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Molecular and stable carbon isotopic composition of monomethylalkanes from one oil sand sample: source implications

Hong Lu, Ping'an Peng, Yongge Sun*

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

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Abstract

Unusually abundant long-chain monomethylalkanes (MMAs) (C_{25}–C_{36}) and their short-chain homologues (C_{14}–C_{22}) have been tentatively identified in a Late Triassic oil sand sample from the Lunnan oilfield, Tarim Basin, NW China. Molecular distributions and stable carbon isotopic compositions of these compounds have been determined to investigate their bio- and/or geosynthetic sources. The results show that the most abundant isomers of short-chain MMAs were 4-methyl (*m*/*z* 70), 5-methyl (*m*/*z* 84), 6-methyl (*m*/*z* 98) and 7-methyl (*m*/*z* 112) alkanes, whereas in long-chain MMAs, there is a clear predominance of the 9-methyl and 10-methyl isomers. Combined with the compound-specific stable carbon isotopic analysis, it is concluded that short-chain MMAs and long-chain MMAs must have different sources. The similar isotopic compositions of MMAs and *n*-alkanes in this sample suggest that they may share the same sources. The short-chain MMAs, as previously suggested, are probably related to a cyanobacterial origin, while the long-chain MMAs may be mainly associated with microorganisms or heterotrophic bacteria, rather than cyanobacteria.

1. Introduction

Monomethylalkanes (MMAs) with mid-chain branching have been identified in hot spring microbial mats (Shiea et al., 1990; Robinson and Eglinton, 1990), crude oils (Jackson et al., 1986; Klomp, 1986; Fowler and Douglas, 1987; Hoffmann et al., 1987; Kissin, 1987; Summons, 1987; Summons et al., 1988a,b) and sediments of various ages (Summons et al., 1988a,b). Several origins for MMAs have been proposed in the earlier stage, including: (i) direct input of biogenic hydrocarbons (Fowler and Douglas, 1987); (ii) diagenetic transformations of functionalized lipid precursors such as carboxylic acids (Summons, 1987; Summons et al., 1988b); (iii) long-term equilibration products of limited iso- and anteiso-alkane isomers (Hoering, 1981); (iv) acid clay mineral catalyzed products of α-olefins formed by thermal cracking (Kissin, 1987). These hypotheses mainly proposed biological and geosynthetic origins for MMAs. In the biogenic hypotheses, the specific organisms involved were mainly focused on cyanobacteria (Han et al., 1968; Gelpi et al., 1970; Han and Calvin, 1970; Fehler and Light, 1970). Furthermore, it has long been recognized that the short-chain (C_{15}–C_{20}) MMAs, in particular 7-methylheptadecane, 8-methylheptadecane and 7,11-dimethylheptadecane, are mainly biosynthesised by a small subgroup of cyanobacteria (Han et al., 1968; Gelpi et al., 1970; Han and Calvin, 1970; Fehler and Light, 1970; Robinson and Eglinton, 1990; Shiea et al., 1990; Kenig et al., 1995; Summons et al., 1988a,b). Trimethylbranched alkanes identified in cultures of filamentous cyanobacteria give strong support for this conclusion (Köster et al., 1999).

* Corresponding author. Fax: +86-20-8529-0706.
E-mail address: ygsun@gig.ac.cn (Y. Sun).

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Recently, long-chain MMAs have been identified in various geological samples and microbial mats. For example, Van Kaam-Peters and Sinninghe Damsté (1997) observed a series of 9-MMAs (C_{18}–C_{32}) in bitumens from the Kimmeridge Clay Formation (Upper Jurassic, Southern Jura, France) and tentatively assigned them to cyanobacteria. Thiel et al. (1999) found abundant C_{15}–C_{25} mid-chain branched carboxylic acids present in demosponges and suggested a heterotrophic bacterial source for these compounds. Höld et al. (1999) identified a homologous series of C_{14}–C_{28} MMAs in oils and sediments of the Huqf Formation (Infra–Cambrian, Oman) and attributed these compounds to C_{28+} functionalized precursor lipids with alkyl substituents at C-12 or C-13. Kenig (2000) identified MMAs (C_{16}–C_{29}) in the pyrolysate of Holocene microbial mats and suggested those MMAs to be partly associated with a microbial assemblages or a heterotrophic bacteria origin. Audino et al. (2001) identified four homologous series of MMAs (C_{23}–C_{31+}) in the extractable hydrocarbon fraction and the hydrous pyrolysate of Permian torbanites, and suggested these compounds derived from freshwater algae or heterotrophic reworking of *B. braunii* biomass. This was further supported by work on torbanite samples from different palaeogeographical locations observed by Grice et al. (2001). Nevertheless, Logan et al. (1999, 2001) argued on the basis of comprehensive evidence (including depleted stable carbon and sulfur isotopic compositions, $\delta^{13}C = -34$ to 32‰; $\Delta^{34}S_{pyrite} = 40$–50‰) that the C_{24+} MMAs might be related to the presence of sulfide-oxidising bacteria; this was partly supported by Arouri et al. (2000).

