



Note

Distribution and origin of ethyl-branched alkanes in a Cenomanian transgressive shale of the Western Interior Seaway (USA)

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Received 15 February 2001; accepted 7 April 2001
(returned to author for revision 7 March 2001)

Abstract

Monoethylalkanes (MEA, C₁₆–C₂₂) with an even number of carbon atoms are relatively abundant in the saturated hydrocarbon fraction of the basal Graneros Shale (Cenomanian, Western Interior Seaway, USA). On the basis of isomer distribution and isotopic composition, it is proposed that MEA derive from eubacterial organisms, possibly cyanobacteria, living in fresh to brackish water environments. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Monoethylalkanes; Branched alkanes; Black shales; Cenomanian; Graneros Shale; Biomarker

1. Introduction

Short-chain (C₁₅–C₂₀) monomethylalkanes (MMA), dimethylalkanes (DMA) and trimethylalkanes (TMA) have been identified in numerous cyanobacterial cultures (e.g., Han et al., 1968; Gelpi et al., 1970; Köster et al., 1999), Modern and Holocene microbial mat assemblages (e.g., Kenig et al., 1990, 1995; Shiea et al., 1990), and ancient sediments (e.g., Summons and Walter, 1990). Short-chain monoethylalkanes (MEA, C₁₇–C₂₃) have been reported in ancient sediments, coals and petroleum only by Warton et al. (1997, 1998). Warton et al. (1998) suggest that MEA are derived from “defunctionalization of specific natural product precursors,” but that catalyzed rearrangement of *n*-alkenes might also be responsible for the formation of MEA in thermally mature sediments. Here, we present a report of the unusual abundance, distribution (C₁₆–C₂₂) and isotopic composition of MEA (C₁₆–C₂₀) in marginally mature

sediment of an early transgressive, laminated shale from the Cenomanian Graneros Shale, Western Interior Seaway (WIS). The origin of these compounds is discussed.

2. Sample and methods

An outcrop sample from the basal Graneros Shale was collected at the type section of the Greenhorn Cyclothem (Cenomanian–Turonian of the Western Interior Seaway, USA) near the reservoir in the Park District of Pueblo, Colorado (USA). The Graneros Shale represents the early transgressive interval of the Late Cretaceous Greenhorn Cyclothem (Kauffman, 1977). This sample, a finely laminated black shale, has a total organic carbon (TOC) content of 0.8 wt.% and was collected 25 cm above the Dakota Sandstone.

The sample was extracted, separated and analysed following the procedure described in Simons and Kenig (2001). The carbon isotopic composition of the total organic carbon was measured by an automated Carlo Erba NC2500 elemental analyzer interfaced to a Finnigan Conflow II mass spectrometer. The isotopic composition of individual compounds was measured by

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isotope ratio monitoring–gas chromatography–mass spectrometry (IRM–GCMS) following the method of Hayes et al. (1990).

3. Results

The saturated hydrocarbon fraction extracted from the basal Graneros Shale sample (Fig. 1a) is dominated by *n*-alkanes with a bimodal distribution. The most abundant compounds of the first mode are *n*-C₁₄, *n*-C₁₅ and *n*-C₁₆. *n*-C₁₇ is present in very low relative concentration. The second mode is dominated by *n*-C₂₇ and *n*-C₂₉ and shows a slight odd-over-even predominance, indicating that a direct contribution of land plant waxes was mixed with long-chain *n*-alkanes released from other sources. Pristane is more abundant than phytane, but both compounds are only present in minor concentration relative to the *n*-alkanes. Steroid hydrocarbons are only

present in trace amounts (not visible in Fig. 1, but detectable by mass chromatography of ion *m/z* 217). The only triterpenoids present in significant amounts are hopanes with a distribution dominated by 17 α , 21 β (H)-isomers (Fig. 1a and b). The 22S isomer dominates over 22R-homohopanooids, and the average 22S/(22S+22R) ratio of 0.6 (*n*=3, homohopane, bishomohopane and trishomohopane) indicates that these compounds are close to thermodynamic equilibrium, and that this sample is at or beyond the onset of oil generation (Peters and Moldowan, 1993).

