Application of Rare-Earth Elements and Comparison to Molecular Markers in Oil–Source Correlation of Tight Oil: A Case Study of Chang 7 of the Upper Triassic Yanchang Formation in Longdong Area, Ordos Basin, China

Ruiliang Guo, Yande Zhao,* Weibin Wang, Xinyou Hu, Xinpeng Zhou, Lewei Hao, Xiaofeng Ma, Dongxu Ma, and Shutong Li

ABSTRACT: The biomarker features of 10 Chang 7 crude oil samples were investigated by gas chromatography–mass spectrometry (GC–MS), and the rare-earth element (REE) compositions of 16 Chang 7 and Chang 8 crude oil samples were determined by inductively coupled plasma–mass spectrometry (ICP–MS) for the first time in Longdong area. Oil–source correlation analysis was improved by biomarkers and REEs. The distribution and relative ratios of a series of biomarker parameters in saturated hydrocarbons and aromatic hydrocarbons of crude oil samples indicate that Chang 7 tight oil has already reached the mature stage. The organic matter mainly comes from lower aquatic organisms of algae, with some contribution of micro-organisms and bacteria, while the forming environment of tight oil is mainly the transitional environment of sub-oxidizing to sub-reducing. The V/(V + Ni) and Ni/Co ratios of crude oil samples suggest that the specific redox conditions of Chang 71 and Chang 72 samples were slightly oxic, while Chang 73 and Chang 8 samples were formed under an anoxic environment. The results of both biomarker-based and REE-based oil–source correlation analysis indicate that Chang 71 and Chang 72 tight oils come from Chang 7 mudstone, while most of the Chang 73 tight oils are from Chang 7 oil shale, with part of mixed from Chang 7 mudstone. This recognition may indicate that Chang 7 mudstone and oil shale are two relatively independent hydrocarbon self-generation and near-storage systems. The analysis results demonstrate that the REE composition in crude oil is an efficient and accurate tool for oil–source correlation in the petroleum system.

1. INTRODUCTION

As the recoverable reserves of conventional oil and gas resources continue to decline, unconventional resources with great potential represented by tight oil have gradually become a new exploration field and are attracting the attention of the energy industry.1−7 In China, tight oil is defined as a hydrocarbon resource that occurs in the source rock or the tight reservoir adjacent to the source rock in adsorbed or free state, without large-scale and long-distance migration.5,6 Tight oil resources are widely distributed in major basins in China, such as Lucaogou Formation of Permian in Junggar Basin, Middle to Lower Jurassic in Sichuan Basin, and Upper Triassic Yanchang Formation in Ordos Basin.1,5 Among them, Chang 7 section of Yanchang Formation is typical deep lacustrine gravitational flow type tight oil, with proved geological reserves of 10 × 108 ton.2,3 In previous studies, Chang 7 section is generally regarded as the main source rock of the whole Yanchang Formation and is the main hydrocarbon contributor to the overlying Chang 6, Chang 8, and Chang 9 reservoirs, while its attribute as a tight oil reservoir and the source of its inner tight oil was ignored.8−10 With the focus of tight oil exploration shifting from the traditional strata to the new target for increasing reserves and production, Chang 7 tight oil and further shale oil resources have been paid attention to. In Ordos Basin, tight oil is mainly from tight massive sandstone reservoirs, while shale oil refers to oil resources in tight sandstone–mudstone interbedded and shale reservoirs.13,14 Longdong area is located in the depocenter of the lacustrine basin at the Chang 7 section depositional stage, where organic-rich source rock and turbidite sandstones are developed, thus forming a lithologic combination of source rock–reservoir...
interbedding. This makes the tight oil reserves of this area particularly rich.²,³,¹³ However, the cyclic development of the lacustrine basin and the frequent transgression−regression lacustrine water in Chang 7 period results in strong heterogeneity of the source rock and reservoir vertically and horizontally. Meanwhile, as the source rock of Chang 7 section, the dark mudstone and oil shale have different hydrocarbon generation potentials, hydrocarbon expulsion thresholds, deposition conditions, and redox states.¹⁴,¹⁵ All these features make it difficult to predict the distribution of tight oil pool; also, the source of crude oil is not well understood, which limits the exploration and exploitation of tight oil and further shale oil to a certain extent.