In summary, the main proposed sources for MMAs include cyanobacteria (C_{15}–C_{20}), insects (C_{17}–C_{50}) (Nelson and Sukkestad, 1975), leaf waxes (Brieskorn and Beck, 1970), freshwater algae or heterotrophic reworking of *B. braunnii* biomass (Audino et al., 2001; Grice et al., 2001), functionalized lipids (Summons, 1987; Summons et al., 1988b; Höld et al., 1999) and sulfide-oxidising bacteria (Logan et al., 1999, 2001; Arouri et al., 2000). Long-chain MMAs in sediments and oils are still of unknown origin.

Previous studies showed that the position of methyl branching and the carbon number range in MMAs are usually source specific. Compound-specific stable carbon isotopic analysis can provide additional information about sources at the molecular level (Freeman et al., 1990). However, MMAs are generally at a low concentration level and cannot be acquired effectively for stable carbon isotopic analysis; thus, the literature on reliable stable carbon isotopic compositions of MMAs is limited. Here, we report on the distribution of unusually abundant long-chain and short-chain MMAs extracted from an oil sand sample from the Lunnan oilfield, Tarim Basin, NW China. In particular, the possible origin of these long-chain MMAs is discussed on the basis of their molecular distribution and their stable carbon isotopic compositions compared with those of short-chain MMAs.

2. Analytical procedures

The oil sand sample was collected from a Late Triassic reservoir, Lunnan oilfield, Tarim Basin, NW China. After the surface layer had been stripped off, the sample was rinsed with dichloromethane. The sample was crushed and Soxhlet extracted with chloroform for approx. 72 h. Asphaltenes were removed from the extract by precipitation with hexane followed by filtration. The deasphalted extract was separated into saturated, aromatic and polar (NSO) fractions by silica column chromatography, using *n*-hexane, benzene and ethanol as eluants, respectively. The aliphatic fraction was further separated into straight chain and branched/cyclic hydrocarbon fractions by urea adduction. The results show that all the MMAs fall into the straight chain hydrocarbon fraction and no MMAs were detected in the non-adduction fraction (Figs. 1b and 2a).

2.1. Gas chromatography

Aliphatic hydrocarbon fractions were analyzed by GC using a Hewlett-Packard 6890 gas chromatograph equipped with a 30 m×0.32 mm i.d. fused silica capillary column coated with a 0.25 μm film of HP-5. The temperature program started at 60 °C, held isothermally for 2 min and then increased to 290 °C at 3 °C/min, followed by a 30 min hold at 290 °C. The carrier gas was nitrogen at a flow rate of 1.0 ml/min.

2.2. Gas chromatography–mass spectrometry

GC–MS analysis was conducted on a Micromass Platform II mass spectrometer coupled to a Hewlett-Packard 6890 gas chromatograph. Chromatographic separation was achieved with a 30 m×0.32 mm i.d. fused silica capillary column coated with a 0.25μm film of DB-5 (Chrompack). The oven temperature program started at 65 °C (1 min), and then increased from 65 to 290 °C at 3 °C/min and held for 30 min. Helium was used as carrier gas at a flow rate of 1.0 ml/min. The transfer line temperature was 250 °C, and the ion source temperature was 200 °C. The ion source was operated in the electron impact (EI) mode at 70 eV.

2.3. Gas chromatography–isotope ratio mass spectrometry

The GC–IRMS analysis was performed on a ThermoQuest-Finnigan Delta Plus^{XL} system interfaced to a

Hewlett-Packard 6890 gas chromatograph. The GC was fitted with a fused silica column (HP-5, 30 m×0.32 mm i.d.) leading directly into the combustion furnace. For the straight chain alkane fraction, the initial temperature of the GC oven was 80 °C and then programmed to 290 °C at 3 °C/min, followed by a 30 min hold. For the acyclic isoprenoid fraction, the GC oven temperature was programmed from 80 to 140 °C at 10 °C/min, and then from 140 to 290 °C at 3 °C/min, followed by a 20 min hold. Helium (1.5 ml/min) was used as carrier gas. The injection of samples was conducted in splitless mode. The isotope values were calibrated against the reference gas and reported in the usual "del" notation relative to VPDB. The accuracy of the instrument was tested daily before and after sample analysis, by analyzing a mixture of *n*-alkanes and isoprenoid alkanes with known $\delta^{13}C$ values. The standard deviation for the standard sample was typically less than ±0.5‰. Five

