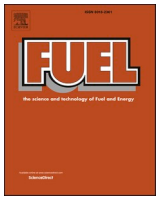
Fuel 355 (2024) 129360

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Short communication

Even carbon number predominance observed in C_{50}-C_{110} n-alkanes and monocyclic alkanes in the highly mature source rock

Chenglong Dong [a,1], Jia Wu [a,1], Jikun Liu [a], Weilai Zhang [a], Sara Grimay [a], Peng Fang [a], Xiaowan Tao [b], Guangyou Zhu [b], Yehua Han [a,*]

[a] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, PR China
[b] Research Institute of Petroleum Exploration and Development, PetroChina, Beijing 100083, PR China

ARTICLE INFO

Keywords:
n-alkanes
Monocyclic alkanes
Carbon number predominance
Petroleomics
HPLC-UHRMS

ABSTRACT

Carbon number predominance of n-alkanes and monocyclic alkanes reveals essential geological information such as biological source, sediment maturity, and paleoenvironmental conditions. The carbon number range of the special distribution pattern is reported to lower than C_{40}, prominantly in the range of C_{24}-C_{34}. Generally, this special distribution pattern fades away with the increase of maturity. However, these well-accepted beliefs are challenged by our investigations. In this work, C_{10}-C_{125} n-alkanes and monocyclic alkanes were identified for the first time in the highly mature source rock of Well Luntan-1 in Tarim Basin (China). Both series exhibited significant even carbon number predominance observed in C_{50} and C_{110}, but there was no carbon-number predominance observed before C_{50}. The similar distribution patterns of n-alkanes and monocyclic alkanes indicated that they might have the same biological precursors. The discovery of higher alkanes with ultra-long carbon chains and their extraordinary display of carbon number predominance provided us with a new perspective, which may open up the era of macromolecular biomarkers exploration.

1. Introduction

Using molecular fossils to reconstruct paleoclimate and paleoenvironmental history has become an important part of molecular stratigraphy [1,2]. n-alkanes are a type of biomarker that are widely abundant in source rock and crude oil, and their distribution patterns are characterized by the predominance of even or odd carbon numbers [3,4]. The special distribution pattern depends on the source material and its microbial or geochemical changes, so it has been applied to determine the biological origin, the maturity of sediments, and the paleoenvironmental conditions. n-alkanes in immature source rocks generally show odd carbon-numbered predominance, especially in the range of C_{27}-C_{31} [5–7]. These n-alkanes are directly synthesized by higher plants or generated by defunctionalization of fatty acids, alcohols and esters with even carbon numbers. The n-alkanes derived from marine organic matter have no carbon-numbered predominance in the C_{24}-C_{35} [5], but high-salt carbonate and evaporite source rocks have a slight even carbon-numbered predominance [8]. Some saline lacustrine oils have an odd carbon-numbered predominance of C_{11}-C_{17} and even carbon-numbered predominance of C_{18}-C_{26} [2]. Monocyclic alkanes were found to have a carbon number distribution pattern similar to n-alkanes, indicating that monocyclic alkanes may be derived from the same precursors as n-alkanes, possibly through the cyclization of algal fatty acids [9,10]. Monocyclic alkanes mainly show the odd carbon-numbered predominance, whereas the even carbon-numbered predominance of monocyclic alkanes is rarely identified. At present, the even carbon-numbered predominance of C_{17}-C_{31} monocyclic alkanes has been found only in some coal-bed samples [10].

In terms of maturity, odd–even predominance (OEP) [3] was proposed to describe the distribution pattern of n-alkanes, and the sediment maturity was determined according to the OEP values. OEP $>$ 1.4 refers to immature organic matter and 1.2 $<$ OEP $<$ 1.4 refers to low mature organic matter.

