Diagenetic and Detrital Origin of Moretane Anomalies through the Permian-Triassic Boundary

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<td><a href="http://dx.doi.org/10.1016/j.gca.2012.01.004">http://dx.doi.org/10.1016/j.gca.2012.01.004</a></td>
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<tr>
<td>Publisher</td>
<td>Elsevier Ltd.</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
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<tr>
<td>Accessed</td>
<td>Mon Apr 01 02:21:02 EDT 2019</td>
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<tr>
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Diagenetic and detrital origin of moretane anomalies through the Permian–Triassic boundary

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Received 20 August 2011; accepted in revised form 11 January 2012; available online 28 January 2012

Abstract

Many biogeochemical anomalies coincide with the Late Permian Extinction (LPE; 252.28 Ma). Several mechanisms have been proposed to explain the moretane/hopane anomaly that has been identified in samples from Meishan GSSP section in southeastern China. Here, we report homohopane, 2α- and 3β-methylhomohopane and lithological data for a drill core from the Meishan section in southeastern China. Three intervals of elevated C30 moretane/hopane ratios are recorded in the Lungtan, Yinkeng and Helongshan Formations. Moretane/hopane ratios of C31–34 homohopanes and the 2α- and 3β-methylhomohopanes display the same stratigraphic patterns as the C30 moretane/hopane record. In light of the multiple and parallel moretane anomalies for the homohopane and 2α- and 3β-methylhomohopane series, enhanced input from higher plant organic matter, such as coal and peat, does not adequately explain the observed isomer patterns. Correlation of high moretane/hopane ratios with low C35 Homohopane Index (HHI) and high hopane/sterane values suggest increased input of hopanoids from oxic soils. Additionally, moretane/hopane ratios show excellent correlations with total clay percentages and specific clay types, particularly chlorite, illite, and mixed layer illite/smectite. We conclude that a combination of episodic hopanoid input from soil bacteria and diagenetic effects related to redox and detrital clays generated the unique moretane/hopane patterns at Meishan.

Similar relationships of Ts/(Ts + Tm) with redox, source indicators, and lithology indicate that Ts/(Ts + Tm) is affected by the same factors controlling the moretane/hopane ratios. Berthierine, a clay that requires reducing conditions for formation, was detected in samples from the Lungtan Formation. We are unable to determine from our results whether the berthierine is authigenic or detrital, but future determination of the origin of berthierine at Meishan may offer additional environmental insight. No link between diasteranes and lithology was observed in this study suggesting that diasteranes are relatively unaffected by the detrital clay component of the Meishan sediments. In total, the results point toward the complex role of source input, lithology, and depositional redox conditions in the transformation of organic matter during maturation. Future work is required to elucidate the lithological effects on diagenetic processes, including biomarker genesis isomerization, and thermal degradation.

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1. INTRODUCTION

Through the course of Earth’s 4.5 billion year history, there have been five mass extinction events in which at least 75% of species became extinct in a geologically short time interval. Given the rapid loss of biodiversity over the past centuries, some researchers have suggested that Earth may currently be entering its sixth mass extinction (Barnosky et al., 2011). Humans are suspected to have a role in today’s loss of biodiversity, but other conditions and series of events must have caused the previous five mass extinctions. The Late Permian Extinction (LPE; 252.28 Ma) (Shen et al., 2011a), which occurred shortly before the biostatigraphic Permian Triassic Boundary (PTB) as defined by the first appearance of *Hindeodus parvus*, marks the greatest loss of biodiversity in Earth history with over 90% of marine species becoming extinct (Raup, 1979; Mundil et al., 2001, 2004; Sepkoski, 2002; Erwin, 2006; Metcalfe and Isozaki, 2009). Many mechanisms have been proposed to trigger the LPE event, including Siberian floodbasalt volcanism, sea level change, extraterrestrial impact, ocean deoxygenation, water column stratification and climate change driven by methane hydrate collapse (Campbell et al., 1992; Wignall and Hallam, 1992; Renne et al., 1995; Becker et al., 2001; Benton and Twitchett, 2003; Kamo et al., 2003). Whatever the trigger or combination of triggers, accumulating evidence points to the rapid deterioration of both the marine and terrigenous ecosystems (Retallack, 1995; Looy et al., 2001; Twitchett et al., 2001; Michaelsen, 2002).

Geochemical techniques have helped to elucidate the nature of the events that unfolded during the Late Permian, yet additional questions have arisen as a result. In addition to a distinctive negative stable carbon isotopic excursion and trace metal enrichment at the boundary (Kaiho et al., 2001, 2006; Cao et al., 2002, 2009), anomalous distributions of lipid biomarkers, including isorenieratane and derived aryl isoprenoids, 2-methylhopanes and crocetane, are defining features of the PTB (Grice et al., 2005; Wang et al., 2005; Xie et al., 2005; Wang, 2007; Cao et al., 2009). Additionally, anomalous values of molecular ratios, including C₃₀ 17β,21α(1H)-hopane/C₃₀ 17α,21β(1H)-hopane (referred to as the C₃₀ moretane/hopane ratio), C₃₂ 18α-trisnorhopane/C₃₂ 17α-trisnorhopane (referred to as Ts/(Ts + Tm)), Tm/C₃₀ hopane, C₃₁/C₃₂ hopane, C₃₅ Homohopane Index (C₃₅ HHII), and hopane/sterane, are recorded in sediments deposited at the PTB (Wang, 2007; Xie et al., 2007; Cao et al., 2009).

Multiple scenarios have been proposed to explain the elevated moretane/hopane ratios at the PTB. Geochemical maturity parameters throughout the Meishan GSSP section in southeastern China are nearly uniform, and thus, thermal maturity variations cannot adequately explain the moretane/hopane and Ts/(Ts + Tm) variability observed through the section (Cao et al., 2009). Accordingly, additional mechanisms have been proposed to account for the moretane variability, including increased input of higher plant organic matter to the marine system, increased acidification, freshening of the upper water column, or lithological effects (Wang, 2007; Xie et al., 2007; Cao et al., 2009).

In order to further assess and correctly interpret the moretane anomalies at the PTB, homohopane, 2α- and 3β-methylhomohopane and lithological data for a drill core taken from the Meishan section in China were critically examined. The possible mechanisms for generating the observed moretane record, including thermal maturity, source input, redox conditions, and lithology, were examined in light of the new hopane and lithological data.

