26.6°C; NOAA, 1998) and agrees with the SST in May and September–October at this site (~28.0°C and ~27.7–28.6°C, respectively; NOAA, 1998). It has been reported that the GDGT concentration in surface waters is higher during non-blooming seasons in the North Sea and the Bermuda Rise (Wuchter et al., 2005). By analogy with this case, although there is no information on the production season and depth of GDGTs at the study site, it is reasonable to infer that GDGT are produced during the summer season when blooms cease. We infer, therefore, that the TEX_{86}^H -derived temperature reflects the SST weighted in warmer seasons at the study site.

The U_{37}^K -derived temperature shows a different temporal evolution in comparison with TEX_{86}^H -derived temperatures (Figs. 3A and 3B). We interpret U_{37}^K -derived temperatures as reflecting mean annual SST (Shintani et al., 2008). The average of summer and winter SSTs estimated by a regional Imbrie–Kipp transfer function method (FP-12E; Thompson, 1981) of planktonic foraminifera in core 19740 (Wang et al., 1999b) agreed with U_{37}^K -derived temperature in core MD97-2146 (Fig. 3B), supporting this interpretation.

On the other hand, we interpret the TEX_{86}^H -derived temperature estimate at a core top sediment sample to reflect the SST weighted in warmer seasons. The TEX_{86}^H -derived temperatures in core MD97-2146 range between summer and annual mean SSTs estimated by a transfer function method in core 19740 (Wang et al., 1999b) during the Holocene, whereas they agree with the annual mean SSTs during the last glacial period between 18

and 27 ka (Fig. 3A). There are three possible interpretations of this phenomenon, such as 1) the seasonal shift of GDGT production, 2) the overestimation of temperature change by $\text{TEX}_{86}^{\text{H}}$, and 3) the underestimation of temperature change by U_{37}^{K} and transfer function approaches.

First, the seasonal shift of GDGT production from warmer seasons to cooler seasons is one of the candidate mechanisms accounting for larger variation in $\text{TEX}_{86}^{\text{H}}$ -derived temperature than in U_{37}^{K} - and transfer function-derived mean annual SSTs. The GDGT concentration in surface waters has been reported to be higher during non-blooming seasons in the North Sea and the Bermuda Rise (Wuchter et al., 2005). If the phytoplankton blooms shifted to warmer seasons due to the temperature limitation of phytoplankton growth, the production of GDGTs would decrease in warmer seasons, and $\text{TEX}_{86}^{\text{H}}$ should reflect the SST in cooler seasons.

Second, the overestimation of temperature change by $\text{TEX}_{86}^{\text{H}}$ is possible due to calibration at this stage. Global core top calibration was revised by increasing surface sediment samples (Schouten et al., 2002; Kim et al., 2008; 2010). The most recently revised calibration gives smaller temperature change than did previous versions. Kim et al. (2010) also pointed out that crenachaeotal ecology is different between subpolar and subtropical water masses and may have different responses to temperature change. If a water mass is displaced by another water mass, a complex response to temperature change results. Caution is necessary when discussing the degree of variation in TEX_{86} -derived temperature until temperature calibration is practically established.

Last, possible underestimations of temperature change by U_{37}^{K} and the transfer function methods are not negligible. Because the production of coccolithophores is temperature dependant (Conte et al., 1998), the season of maximum production may have

shifted to the warmest times of year, during periods of decreasing mean annual SST. It is thus possible that the drop in U_{37}^K -derived temperatures may be an underestimate. Temperature at core 17940 was estimated by a regional Imbrie–Kipp method (Wang et al., 1999b). Chen et al. (2005) compared the results of temperature estimates by different transfer function techniques and found that the Imbrie–Kipp method tends to show smaller temperature variation than those obtained by other methods. In addition, Steinke et al. (2008) showed that transfer function methods give smaller glacial–interglacial variation in SST compared with those inferred by geochemical proxies in the SCS because there are no modern analog planktonic foraminiferal faunas in the glacial SCS. These lines of evidence suggest that glacial cooling may be underestimated by U_{37}^K and transfer function methods.

It is now not clear which of the above mechanism is critical in causing the difference between proxies. Further comparison studies of proxies are necessary to answer this question.

The TEX_{86}^H -derived temperatures in core MD97-2146 generally agree with the foraminiferal Mg/Ca-derived temperatures at ODP Site 1145, located ~100 km south of Site MD97-2146 (Fig. 3; Oppo and Sun, 2005), but the disagreement is again observed in the period between 18 ka and 15 ka (Figs. 3A and 3C). The cooling observed in TEX_{86}^H -derived temperatures during the 15–18 ka could be somehow overestimated, as other proxies do not indicate such a cooling. The anomalies of TEX_{86}^H -derived temperatures are potentially attributable to seasonal shift of GDGT production, changes in the GDGT production depth, lateral transport of GDGTs and additional contribution of GDGTs by archaeal communities other than Marine Group I Crenarchaeota (Kim et al., 2008). There is now no evidence to support the above possibilities, but they must be

considered by further studies.