Between *n*-C₁₅ and *n*-C₁₆, *n*-C₁₇ and *n*-C₁₈, *n*-C₁₉ and *n*-C₂₀, clusters of peaks (Fig. 1a) were identified on the basis of their elution time and mass spectral characteristics, as monoethylalkanes (MEA), with 16, 18 and 20 carbon atoms respectively (Warton et al., 1997, 1998). The distribution of MEA was monitored by mass chromatography of the M⁺-30 ions (Fig. 1c) corresponding to the loss of the ethyl-substituent (Warton et al., 1997).

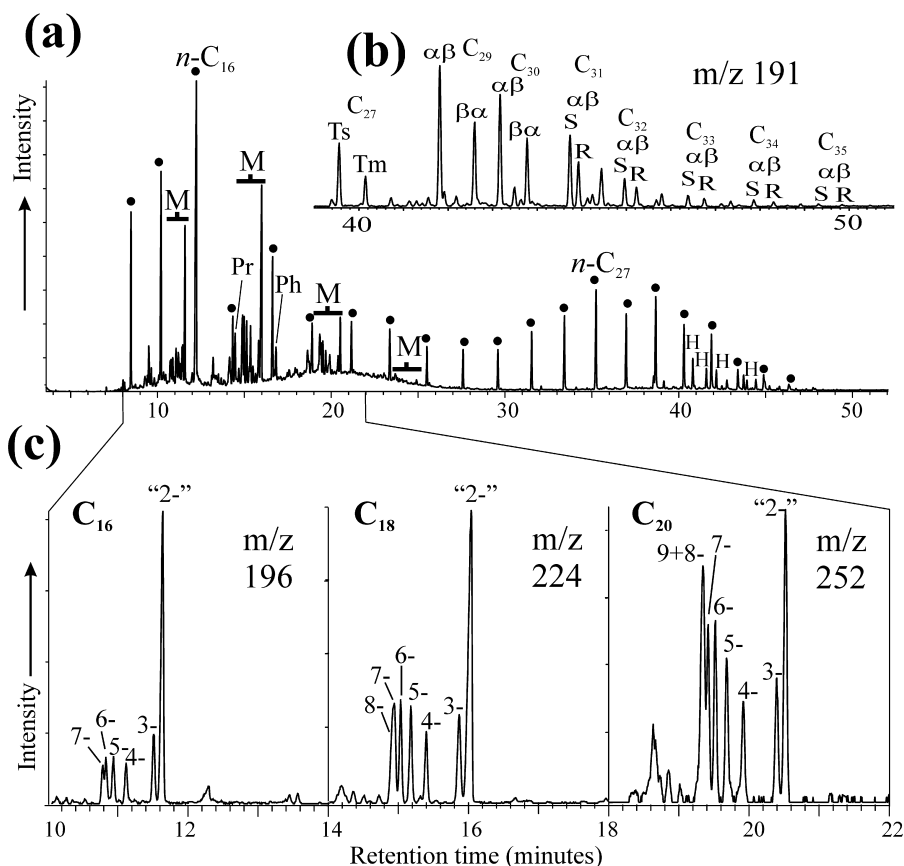


Fig. 1. (a) Reconstructed ion chromatogram of the saturated hydrocarbon fraction of a Graneros Shale sample. Filled circles indicate *n*-alkanes; M, clusters of monomethyl- and monoethylalkanes (MEA); Ph, phytane; Pr, pristane; H, hopanoids. (b) Partial mass chromatogram *m/z* 191 shows the distribution of hopanoid hydrocarbons. (c) Partial mass chromatogram *m/z* 196, 224, 252 shows the distribution of MEA with 16, 18 and 20 carbon atoms, respectively. Numbers on peaks indicate the substitution position of the ethyl side-chain.

The mass spectrum of 3-ethylhexadecane is identical to that of the authentic standard of Warton et al. (1997). The presence of minor amounts of monoethylcosane (C_{22}) was also detected by mass chromatography of the ion m/z 280. Only the 3-ethylcosane and the centrally branched isomers are visible in the reconstructed ion chromatogram (Fig. 1a). The ethyl side-chains of MEA are located at both odd and even numbered carbon atoms of aliphatic chains having only even numbers of carbon atoms. Within each cluster, MEA are not distributed evenly. The 3-methylalkanes (“2-ethylalkanes”, see Fig. 1c) dominate over the MEA cluster. All possible isomers of MEA are present, up to the most centrally branched (i.e. 7-ethyltetradecane and 9-ethyloctadecane for the C_{16} and C_{20} clusters, respectively).

