PS 4-Methyl-24-Ethylcholestane in Upper Permian Fossil Conifer Wood from Paleo-Midlatitude of NE Pangea, Wutonggou Low-Order Cycle, Southern Bogda Mountains, NW China*

Xin Zhan[1], Wan Yang[2], Qiao Feng[3], Yujiao Zhang[4], and Yankuan Tian[4]

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[1]Missouri University of Sciences and Technology, Rolla, Missouri, United States (xz793@mst.edu)
[2]Missouri University of Sciences and Technology, Rolla, Missouri, United States
[3]Shandong University of Science and Technology, Qingdao, China
[4]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

Abstract

The use of C30 4-methylsteranes as an indicator of source organic matter relies on accurate identification of the compounds from their isomers and distribution of their precursors (i.e. sterols) in contributing organisms. C30 4-methylsteranes have been reported in many Mesozoic and pre-Mesozoic samples but not in Permian rocks. They may be produced from dinoflagellates or aquatic plants or methylotrophic bacteria. Significant amount of C30 4-methylsteranes was detected in preserved materials in two Upper Permian fossil conifer stems. The 4-methylsteranes have a 4-methyl-24-ethylcholestane structure, without 4α, 23, 24-trimethylcholestanes (also known as dinosteranes). The preservation of C30 4-methylsteranes with C29 steranes and absence of C27-28 steranes with rare hopanes suggest that the 4-methyl sterols produced by conifers may be an important potential precursor for 4-methylsteranes. Alternative sources include freshwater dinoflagellates or methylotrophic bacteria in the environments where the conifers lived, transported, and deposited. Significant amount of C30 4-methylsteranes in Permian fossil conifer in fluvial-lacustrine environments shows that regarding the 4-methylsteranes as an indicator of diagnostic marine input can lead to erroneous conclusions. The rarity of this biomarker in geological records makes it an effective proxy for nonmarine sequence stratigraphic correlation and oil-oil and oil-source rock correlation.

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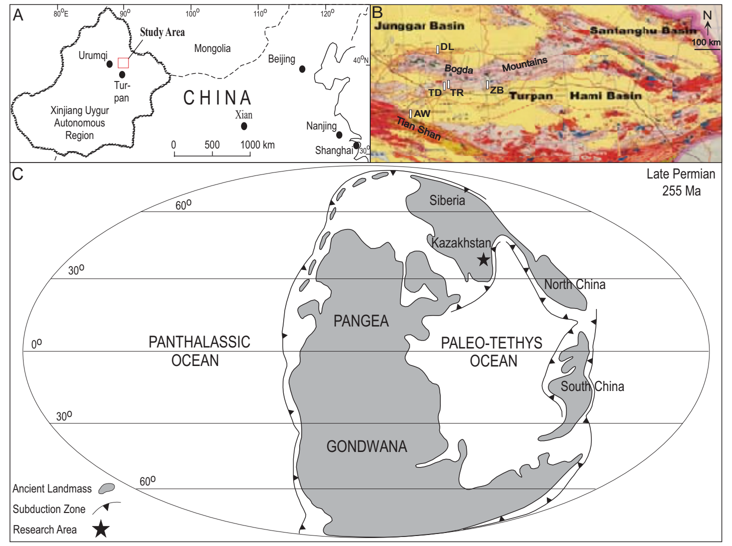
Xin Zhan[1], Wan Yang[1], Qiao Feng[2], Yujiao Zhang[3], Yankuan Tian[3]

1. Missouri University of Sciences and Technology, Rolla, MO 65409, U.S.A.
2. Shandong University of Science and Technology, Qingdao, 310003, China.
3. Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.