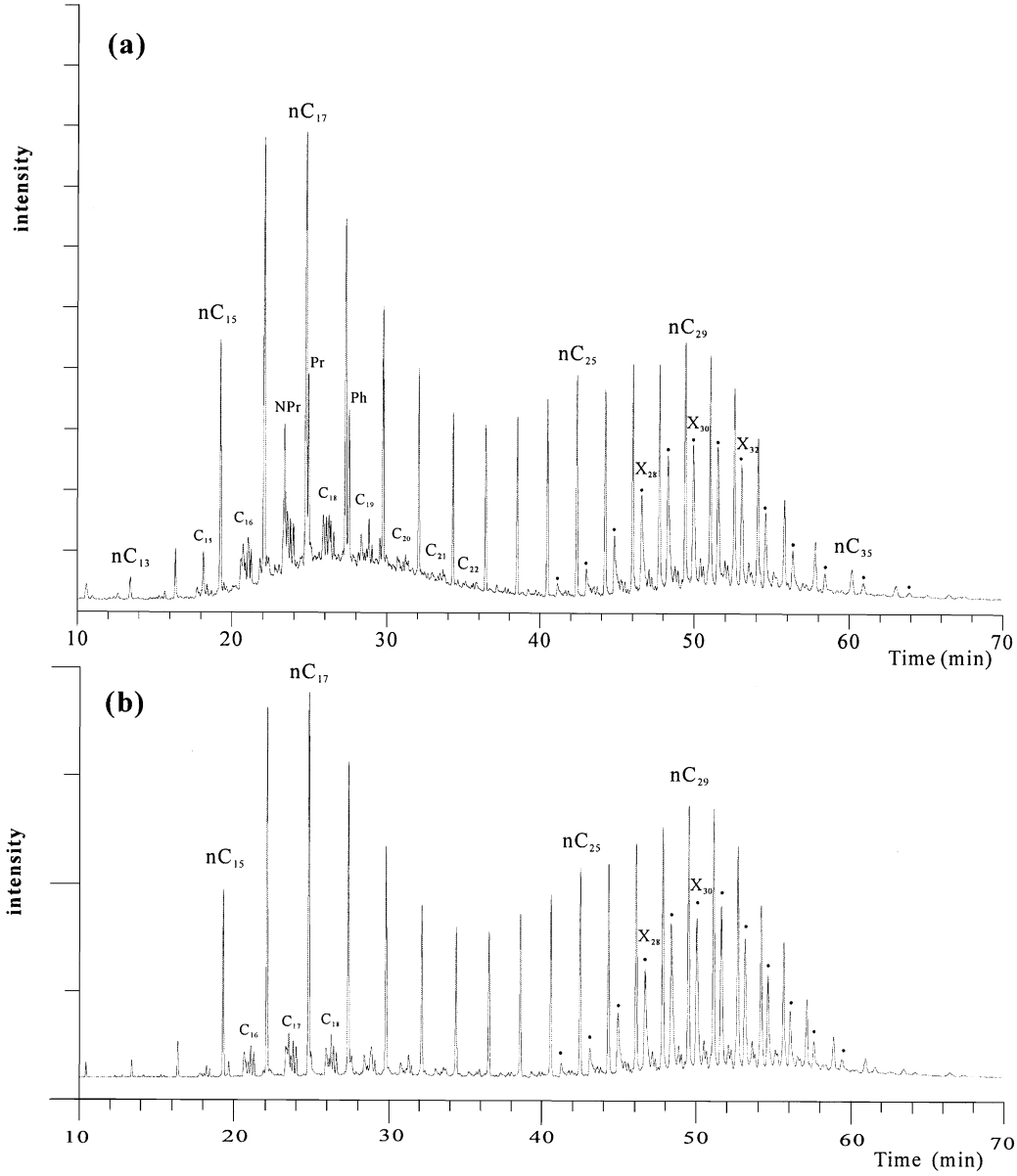

Fig. 1. (a) Gas chromatogram of the saturated hydrocarbon fraction of an oil sand sample from the Lunnan oilfield, Tarim Basin, NW China. Filled circles indicate suites of long-chain MMAs and are labeled "*X*". A homologous series of short-chain MMAs is detected in the range nC_{13}–nC_{22} and are labeled as "C". (b) Gas chromatogram of the straight chain hydrocarbon fraction after urea adduction, which show high concentrations of MMAs.

parallel analyses were also performed on our samples. The standard deviation for each compound is mostly in the range of 0.20–0.55‰ and show good reproducibility (Fig. 6).

3. Results and discussion

3.1. Biomarker distributions

The aliphatic hydrocarbon fraction from the oil sand sample is dominated by *n*-alkanes with a bimodal distribution maximizing at nC_{17} and nC_{29}, respectively (Fig. 1a). There is a slight odd-over-even predominance in the range nC_{22}–nC_{30} (CPI = 1.08, OEP = 1.06), suggesting marginal maturity. In addition, a little "UCM" can be seen in the nC_{14} to nC_{22} range. Pristane is slightly more abundant than phytane, combined with the presence of a relatively high concentration of gammacerane in the sample (see below), it seems to indicate that they formed in a weak-oxic to weak-redox depositional environment. Pristane and phytane are present in lower amounts than the C_{17} and C_{18} *n*-alkanes (Pr/Ph = 1.20, Pr/nC_{17} = 0.47, Ph/nC_{18} = 0.48).

An unusual feature is suites of peaks detected in the range nC_{24}–nC_{36} (filled circles in Fig. 1a). These peaks show a maximum intensity at the peak eluting after nC_{29}. At the same time, the GC trace (Fig. 1b) for products of urea adduction show that these peaks fall into the straight chain hydrocarbon fraction, which indicates they are acyclic.