As mentioned before, previous studies on oil−source correlation in the Longdong area mainly focused on the relationship between the crude oil in Chang 6, Chang 8, and Chang 9 tight reservoirs and the source rocks of Chang 7 and Chang 9.⁶,¹⁰,¹⁶,¹⁷ There is no doubt that the tight oil in the Chang 7 reservoir comes from the Chang 7 source rock, but it is rarely mentioned whether it comes from mudstone or oil shale. It is well accepted that Chang 7 mudstone and oil shale have different hydrocarbon generation potentials and times, sedimentary environments, and accumulation patterns.¹⁴,¹⁵,¹⁸−²⁰ Though Xu et al. proposed that Chang 7 mudstone controls the occurrence of the Chang 7 tight oil pool and Chang 7 oil shale mainly controls the occurrence of the Chang 8 tight oil pool, evidence is lacking from crude oil samples.¹⁴ Also, the geochemical reports of crude oil in Ordos Basin are mainly on the biomarkers.⁸,¹⁰,¹⁸ Biomarkers, as a traditional tool for oil−source correlation, are not effective in facing with the complicated hydrocarbon accumulation and refined oil−source correlation, not to mention that they will lose original significance because of the influence of thermal maturity and secondary alterations such as biodegradation.²¹,²² In addition, the concentration ratio of biomarkers which is commonly used in oil group classification and oil−source correlation vary as a nonlinear function of the amount of different types of oils, thus affecting the comparison results of mixed-source crude oil.²³ However, some elemental ratios of crude oil remain stable in most instances, such as the V/Ni ratio.²⁴,²⁵ At the same time, extensive studies demonstrate that the concentration and distribution of trace elements in crude oil can provide information about the source rock sedimentary environment, oil maturity, and origin and also be a potential tool for oil−oil correlation and oil−source correlation.²⁶−²⁷ Rare-earth elements (REEs), as lanthanide elements from La to Lu, have been widely used on material origin and systematic division in various geological processes for their similar chemical properties.²⁸−³⁰ Also, there are some successful applications to crude oil classification and oil−source correlation in Tarim Basin and Anadarko Basin.³¹,³² However, data on the concentration and distribution of REEs in crude oil are rare in Ordos Basin, and few studies compare the application effects between REEs and biomarkers in oil−oil
correlation and/or oil−source correlation. Hence, in view of the deficiencies in previous studies and the difficulties in the exploration and exploitation of tight oil, the main purpose of this study is to analyze biomarker and REE compositions of Chang 7 tight oil in the Longdong area, using traditional biomarker ratios and REE compositions to carry out the crude oil group classification, to compare the results and ultimately carry out the oil−source correlation analysis.