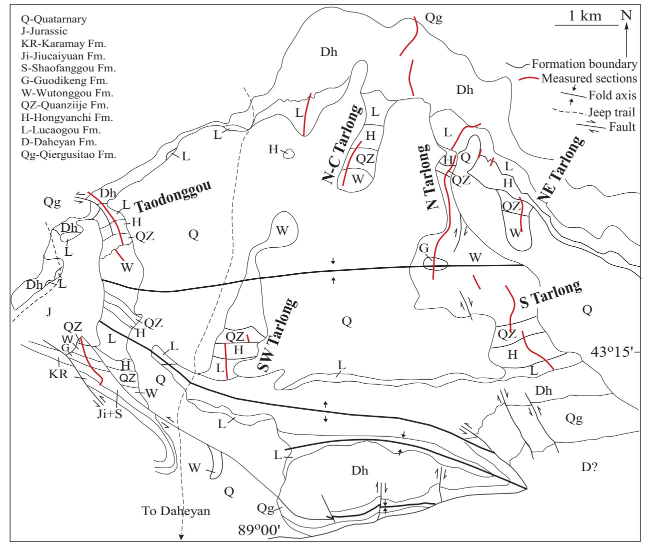
The use of C_{30} 4-methylsteranes as an indicator of source organic matter relies on accurate identification of the compounds from their isomers and distribution of their precursors (i.e. sterols) in contributing organisms. C_{30} 4-methylsteranes have been reported in many Mesozoic and pre-Mesozoic samples but not in Permian rocks. They may be produced from dinoflagellates or aquatic plants or methylotrophic bacteria. Significant amount of C_{30} 4-methylsteranes was detected in preserved materials in two Upper Permian fossil conifer stems. The 4-methylsteranes have a 4-methyl-24-ethylcholestane structure, without 4a, 23, 24-trimethylcholestanes (also known as dinosteranes). The preservation of C_{30} 4-methylsteranes with C_{29} steranes and absence of C_{27}-C_{28} steranes with rare hopanes suggest that the 4-methyl sterols produced by conifers may be an important potential precursor for 4-methylsteranes. Alternative sources include freshwater dinoflagellates or methylotrophic bacteria in the environments where the conifers lived, transported, and deposited. Significant amount of C_{30} 4-methylsteranes in Permian fossil conifer in fluvial-lacustrine environments shows that regarding the 4-methylsteranes as an indicator of diagnostic marine input can lead to erroneous conclusions. The rarity of this biomarker in geological records makes it an effective proxy for nonmarine sequence stratigraphic correlation and oil-oil and oil-source rock correlation.

Research Area



(A) Location of the study area in Xinjiang Uygur Autonomous Region, NW China. (B) Geological map of Turpan-Hami Basin, showing the location of Tarlong (TR), Taodonggou (TD), Dalongkou (DL), Zhaobishan (ZB), and Aiweiergou (AW) sections (white column). Modified from XBGMR (1993) and Yang et al. (2010). (C) Paleotectonic and paleogeographic reconstruction of Pangea at Late Permian (255 Ma) of Scotese (2001).

Geological Map of Tarlong and Taodonggou



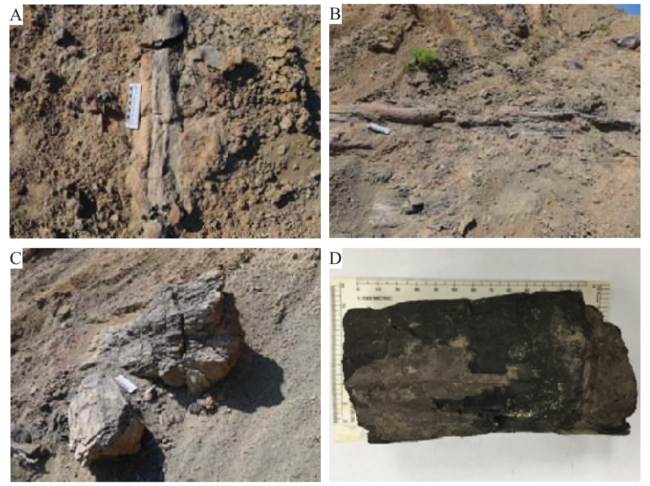
Geological map of the study area showing location of measured sections (thick red lines) in a syncline (named as Tarlong– Taodonggou half graben). Alluvial and lacustrine deposits exposed were deposited during Late Carboniferous – Early Triassic. Basemaps are 1:10,000-scale topographic maps. Modified from Yang et al., (2010).