The TIC chromatograms (Fig. 2a) of the branched/cyclic hydrocarbon fraction for this oil sand sample show that the acyclic isoprenoids are present in greatest abundance with a predominance of norpristane (NPr), pristane (Pr) and phytane (Ph). At higher carbon numbers, hopanes are detected and dominated by 17α, 21β(H)–C_{30} hopane (Fig. 2b). Relatively high concentrations of gammacerane (Ga/C_{30}H = 0.4, Ga/C_{31}H = 1.4) indicates water column stratification in the depositional environment (Sinninghe Damsté et al., 1995). Other terpenoids detected in the sample include C_{19}–C_{26} tricyclic terpanes, C_{24} tetracyclic terpane, and sesquiterpanes mainly dominated by 8β(H) drimane and 8β(H) homodrimane. Steroid hydrocarbon distributions show higher concentrations of C_{29} steranes than C_{27} and C_{28} steranes, and diasteranes and 4-methyl steranes are present at very low concentrations (not shown).

3.2. Identification of MMAs

In the GC–MS analyses of the saturated hydrocarbon fraction, the X-peaks show that their molecular weights are identical to those of the succeeding normal alkanes which suggest they are acyclic branched alkanes. A predominant $(M-15)^+$ fragment ion indicates methyl substitution. A pronounced series of even mass peaks corresponding to C_nH_{2n} fragments were detected which is typical for mid-chain branched alkanes (McCarthy et al., 1968; Fig. 3). These compounds were firstly called "*X*-peaks" by Klomp (1986) and are thus labeled as X_n in this paper, where "*n*" is the carbon number.

In the *X* peaks, each peak is an unresolved mixture of mid-chain monomethyl isomers. For example, the major fragments in the mass spectrum of the X_{30} peak are *m*/*z* 98, 112, ···, 266, 280, 294 ···(as shown in Fig. 3). The corresponding methyl substituted positions range from 6-methyl to 15-methyl and mid-chain methyl-substituted isomers (e.g., 15-methyl) are eluted earlier than methyl-substituted isomers near the terminals of the chain (e.g.,

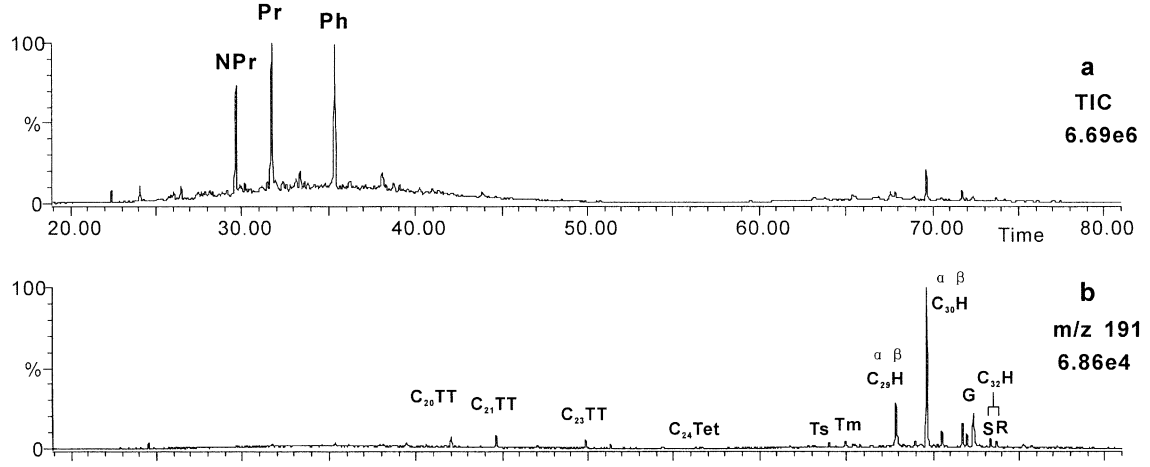

Fig. 2. (a) Reconstructed ion chromatogram of the urea non-adducted branched/cyclic hydrocarbon fraction of an oil sand sample from the Lunnan oilfield, Tarim Basin, NW China. (b) Partial mass chromatogram *m*/*z* 191 showing the distribution of tricyclic (TT), tetracyclic terpanes (Tet), hopanes (H) and gammacerane (G).

7-methyl) (Fig. 4). This kind of chromatographic behaviour is consistent with previous reports for *X*-peaks by Klomp (1986) and Fowler and Douglas (1987).

Similarly, the peaks present as clusters in the range nC_{13}–nC_{22} were examinated for additional information on MMAs. Further mass spectral analyses demonstrate that most of these peaks in the clusters can be identified as homologous series of MMAs (C_{14}–C_{22}, labeled as C_n in Fig. 1a) on the basis of their elution time and mass spectral characteristics. These compounds are only in abundance between nC_{13} and nC_{22} and between nC_{24} and nC_{36}. According to their carbon number ranges, the suites of compounds between C_{14}–C_{22} and C_{25}–C_{36} in this sample are defined as short-chain MMAs and long-chain MMAs, respectively.