1.1. Moretane background

Hopanes are pentacyclic triterpanes and are arguably the most ubiquitous natural product found on Earth (Ourisson and Albrecht, 1992). Bacteria are the dominant source of hopanes in marine sediments, and bacteriohopanepolys (BHP) are the primary precursor of C₃₀ and higher hopane homologues. Hopanes have readily isomerized asymmetric carbon atoms at C-17 and C-21, where α and β denote whether the hydrogen is below or above the plane of the ring system, respectively. Consequently, when considering C-17 and C-21, there are four possible stereoisomers (Fig. 1): 17β,21β-H(hopane) (ββ-hopane), 17β,21α-H(hopane) (ββ-moretane), 17α,21β-H(hopane) (ββ-hopane), and 17α,21β-H(hopane) (αα-hopane; this isomer is not generally encountered in sediments). The term “moretane” distinguishes the 17β,21α-H(hopane) stereoisomers from the other hopane stereoisomers, while the others are simply referred to as ‘hopanes’. The ββ-hopanoids are the commonly observed biological configuration and are found in bacterial cultures and immature organic material. The αα configuration is nearly planar, which enables the molecule to fit into the membrane lipid bilayer (Peters et al., 2005), but the ββ-hopane is the least thermodynamically stable of the hopane stereoisomeric series (Seifert and Moldowan, 1980; Kolaczkowska et al., 1990; Peters et al., 2005). During diagenesis and catagenesis, ββ-hopane is removed by thermal degradation or interconversion to the more thermodynamically stable βα-moretane and αβ-hopane. According to the scheme illustrated in Seifert and Moldowan (1980), βα-moretane can overcome an energy barrier given sufficient thermal energy to be converted to the thermodynamically preferred αβ-hopane via the ββ-hopane intermediate (Peters et al., 2005). The αα-hopane is less thermodynamically stable than either 17β,21α(1H)-moretane or 17α,21β(1H)-hopane, and it is largely undetected in petroleum and mature petroleum source rocks (Bauer et al., 1983; Kolaczkowska et al., 1990).

The distributions of terpane isomers can be used to estimate thermal maturity. Predictions of thermodynamic stability of the different hopane stereoisomeric series and observations of the degree of isomerization of hopanes in immature organic matter and petroleum have led to use of the βα-moretane to αβ-hopane ratio as a thermal maturity indicator (Seifert and Moldowan, 1980; Peters et al., 2005). The βα-moretane/αβ-hopane ratio is used to characterize immature to mildly mature oils. However, thermal maturity is not the only factor that influences the βα-moretane/αβ-hopane ratio. The source of organic matter input and depositional environment influence the terpane fingerprint of petroleum and can significantly affect thermal maturity parameters (Peters et al., 2005). Based on reports
of 17β,21α(H) hopanoids in hypersaline environments, peat, coal, lacustrine environments, and in living systems (Quirk et al., 1984; Rullkötter and Marzi, 1988; Uemura and Ishiwatari, 1995; Rosa-Putra et al., 2001), some authors have invoked increased input of higher plant organic matter to explain anomalous moretane abundance in marine sediments where thermal maturity is not the cause of variability (Grantham, 1986; Isaksen and Bohacs, 1995; Wang, 2007; Xie et al., 2007). However, in a number of instances, depositional environment has been shown to strongly modulate terpane distributions, including the abundance of moretane relative to ab-hopane (Peters et al., 2005).

2. SAMPLES AND EXPERIMENTAL METHODS

2.1. Geographic setting

The Meishan quarries in South China have produced detailed information about the Permian–Triassic mass extinction. The Meishan section is the Global Stratotype Section and Point (GSSP) for the PTB, as well as for the base of Changhsingian Stage. In order to avoid sampling material that was altered and contaminated during surficial weathering, a drilling project was undertaken by the Nanjing Institute of Geology and Paleontology in 2004. A detailed description of the Meishan section and the drilling project are provided in the supplementary online material of Cao et al. (2009).

2.2. Biomarker analyses

As described by Cao et al. (2009), the exterior of the samples were brushed clean and rinsed with methanol (MeOH) and dichloromethane (DCM) prior to being powdered using a solvent-cleaned ceramic puck mill. Procedural blanks were prepared along with the samples and showed no evidence of laboratory contamination. Samples were solvent extracted using a Dionex ASE-200 extractor and a solvent mixture of DCM and MeOH (9:1). Elemental sulfur was removed from the total lipid extracts using acid-washed copper granules. Aliphatic, aromatic, and polar fractions of 17β,21α(H) hopanoids in hypersaline environments, peat, coal, lacustrine environments, and in living systems (Quirk et al., 1984; Rullkötter and Marzi, 1988; Uemura and Ishiwatari, 1995; Rosa-Putra et al., 2001), some authors have invoked increased input of higher plant organic matter to explain anomalous moretane abundance in marine sediments where thermal maturity is not the cause of variability (Grantham, 1986; Isaksen and Bohacs, 1995; Wang, 2007; Xie et al., 2007). However, in a number of instances, depositional environment has been shown to strongly modulate terpane distributions, including the abundance of moretane relative to ab-hopane (Peters et al., 2005).

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were collected by silica column chromatography using hexane, hexane/DCM (4:1), and DCM/MeOH (4:1) solvents, respectively. Each fraction was dried and weighed before adding analytical standards to 1 mg of the saturated fraction. The saturated hydrocarbon biomarkers were analyzed by gas chromatography–mass spectrometry (GC–MS) in full scan and metastable reaction monitoring (MRM) modes. The characteristic m/z 191 and 205 mass fragments were used to identify the C_{30}–C_{34} homohopanes and 2α- and 3β-methylhomohopanes in MRM mode, respectively (see Fig. 2). The 22S and 22R isomers of C_{31–34} homohopanes and C_{32–33} methylhomohopanes were identified, and both isomers were used in the calculation of the βα/(βα + ββ) ratios. The 22S and 22R isomers of βα-C_{31} homohopane and βα-C_{32} methylhomohopane coelute, so these compounds were integrated as a single peak as illustrated in Fig. 2. The supplementary online material of Cao et al. (2009) describes the biomarker analytical methods in greater detail.