Stratigraphy

Period		Epoch	Lithostratigraphy	Cyclostratigraphy Low-Order Cycles (Yang et al., 2010; Obrist-Farner and Yang, 2015)	Revised Cyclostratigraphy (Yang et al., 2010, 2013) New dates	Stages
Triassic		Middle	Karamay	Karamay		245.9 Anisian
Triassic		Lower	Shaofanggou	Shaofanggou		249.5 Olenekian
Triassic		Lower	Jiucaiyuan	Jiucaiyuan		251.0 Induan
Permian		Lopingian	Guodikeng	Wutonggou	253.11 253.63	Changshingian 253.8
Permian		Lopingian	Wutonggou	Wutonggou	254.22	Wuchiapingian 260.4
Permian		Guadalupian	Quanzijie	Upper Quanzijie		Capitanian 265.8
Permian		Guadalupian		Lower Quanzijie		Wordian 268.0
Permian		Guadalupian				Roadian 270.6
Permian		Cisuralian				Kungurian 275.6
Permian		Cisuralian	Hongyanchi	Hongyanchi	281.42	Artinskian 284.4
Permian		Cisuralian	Lucaogou	Lucaogou		Sakmarian 294.6
Permian		Cisuralian	Daheyan	Upper Daheyan		Asselian 299.0
Carboniferous	Pennsylvanian	Upper	Daheyan	Middle Daheyan		
Carboniferous	Pennsylvanian	Upper	Daheyan	Lower Daheyan	301.26 ± 0.05 301.37 ± 0.07	Gzhelian 303.4
Carboniferous	Pennsylvanian	Upper	Qiergusitao		305.50 ± 0.11 306.48 ± 0.32	Kasimovian 307.2

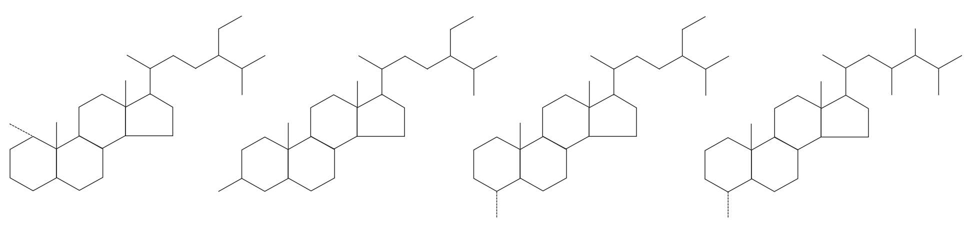
Chrono-, litho, and cyclostratigraphy of Upper Carboniferous-Middle Permian strata in the Tarlong-Taodonggou area. Hachured areas indicate missing strata; wavy lines are major unconformities; and dashed lines are disconformities; Absolute ages at stage boundaries are from Gradstein et al. (2004). The Wutonggou low-order cycle is defined on the basis of interpreted depositional environments and palaeoclimatic conditions (Yang et al., 2010). The environments range from meandering stream, lacustrine deltaic, to lake margin; the climatic conditions are dominantly humid to subhumid. Modified from Yang et al., (2010).

Photographs of Petrified Woods



(A,B,C) Photographs of petrified woods in Wutonggou low-order cycle at northeast Tarlong section (Yang et al., 2010). The Wutonggou interval is composed of distributary channel sandstones overlaying delta-front sandstones. The stems are parallel to the bedding plane, suggesting that they were transported from upstream or a nearby interdistributary area. The systematic study of the stems collected in Wutonggou low-order cycle at southwestern Tarlong section indicate that wood was Coniferopsida (Wan et al., 2014). (D) The outer layers of the stem are well silicified while the inner layers are organic-rich, with the TOC value of 3.16% and bulk organic carbon isotope value of -23.6‰.

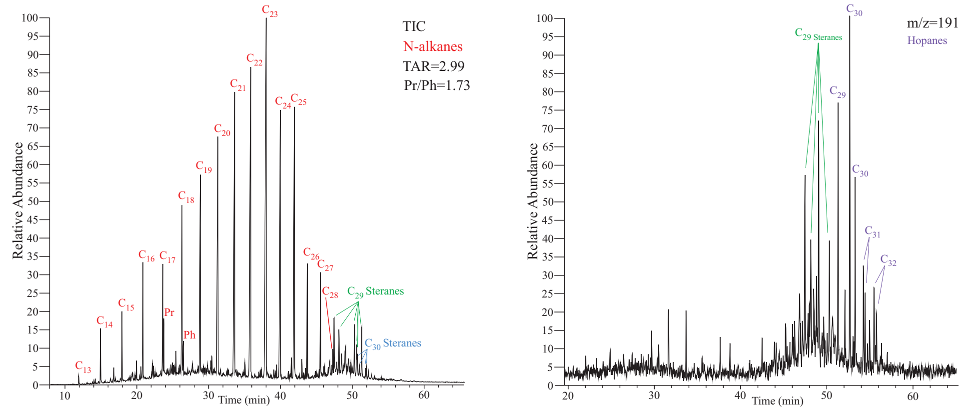
Four Major Classes of 4-Methylsteranes C_{30}



2a-Methyl-24-ethylcholestane　3ß-Methyl-24-ethylcholestane　4a-Methyl-24-ethylcholestane　4 ,23,24-Trimethylcholestane (C_{30} dinosteranes)