In order to elucidate the distributions of isomers in short-chain and long-chain MMAs, every diagnostic even number fragment ion peak was integrated manually. After normalization of peak areas, the percentages of each peak for all the homologous MMAs are plotted together with their characteristic mass ion numbers (Fig. 5). It is evident that the short-chain and long-chain MMAs in this study have different isomer distributions. In the short-chain MMAs series, the different isomers are mainly 4-methyl (m/z 70), 5-methyl (m/z 84), 6-methyl (m/z 98) and 7-methyl (m/z 112) isomers, which show a slight predominance for lower methyl-substituted isomers. Furthermore, the percentage of higher carbon number isomers exponentially decreased with higher characteristic mass ions (Fig. 5a). However, in the long-chain MMAs, there is a clear preference for 9-methyl (partly 10-methyl) isomers (Fig. 5b). This distribution of the methyl position (9-, 10-methyl) in the long-chain MMAs significantly differs from that of 7- and 8-methyl heptadecane often reported in cyanobacteria (Han et al., 1968; Gelpi et al., 1970; Robinson and Eglinton, 1990; Shiea et al., 1990, 1991).

3.3. Compound-specific stable carbon isotopic composition analysis

Stable carbon isotopic compositions of normal alkanes, isoprenoids, and MMAs are shown in Fig. 6. Compared to the lower carbon number *n*-alkanes (nC_{15}–nC_{21}, −33.5 to 32.4‰), $\delta^{13}C$ values of higher molecular weight *n*-alkanes (nC_{22}–nC_{34}, −32.0 to 30.5‰) are slightly enriched in ^{13}C. The $\delta^{13}C$ values of norpristane, pristane and phytane are −31.6, −32.8 and −32.4‰, respectively, which are slightly heavier than that of the C_{16-18} *n*-alkanes. This is in agreement with previous observations (Bjorøy et al., 1991; Hayes, 1993; Collister et al., 1994; Clayton and Bjorøy, 1994; Pancost et al., 2001). The relationships of $\delta^{13}C$ values between acyclic isoprenoids and the corresponding *n*-alkanes have been explained by the intramolecular distribution of ^{13}C (Monson and Hayes, 1982) and fractionation in the biosynthesis pathways (Fang et al., 1993; Hayes, 1993; Collister et al., 1994). The $\delta^{13}C$ values of hopanoids cannot be reliably obtained because of their low concentration as shown in Fig. 2b.

Relatively high concentrations of long-chain MMAs enabled the reliable analysis of stable carbon isotopic compositions. The $\delta^{13}C$ values of these long-chain MMAs range from −31.4 to −30.1‰, which is similar to those of long chain *n*-alkanes (Fig. 6). The stable carbon isotopic compositions of several short-chain MMAs were also successfully obtained and ranged from −33.4 to −31.9‰.

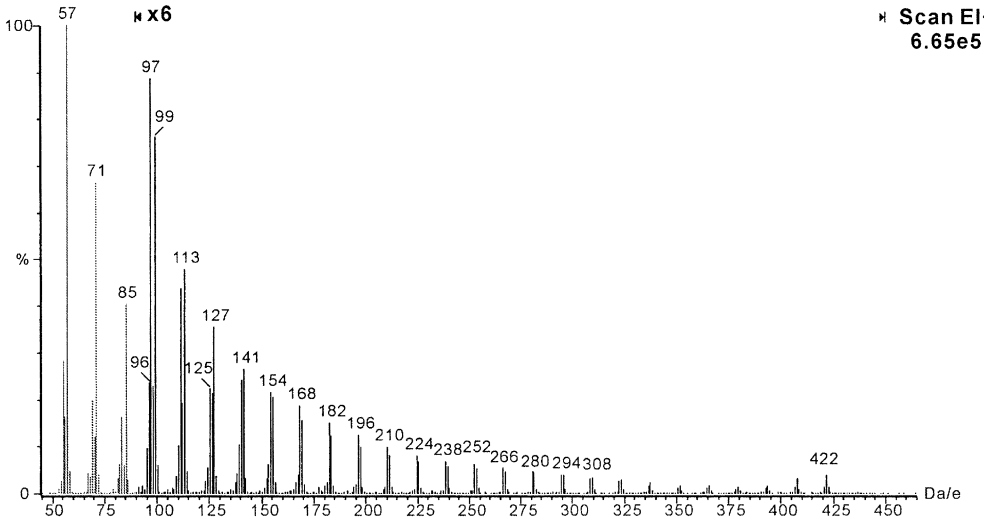

Fig. 3. The mass spectrum of the X_{30} compound. Dominant even-mass fragment ions indicate mid-chain MMAs, and the $(M-15)^+$ ion indicates methyl branching.

3.4. Source implications for long-chain MMAs

The bimodal distribution of *n*-alkanes and the different $\delta^{13}C$ compositions between the lower carbon number and higher carbon number *n*-alkanes both indicate that there must be two different source inputs to the oil sand sample.