Fig. 2. Multiple reaction monitoring (MRM) chromatograms from sample MS-core1-35-1 at 94.53 m depth are shown. The MRM transitions are written to the right of the chromatogram. In the left column, the 191.179 fragment corresponds to the A/B rings for homohopanes (see Fig. 1). In the right column, the 205 mass fragment corresponds to the A/B ring fragment for 2α- and 3β-methylhomohopanes. All peaks are marked numerically with the corresponding identification to the right.
2.3. Mineralogical analyses

2.3.1. Carbonate contents

Approximately 0.5 g of each powdered sample was accurately weighed into a clean Teflon tube. Methanol was added to wet the sample prior to acidification. Each sample was acidified with a 10% aqueous hydrochloric acid (HCl) solution. The samples were treated again with a 15% HCl solution and left for 24 h to allow the reaction to reach completion. The samples were rinsed with water five times to remove any remaining acid before being dried in a 60 °C oven for 48 h. The samples were reweighed, and the percentage carbonate was calculated based on the difference between the initial and final weights.

2.3.2. Clay analyses

Preparation for bulk mineralogical analysis of all samples involved crushing rock samples in an agate swing mill, addition of 10 wt.% ZnO and further milling to ensure mixing and homogeneous distribution. Bulk mineralogical analysis was performed on randomly oriented samples using a Bruker D8 X-ray diffractometer at 40 kV and 30 mA with CuKa radiation. Analyses were performed from 2–65° 2θ (for any diffracted X-ray obeying Bragg’s Law, 2θ is referred to herein is equal to two times the angle between the sample plane and the incident X-ray beam) at a step size of 0.02° and counting times of 4 s per step. Quantitative analysis was performed with single line and full profile fitting using pure mineral standards for reference intensity ratios (Srodon et al., 2001).

Determination of clay mineralogy involved light crushing of samples by hand in a steel mortar and pestle and for samples containing appreciable carbonate content, decarbonation with 1 M acetic acid while monitoring pH. Decarbonated samples were rinsed three times with deionised water and all samples were resuspended with sodium phosphate, sonicated and the <2 and <0.2 μm size fractions were obtained by timed centrifugation. Centrifuged samples were decanted and oriented Ca-saturated aggregates were prepared by using a filter membrane technique and transfer of clay films for glass substrates. X-ray diffraction was performed using a Siemens D5000 diffractometer at 30 kV and 20 mA, with CuKa radiation from 2–35° 2θ a step size of 0.03° and counting times of 8–10 s. Divergence, receiving and anti-scatter slits were 0.2 and 1 mm in size, respectively, and a Ni filter was used. Clay samples were analysed in the air-dried Ca-saturated state, after ethylene glycol solvation overnight at 60 °C (to identify expandable minerals), heating at 400 °C for 2 h (to quantify collapsible/expanding mineral proportions), and heating to 550 °C for 2 h (to aid in quantifying kaolinite and chlorite proportions). Relative clay abundances were determined by peak area measurement, expressed in relative percent and normalized to total clay content by total clay mineral abundance determined by bulk mineralogical analyses. The composition of mixed-layered species was determined using one dimensional X-ray diffraction pattern modeling with the software package NEWMOD (Reynolds and Reynolds, 1996).

3. RESULTS

3.1. Stratigraphic variation of lithology and hopane distributions

The β3/(β3 + α3) ratios for C30 hopane, C31–34 homohopanes, C31–33 2α-methylhopanes, and C31–33 3β-methylhopanes were calculated for each sample (Table 1). The precise determination of β3/(β3 + α3) for the C31 and C32 3β-methylhopanes was precluded by interfering peaks and will not be further discussed. The β3/(α3 + β3) values vary from 0.04 to 0.34 for all of the other hopane series measured. The profiles of C30 hopane, the homohopanes, and the 2α- and 3β-methylhomohopanes show parallel down-core trends and similar values (Fig. 3). Ts/(Ts + Tm) and C35 Homohopane Index (HHI) data from Cao et al. (2009) were plotted in Fig. 3 for comparison. Notably, the rocks record three positive moretane enrichments. The first interval of enhanced moretane/hopane ratios occurs in the Lungtan Formation, followed by the second interval at the PTB in the Yinkeng Formation, and the last interval of moretane enrichment at the end of the Griesbachian in the Helongshan Formation.

The bulk lithology, including percent carbonate, total clay, and quartz was determined (Table 2). The lithology was highly variable through the drill core section (Fig. 4). The percent carbonate fluctuates from 8.5% to 99%. The percent total clay and the percent quartz both vary from close to 0% to nearly 50%. The Lungtan Formation is a clay-rich unit that is enriched in quartz and is characterized by low carbonate (8.5–14%). The percent carbonate increases significantly in the overlying Changxing unit, although the carbonate and quartz percentages are more variable through this interval. Unlike the Lungtan Formation, clay is a minor component through the Changxing Formation. The percent total clay returns to elevated values in the Yinkeng Formation, while the percent carbonate is significantly lower than the Changxing or Helongshan formations. Through the Helongshan Formation, the samples are all over 95% carbonate with very little clay or quartz. Similar to the observations of Rullkötter and Marzi (1988), elevated abundances of moretanes relative to 3β-hopane are associated with carbonate-poor facies.

Further clay mineralogical analyses provided the absolute and relative percentages of specific clay types, including illite, chlorite, smectite, kaolinite, berthierine, and mixed layer illite/smectite (Table 3). The total percent clay and the absolute and relative percentages of the clay type varied through the section (see Fig. 5). Illite and mixed layer illite/smectite represent the dominant clay types, where the sum of percent illite and mixed layer illite/smectite represents over 50% through the entire section. The relative percentage of illite/smectite mixed layer clay is largely constant throughout the clay mineral assemblage. Although more variable, kaolinite, chlorite, and smectite clays become a significant fraction of the total clay through some intervals of the assemblage. Notably, berthierine, which is usually formed under reducing conditions (Taylor and Curtis, 1995; Fritz and Toth, 1997), is present in the Lungtan Formation at the base of the section. Measurable differ-
Table 1
Summary of geochemical data.

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<td>0.151</td>
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<td>0.133</td>
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<tr>
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<td>0.060</td>
<td>0.098</td>
<td>0.041</td>
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<td>0.063</td>
<td>0.047</td>
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<td>0.135</td>
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<tr>
<td>MS-1-core</td>
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<td>0.267</td>
<td>0.246</td>
<td>0.302</td>
<td>0.304</td>
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</table>
ences between the glycolated and heated (400 °C) samples in the 7 Å peak suggest that trace abundances of berthierine may be present in the samples between 92 and 103 m. It is not possible to determine from our results whether the berthierine is detrital or authigenic.