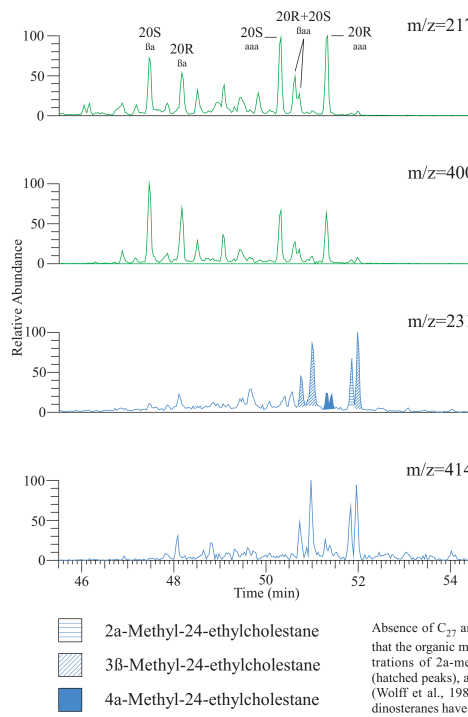
2a-Methyl-24-ethylcholestane, 3ß-Methyl-24-ethylcholestane, and 4a-Methyl-24-ethylcholestane are detected in the sample. No dinosteranes are detected.

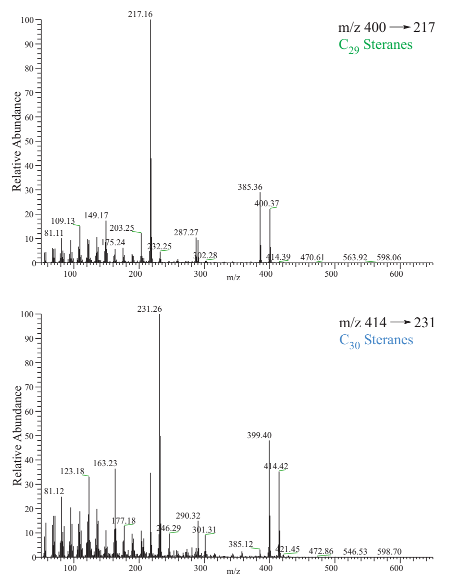
Biomarkers in the Saturated Fractions



The total ion chromatogram (TIC) shows that the intermediate- and long-chain n-alkanes are dominated in the saturated hydrocarbons, suggesting major contribution of terrestrial higher plants to the organic matter. Terrestrial aqueous ratio (TAR) = $(C_{23}+C_{25}+C_{27})/(C_{15}+C_{17}+C_{19})$. High TAR (>1) indicate dominance of organic matter input from terrestrial higher plants. Moderate Pristane/Phytane ratio (1<Pr/Ph<3) may suggest relatively dysoxic water conditions. Relatively low amount of 17a-homohopanes of C_{29} - C_{32} are detected on the m/z 191 chromatogram.