Monomethylalkanes (MMA) were also detected in the C_{16} – C_{20} range by mass chromatography, but in minor concentration relative to MEA (Fig. 2). MMA with an even number of carbon atoms are relatively more abundant than MMA with odd carbon numbers, and elute within the MEA clusters (e.g., monomethylheptadecanes are eluting within the monoethylhexadecane cluster). Centrally branched MMA coelute with 4-ethylalkanes and, thus, elute after centrally branched MEA. 3-Ethyl- and 2-methylalkanes nearly coelute. As noted above, the 3-methylalkanes dominate over other isomers of MMA and MEA (Fig. 2).

The carbon isotope compositions of MEA were measured for the well-resolved 5-ethylhexadecane and 5-ethyloctadecane and for groups of pure centrally branched MEA with 16 and 18 carbon atoms (Fig. 3). 2-Methyl, 3-methyl- and 3-ethylalkanes were measured as one group for the C_{16} and C_{18} clusters. There are no significant differences between the average of all values obtained for pure MEA peaks ($-26.9 \pm 0.2\text{‰}$, $n = 5$) and for MEA–MMA coeluting groups ($-27.0 \pm 0.6\text{‰}$, $n = 4$). This indicates that $\delta^{13}\text{C}$ values of MMA, even if in low relative abundance to MEA, are not significantly different from those of MEA.

The mean $\delta^{13}\text{C}$ of pure MEA peaks is depleted relative to $\delta^{13}\text{C}_{\text{TOC}}$ (-24.5‰) by 2.4‰ and is significantly enriched in ^{13}C (3.4‰) relative to the average $\delta^{13}\text{C}$ of odd long-chain n -alkanes in the $n\text{-}C_{25}$ – $n\text{-}C_{31}$ range. This suggests that MEA are not derived from higher-plants. The $\delta^{13}\text{C}$ of the abundant $n\text{-}C_{15}$, $n\text{-}C_{16}$ and $n\text{-}C_{18}$ fall close to those of MEA (Fig. 3). The isotopic composition of $n\text{-}C_{17}$ and $n\text{-}C_{19}$ are similar to those of the odd long-chain n -alkanes in the $n\text{-}C_{25}$ – $n\text{-}C_{31}$ range. Therefore, it is possible that the organisms producing MEA also synthesized relatively short chain ^{13}C -enriched n -alkanes dominated by $n\text{-}C_{15}$, $n\text{-}C_{16}$ and $n\text{-}C_{18}$. Hopanes (average of $\alpha\beta$ and $\beta\alpha$ hopanes, Fig. 3) are enriched in ^{13}C ($\delta^{13}\text{C} = -28.5 \pm 0.6\text{‰}$, $n = 2$) relative to homohopanes ($\delta^{13}\text{C} = -30.2 \pm 0.2\text{‰}$, $n = 2$) and $17\alpha,21\beta(\text{H})$ -norhopane (Fig. 3).

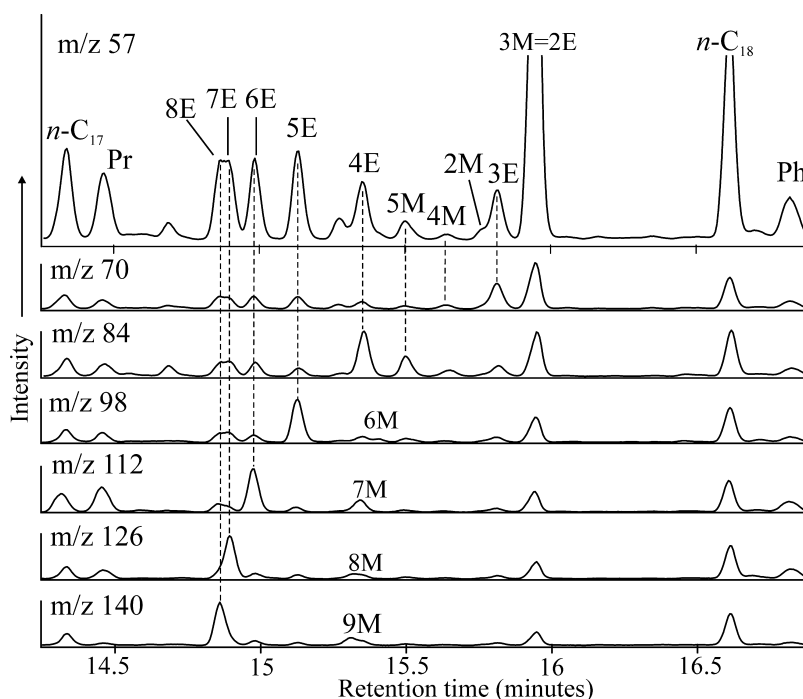


Fig. 2. Partial mass chromatogram m/z 57, 70, 84, 98, 112, 126 and 140, in the $n\text{-}C_{17}$ – $n\text{-}C_{18}$ region. E indicates peaks identified as monoethylhexadecanes. M indicates monomethylheptadecanes. Numbers indicate the position of the ethyl or methyl substituents. Pr, pristane; Ph, phytane.