Currently, hydrocarbon biomarkers are mainly analyzed by gas chromatography-mass spectrometry (GC–MS). The carbon-numbered predominance is limited below C_{40} and concentrated in C_{24}-C_{34} [11–13] due to instrument temperature limitations. High temperature gas chromatography (HTGC) with the programming temperature up to

* Corresponding author.
E-mail address: hanyehua@cup.edu.cn (Y. Han).
[1] The two authors contributed equally to this work.

https://doi.org/10.1016/j.fuel.2023.129360
Received 8 February 2023; Received in revised form 29 July 2023; Accepted 30 July 2023
Available online 11 August 2023

430 ℃ could extend the carbon number of n-alkanes in wax sample up to 120 [14]. However, HTGC still shows poor resolution, low sensitivity to detect higher n-alkanes in source rock or crude oil samples. Predominance of carbon-number will gradually reduce as maturity increases due to the mixing of n-alkanes created by kerogen and the decomposition of hydrocarbon in the early diagenetic stage. Therefore, the distribution pattern of n-alkanes cannot characterize the maturity, biological origin, and paleoenvironment of high-maturity source rocks and crude oil samples.

The integration of ultrahigh-resolution mass spectrometry and soft ionization technology provides the possibility to investigate the composition of high molecular weight hydrocarbons [15–17]. In this work, on-line coupling of high-performance liquid chromatography (HPLC) and ultrahigh resolution mass spectrometry (UHRMS) was utilized to explore alkanes and monocyclic alkanes as much as possible. An unexpected wide range of C_{10} to C_{125} was discovered and identified in the extracts of highly mature source rocks from Luntan-1 well in the Tarim Basin, China. Moreover, they showed different carbon-numbered predominance from reported results, which was beyond the conventional understanding of the distribution patterns of n-alkanes and monocyclic alkanes in highly mature samples.

2. Materials and methods

2.1. Materials

HPLC-grade n-hexane (HEX) and dichloromethane (DCM) were purchased from Fisher Scientific. The source rock sample was obtained from the Luntan-1 well in Tarim Basin (China), with a depth of 8882 m, which penetrated the lower Cambrian. The sample was of high thermal maturity with equivalent vitrinite reflectance (Ro) values of 1.6%. The pretreatment procedure of samples was described in supplemental materials.

2.2. GC–MS analysis

The GC–MS analysis was carried on a mass spectrometer coupled with an Agilent 7890 gas chromatography (GC). The GC was equipped with a HP-5 MS (60 m × 0.25 mm × 0.25 μm) fused silica capillary column. The oven temperature was set at 80 °C for 2 min and heated at 10 °C/min to 300 °C, and then held constant for 20 min. The 70 eV electron impact ion source was operated at 250 °C.

2.3. HPLC-UHRMS analysis

The chromatographic separation utilized an Agilent 1200 HPLC system (Agilent Technologies, USA). The column was a Zorbox NH_2 (4.6 × 250 mm, 5 μm) column (Agilent Technologies, USA). HPLC-grade n-hexane was used as mobile phase at a flow rate of 0.8 mL/min. 5 μL saturates (5 mg/ml) was injected by autosampler. HPLC was directly coupled with Orbitrap Fusion MS (Thermo Fisher Scientific, USA) through atmospheric pressure chemical ionization (APCI) source. The ionization conditions were shown in Table S1.

3. Results and discussion

3.1. The development of HPLC-UHRMS method

On-line coupling of high-performance liquid chromatography (HPLC) and ultrahigh-resolution mass spectrometry (UHRMS) was developed to detect high molecular weight n-alkanes and monocyclic alkanes as full range as possible.

Generally, the carbon range of n-alkanes and monocyclic alkanes detected by gas chromatography-mass spectrometry (GC–MS) is lower than C40 due to the limitation of instrument temperature. High temperature gas chromatography (HTGC) extend the boiling point of detectable hydrocarbons, while it still could not resolve n-alkanes from *iso*-alkanes and cycloalkanes, especially when carbon numbers increase. UHRMS is used in petroleomics to analyze large molecular weight compounds. However, soft ionization limits the analysis of saturated hydrocarbons. To overcome that, a solvent-assisted chemical ionization method was developed for the soft ionization of n-alkanes and monocyclic alkanes. Thus, enabled the regulation of the gas-phase chemical behaviors of the secondary ions, and reactive ions generated from different compounds by controlling the processes of hydrogen abstraction and charge transfer. In particular, n-alkanes and monocyclic alkanes produced $[M-H]^+$ ions while *iso*-alkanes produced $[M-2H]^+$ ions [18,19]. Therefore, n-alkanes and *iso*-alkanes could be distinguished by the type of product ions. n-alkanes and monocyclic alkanes were distinguished by the double-bond equivalence (DBE) values, where the DBE values of n-alkanes and monocyclic alkanes were 0 and 1, respectively.