2. GEOLOGICAL SETTINGS

2.1. Tectonics and Structure. Ordos Basin, formed in the west of North China Craton, is the second largest sedimentary basin in China. Ordos Basin developed on the Paleozoic North China Craton with Paleoproterozoic crystalline basement in the Mesozoic and Cenozoic. From Paleozoic to Mesozoic, the Ordos Basin experienced evolution from the Cambrian−Early Ordovician craton basin with a divergence margin to the Middle Ordovician−Middle Triassic craton basin with a convergence margin and then to the Late Triassic−Early Cretaceous intraplate residual craton basin. Among them, it was a huge interior freshwater lacustrine basin in the Late Triassic (Figure 1a). The basin can be divided into six tectonic units: the Jinxia flexure belt in the east, the Yi-Shan slope gently westward with a dip angle of 1°, is stable in structure, and is the main petroleum production area in Ordos Basin. The Longdong area is mainly located in the south-
2.2. Lithostratigraphy. The sedimentary facies of Ordos Basin experienced a transition from marine-continental to continental facies in Late Triassic, which was mainly a lacustrine environment at that period. \cite{34} Yinshan in the north and Qinling orogenic belt in the south are the main sediment source supply areas in the southwest of the basin and gradually formed Yanchang Formation, which mainly consists of fluvial-lacustrine-deltaic deposits, including sandstone, siltstone, mudstone, shale, and tuff intercalation. \cite{35} The Yanchang Formation, which can be further separated into 10 sections (Chang 1–10 from top to bottom) just experienced an integral lacustrine basin evolution process: the formation and development period (Chang 10 to Chang 8), the peak period (Chang 7 to Chang 4 + 5), and the extinction period (Chang 3 to Chang 1) (Figure 2). \cite{35,36} Among them, Chang 7 section is the largest flooding deposit. Organic-rich dark mudstone and oil shale are developed over a large area on the plane and overlapped with a delta front or gravity flow sand body to form a favorable lithologic trap (Figure 2). \cite{35,36} Chang 7 section can be further divided into three sub-sections from top to bottom, namely, Chang 7_1, Chang 7_2, and Chang 7_3 sub-sections, respectively. Oil shale is mainly developed at the bottom of Chang 7_3, while mudstone is mainly overlying shale, which is located from Chang 7_1 to Chang 7_3 (Figure 2). Dark mudstone and oil shale are both formed in deep and semi-deep lacustrine environments. Mudstone is thick, homogeneous, massive, with partly developed horizontal lamination, and the particle diameter is generally less than 4 μm. \cite{3,12} It is gray-black to black due to its rich aromatic organic matter. \cite{12} Oil shale is black to brown-black flakes with horizontal lamination and a smaller grain size than mudstone. \cite{12} Mudstone contains more sandy components than oil shale, approximately 5–20% in mudstone, while in oil shale it is generally less than 5%; the quartz content is also higher in mudstone than that in oil shale (on average, at 21.5 and 12.5%, respectively), while oil shale has more clay mineral content than mudstone (on average, at 52.1 and 43.3%, respectively). \cite{40} In addition, the pyrite content of oil shale is 3 times more than that of mudstone. \cite{40}

2.3. Characteristics of Chang 7 Source Rock. Part of the hydrocarbon generation center of Chang 7 section is located in the Longdong area, with the source rock thickness of 10–40 m (Figure 1b,c). The organic matter type of Chang 7 source rock is dominated by lower aquatic organisms, with an average TOC of 13.75%, and the kerogen is mainly of type I, II_1, and II_2 based on the classification of Peters and Cassa, 1994. \cite{14,15,40,41} Kerogen accounts for a high proportion of 15–35% approximately in the source rocks. \cite{3} Specifically, oil shale is dominated by type I kerogen, while mudstone is mainly type II_1 and II_2 kerogen. \cite{40} The average TOC of oil shale is 18.5%, which is 5 times more than that of mudstone. \cite{40} This reveals that Chang 7 oil shale has better hydrocarbon generation potential than mudstone. Biomarker data demonstrate that the organic matter in oil shale has more alga and other aquatic micro-organism input than that of mudstone, and the reducing
level of oil shale sedimentary environment is higher than that of mudstone.14 This is supported by trace element evidence that the paleoenvironment of oil shale is anoxic, while that of mudstone is sub-oxic.19,20 Also, the relative salinity of the mudstone deposit water body is slightly higher than that of shale, and the depth is deeper as well.20

3. RESULTS

3.1. Physical Properties of Crude Oil. By summarizing the 87 physical property data of crude oil samples from the Changqing Oilfield Company, it is concluded that for Chang 7 crude oil in Longdong area, the average ground density is 0.836 g/cm³, the average viscosity is 4.26 mPa s, the gel point averages at 16.4 °C, the gas/oil ratio averages at 118.0 m³/t, and the average formation volume coefficient is 1.261 (Changqing Oilfield Company). This reveals that Chang 7 tight oil is characterized by low density, low viscosity, and low gel point, with relatively strong fluidity. The group components of 10 Chang 7 crude oil samples are listed in Table 1. It can be seen that the contents of saturated hydrocarbon, aromatic hydrocarbon, resins, and asphaltene are 20.24%, 13.44%, 6.25%, and 0.83%, respectively (Table 1). Resins and asphaltene account for less than 10% in crude oil samples, respectively (Table 1). The saturated/aromatic hydrocarbon ratio is 4.70–8.80, with an average of 5.34 (Table 1). Saturated hydrocarbon accounts for the highest proportion in crude oil, showing the typical group composition characteristics of mature oils.