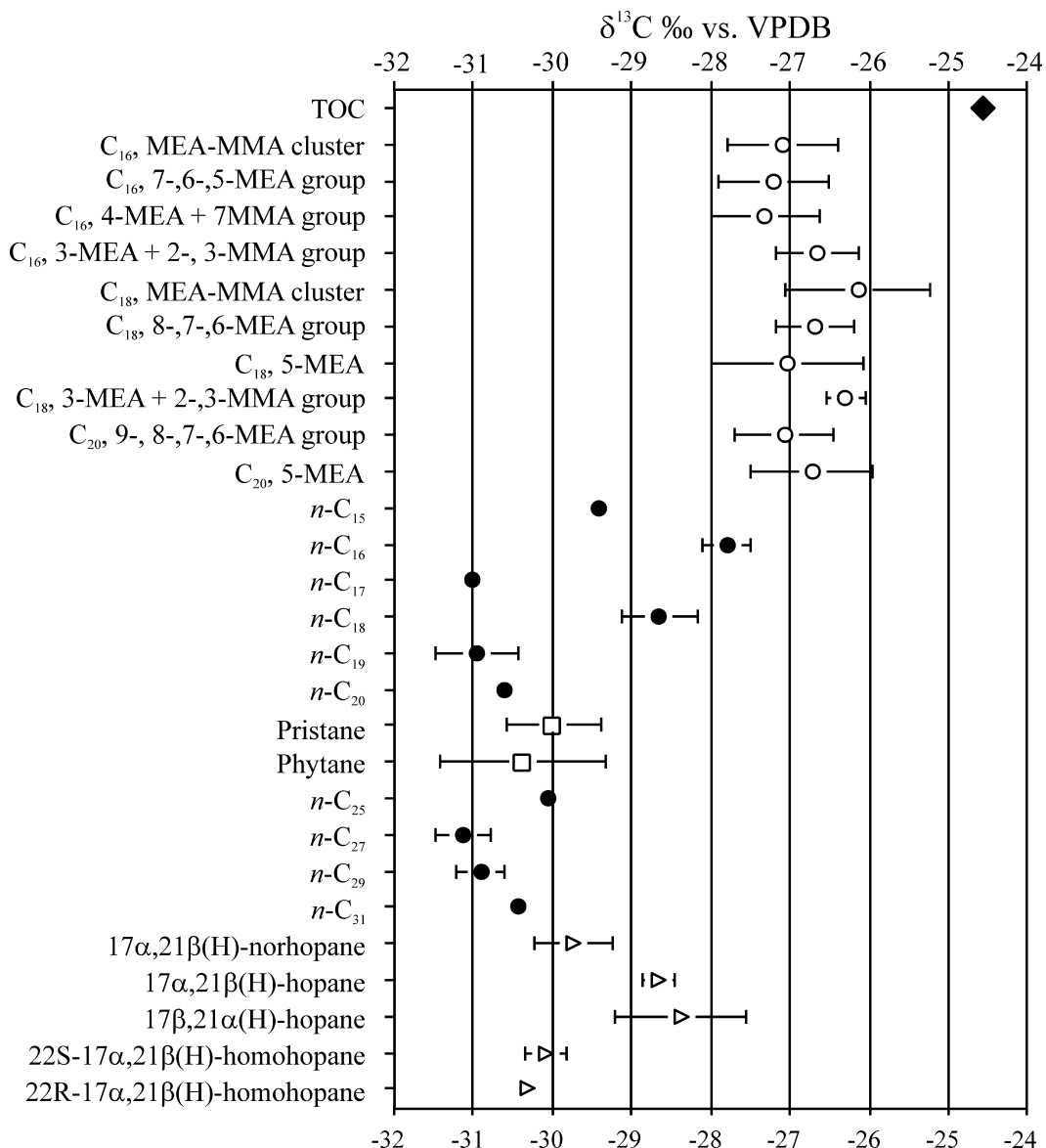


Fig. 3. $\delta^{13}\text{C}$ vs. VPDB (‰) of total organic carbon (TOC), and biomarkers from the basal Graneros Shale. Error bars correspond to the standard deviation calculated for duplicate analyses; if not visible, the error bar is smaller than the data point. MEA, monoethylalkanes; MMA, monomethylalkanes. $\delta^{13}\text{C}$ values of clusters represent the integration of the whole area between the first eluting centrally branched MEA and the last eluting MEA, and include MMA with the same number of carbon atoms.

4. Discussion and conclusions

MEA in the basal Graneros shale sample are only present with an even number of carbon atoms in the C_{16} – C_{22} range (Fig. 1). This distribution is completely different from that of MEA in samples of the Late Cretaceous Gippsland Basin (Australia) analyzed by Warton et al. (1998) where, in immature samples, the 3- and 5-MEA in the C_{17} – C_{24} MEA clusters dominate over other isomers in clusters with an odd number of carbon

atoms. This pattern disappears with increasing maturity. The very distinctive distribution and $\delta^{13}\text{C}$ of MEA in the Graneros Shale sample points to a single source or group of related source organisms, and indicate that MEA are unlikely to derive from kerogen thermal degradation. The very low concentration of steroids, compounds usually abundant in eukaryotic algae (e.g., Volkman, 1986), is consistent with MEA being derived from eubacteria. The co-occurrence of a distinctive C_{16} – C_{20} distribution of MMA, considered cyanobacterial

biomarkers (e.g., Kenig et al., 1990, 1995; Shiea et al., 1990), with MEA, and their equivalent isotopic composition, also suggest cyanobacteria as a potential source for MEA. The $\delta^{13}\text{C}$ of the C_{30} hopanes is enriched relative to homohopanes and norhopanes (Fig. 3), and it can be speculated that this resulted from the mixed contribution of C_{30} hopanes derived from eubacteria (primary producers or heterotrophs) including those producing the MEA.

