



Research paper

Geochemical significance of $17\alpha(\text{H})$ -diahopane and its application in oil-source correlation of Yanchang formation in Longdong area, Ordos basin, China

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ABSTRACT

Relatively high abundance of $17\alpha(\text{H})$ - C_{30} rearranged hopane has been detected in some oils and rock extracts from Yanchang Formation of Longdong area, southwestern Ordos basin. Oil shale, silty mudstone and carbonaceous mudstone extracts from Yanchang Formation all have low abundance of C_{30} rearranged hopane, while high concentrations of C_{30} rearranged hopane were observed in the dark mudstone extracts. Analysis on the geochemical parameters of the organic matter origin, thermal maturity, and sedimentary organic facies were carried out. The result showed that the depositional-redox environment and lithology may be the critical factors for the rearrangement of hopanes which usually occurred in suboxic condition with clay-catalyzed reactions, as is consistent with the viewpoint of Peters and Moldowan (1993). According to the relative abundance of diahopane, three oil classes can be identified. Class 1 oil with low abundance of diahopanes was originated from oil shale of Chang 7 member, while Class 2 oil and Class 3 oil with middle to high abundance of diahopanes were derived from dark mudstones of Chang 4 + 5 to Chang 9 members of Yanchang Formation. Of the 151 analyzed oil and extracts samples from different stratigraphic intervals, 105 samples belong to Class 1 oil coming from oil shale, while 46 samples belong to Class 2 and Class 3 oil derived from mudstones. So oil shale of Chang 7 member is the main effective source rock of Longdong area, and dark mudstones of Chang 4 + 5 to Chang 9 member are also important source rocks.

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1. Introduction

Rearranged hopanes refer to a class of biomarkers with carbon skeleton identical to that of regular hopanes, while the methyl side chain position is distinct from that of regular hopane. Multiple homologues of rearranged hopanes occur in hydrocarbon source rocks or crude oils, including $17\alpha(\text{H})$ -diahopane, $18\alpha(\text{H})$ -neohopane, an unidentified early-eluting series and 21-methyl-28-norhopanes (Whitehead, 1973; Philp and Gilbert, 1986; Moldowan et al., 1991; Farrimond and Telnæs, 1996; Nytoft et al., 2006). The first member of the rearranged hopane detected from the sediments is $18\alpha(\text{H})$ -22,29,30-trinor-neohopane(Ts) (Whitehead, 1973; Smith, 1975), then another important compound of the $18\alpha(\text{H})$ -

neohopane series (named " C_{29}Ts ") was identified by NMR techniques (Moldowan et al., 1991). Moldowan et al. (1991) determined the structure of $17\alpha(\text{H})$ -15 α -methyl-27-norhopane (" $17\alpha(\text{H})$ -diahopanes") by X-ray crystallography, which was another series of rearranged hopanes. The C_{30} member of this series had been observed earlier by Philp and Gilbert (1986) (denoted "Hopane X"). Furthermore, Moldowan et al. (1991) observed a pseudo-homologous series of C_{29-34} $17\alpha(\text{H})$ -diahopanes by GC-MS-MS from a Prudhoe Bay crude oil in Alaska and believed that this series had been recognized by Summons et al. (1988a,b) and they were erroneously assigned as the pseudo-homologous series of Ts detected in the middle Proterozoic crudes of McArthur Basin, Australia. A further series of unidentified rearranged hopanes has been reported by Killops and Howell (1991), Telnæs et al. (1992) and Farrimond and Telnæs (1996). Compounds in this pseudohomologous series including C_{27} and C_{29-35} members are notable in eluting approximately two carbon numbers earlier than the regular hopanes, so they were called an early-eluting series. Recently, a

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novel series of rearranged hopanes ranging from C₂₉ to at least C₃₄ has been identified as 21-methyl-28-nor-hopanes (Nytoft et al., 2006).

After rearranged hopanes were identified, they have received increasing attention as biological markers with applications for geochemical studies of petroleum source rocks and oils. The series of 17 α (H)-diahopane and 18 α (H)-neohopane have been applied widely in maturity and oil-source correlation, but the other two series of rearranged hopanes have rarely been studied. Ts/Tm, C₂₉Ts/[C₂₉17 α (H)-hopane + C₂₉Ts] are maturity parameters (Seifert and Moldowan, 1978) and the values of C₃₀ 17 α (H)-diahopane/[C₃₀ 17 α (H)-diahopane + C₂₉ 17 α (H)-hopane] increase with increasing maturity (Wang et al., 2000). Moreover, 17 α (H)-diahopanes and C₂₉Ts can be used to distinguish oil families and oil-source correlation (Smith and Bend, 2004; Xiao et al., 2004).