3.2. Biomarker Compositions. The mass chromatograms of m/z 85, m/z 191, and m/z 217 were used to determine the characteristics of n-alkanes, isoprenoid alkanes, terpenoids, and steroids in saturated hydrocarbons of Chang 7 crude oil. The distribution and characteristics of polycyclic aromatic hydrocarbons were identified from m/z 178, m/z 192, m/z 168, m/z 166, and m/z 184 mass chromatograms. The related biomarker parameters of saturated and aromatic hydrocarbons were calculated from the ratio of the relevant peak area.

3.2.1. n-Alkanes and Isoprenoids. Figure 3 illustrates the m/z 85 mass chromatograms of four representative Chang 7 crude oil samples, most of which have a bimodal distribution. The carbon number of all the samples is in the range of C_{27}−C_{35} with the main peak carbon number of C_{27}−C_{28} (Table 2). The carbon preference index (CPI) and odd–even predominance (OEP) are generally low, ranging 1.13–1.24 and 1.21–1.33, averaging at 1.17 and 1.28, respectively (Table 2). The ∑nC_{21}/∑nC_{23}+ (and C_{21}+ C_{22})/(C_{24} + C_{29}) ratios are relatively high, which are 1.69–3.16 and 2.68–3.96, and averaging at 2.30 and 3.22, respectively, revealing the absolute advantage of short chain n-alkanes (Table 2). There is no significant difference between the content of pristane and phytane in crude oil; the Pr/Ph ratios range from 0.77 to 1.26 with an average of 1.03 (Table 2). Pr/nC_{17} and Ph/nC_{18} ratios of crude oil samples are relatively low with value variations of 0.24–0.53 and 0.23–0.71, respectively (Table 2).

3.2.2. Terpenoids. Based on the m/z 191 mass chromatogram of the saturated hydrocarbon (Figure 3), it can be found that terpane biomarkers such as gammacerane, Ts (C_{27} 18α(H)-trisnemohopane), Tm (C_{27} 17α(H)-trisnemohopane), and C_{31}-hopane are relatively abundant, and their relationship is pentacyclic terpane > tricyclic terpane > tetracyclic terpane. The homopane series compounds of pentacyclic terpane are characterized by relatively high contents, mainly distributed between C_{27} and C_{35}, with C_{30}-hopane as the main peak (Figure 3). C_{31}−C_{35} homopanes are relatively low in abundance and decrease in order (Figure 3). The ∑tricyclic terpene/∑homopane ratios of all crude oil samples vary significantly, most of which are greater than 1, ranging from 0.26 to 10.70, with an average of 4.46 (Table 2). The content of Ts is absolutely higher than that of Tm, with Ts/(Ts + Tm) ratios ranging from 0.51 to 1.00 and averaging at 0.74 (Table 2). Meanwhile, the gammacerane/C_{30} homopane ratios are pretty low at 0.02–0.21, with a mean value of 0.08, demonstrating the relatively low concentration of gammacerane (Table 2). C_{31} homopane is dominant in the homopane distribution, which C_{31} homopane 22S/(22S + 22R) ratios are in the range of 0.43–1.00, with a mean of 0.61 (Table 2).