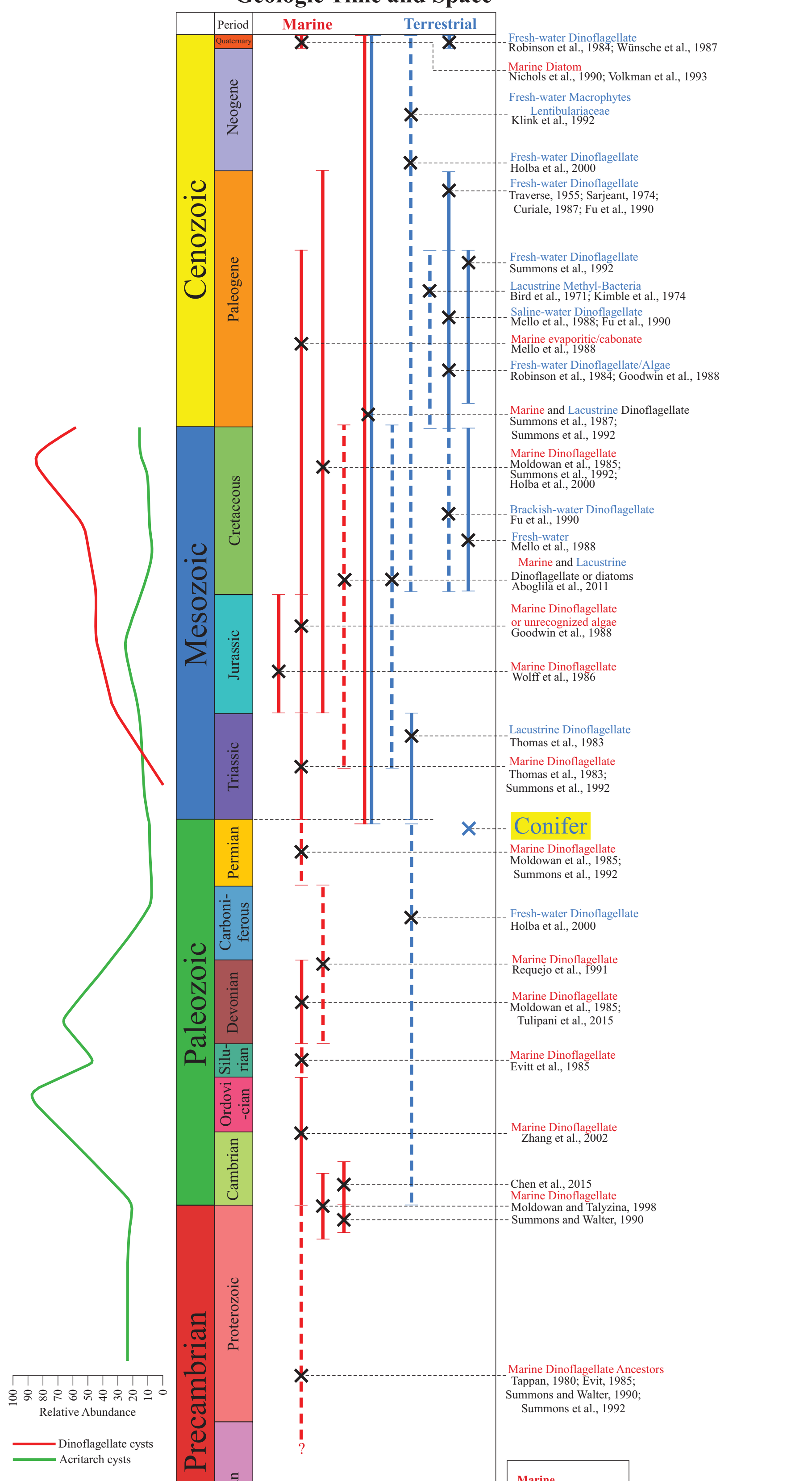
Identification of 4-Methyl-24-Ethylcholestane





Absence of C_{27} and C_{28} steranes and abundant C_{29} and C_{30} steranes in the fossil conifer wood, suggesting that the organic matter are derived from terrestrial higher plants instead of lacustrine algae. Relative concentrations of 2a-methyl-24-ethylcholestanes (horizontally striped peaks), 3ß-methyl-24-ethylcholestanes (hatched peaks), and 4a-methyl-24-ethylcholestanes (solid) are indicated on the m/z 414-231 chromatogram (Wolff et al., 1986; Peters et al., 2005). No 4a,23,24-trimethylcholestanes (dinosteranes) are detected as dinosteranes have an additional m/z 98 fragment on the m/z 414-231 chromatogram (Summons et al., 1987).