3.2. Crossplots of molecular indices and lithological data

Cross-correlation diagrams were generated to evaluate the relationships between the geochemical and lithological data. The $\beta\gamma/(\alpha\beta + \beta\alpha)$ ratios of C$_{30}$ hopane were plotted
against the $\beta\alpha/(\alpha\beta + \beta\alpha)$ ratios of C₃₁–C₃₄ homohopanes and the 2α and 3β-methylhomohopanes (Fig. 6A and B). In both cases, an excellent positive correlation is observed with $R^2$ values ranging from 0.88 to 0.99. Cao et al. (2009) found that $T_s/(T_s + T_m)$ varied inversely with the C₃₀ hopane $\beta\alpha/(\alpha\beta + \beta\alpha)$ ratio. Likewise, the $T_s/(T_s + T_m)$ data reported by Cao et al. (2009) also correlate inversely with the homohopane and 2α- and 3β-methylhomohopane $\beta\alpha/(\alpha\beta + \beta\alpha)$ ratios with $R^2$ values ranging from 0.64 to 0.77 (Fig. 6C and D).

The carbonate percentage and total clay percentage were plotted against the moretane/hopane ratios for all of the hopane series and $T_s/(T_s + T_m)$ (Fig. 7). The percent carbonate and percent clay have opposite relationships with the $\beta\alpha/(\alpha\beta + \beta\alpha)$ ratios. Carbonate percentage and the $\beta\alpha/(\alpha\beta + \beta\alpha)$ ratios of all of the hopane series are inversely related, having $R^2$ values ranging from 0.42 to 0.57. The correlation is significantly improved with $R^2$ values from 0.74 to 0.87 when the $\beta\alpha/(\alpha\beta + \beta\alpha)$ ratios are plotted against total clay percentage. Similarly, the correlation of $T_s/(T_s + T_m)$ with the total clay percentage ($R^2 = 0.52$) is stronger than with the percent carbonate ($R^2 = 0.36$). However, the $R^2$ values for $T_s/(T_s + T_m)$ versus carbonate and total clay percentages are less than for the $\beta\alpha/(\alpha\beta + \beta\alpha)$ ratios in both cases.

The $\beta\alpha/(\alpha\beta + \beta\alpha)$ ratios for all of the hopane series were plotted together with the percentages of the different clay types in Fig. 8. Like the total clay percentage, all of the clay types were directly related to $\beta\alpha/(\alpha\beta + \beta\alpha)$, yet some clay types were more strongly correlated to $\beta\alpha/(\alpha\beta + \beta\alpha)$ than others. Kaolinite had the weakest correlation with $\beta\alpha/(\alpha\beta + \beta\alpha)$, having $R^2$ values from 0.024 to 0.222. Likewise, smectite was weakly correlated to $\beta\alpha/(\alpha\beta + \beta\alpha)$, having $R^2$ values spanning 0.215–0.485. On the other hand, the percent chlorite was strongly correlated with $\beta\alpha/(\alpha\beta + \beta\alpha)$, where $R^2$ values ranged from 0.773 to 0.901. Percent illite and percent mixed layer illite/smectite also yielded strong correlations with $\beta\alpha/(\alpha\beta + \beta\alpha)$.

The $T_s/(T_s + T_m)$ values from Cao et al. (2009) were plotted versus the different types of clays. Low values of $T_s/(T_s + T_m)$ occur during intervals of high clay accumulation, in particular, intervals where chlorite, illite, and illite/smectite mixed layer clays comprise a higher proportion of rock lithology. The $R^2$ values for $T_s/(T_s + T_m)$ were less

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**Fig. 4.** Vertical profiles of the bulk lithological components by percentage versus the stratigraphic column (modified from Cao et al., 2009). (A) percentage carbonate; (B) percentage total clay; (C) percentage quartz. See Fig. 3 for the stratigraphic column legend.
### Table 3
Absolute and relative clay type percentages.

<table>
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<tr>
<th>Sample ID</th>
<th>Absolute percent illite</th>
<th>Absolute percent berthierine</th>
<th>Absolute percent kaolinite</th>
<th>Absolute percent chlorite</th>
<th>Absolute percent illite/smectite mixed layer</th>
<th>Absolute percent smectite</th>
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<th>Relative percent kaolinite</th>
<th>Relative percent chlorite</th>
<th>Relative percent illite/smectite mixed layer</th>
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*Note: See Table 1 for sample depths.*
Fig. 5. Vertical profiles of clay types plotted against the stratigraphic column (modified from Cao et al. (2009)). (A) Absolute percent illite; (B) absolute percent chlorite; (C) absolute percent smectite; (D) absolute percent kaolinite; (E) absolute percent mixed layer illite/smectite (I/S); (F) absolute percent berthierine. Note the difference in the x axis scale for clay types. See Fig. 3 for the stratigraphic column legend.

Fig. 6. Cross-correlations of molecular indices. Plots A and B relate moretane/hopane of the C₃₀ hopane to the higher homologues of the homohopane series and 2α- & 3β-methylhomohopane series, respectively. Plots C and D relate Ts/(Ts + Tm) to the higher homologues of the homohopane series and 2α- and 3β-methylhomohopane series, respectively. The $R^2$ value associated with the linear regression for each series relationship is given in the legend.
than the $R^2$ values for the analogous $\beta\beta/(\alpha\beta + \beta\alpha)$ plots. Like $\beta\beta/(\alpha\beta + \beta\alpha)$, kaolinite and smectite produced the weakest correlation coefficients, while illite, chlorite, and mixed layer illite/chlorite had higher correlation coefficients with $Ts/(Ts + Tm)$.