In a typical bimodal distribution of *n*-alkanes, lower carbon number *n*-alkanes ($<C_{20}$) are conventionally presumed to have an algal or a cyanobacterial origin (e.g., Gelpi et al., 1970; Cranwell et al., 1987), while higher carbon number *n*-alkanes ($>C_{20}$) with a marked predominance of odd-carbon numbers are usually presumed to derive from epicuticular waxes of higher vascular plants (Eglinton et al., 1962; Eglinton and Hamilton, 1963; Cranwell et al., 1987). However, the extractable OM from the oil sand sample in this study is believed to be derived from Cambrian and Ordovician marine source rocks, most probably from middle-upper Ordovician rocks (Zhang et al., 2000; Hanson et al., 2000). Microbial organisms and algae were then the most important primary producers, and a large input of terrestrial plant material seems unlikely. Moreover, the above-described biomarker distributions indicate that there is no clear evidence of higher plant inputs.

Several isomer ratios (C_{31} αβ hopane $22S/(22S+22R)=0.61$, C_{29} ααα sterane $20S/(20S+20R)=0.47$, C_{29} sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)=0.41$) indicate that the hydrocarbons in this sample reached isomerization equilibrium. In combination with other maturity parameters (CPI = 1.08, OEP = 1.06, $Ts/Tm=0.82$), we deduce that the sample is at a marginally-mature stage. Thus, some of the long-chain *n*-alkanes may be derived from the thermal cracking of kerogen which would affect the

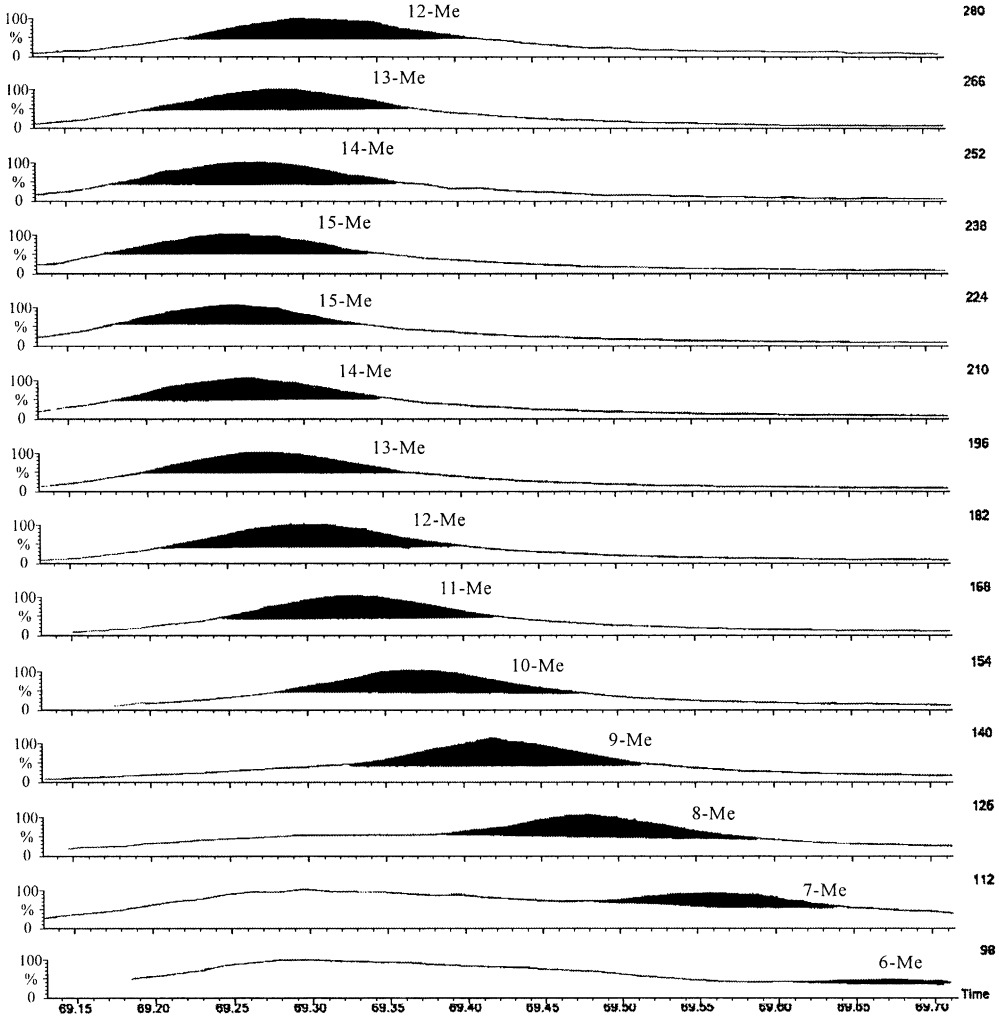

Fig. 4. Fragmentograms of the X_{30} peak from the oil sand sample. The differences in retention time show the presence of different isomers.

stable carbon isotopic composition of these alkanes. Here, source-dependent isotope effects rather than maturation-dependent isotope effects are expected to explain this difference. If maturation-dependent isotope effects were important, *n*-alkanes derived from the thermal cracking of the kerogen would lead to ^{13}C depletion of the higher carbon *n*-alkanes relative to their lower carbon homologous due to the preferential breakage of ^{12}C–^{12}C bonds during progressive maturation.