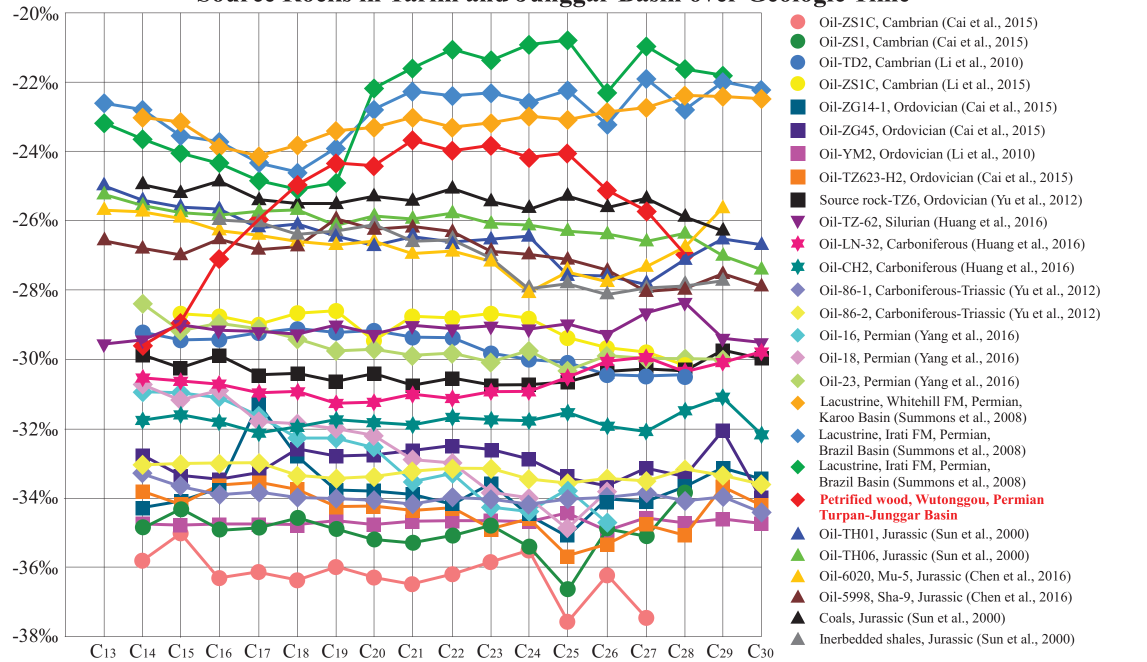
Occurrence of 4-Methyl-24-Ethylcholestane and its Origin over Geologic Time and Space



Schematic representation of relative numbers of species of **dinoflagellate** cysts and **acritarch** cysts. Modified from Moldowan et al., 1996

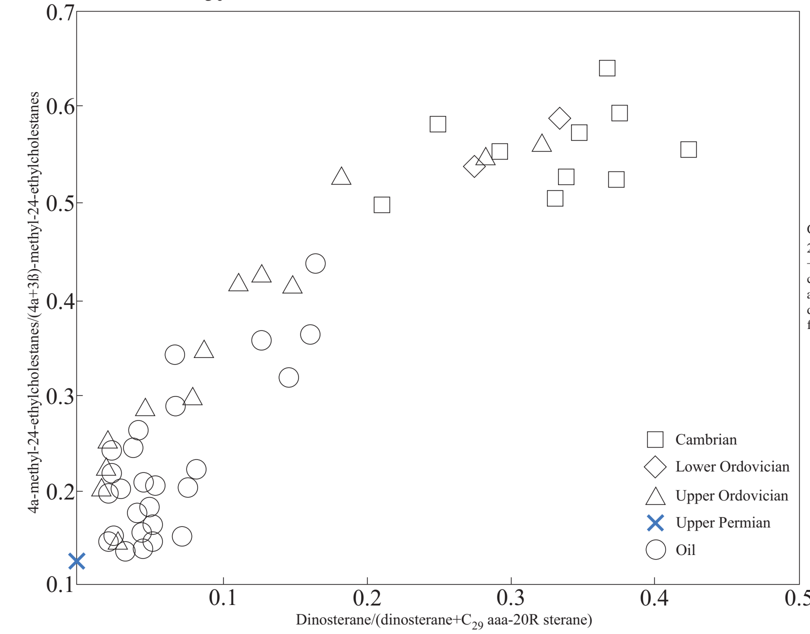
4-Methyl-24-Ethylcholestane have been reported in many Mesozoic and pre-Mesozoic samples but not in Permian rocks. They may be produced from dinoflagellates or aquatic plants or methylotrophic bacteria.

Differences of Compound Specific Organic Carbon Isotope of the Petrified Wood, Oil and Source Rocks in Tarim and Junggar Basin over Geologic Time



Crossplot of compound specific organic carbon isotope values and n-alkanes, suggesting that oil and source rocks from different geologic time have different organic carbon isotope values, thus, the compound specific organic carbon isotope may serve for oil and source rocks correlation.

Application of C_{30} Steranes for Oil and Source Rocks Correlation in Tarim and Junggar Basin



Crossplot of dinosteranes/(dinosteranes + C_{29} aaa-20R steranes) and 4a-methyl-24-ethylcholestanes/(4a + 3ß)-methyl-24-ethylcholestanes for oil and source correlation, suggesting possible decreasing relative abundance of 4a-methyl-24-ethylcholestanes and dinosteranes from Carmbian to Perimian, modified from Zhang et al., 2002.

Conclusion

4a-methyl-24-ethylcholestanes may be generated from higher plants, not from marine/lacustrine dinoflagellate. They constrain the age and depositional environments of sediments and age of oil and source rocks, thus the steranes are indicative markers for oil and source correlation.

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