3.3. Crossplots of C$_{35}$ homohopane index and hopane/sterane ratios with moretane/hopane, $Ts/(Ts+Tm)$ and lithological data

The C$_{35}$ HHI is a redox indicator, and redox conditions are known to affect the distribution of terpanes (Peters et al., 2005). Cross-correlation diagrams were generated to evaluate the relationships between C$_{35}$ HHI data reported in Cao et al. (2009) and moretane/hopane ratios and $Ts/(Ts + Tm)$ (Fig. 9). High moretane/hopane ratios for C$_{30-34}$ homohopanes and C$_{31-33}$ methylhomohopanes correspond to low values of C$_{35}$ HHI, which are indicative of oxic conditions. On the other hand, low values of $Ts/(Ts + Tm)$ correspond with low values of C$_{35}$ HHI. These results are consistent with previous results relating redox indicators to moretane/hopane ratios and $Ts/(Ts + Tm)$ (Moldowan et al., 1986; Rullkötter and Marzi, 1988; Wang, 2007). Interestingly, high values of hopane/sterane percentages reported in Cao et al., 2009 correspond with high values of moretane/hopane ratios for C$_{30-34}$ homohopanes and C$_{31-33}$ methylhomohopanes and low values of $Ts/(Ts + Tm)$ (Fig. 9). This relationship is unexpected because if the abundance of $\beta\beta$-hopanes were driving the correlation between hopane/sterane ratios and moretane/hopane ratios, one would expect an inverse pattern between these two parameters, which is the opposite of what is observed.

The C$_{35}$ HHI and hopane/sterane percentages were plotted against total clay percent and all of the clay types detected in the Meishan section (Figs. 10 and 11). In general, the highest values of percent total clay and individual clay types correspond to C$_{35}$ HHI values less than 5%, but
several samples with significant kaolinite abundances have higher C₃₅ HHI values. High values of hopane/sterane per-
percentages are related to high values of total clay, chlorite, illite, mixed layer illite/smectite (I/S), and smectite. Kaolinite

Fig. 8. Correlations between moretane/hopane ratios and the specific clay types are shown for the homohopane and 2α- and 3β-methylhomohopane series. The R² values are listed in the legend next to the corresponding series. (A) Absolute percent chlorite; (B) absolute percent illite; (C) absolute percent mixed layer illite/smectite (I/S); (D) absolute percent smectite; (E) absolute percent kaolinite.
and berthierine do not display this same relationship with the hopane/sterane percentages (see Fig. 11 F and G).

4. DISCUSSION

4.1. Possible causes of moretane enrichment

The strong positive correlations between the C_{30} hopane \( \beta_2/(\alpha_\beta + \beta_2) \) (A), methylhomohopanes \( \beta_2/(\beta_2 + \alpha_\beta) \) (C), and Ts/(Ts + Tm) (E). Hopane/Sterane (%) versus homohopanes \( \beta_2/(\beta_2 + \alpha_\beta) \) (B), methylhomohopanes \( \beta_2/(\beta_2 + \alpha_\beta) \) (D), and Ts/(Ts + Tm) (F).

Fig. 9. Correlations of geochemical source and redox indicators against moretane/hopane ratios and Ts/(Ts + Tm). C_{35} HHI (%) vs. homohopanes \( \beta_2/(\beta_2 + \alpha_\beta) \) (A), methylhomohopanes \( \beta_2/(\beta_2 + \alpha_\beta) \) (C), and Ts/(Ts + Tm) (E). Hopane/Sterane (%) versus homohopanes \( \beta_2/(\beta_2 + \alpha_\beta) \) (B), methylhomohopanes \( \beta_2/(\beta_2 + \alpha_\beta) \) (D), and Ts/(Ts + Tm) (F).

Thermal maturity can be estimated by measuring the degree of isomerization, including the ratio of \( \beta_2 \)-moretanes to \( \alpha_\beta \)-hopanes, the conversion of 22R to 22S for 17\( \alpha \)21\( \beta \)H-homohopanes and the conversion of 20R to 20S steranes. The moretane to \( \alpha_\beta \)-hopane ratio for the C_{30} compound declines with increasing thermal maturity from \( \sim 0.8 \) in immature rocks to \( <0.15 \) for mature rocks (Peters et al., 2005). While the ratio of moretanes to \( \alpha_\beta \)-hopanes varies significantly through the drill core, the ratio of 22S/(22S + 22R) for C_{31} homohopane is between 54% and 59% throughout the entire Meishan drill core (Cao et al., 2009). According to Larcher et al. (1987), these values are
expected for \( \alpha\beta \)-hopanes when the epimerization reaction that converts the biological 22R epimer to 22S has reached the endpoint. The epimerization end point is met before the main phase of oil generation (Peters et al., 2005). The 20S/(20S + 20R) ratios of the \( \mathrm{C}_{27} \) steranes varies between 45% and 50%, which further supports the conclusion that the whole cored interval is within the early stages of petroleum generation and shows little variation throughout (Cao et al., 2009). The largely constant relative percent of illite/smectite mixed layer clay in the section is also consistent with constant thermal maturation throughout the Meishan drill core (Pollastro, 1993). Accordingly, thermal maturity can be ruled out as the factor responsible for moretane variability. Likewise, Wang (2007) and Xie

Fig. 10. Correlations of \( \mathrm{C}_{35} \) HHI (%), a redox indicator, against percent total clay and clay types. \( \mathrm{C}_{35} \) HHI (%) vs. percent total clay (A), absolute percent chlorite (B), absolute percent illite (C), absolute percent illite/smectite mixed layer clay (I/S) (D), absolute percent smectite (E), absolute percent kaolinite (F), absolute percent berthierine (G).
et al. (2007) eliminated thermal maturity as a possible mechanism for generating the moretane anomaly based on additional lines of evidence.

The sources of organic matter profoundly affect biomarker distributions (Peters et al., 2005). Previous studies have argued that increased terrigenous organic matter input from higher plants, peat, or coal explains elevated moretane/hopane ratios in cases where thermal maturity does not sufficiently explain the pattern of moretane/hopane ratios (Grantham, 1986; Rullkötter and Marzi, 1988; Isaksen

Fig. 11. Correlations of Hopane/Sterane (%), a geochemical source indicator, against percent total clay and clay types. Hopane/Sterane (%) vs. percent total clay (A), absolute percent chlorite (B), absolute percent illite (C), absolute percent illite/smectite mixed layer clay (I/S) (D), absolute percent smectite (E), absolute percent kaolinite (F), absolute percent berthierine (G).
Second, although ββ-hopanes have been isolated from ferns and lichens (Hveding-Bergseth et al., 2005; Aichner et al., 2010; Kristen et al., 2010). Quirk et al. (1984) detected C_{32} βα-alcohols, C_{31} methylmoretan-29-ol, and C_{32} and C_{33} βα hopanoic acids in peat samples, and elevated levels of moretane were reported for coals (e.g., Hughes and Dzou, 1995; Shen and Huang, 2007). The data presented in this paper do not support this explanation. None of the previous reports linking higher plant organic matter input to elevated moretane abundances provide a viable explanation for the parallel trends of the extended homohopanes and the 2α- and 3β-methylhomohopanes because, with the exception of the peat samples reported by Quirk et al. (1984), the ββ-hopanoids detected in organisms, peat, and coal are C_{32} or C_{30} compounds. Because thermal maturity and a change in input of higher plant organic matter fail to account for the observed moretane anomalies, other source input changes and diageneric effects must be considered.