The changing pattern of TEX₈₆^H-derived temperature record from 15 to 10 ka shows a good correspondence to the millennial-scale pattern of stalagmite oxygen isotopes from the Hulu Cave, eastern central China (Wang et al., 2001), and the Dongge Cave, south China (Yuan et al., 2004). The variation in stalagmite $\delta^{18}\text{O}$ is thought to reflect changes in the relative abundance of summer vs. winter precipitation: low values correspond to larger contributions of summer precipitation due to an increased intensity of the East Asian summer monsoon. The correspondence of the pattern of change between TEX₈₆^H-derived temperature at the study site and Chinese stalagmite $\delta^{18}\text{O}$ suggests that changes in TEX₈₆^H-derived temperature in this period reflected atmospheric and oceanic reorganization on a millennial timescale.

5.2. Inflow of terrestrial organic matter to the study site

The total long-chain n-alkane concentration decreases in the interval from 15 ka to 13 ka (Fig. 4). The similar trend of long-chain n-alkane concentration was previously reported in nearby core 17940 (Pelejero, 2003; Kienast et al., 2010) and was attributed to the emergence and flooding of the shelves caused by sea level variations, together with SCS SSTs, have a clear dependency on the Northern Hemisphere climate evolution.

In this study, the long-chain n-alkanes were separately determined as higher plant-derived n-alkanes and lithic n-alkanes. The long-chain n-alkanes are mainly of higher plant origin before ~14–15 ka and a mixture of higher plant and lithic origins after ~14–15 ka (Fig. 4A). The sudden decrease of higher plant n-alkane concentration was accompanied by a decrease in the ratio of long-chain to short-chain n-fatty acids (Fig. 4B). These observations suggest that the relative contribution of fresh higher plants decreased and that the

contribution of mature organic matter derived from sedimentary rocks increased between 14 and 15 ka, indicating a drastic change in sediment provenance at this time.

Wang et al. (1999a) showed that the median grain size of silt and the total modal grain size of sediments decreased, while the clay content increased, at the onset of the Bølling-Allerød (B-A) period at core site 17940. This decrease in the average grain size and increase in clay content was interpreted as indicating a decrease in the supply of dust and an increase in the supply of fine fluvial material from the Pearl River at ~14.5 ka. Wang et al. (1999a) stressed that this change reflects the shift from a winter monsoon-dominated glacial regime to a summer monsoon-dominated Holocene regime.

Tamburini et al. (2003) found higher illite content in SCS sediment during the Holocene, while smectite and kaolinite were elevated during glacial periods. Because illite is abundant in sediments derived from the Asian continent, and smectite and kaolinite are relatively abundant in sediments from the southern tropical islands, the change in clay-mineral composition may reflect changes in sediment provenance. Studies on modern sediments indicate that reworking of material from the Pearl River (Wang et al., 1999a) and current transport from the East China Sea through the open Taiwan Strait (Chen, 1978) should be considered the main transport mechanism responsible for clay and mineral distribution in the northern SCS (Tamburini et al., 2003). The low illite content during the last glacial period was attributed to the interruption of the input of illite-rich material from the East China Sea shelf when a low sea level stand closed the Taiwan Strait (Tamburini et al., 2003).

The sill depth of the Taiwan Strait is ~70 m, and a marine connection was established by ~13 ka, later than the decreases of fresh higher plant-derived n-alkane and n-fatty acids (Fig. 4). This implies that the opening of the Taiwan Strait was not a cause of the low

content of higher plant biomarkers.

On the other hands, the decrease of fresh higher plant n-alkanes at 15 ka coincides with the increase of the Asian summer monsoon intensity recorded in Chinese stalagmites (Wang et al., 2001; Yuan et al., 2004). The greater content of fresh higher plant n-alkanes and long-chain n-fatty acids in sediments prior to 14–15 ka is attributable to enhanced aeolian transportation and/or arid environments in South China (Sun and Li, 1999). Enhanced precipitation due to the intensified East Asian summer monsoon after ~14–15 ka increased the erosion of sub-aerially exposed sedimentary rocks, increasing the relative proportion of lithic n-alkanes.