3.2.3. Steroids. Pregnane, homopregnane, C_{27}−C_{29} regular steranes, and diasterane were detected by the m/z 217 mass chromatogram of saturated hydrocarbon in crude oil samples (Figure 3). For regular steranes, the content of C_{27} sterane is absolutely greater than those of C_{28} sterane and C_{29} sterane, while C_{29} sterane is slightly greater than C_{28} sterane in relative content. The specific relative content relationship is C_{27}(0.42–0.50%) > C_{28}(0.26–0.32%) > C_{29}(0.24–0.26%) (Figure 3 and Table 2). The C_{27}, C_{28}, and C_{29} regular steranes are generally distributed in V-shape on the m/z 217 mass chromatogram (Figure 3). The regular steranes are pretty discrepancy from hopanes in abundance, which lead to the significant variation on ∑regular steranes/∑(α)S'H-hopane ratios of 0.22–6.05, with an average of 1.91 (Table 2). The C_{29} sterane 20S/20S + 20R and C_{29} sterane ββ/αα + ββ ratios are generally high, which range from 0.44–0.50 and 0.55–0.61, with mean values of 0.47 and 0.59, respectively (Table 2). The (pregnane + homopregnane)/C_{30} regular sterane ratios are also calculated to be slightly high at 0.55–3.07 (Table 2).

3.2.4. Polycyclic Aromatic Hydrocarbons. The aromatic compounds of phenanthrene (Phen) series, fluorenes (Flu), dibenzothiophenes (DBT), and dibenzofuranes (DBF) were detected by the combination of the total ion chromatogram (TIC) and m/z 178, m/z 192, m/z 168, m/z 166, and m/z 184 mass chromatograms of aromatic hydrocarbons in crude oil (Figure 4). Phen series are high in abundance relative to Flu, DBT, and DBF in the distribution of aromatic compounds (Figure 4). Because of the extensive application in identifying the depositional environment, the relative contents of Flu, DBT, and DBF are calculated; 42 the relative content of Flu (0.26–0.52%) is the highest, followed by DBF (0.24–0.53%) which is slightly lower, and then DBT (0.18–0.30%) which is the lowest (Table 2). As the most commonly used maturity parameter of phenanthrene compounds, methylphenanthrene index (MPI) of crude oil is also calculated as 0.64–1.20 (Table 2). 43 The R_{c} (calculated vitrinite reflectance) calculated by MPI is between 0.78 to 1.12%, averaging at 0.91% (Table 2).

3.3. REE Compositions. REE determination results of crude oil samples are listed in Table 3 (the chondrite data are from Sun and McDonough, 1989). 44 The ∑REE (total content of REE) values in crude oil exhibit a wide variation and range from 42.02 to 684.66 ppb, with a mean value of 209.93 ppb (Table 3). The sum content of light REEs (LREEs of La to Eu) is higher than that of heavy REEs (HREEs of Gd to Lu) with the LREE/HREE ratios ranging from 42.02 to 684.66 ppb, with a mean value of 209.93 ppb (Table 3). Both LREEs and HREEs are characterized by relatively strong fractionation, with the (La/Yb)_{CN} values between 5.95 and 15.45, with an average of 9.60 (Table 3). Whereas the higher (La/Sr)_{CN} values (ranging...
Table 2. Molecular Composition and Related Parameters of Chang 7 Crude Oil Samples\(^a\)