Saturates, aromatics, resins, and asphaltenes (SARA) separation is usually used to enrich target compounds and simplify analysis. Due to the complexity of source rock or crude oil and the low separation accuracy of SARA method, some monoaromatic hydrocarbons were eluted in saturates (saturated fraction). The ionization efficiency of aromatic hydrocarbons is much higher than that of saturated hydrocarbons during solvent-assisted chemical ionization, thus the ionization of n-alkanes and monocyclic alkanes is restrained by mono-aromatic hydrocarbons when the saturates is injected into APCI directly. Therefore, normal phase HPLC was utilized to separate saturates into saturated hydrocarbons and monoaromatic hydrocarbons The total ion chromatography obtained by HPLC-UHRMS is shown in Fig. S1. Saturates were separated into saturated hydrocarbons and monoaromatic hydrocarbons. Without the inhibition of monoaromatic hydrocarbons, the intensity of UHRMS peak could be used to semi-quantify n-alkanes and mono-alkanes. The Orbitrap Fusion mass spectrum for saturated hydrocarbons is shown in Fig. 1a. It can be seen that the peak of the mass spectrum showed a normal distribution, and the mass center was located at $m/z = 900$. All peaks were identified as hydrocarbons, and the highest peaks in each cluster were assigned to n-alkanes. The carbon number of n-alkanes were ranged from C_{10}-C_{125}. The relative ion abundance plot of DBE versus carbon number of CH class species was shown in Fig. 1b. n-alkanes with DBE = 0 and monocyclic cycloalkanes with DBE = 1 were detected with the highest carbon number of 125. In addition, there were few cycloalkanes with DBE between 2 and 5, whose carbon number range was also higher than 120. These n-alkanes and monocyclic alkanes with ultra-high molecular weight contained important geological information that was not indicated by low molecular weight hydrocarbons.

3.2. Identification of n-alkanes and monocyclic alkanes by HPLC-UHRMS

HPLC-UHRMS technique enables us to investigate the real characteristic distribution of n-alkanes and monocyclic alkanes in highly mature source rock. Firstly, the saturates of extract was analyzed by GC–MS. GC–MS mass chromatograms of n-alkanes ($m/z = 85$) and monocyclic alkanes ($m/z = 83$) are shown in Fig. 2. The carbon number range of n-alkanes was C_{14}-C_{33} without the carbon-numbered predominance, which was consistent with the trend that the carbon-numbered predominance faded away with the increase of maturity. The distribution of monocyclic alkanes was similar to that of n-alkanes, showing a normal distribution and without carbon-numbered predominance. The carbon number of n-alkanes and monocyclic alkanes did not exceed C_{40} due to limitations in GC separation ability and the temperature.

As shown in Fig. 1, the carbon number of n-alkanes and monocyclic alkanes detected by HPLC-UHRMS was expanded to C_{125}. The relative concentration of n-alkanes and monocyclic alkanes with different carbon number was quantified by the intensity of mass spectrum peaks. Fig. 3a shows the relative abundances of n-alkanes and monocyclic

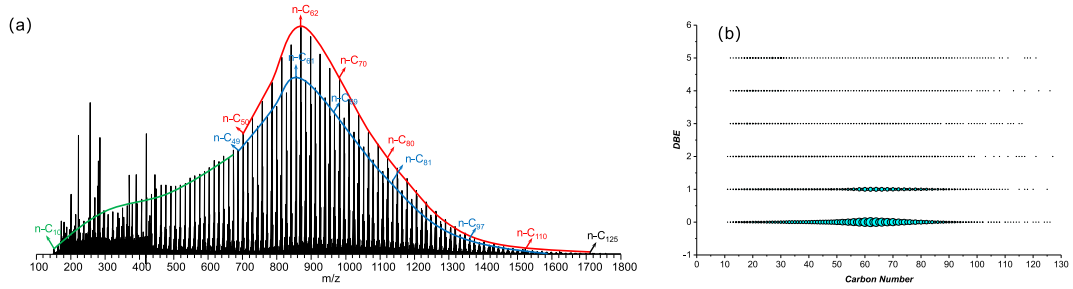


Fig. 1. (a). Orbitrap Fusion mass spectrum of saturated fraction (averaged mass spectrum obtained in 3.5–3.8 min). (b) The relative ion abundance plot of DBE versus carbon number of CH class species.