5.3. *Paleoenvironment after 2 ka*

The ACL is significantly higher in the Oldest Dryas period and after 2 ka (Fig. 4). In general, ACL values are higher in herbs than in trees (e.g., Vogts et al., 2009). A pollen study at the site of core 17940, near our study site, showed that herb pollen (e.g., *Artemisia*, *Gramineae*, and *Cyperaceae*) was abundant during the Oldest Dryas period, due to the cold and dry climate, and decreased during the Bølling-Allerød period (Sun and Li, 1999). The high ACL in the Oldest Dryas period is consistent with the high abundance of herb pollen. Fern spores significantly increased after 1.4 ka in core 17940, possibly due to human activity (Sun and Li, 1999). This increase corresponds to the increase of ACL in the study core. There is one report for a fern *Hydrilla verticillate* having high ACL (Chikaraishi and Naraoka, 2003), but we do not fully understand the ACL in ferns. Thus we cannot attribute this change to the increase of ferns; future investigations of fern ACLs are necessary. The core site is proximal to South China and is thus in an ideal position to trace environmental changes by human activities in historical times. Further applications of new techniques will

contribute to better understanding the environmental changes in South China.

Conclusions

We applied $\text{TEX}_{86}^{\text{H}}$ paleothermometry to sediment from the SCS and demonstrated measurable SST variations over the past 28 kyr. The $\text{TEX}_{86}^{\text{H}}$ -derived temperature of a core-top sample corresponds to the SSTs in warmer seasons. The glacial–interglacial contrast in $\text{TEX}_{86}^{\text{H}}$ -derived temperature is almost the same as that in foraminiferal Mg/Ca ratio-derived temperature, but it is larger than those in U_{37}^{K} and transfer function-derived temperatures. The similar variation in $\text{TEX}_{86}^{\text{H}}$ -derived temperature at the study site and Chinese stalagmite $\delta^{18}\text{O}$ during the last deglaciation suggests that changes in $\text{TEX}_{86}^{\text{H}}$ -derived temperature in this period reflected atmospheric and oceanic reorganization on a millennial timescale.

We also examined terrestrial biomarkers such as n-alkanes and n-fatty acids that show a remarkable change from abundant fresh higher plants to the mixture of fresh higher plants and mature organic matter at 14–15 ky BP. We consider this is a result of a considerable change in sediment delivery at that time. Terrestrial organic matter was presumably supplied by enhanced aeolian transportation prior to 14–15 ka, with the contribution from river discharge becoming more important thereafter presumably due to intensified summer monsoon.

Acknowledgements: We thank shipboard members of IMAGES 1997 cruise. We also thank Ellen Hopmans and Stefan Schouten (Royal Netherlands Institute for Sea Research) for kindly giving us advice about GDGT and TEX_{86} analysis. Thanks go to Tatsufumi Okino, Yusuke Izawa, Masao Minagawa, and Tomohisa Irino (Hokkaido University) for help with

analysis. Comments by four anonymous reviewers improved this manuscript. This study was supported by a grant-in-aid for Scientific Research (A) the Japan Society for the Promotion of Science, No. 19204051 (to MY).

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Figure captions

Fig. 1. Map showing the locations of core MD97-2146 and other cores referred to in this paper.

Fig. 2. Depth and seasonal variation of water temperatures at the study site (Compiled data from NOAA, 1998). “J” to “D” means January to December.

Fig. 3. (A) $\text{TEX}_{86}^{\text{H}}$ and (B) U_{37}^{K} -derived temperatures in core MD97-2146, and (C) Mg/Ca-derived SST in ODP Site 1145 (Oppo and Sun, 2005) during the last 28 kyr. The summer, winter and annual mean SSTs estimated by a regional Imbrie–Kipp transfer function method (FP-12E; Thompson, 1981) of planktonic foraminifera in core 19740 (Wang et al., 1999b) are also shown in each panel.

Fig. 4. (A) Concentrations of total, higher plant, and lithic long-chain $\text{C}_{25}\text{-C}_{33}$ n-alkanes, and the CPI and ACL of n-alkanes. (B) Concentrations of total ($\text{C}_{14}\text{-C}_{34}$), short-chain ($\text{C}_{14}\text{-C}_{18}$), and long-chain ($\text{C}_{26}\text{-C}_{34}$) n-fatty acids, and the CPI of n-fatty acids and abundance ratio of long-chain to short-chain (L/S ratio) n-fatty acids in core MD97-2146 during the last 28 kyr. (C) Reconstructed sea level (Lambeck *et al.*, 2002) and the sill depths of straits to the East China Sea, the Sulu Sea, the Indian Ocean and the Java Sea (Wyrтки, 1961).

Fig. 1

Fig. 2

Fig. 3

Fig. 4