| Sample | \(n\)-alkanes (C\(_{\text{main}}\)) | \(n\)-alkanes (C\(_{\text{range}}\)) | CPI | OEP | A | B | C | D | E | F | GI | H | I | J | K | L | M | C\(_{27}\) | C\(_{28}\) | C\(_{29}\) | DBT (%) | DBF (%) | Flu (%) | MPI | \(R_c\) (%) |
|--------|-----------------|-----------------|-----|-----|---|---|---|---|---|---|---|---|---|---|---|---|---|-----|-----|-----|--------|--------|--------|------|--------|
| B246   | 1.13            | 1.33            | 2.05| 2.77| 1.19 | 0.27 | 0.23 | 9.33 | 0.04 | 0.54 | 1.00 | 0.46 | 0.59 | 6.05 | 1.26 | 0.46 | 0.25 | 0.29 | 0.22 | 0.24 | 0.53 | 1.20 | 1.12 |
| H56    | 1.20            | 1.26            | 1.78| 2.80| 1.03 | 0.42 | 0.42 | 0.29 | 0.06 | 0.56 | 0.51 | 0.50 | 0.57 | 0.26 | 0.62 | 0.47 | 0.26 | 0.26 | 0.19 | 0.53 | 0.28 | 0.65 | 0.79 |
| H69    | 1.24            | 1.22            | 1.69| 2.68| 1.09 | 0.53 | 0.51 | 0.26 | 0.06 | 0.57 | 0.58 | 0.48 | 0.55 | 0.22 | 0.55 | 0.50 | 0.24 | 0.26 | 0.17 | 0.56 | 0.27 | 0.64 | 0.78 |
| N50    | 1.14            | 1.31            | 2.30| 2.96| 1.03 | 0.31 | 0.31 | 7.98 | 0.05 | 1.00 | 0.87 | 0.46 | 0.59 | 2.62 | 1.52 | 0.47 | 0.24 | 0.29 | 0.32 | 0.27 | 0.41 | 1.00 | 1.00 |
| W67    | 1.14            | 1.30            | 2.38| 3.16| 1.02 | 0.36 | 0.37 | 0.89 | 0.09 | 0.50 | 0.64 | 0.47 | 0.60 | 0.54 | 0.92 | 0.50 | 0.24 | 0.27 | 0.32 | 0.30 | 0.38 | 0.80 | 0.88 |
| Z45    | 1.15            | 1.29            | 3.16| 3.96| 1.26 | 0.28 | 0.24 | 10.70 | 0.02 | 0.57 | 0.91 | 0.44 | 0.48 | 0.60 | 3.39 | 2.06 | 0.42 | 0.25 | 0.32 | 0.24 | 0.40 | 0.36 | 0.69 | 0.81 |
| L36    | 1.13            | 1.32            | 2.32| 2.84| 1.09 | 0.24 | 0.23 | 9.13 | 0.06 | 1.00 | 0.84 | 0.46 | 0.58 | 3.00 | 3.07 | 0.48 | 0.25 | 0.27 | 0.27 | 0.28 | 0.45 | 1.02 | 1.01 |
| L87    | 1.17            | 1.27            | 2.86| 3.82| 0.92 | 0.35 | 0.42 | 1.62 | 0.08 | 0.48 | 0.68 | 0.48 | 0.60 | 0.72 | 1.08 | 0.47 | 0.24 | 0.29 | 0.26 | 0.36 | 0.38 | 0.76 | 0.86 |
| N44    | 1.17            | 1.27            | 2.07| 3.93| 0.88 | 0.36 | 0.38 | 1.58 | 0.16 | 0.43 | 0.75 | 0.49 | 0.61 | 1.03 | 0.61 | 0.49 | 0.24 | 0.27 | 0.27 | 0.32 | 0.41 | 0.81 | 0.89 |
| N45    | 1.21            | 1.21            | 2.38| 3.27| 0.77 | 0.51 | 0.71 | 2.63 | 0.21 | 0.43 | 0.58 | 0.47 | 0.60 | 1.30 | 0.81 | 0.46 | 0.26 | 0.28 | 0.28 | 0.30 | 0.43 | 0.88 | 0.93 |

\(^a\) C\(_{\text{main}}\): main peak carbon number; C\(_{\text{range}}\): carbon number range; CPI: carbon preference index = \(2[C_{23} + C_{25} + C_{27} + C_{29}] / [C_{22} + 2(C_{24} + C_{26} + C_{28}) + C_{30}]\); OEP: odd–even predominance = \(((\text{C4}_i + 6\text{C}_i + 4\text{C}_i)/(4\text{C}_i + 4\text{C}_i))^{1.5})^{-1}\); \(i = C_{24} - C_{34}\); A: \(\sum C_{21}\) / \(\sum C_{22}\); B: \(C_{21} + C_{22}\) / \(C_{28} + C_{29}\); C: Pr/Ph; D: Pr/nC\(_{27}\); E: Ph/nC\(_{31}\); F: \(\sum\)tricyclic terpenes / \(\sum\)hopanes; GI: gammacerane index = gammacerane / C\(_{30}\) hopane; H: C\(_{31}\) hopane 22S/(22S + 22R); I: Ts/(Ts + Tm); J: C\(_{29}\) sterane 20S/20S + 20R; K: C\(_{29}\) sterane \(\beta\beta\)/\(\alpha\alpha\) + \(\beta\beta\); L: \(\sum\)regular steranes / \(\sum 17(\alpha)H\)-hopane; M: (pregnane + homopregnane) / \(\sum\) regular sterane; DBT: dibenzothiophenes = DBT/(DBT + DBF + Flu); DBF: dibenzofuranes = DBF/(DBT + DBF + Flu); Flu: fluoranes = Flu/(DBT + DBF + Flu); MPI: methylphenanthrene index = 1.5 \(\times\) [(2 – MP) + (3 – MP)] / [phenanthrene + (1 – MP) + (9 – MP)], where MP-methylphenanthrene; \(R_c\) = 0.6 \times MPI + 0.4. Pr: pristane; Ph: phytane; Ts: C\(_{27}\) 18(\(\alpha\))-trisnorhopane; Tm: C\(_{27}\) 17(\(\alpha\))-trisnorhopane.
Figure 4. TIC and m/z 178, m/z 192, m/z 168, m/z 166, and m/z 184 aromatic hydrocarbon mass chromatograms of W67 crude oil samples.