Redox potential is known to affect the distribution of terpanes in lipid extracts (Peters et al., 2005). Multiple redox indicators are presented for the Meishan section in Cao et al. (2009). Values of 28,30-dinorhopane (28,30-DNH) between 0.5% and 2% and the detection of isoretene and C_{14,27} aryl isoprenoids throughout the cored interval indicates that all of the sediments were deposited in a marine environment. The discrepancy of the C_{35} HHI with the other redox indicators and the strong relationship of the C_{35} HHI with the moretane/hopane ratios, Ts/(Ts + Tm), and lithological data suggest a detrital source for the clays and hopanes in the intervals of elevated moretane/hopane ratios.

Multiple lines of evidence suggest increased soil erosion, forest fires, continental weathering, and terrigenous input during the PTB (Ward et al., 2000; Retallack, 1998; Retallack, 2005; Septon et al., 2005; Wang and Visscher, 2007; Cao et al., 2009; Nabbefeld et al., 2010b; Shen et al., 2011a,b). Although most studies do not examine evidence earlier than the Changhsingian, detection of particular polycyclic aromatic hydrocarbons (PAHs) in samples from Meishan prior to the extinction horizon suggests that there may have been earlier pulses of land-derived organic matter to the marine system (Nabbefeld et al., 2010b). Interestingly, the highest values of retene, a PAH thought to be derived from coniferous resin (Peters et al., 2005), is concurrent with the earliest interval of moretane/hopane enrichment in the Lungtan Formation. Accordingly, there may have been increased terrigenous input to the marine system during the PTB and the Wuchiapingian, which is consistent with a detrital origin of clays and hopanes during these intervals.

Increased organic matter input from higher plant matter cannot explain the parallel patterns of ββ/(αβ + ββ) for C_{30–34} homohopanes and C_{31–33} methylhomohopanes, but increased input of hopanoids from soil bacteria may explain the anomalous moretane/hopane ratios observed in all hopane series. The hypothesis that there was an influx of hopanoids from soil bacteria to the marine system is supported by the observation that high moretane/hopane ratios for all hopane series are associated with high hopane/stereane percentages. This hypothesis is further supported by the observation that high hopane/stereane percentages are associated with high abundances of the clay types that are most tightly related to moretane/hopane ratios (chlorite, illite, mixed layer illite/smectite, and smectite). We conclude that the multiple intervals of elevated moretanes were characterized by increased input of hopanoids derived from soils. However, this change in source input alone does not fully explain the moretane stereochemochemical anomalies. While ββ-hopanoids have been identified in one type of soil bacteria (Rosa-Putra et al., 2001), it is more likely that the detrital clays and redox conditions of the original depositional environment controlled the stereochemochemistry of the soil-derived hopanoids that were ultimately deposited in marine sediments. Therefore, a combination of hopanoid input from soils and diageneric effects generated the unique moretane/hopanes patterns observed at Meishan.

4.2. Discussion of possible mechanisms for mineral preservation of ββ-hopanoid stereochemochemistry

Certain minerals are known to mediate diageneric reactions. In addition to thermal maturity and the source of organic matter, depositional environment and lithology are known to affect the distribution of biomarkers, including the moretane/hopane ratio (Moldowan et al., 1986; Curiale and Odermatt, 1989; Peters et al., 2005). If given sufficient time and heat, the biological isomers decline relative to the thermodynamically preferred isomers. However, this simplistic view is further complicated by factors that affect the relative rates of hydrocarbon generation, isomerization,
and thermal degradation (Lu et al., 1989; Farrimond et al., 1998). Mineral composition has been shown to affect the degree of isomerization for steranes and hopanes in natural systems as well as laboratory pyrolysis experiments (Rullkötter et al., 1985; Eglinton et al., 1986; Curiale and Odermatt, 1989; Lu et al., 1989; Peters et al., 1990; Farrimond et al., 1998; Pan et al., 2010), but distinguishing between mineral effects on biomarker genesis, isomerization, and thermal degradation is difficult. Moreover, it is possible that a combination of these mineral composition effects plays a role in controlling biomarker stereoisomer distribution.

Originally, it was believed that the biologically preferred \( \beta \)-hopane was converted to the \( \beta \alpha \)-hopane and \( \alpha \beta \)-hopane according to the energy diagram and schematic depicted in Seifert and Moldowan (1980). The thermodynamic stabilities of the hopane stereoisomers were later confirmed by molecular mechanics (Kolaczkowska et al., 1990). However, it was recognized that minerals could modulate the rates of epimerization. In particular, acidic surface sites of certain clay types were shown to catalyze isomerization, rearrangement, and hydrogen exchange reactions (Solomon and Swift, 1967; Sieskind et al., 1979; Saxby et al., 1992). Alexander et al. (1984) proposed an epimerization mechanism that proceeded through a planar sp\(^2\) hybridized intermediate. Due to the enhanced stabilities of tertiary, allylic, or benzylic carbocation and radical intermediates, these positions interact with clay surface sites. The carbon adjacent to the carboxylation or radical intermediate then undergoes hydrogen exchange and loss of the original stereochemistry if the hydrogen is added from the opposite face (Alexander et al., 1984). If the mechanism proposed by Alexander et al. (1984) is correct, clay-catalyzed epimerization may be stereoselective. In which case, the conversion of \( \beta \)-hopane to \( \alpha \beta \)-hopane would be less favorable than the conversion to \( \beta \alpha \)-hopane because \( \text{C}_{22} \) is arguably the most accessible tertiary carbon in the hopane skeleton that could interact with the clay surface and form a carbocation intermediate, thus promoting epimerization at the adjacent C-21.