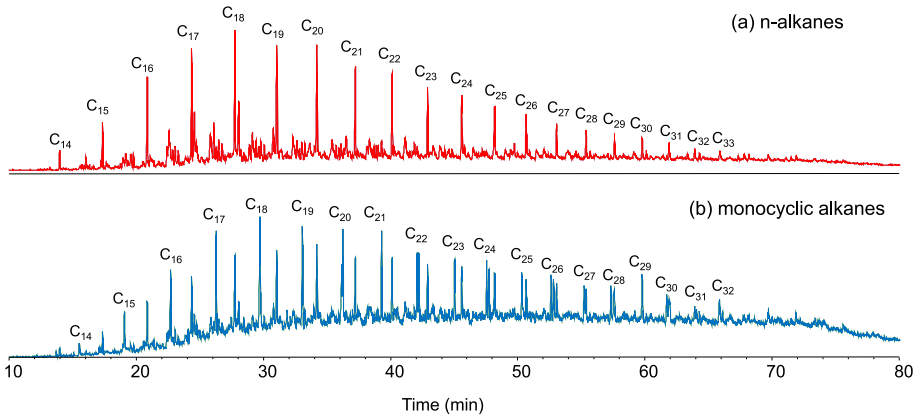


Fig. 2. Mass chromatograms of n-alkanes (m/z = 85) and monocyclic alkanes (m/z = 83) detected by GC–MS.

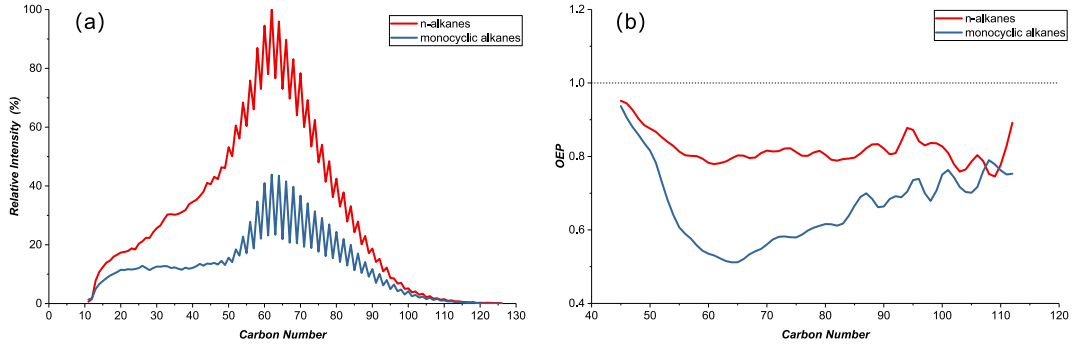


Fig. 3. Qualitative and relative quantitative analysis. (a) The relative intensity of n-alkanes and monocyclic alkanes with different carbon numbers. (b) OEP curves for n-alkanes and monocyclic alkanes.

alkanes. The relative abundances of n-alkanes and monocyclic cycloalkanes showed a continuous distribution without any carbon-numbered predominance when carbon number was less than 50, which was consistent with the results obtained by GC–MS. While C_{50}-C_{110} n-alkanes and monocyclic alkanes showed a strong predominance of even carbon number over adjacent odd carbon number. OEP curves for n-alkanes and monocyclic alkanes are shown in Fig. 3b. All OEP values are less than 1. Even carbon-numbered predominance of ultrahigh molecular weight n-alkanes and monocyclic alkanes is inconsistent with the traditional cognition that the carbon-numbered predominance will disappear with the increase of maturity. Therefore, it is controversial to conclude that there is no carbon-numbered predominance in high maturity crude oil and source rocks based on traditional GC–MS data. The data in this paper show that the ultrahigh carbon numbered n-alkanes and monocyclic alkanes in high maturity source rocks still retain their carbon number distribution characteristics.