So far, a lot of researches have been done on the geochemical significance of 17 α (H)-diahopanes, but the disputes over their origins and geochemical significance still exist. On the aspect of origins, Moldowan et al. (1991) suggested that the 17 α (H)-diahopanes may be of a bacterial origin on the basis of isotopic similarity to the regular hopanes and their occurrence in an extended pseudohomologous series, whereas Philp and Gilbert (1986) proposed that the 17 α (H)-diahopanes were considered as terrestrial markers due to their recognition in coals and terrestrially sourced oils. However, through the geochemical study of oil shales from the Neoproterozoic, Qingbaikou System, Xiamaling Formation of Xiahuayuan town, Hebei Province, Zhang et al. (2007) reported that some special origin, such as the red algae may be the reason for high abundances of diahopanes. About the forming mechanism, the rearranged hopane series most likely arise from precursor bacterial hopanoids, which undergo rearrangement with clay-mediated acidic catalysis during diagenesis (Moldowan et al., 1991; Philp and Gilbert, 1986; Wang et al., 2000; Zhao and Zhang, 2001; Zhu et al., 2007). However, Xiao et al. (2004) suggested that the alkali condition with clay catalysis may be favorable for rearrangement occurring. Nevertheless, it should be noted that according to Telnaes et al. (1992), the abundances of diahopanes co-vary with the salinity of the depositional environment and type of bacterial organisms living there, not with the presence or absence of active catalytic sites on clay minerals as previously suggested. Furthermore, high abundance of diahopanes may have relationship with thermal maturity, increasing maturity should result in increased ratios of 17 α (H)-diahopane/17 α (H)-hopane, particularly in the late oil window (Moldowan et al., 1991). Kolaczowska et al. (1990) proposed that compounds of the 17 α (H)-diahopane series are more stable than those of the 17 α (H)-hopane series by molecular mechanics calculations. Thus, the ratio of 17 α (H)-diahopane/(17 α (H)-diahopane+17 α (H)-hopane) along with the sterane isomerization can be used to study the oil maturities in the North Sea oil fields (Horstad et al., 1990). But not all high mature sources and related oils have high abundances of diahopanes. In summary, divergent factors can affect the occurrence of 17 α (H)-diahopanes, but the critical factor may be different in various geological conditions.

Source rock extracts and oils with relatively abundant 17 α (H)-diahopane have been observed from Yanchang Formation of Longdong area, Ordos basin. Nevertheless, the precise reason for high abundances of rearranged hopanes remains unresolved, which has hindered the oil-source correlation of the studied area. The purpose of this paper is to investigate the geochemical significance of 17 α (H)-C₃₀diahopane and determine the origin of crude oils through a systematic geochemical characterization of Yanchang formation in Longdong area. This information may contribute to a better understanding of hydrocarbon generation, migration and accumulation mechanisms in Longdong area and therefore provide a better model for further petroleum exploration.

2. Geological setting

The Ordos basin, located in central China, is the second largest sedimentary basin in China, encompassing an area of about 250,000 km² (Fig. 1). It is surrounded by the Yinshan Mountains in the north, the Qinling Mountains in the south, the Liupanshan Mountains in the west and the Luliangshan Mountains in the east. Since the Middle Proterozoic, the Ordos basin has experienced five discernable stages including a Middle-Late Proterozoic aulacogen basin, an Early Paleozoic marginal basin, a Late Paleozoic intracratonic basin, a Mesozoic reactivated cratonic basin and a Cenozoic rift basin (He, 2003). This basin can be divided into six structural units: the Yimeng uplift, Weibei uplift, Western edge thrusting belt, Tianhuan depression, Shanbei slope, and the Jinxi flexural fold belt (Fig. 1; Yang, 2002). The Shanbei slope, where faults and folds were not developed, is a smooth monocline with an east-to-west dip angle of less than 1° and it is the major area of petroleum production in the Ordos basin. Longdong area is in the southwestern part of the Ordos basin, extending across the Tianhuan depression and Shanbei Slope (Fig. 1; He, 2003).

Paleozoic, Mesozoic, and Cenozoic sedimentary strata were developed in the Ordos basin. Paleozoic sediments deposited in marine and delta environments are rich in natural gas, whereas Mesozoic sediments of lacustrine-fluvial reservoirs are abundant in oil resources (Yang, 2002). The Mesozoic petroleum system mainly includes the Lower Jurassic Yan'an Formation and the Upper Triassic Yanchang Formation. Approximately 75% of the oil resources in Ordos basin are found in the Upper Triassic Yanchang Formation, which is part of a lacustrine sedimentary system with a thickness of about 1300 m. The Upper Triassic Yanchang Formation can be divided by lithology into ten members (Chang 1 to Chang 10) from top to bottom (Fig. 2; Zhao et al., 2004). Specifically, sandstones from the sixth and eighth members are the main oil reservoirs which were deposited in delta environments. The porosity of reservoirs is mainly between 6% and 14%, and the permeability is generally 0.01–1 × 10⁻³ μm² (0.01–1md). Thus, they are typical sandstone reservoirs with high heterogeneity, poor porosity and ultra-low permeability.

Previous researches showed that there were four possible types of oil source rocks in Yanchang Formation of Longdong area including oil shale, mudstones, silty mudstones and carbonaceous mudstones (Yang et al., 1992). According to the empirical statistics, the total organic carbon (TOC) content of the oil shale is mostly higher than 6%, and that of the mudstones is between 1% and 6%, while the TOC of silty mudstones is lower than 1%. The carbonaceous mudstones, which mainly developed in Chang 4 + 5 and Chang 6 member, are mudstones with amounts of carbonized organic matter. Shang et al. (1982) and Zhang and Li (2001) suggested that the organic-rich oil shale matter of Chang 7 member is the best source rock of Yanchang Formation, Ordos basin. However, no systematic oil-source correlation has been performed in Yanchang Formation of Longdong area.

3. Samples and analytical methods

Seventy representative Drill Stem Test (DST) oil samples and eighty-one reservoir samples from different stratigraphic intervals, as well as ninety-three source rocks were collected (Fig. 1). All the oil samples, reservoir samples and source rock samples were analyzed for their biomarker compositions. These analytical tests were operated in the State Key Laboratory of heavy oil in Chinese University of Petroleum.

Rock samples were crushed into 100 mesh grain size and the powdered samples were extracted with chloroform using a YSB-automatic multifunctional extractor with leaching method, which

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