However, direct epimerization of the free \( \beta \)-hopane to \( \beta \alpha \)-hopane and \( \alpha \beta \)-hopane isomers is not the only factor that affects the isomeric distribution of hopanes. Indeed, the rates of hydrocarbon release from kerogen and asphaltene, rates of generation of hydrocarbons from functionalized moieties, and rates of hydrocarbon thermal degradation may also play significant roles in controlling isomer distributions of biomarkers. Mineralogy may mediate these processes, thus influencing the initial and final biomarker distribution (Eglinton et al., 1986; Huizinga et al., 1987; Larcher et al., 1988; Lu et al., 1989; Abbott et al., 1990; Bishop and Abbott, 1993; Bishop et al., 1998; Farrimond et al., 1998, 2002; Koopmans et al., 1998; Wei et al., 2006; Pan et al., 2009, 2010). Furthermore, both organic and inorganic protective matrices can affect lipid biomarker distributions (Hedges and Keil, 1995; Huang et al., 2008; Mead and Goni, 2008). Active clay surfaces, in particular, tend to selectively adsorb polar compounds (Pan et al., 2005). For this reason, the preservation and generation mechanisms of polar hopane precursor compounds may offer insight to the moatane anomalies at Meishan detailed in this report.

Hopanoic acids can be a significant source of free hopanes (Bennett and Abbott, 1999). Laboratory and field results have demonstrated that the degree of isomerization of free hopanes is greater than kerogen-bound and functionalized hopanoids, including hopanoic acids (Tannenbaum et al., 1986; Peters and Moldowan, 1991; Bishop et al., 1998; Murray et al., 1998; Farrimond et al., 2002; Lockhart et al., 2008). Isomerization in the hopane E-ring may occur during the decarboxylation of hopanoic acids to yield free hopanes or during bond cleavage of kerogen-bound hopanoids (Farrimond et al., 1998, 2002). Alternatively, rates of isomerization may be slower for bound hopanoids and functionalized hopanoids than for free hopanes, as discussed below.

Hopanoic acids released from kerogen or produced during early diagenesis may become adsorbed on the mineral matrix and/or polar organic matter by ionic interactions (Huizinga et al., 1987; Thomas et al., 1993; Kubicki et al., 1999). Previous works show that “trapped” or “bound” hydrocarbons isomerize at slower rates than free hydrocarbons (Derenne et al., 1988; Jaffé and Gardinali, 1990; Jaffé et al., 1997). Likewise, adsorption of polar moatane precursors to the surface of a protective matrix could effectively retard the rates of isomerization until release at high maturities. Carboxylic acids tend to adsorb strongly on inorganic surfaces (Thomas et al., 1993). However, the preservation potential of the less mature hopanoic acid signature depends on the adsorptive capacity of the mineral surface (Ransom et al., 1998; Kubicki et al., 1999). The different surface chemistries associated with individual clay types have unique affinities for organic matter, which could explain the different correlation strengths observed for \( \beta \alpha/(\alpha \beta + \beta \alpha) \) and the different clay types at Meishan. However, a more comprehensive study is required that characterizes the interaction of polar precursors of hopanoic acids with the clay types at Meishan and monitors hopanoic acid interactions with the mineral surface over a range of temperature and times.

4.3. Discussion of depositional environment, source input, and Ts/(Ts+Tm)

Like the moatane/hopane ratios, the Ts/(Ts + Tm) thermal maturity parameter is also strongly influenced by source input, lithology, oxygen, and acidity of depositional environment (McKirdy et al., 1983; Moldowan et al., 1986; Waples and Machihara, 1990; Dahl et al., 1993; Peters et al., 2005; Bennett and Olsen, 2007). According to molecular mechanics and observation, Tm (or C\(_{27}\) 17α-trisnorhopane) is less stable than the rearranged Ts isomer (or C\(_{27}\) 18α-trisnorhopane) (Seifert and Moldowan, 1978; Kolaczkowska et al., 1990). According to Fig. 6, Ts/(Ts + Tm) seems to be related not only to C\(_{30}\) \( \beta \alpha/(\alpha \beta + \beta \alpha) \) as shown in Cao et al. (2009), but it is also inversely related to the \( \beta \alpha/(\alpha \beta + \beta \alpha) \) values of the homohopane and 2α- and 3β-methyllumohopane series. This inverse relationship would be expected for Ts/(Ts + Tm) and \( \beta \alpha/(\alpha \beta + \beta \alpha) \) if thermal maturity was the primary control on these parameters. Like \( \beta \alpha/(\alpha \beta + \beta \alpha) \), Ts/(Ts + Tm) co-varies with total clay percent, specific clay type abundances, C\(_{35}\) HHI, and
hopane/sterane percentages at the Meishan section. As discussed above, maturity parameters that more appropriately evaluate the thermal history of this section, indicate relatively constant thermal maturity through the section, so the same mechanisms that are influencing the moretane/hopane ratios are likely affecting $T_s/(T_s + T_m)$. Unlike previous studies that show that carbonate source rocks tend to generate oil with lower $T_s/(T_s + T_m)$ values than clay-rich source rocks (McKirdy et al., 1983; Waples and Machihara, 1990; Peters et al., 2005; Bennett and Olsen, 2007), our results show that low values of $T_s/(T_s + T_m)$ coincide with intervals of high clay content. However, our results are consistent with previous work that indicates $T_m$ is favored over the rearranged, more stable isomer $T_s$ in oxidizing conditions (Moldowan et al., 1986). Like our results that show high values of $T_s/(T_s + T_m)$ in carbonate-rich rocks deposited under reducing conditions, Rullkötter and Marzi (1988) found higher values of $T_s/(T_s + T_m)$ associated with the relatively carbonate-rich Liassic $\sigma$ unit which was deposited under reducing conditions compared to the adjacent carbonate-poor mudstone facies that was deposited under oxic conditions. Input of soil-derived hopanoids seems to play a role in the moretane/hopane ratio patterns, and the relationship of $T_s/(T_s + T_m)$ with hopane/sterane percentages suggests that source input may be affecting $T_s/(T_s + T_m)$ as well. In total, these results indicate that a combination of source input effects and depositional factors, including oxicity and lithology, control $T_s/(T_s + T_m)$ and complicate the interpretation of this geochemical indicator.