3.3. Origin of n-alkanes and monocyclic alkanes in Luntan-1 source rock

Based on current knowledge of organic geochemistry of such biomarkers and the characteristics of the sample's stratigraphy, there are two possible origins of n-alkanes and monocyclic alkanes: biological and thermal origins. The distribution pattern of monocyclic alkanes in Luntan-1 source rock is similar to n-alkanes, particularly in the predominance of their C_{50}-C_{100} members. This similarity suggests that both series of compounds may have the same biogenic precursors. Generally, medium molecular weight n-alkanes with even carbon-numbered predominance are considered to be transformed from even-carbon dominant fatty acids or alcohols by β-cleavage reaction in the presence of $CaCO_3$. This assumption has been verfied by simulation experiments [20,21]. Medium molecular weight monocyclic alkanes are considered to be transformed from even-carbon dominant fatty acids or alcohols by cyclization reaction. Therefore, ultrahigh molecular weight fatty acids and alcohols with the same carbon number as n-alkanes and monocyclic

alkanes are the potential precursors of ultrahigh molecular weight n-alkanes and monocyclic alkanes, despite the fact that these kind of fatty acids and alcohols have not been reported in either modern or ancient biological materials. From the point of view of chemical stability, n-alkanes and monocyclic alkanes with long carbon chains have higher melting points and are more likely to aggregate with solid sedimentary organic matter in the formation, so the steric hindrance and energy barrier of corresponding molecules are larger than those of small-molecule alkanes. Therefore, they can be preserved for a long time.

From a thermal perspective, the formation of n-alkanes with ultra-long carbon chains can be attributed to the polymerization of fatty acids with medium-length carbon chains during the maturation process. Akira Shimoyama [20] conducted the pyrolysis expertiment with C_{19} and C_{22} fatty acids in the presence of $CaCO_3$ at 250 ℃ for 300 h. This experimental setup resulted not only in the formation of C_{17} and C_{20} n-alkanes via β-cleavage reaction, but also in the detection of a series of n-alkanes with carbon number exceeding those carbon number of the original fatty acids. However, these higher carbon-numbered n-alkanes were observed only at significantly low concentration. Additionally, a notable predominance of even carbon number was evident in the products, suggesting the possible involvement of fatty acids polymerization facilitated by $CaCO_3$. To improve the understanding of the authentic origins of these n-alkanes and to explore their geochemical significance, a comparative analysis of sedimentary organic samples from different depths within the Luntan 1 well is imperative. Futher investigations will primarily focus on determining the precise origins of these compounds and delving into their broader geochemical implications.

4. Conclusion

C_{10}-C_{125} n-alkanes and monocyclic alkanes were detected for the first time in the highly mature source rock of Luntan-1 well in Tarim Basin. Both series exhibited no carbon number predominance in the carbon range of C_{10}-C_{50}, but even carbon-number predominance in the carbon range of C_{50}-C_{110}. This distribution pattern breaks the conventional understanding that n-alkanes have no carbon number predominance in highly mature samples. The similar distribution pattern of n-alkanes and monocyclic alkanes indicate that they have the same biological precursors. It is speculated that they are formed by reduction and cyclization of ultrahigh molecular weight fatty acids and alcohols or polymerization of medium molecular weight fatty acids under the catalytic action of $CaCO_3$.

CRediT authorship contribution statement

Chenglong Dong: Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Jia Wu:** Writing – review & editing, Resources, Investigation, Formal analysis, Data curation. **Jikun Liu:** Methodology. **Weilai Zhang:** Methodology. **Sara Grimay:** Methodology. **Peng Fang:** Methodology. **Xiaowan Tao:** Resources. **Guangyou Zhu:** Resources. **Yehua Han:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

This work was financially supported by the National Key R&D Program of China (No. 2021YFA1501201), and the National Natural Science Foundation of China (No. 21874153). The authors acknowledge support from State Key Laboratory of Heavy Oil Processing, China University of Petroleum-Beijing.

Thanks for the technical support from Yahe Zhang and Hao Wu.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2023.129360.