Considering the marginally mature character of the Graneros shale sample, and despite the absence of identifiable functionalized MEAs in the polar fraction and pyrolysis products, the possibility of functionalized precursors cannot be excluded, as suggested by Warton et al. (1998). Catalytic conversion of olefins was also suggested to result in MEA formation in thermally mature sediments (Warton et al., 1998). However, catalytic conversion of olefins preferentially produces MMA (e.g., Kissin, 1987; Warton et al., 1998). The distribution of MMA (every carbon number) and MEA (every other carbon number) and the dominance of MEA over MMA does not support the formation of MEA via such a pathway in our sample.

MEA with the same distribution in carbon number and substituent location were identified in the extract of Eocene massive algal deposits (Axel Heidberg, Canadian Arctic; Anderson, Kenig, Simons, unpublished results). These deposits are associated with coals and are considered lacustrine. Similarly, 12 of the 16 MEA-containing samples analysed by Warton et al. (1998) are considered of fresh water or terrestrial origin. The Hydrogen Index (6 mgHC/gTOC) and Oxygen Index (72 mgCO₂/gTOC) suggest that transported terrestrial organic matter dominates the total organic matter of the basal Graneros Shale sample (Kenig et al., in prep.). The uppermost unit of the Dakota Sandstone was deposited in brackish, near-shore water conditions and the base of the Graneros Shale was deposited in an initially shallow, not fully developed seaway, likely to be brackish (Kauffman, 1985). Therefore, it can be hypothesized that MEA are derived from freshwater microbes, possibly cyanobacteria, which grew in fresh to brackish water environments of the marginally developed WIS at the onset of the transgressive leg of the Greenhorn Cyclothem.

Acknowledgements

This research was supported by NSF award EAR-9614769 to F.K. K.B.A. gratefully acknowledges the support of the US Department of Energy under contract W-31-109-ENG-38. The authors wish to thank Erle Kauffman (Indiana University, USA) for good advice at the onset of our WIS project. The Park District of the City of Pueblo (CO, USA) is thanked for permission to sample.

Terri Rust and Brian Popp (University of Hawaii, USA) are thanked for the $\delta^{13}\text{C}$ analysis. J.A. Curiale and P. Greenwood are thanked for providing constructive reviews of the manuscript.

Associate Editor—J. Curiale

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