4.4. Discussion of lithology, $C_{35}$ homohopane index and additional molecular parameters

Lithology and redox conditions affect other molecular maturity parameters in addition to moretane/hopane ratios and $T_s/(T_s + T_m)$ (Peters et al., 2005). Molecular parameters from Cao et al. (2009), including 28,30-bisnorhopane/$C_{30}$ hopane, gammacerane/$C_{30}$ hopane, $C_{29}$ diasterane/regular sterane, and $C_{27}$ diasterane/regular sterane were plotted against percent carbonate, percent total clay, percent total clay/TOC, $C_{35}$ HHI, and hopane/sterane percentages. No significant correlations were identified with the exception of an inverse correlation of $C_{29}$ diasterane/regular sterane and $C_{27}$ diasterane/regular sterane with hopane/sterane percentages. The absence of any relationship with clay/TOC is countered to the results of van Kaam-Peters et al. (1998) and Nabbefeld et al. (2010a), although the different environmental settings, lithologies, and methods may partially explain the discrepancy.

Having recognized a detrital, clay-borne contribution to the hopanoid inventory during intervals of enhanced moretane accumulation at Meishan, the absence of a relationship between diasterane/regular sterane ratio and lithology comes into focus. Terrigenous organic matter tends to have higher abundances of hopanoids and lower contents of steroids relative to TOC compared to marine organic matter (Peters et al., 2005; Handley et al., 2010; Sáenz et al., 2011). Thus, in marine settings the sources of steroids are mainly marine algae from the water column. During sedimentation in a strongly reducing setting, steroids may be relatively unaffected by diagenetic processes associated with the clays. In other words, in this particular environment steroidal and hopanoid diagenetic processes are decoupled to the degree that some fraction of the hopanoids is derived from detrital sources while the sterols are predominantly of local origin.

4.5. Potential sources of berthierine

The discovery of measurable berthierine and evidence of trace berthierine in the Lungtan and Yinkeng Formations, respectively, is an observation with multiple possible environmental implications. Berthierine forms in reducing environments, but low levels of sulfide and bicarbonate are also required because pyrite or siderite formation is favored over berthierine formation in reducing conditions in the presence of sulfide and bicarbonate, respectively (Taylor and Curtis, 1995; Fritz and Toth, 1997; Sheldon and Retallack, 2002). Interestingly, the berthierine-rich samples occur in the only kaolinite-rich interval of the section, and kaolinite is implicated in the formation of berthierine (Sheldon and Retallack, 2002). In contrast, samples from the Yinkeng Formation with evidence of trace berthierine are kaolinite-poor and smectite-rich. Smectite and kaolinite signify different weathering conditions, and as a result, the clay composition of these two intervals indicates that two different soil types are contributing to the sediments.

The detection of berthierine in samples from the Lungtan Formation where low $C_{35}$ HHI values indicates oxic conditions suggests that one or both of these redox indicators have a detrital component. While it is not possible to conclusively determine from our results whether the berthierine is authigenic or detrital, it is interesting to note that berthierine was discovered in high latitude paleosols deposited in the Early Triassic following the PTB (Sheldon and Retallack, 2002). Formation of berthierine in soils is rare because of the environmental requirements for formation, but weathering or erosion of berthierine-containing paleosols could contribute detrital berthierine to marine sediments. The berthierine-containing paleosols reported in Sheldon and Retallack, 2002 do not correspond well spatially or temporally with the berthierine-rich samples in the Lungtan Formation, but the discovery of berthierine in paleosols may offer a possible mechanism for delivery of berthierine to marine sediments in the event that the berthierine is detrital.

5. Conclusions

Three periods of moretane enhancement, two in the Triassic and one in the Permian, are recorded in the core from the Meishan section in southeastern China. These $C_{30}$ moretane/hopane excursions are echoed in the homohopanes and 2α- and 3β-methylhomohopanes. In light of the multiple and parallel moretane ‘anomalies’ for the homohopane and 2α- and 3β-methylhomohopane series, enhanced input from higher plant organic matter does not adequately explain the observed hopane isomer patterns at Meishan. Correlation of high moretane/hopane ratios
with low C35 HH1 and high hopane/sterane ratios suggest increased input of hopanoids from soils that are influenced byoxic conditions during transport. However, this shift in source input alone cannot explain the hopane stereochemical patterns at Meishan. Based on C35 HH1 and mineralogical analyses, we conclude that diagenetic processes related to lithology and redox determine the [βs-moretane/βa]-hopane distribution for all of the hopane series throughout the cored interval. It seems likely that certain clay types preferentially bind triterpanes having the moretane configuration. Berthierine, a clay that is formed in reducing conditions, was detected in samples from the Lungtan Formation. It is unclear from our results whether the berthierine at Meishan may offer additional environmental insight.

Additional molecular parameters were tested for relationships with lithology. Hopane/sterane ratios, C35 HH1, percent total clay, chlorite, illite, and illite/smectite mixed layer clay showed significant relationships with Ts/Tm, suggesting source input, lithology, and redox also affect this ratio. However, unlike previous studies (van Kaam-Peters et al., 1998; Nabefeld et al., 2010a) that reported a link between diasteranes and percent clay/TOC, this relationship was noticeably absent in the sediments at Meishan. Therefore, it seems likely that the diageneis of steroids here was decoupled from the clay component and more under the control of the intense reducing conditions that prevailed in the water column. In total, our results point toward a complex role of redox and lithology in the transformation of organic matter during diageneis and maturation. Future work is required to disentangle the lithological effects on diagenetic processes, including biomarker genesis isomerization, and thermal degradation. We conclude that a combination of episodic hopanoic input from soil bacteria and diagenetic effects related to redox and detrital clays generated the distinctive moretane/hopane patterns at Meishan.

ACKNOWLEDGMENTS

We wish to thank Christian Hallman and Jürgen Rullkötter for discussions and constructive suggestions, and Gordon Love for his contributions to the early stages of this work, and Bob Burruss, Simon George, and Ken Peters for informative reviews and insightful comments that strengthened this work. K.L.F. is supported by a National Science Foundation Graduate Research Fellowship. Research at MIT was supported by an award (NNX09AM88G) from the NASA Exobiology Program to R.E.S. Research at Nanjing was supported by the 973 Project of the MST of China (2011CB808905) and NSF of China. N.J.T. acknowledges support from Churchill College and the Royal Society (RG 2009/R2).

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*Associate editor: Robert C. Burruss*