References

[1] Wang N, Xu Y, Wang F, Liu Y, Huang Q, Huang X. Identification and geochemical significance of unusual C24 tetracyclic terpanes in Shahejie Formation source rocks in the Bozhong subbasin. Bohai Bay Basin Petroleum Science 2022;19(5):1993–2003.
[2] Wang Y, Fang X, Zhang T, Li Y, Wu Y, He D, et al. Predominance of even carbon-numbered n-alkanes from lacustrine sediments in Linxia Basin, NE Tibetan Plateau: implications for climate change. Appl Geochem 2010;25(10):1478–86.
[3] Scalan E, Smith J. An improved measure of the odd-even predominance in the normal alkanes of sediment extracts and petroleum. Geochim Cosmochim Acta 1970;34(5):611–20.
[4] Herrera-Herrera AV, Leierer L, Jambrina-Enríquez M, Connolly R, Mallol C. Evaluating different methods for calculating the Carbon Preference Index (CPI): Implications for palaeoecological and archaeological research. Org Geochem 2020;146:104056.
[5] Evans E, Kenny G, Meinschein W, Bray E. Distribution of n-paraffins and separation of saturated hydrocarbons from recent marine sediments. Anal Chem 1957;29(12):1858–61.
[6] Bray E, Evans E. Distribution of n-paraffins as a clue to recognition of source beds. Geochim Cosmochim Acta 1961;22(1):2–15.
[7] Brunnock J. Distribution of normal paraffins in Libyan and Nigerian crude oils. Nature 1966;212(5060):385–7.
[8] Dembicki Jr H, Meinschein W, Hattin DE. Possible ecological and environmental significance of the predominance of even-carbon number C20–C30n-alkanes. Geochim Cosmochim Acta 1976;40(2):203–8.
[9] Fowler M, Abolins P, Douglas A. Monocyclic alkanes in Ordovician organic matter. Org Geochem 1986;10(4–6):815–23.
[10] Dong V. Origin of long-chain alkylcyclohexanes and alkylbenzenes in a coal-bed wax. Geochim Cosmochim Acta 1993;57(4):837–49.
[11] Murray AP, Summons RE, Boreham CJ, Dowling LM. Biomarker and n-alkane isotope profiles for Tertiary oils: relationship to source rock depositional setting. Org Geochem 1994;22(3–5):521–42.
[12] Bourbonniere RA, Meyers PA. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. Limnol Oceanogr 1996;41(2):352–9.
[13] Bush RT, McInerney FA. Leaf wax n-alkane distributions in and across modern plants: Implications for paleoecology and chemotaxonomy. Geochim Cosmochim Acta 2013;117:161–79.
[14] Barman BN, Cebolla VL, Membrado L. Chromatographic techniques for petroleum and related products. Crit Rev Anal Chem 2000;30(2–3):75–120.
[15] Marshall AG, Rodgers RP. Petroleomics: The next grand challenge for chemical analysis. Acc Chem Res 2004;37(1):53–9.
[16] Rodgers RP, Schaub TM, Petroleomics MAG. MS returns to its roots. Anal Chem 2005;77(1):20 A-27. A.
[17] Marshall AG, Rodgers RP. Petroleomics: Chemistry of the underworld. Proc Natl Acad Sci 2008;105(47):18090–5.
[18] Dong C, Hu W, Wang Y, Zhang Y, Zhu G, Han Y. Double-bond equivalence linear equations for structural interpretation of fossil hydrocarbons. Fuel 2023;332:126206.
[19] Dong C, Jia C, Zheng S, Zeng H, Fu D, Xu L, et al. Molecular composition analysis using ultra-high resolution mass spectrometry for lubricating oil process optimization. Petroleum Sci Bull 2019;04:430–9.
[20] Shimoyama A, Johns WD. Formation of alkanes from fatty acids in the presence of CaCO3. Geochim Cosmochim Acta 1972;36(1):87–91.
[21] Wu L, Zhu G, Yan L, Feng X, Zhang Z. Late Ediacaran to Early Cambrian tectonic–sedimentary controls on Lower Cambrian black shales in the Tarim Basin, Northwest China. Global and Planetary Change 2021;205:103612.