It has been suggested previously that the two ranges of MMAs originate from different biogenic sources (Summons et al., 1988b). In this study, the discrepancies in isomer distributions (Fig. 5) and stable carbon isotopic compositions (Fig. 6) between the short-chain and long-chain MMAs strongly suggest that they must have different sources. Moreover, previous studies suggested that 7-methylheptadecane, 8-methylheptadecane and 7,11-dimethylheptadecane were typically biosynthesized by a small subgroup of cyanobacteria (Han and Calvin, 1970; Shiea et al., 1990; Robinson and Eglinton 1989; Summons et al., 1988a,b). Thus, a cyanobacterial origin for the short-chain MMAs seems possible since the most abundant methyl substituents in the short-chain MMAs are mainly located at 4-methyl (C-4), 5-methyl (C-5), 6-methyl (C-6) and 7-methyl (C-7).

Although Van Kaam Peters and Sinninghe Damsté (1997) tentatively assigned a series of 9-methylalkanes (C_{18}–C_{32}) in bitumens from the Kimmeridge Clay Formation (upper Jurassic, Southern Jura, France) to a cyanobacterial origin, such an origin for the long-chain MMAs seems unlikely in this study, because the predominant 9-methyl and 10-methyl isomers present in the long-chain MMAs in this study significantly differ from those of 7- and 8-methyl heptadecane often reported in cyanobacteria (Han et al., 1968; Gelpi et al., 1970; Robinson and Eglinton, 1990; Shiea et al., 1990, 1991).

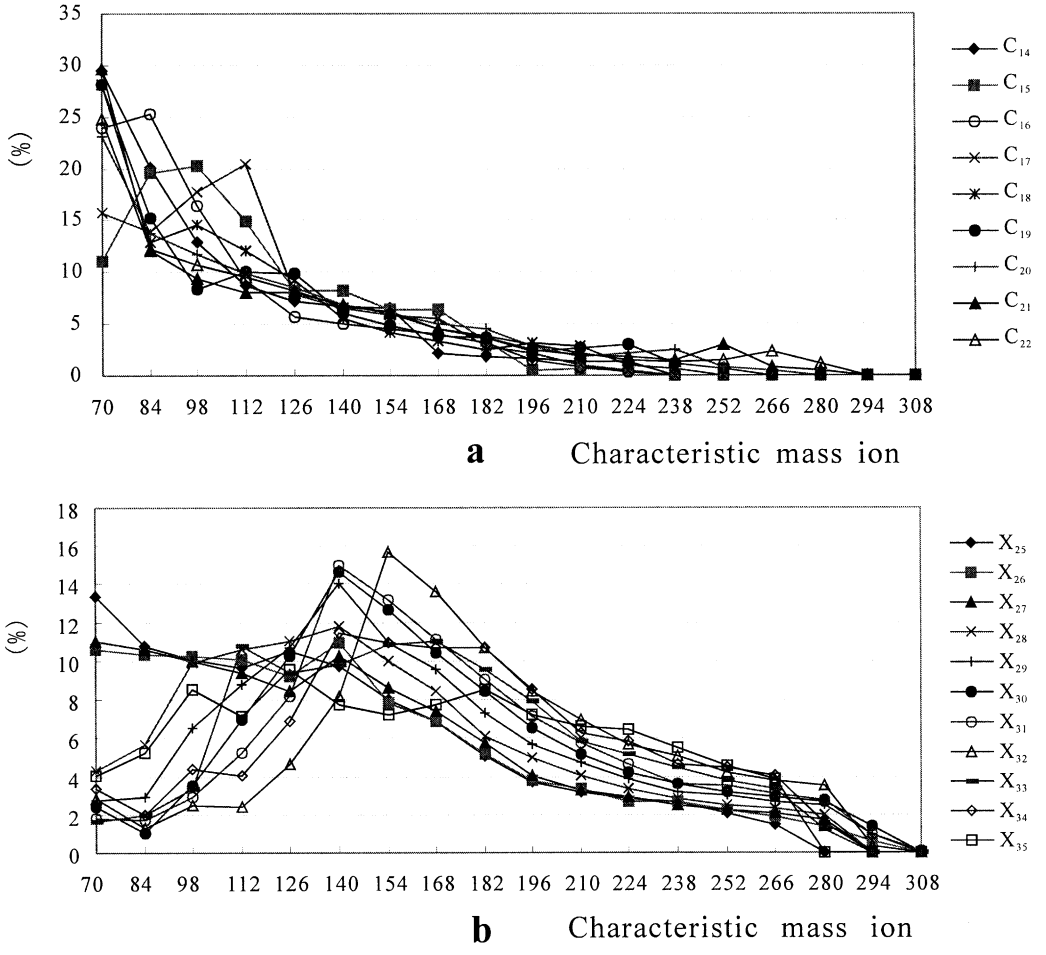

Fig. 5. The normalized distributions of even number fragment ions in the mass spectrum of different MMAs homologues. (a) This indicates that 4-methyl, 5-methyl, 6-methyl and 7-methyl isomers are dominant components in the clusters of peaks representing short-chain MMAs. (b) This demonstrates that 9-methyl and 10-methyl substituted isomers are relatively abundant in the long-chain MMAs.

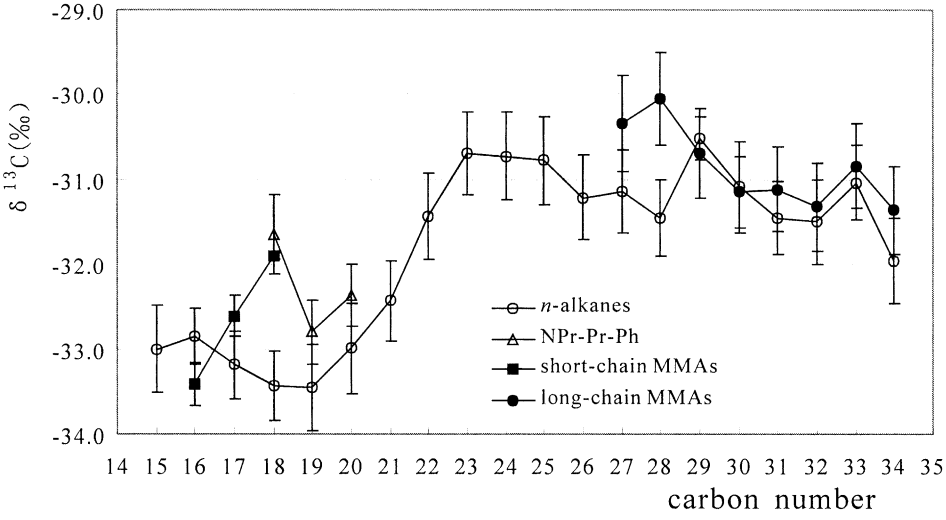

Fig. 6. Distributions of stable carbon isotopic compositions with their carbon numbers for *n*-alkanes, acyclic isoprenoids (NPr = norpristane, Pr = pristane, Ph = phytane), short-chain and long-chain MMAs in an oil sand sample from the Lunnan oilfield, Tarim Basin, NW China.

In addition, to the best of our knowledge, long-chain MMAs have not been reported in cyanobacterial cultures or cyanobacterial mats. Modern and Holocene microbial mat assemblages (e.g., Shiea et al., 1990; Kenig et al., 1990, 1995) and cyanobacterial cultures (e.g., Han et al., 1968; Gelpi et al., 1970; Boon et al., 1983; Köster et al., 1999) are mainly dominated by short-chain monomethyl and dimethyl alkanes. Although long-chain monomethyl, dimethyl and trimethyl alkanes were found in modern and Holocene cyanobacterial mats from Abu Dhabi (Kenig et al., 1990, 1994, 1995; Kenig, 2000), these compounds were finally suggested to be partly associated with microbial assemblages or of heterotrophic bacterial origin. It is important to note that all reported long-chain monomethyl carboxylic acids (Demospongic acids) where isolated from the phospholipids of certain sponges and/or their bacterial symbionts (Walkup et al., 1981; Ayanoglu et al., 1982; Dasgupta et al., 1984). Furthermore, there is strong evidence that their biosynthesis is linked to the metabolism of the large biomass of bacteria living in a symbiotic association with these animals (Dasgupta et al., 1984). Recently, long-chain MMAs were also suggested to be derived from heterotrophic bacteria (Thiel et al., 1999; Audino et al., 2001; Kenig, 2000). There are similarities between the sample reported here and the torbanites observed by Grice et al. (2001) (i.e., drimanes, tetracyclic terpane, long-chain MMAs from two different sources etc), which attributed MMAs to either *B. braunii* or heterotrophic bacteria feeding on *B. braunii* biomass.

Another important clue rests with the $\delta^{13}C$ values of the MMAs from the oil sand sample. They have similar values as the *n*-alkanes, suggesting that they may share the same source. A heterotrophic bacterial origin for long-chain *n*-alkanes is possible as shown in work on samples from the Green River Formation (Collister et al., 1994). We suggest therefore that the long-chain MMAs in this sample may be mainly associated with the microorganisms of phytoplanktonic or heterotrophic bacteria rather than cyanobacteria as a source.

4. Summary

Unusually abundant long-chain monomethylalkanes (MMAs) (C_{25}–C_{36}) and their short-chain homologues (C_{14}–C_{22}) have been tentatively identified in a Late Triassic oil sand sample from the Lunnan oilfield, Tarim Basin, NW China. Molecular distributions and stable carbon isotopic compositions of these compounds suggested that short-chain MMAs and long-chain MMAs have different bio- and/or geosynthetic origins. The origin of the short-chain MMAs may be attributed to a contribution from cyanobacteria, while the long-chain MMAs are most probably associated with microorganisms or heterotrophic bacteria rather than cyanobacteria as a source.

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