3.50–6.59 and averaging at 5.14) than the (Gd/Yb)\textsubscript{CN} values (ranging 0.82–1.57 and averaging at 1.18) indicate that LREEs are more fractionated than HREEs (Table 3). The δEu and δCe values of crude oil are in the range 0.39–1.33 and 0.90–1.46, with an average of 0.79 and 1.12, respectively, demonstrating slightly negative Eu anomalies without an obvious Ce anomaly (Table 3). All REE distribution patterns of crude oil normalized by chondrite data display a right deviation curve with relatively high content of LREE (the obvious Ce anomaly (Table 3). All REE distribution patterns demonstrating slightly negative Eu anomalies without an obvious Ce anomaly (Table 3). All REE distribution patterns of the lower continental crust (UCC) (data from Taylor and McLennan, 1985) (Figure 5a–c).44 According to the distribution pattern of each sample, all crude oil samples can be further divided into three categories, most of which belong to the first group, with the features of slightly negative Eu anomalies, similar to the chondrite-normalized REE distribution of the upper continental crust (UCC) (data from Taylor and McLennan, 1985) (Figure 5a,d).45 There are two Chang 7 crude oil samples in the second group, that is, L140 and Z71, showing slightly positive Eu anomalies, which is consistent with the chondrite-normalized REE distribution of the lower continental crust (LCC) (data from Taylor and McLennan, 1985) (Figure 5b,d).46 Only one Chang 7 crude oil sample of Z182 belongs to the last group, the curve of which is relatively smooth without an obvious Eu anomaly (Figure 5c). This discrepancy may be due to the fact that the first type crude oil is mainly affected by the interaction of the fluids and materials derived from UCC in the migration process, which is also the normal formation process of typical sedimentary rocks. The second type is chiefly mixed by materials from the LCC, while the last type may be in-between.

4. DISCUSSION

4.1. Thermal Maturity of Crude Oil. The maturity of crude oil is of great significance to the inversion and understanding of the thermal history, the fluidity of crude oil in the reservoir, and the oil–source correlation analysis. In this study, a series of relative biomarker parameters including C\textsubscript{29} sterane 20S/20S + 20R, C\textsubscript{30} sterane ββ/αα + ββ, OEP, CPI, C\textsubscript{33} hopane 22S/(22S + 22R), MPI, and Ts/Tm were used to evaluate the maturity of Chang 7 crude oil samples. In the cross-plot of C\textsubscript{29} sterane ββ/αα + ββ and C\textsubscript{30} sterane 20S/20S + 20R, all data points fall in the area of mature (the identification map is from Li et al., 2017) (Figure 6a),47 that is, the C\textsubscript{29} sterane ββ/αα + ββ and C\textsubscript{30} sterane 20S/20S + 20R ratios of all samples are greater than 0.4, which is roughly equivalent to the R\textsubscript{o} (vitrinite reflectance) of oil equal to 0.8%,48 indicating that all crude oil samples are mature. The cross-plot of OEP and CPI continue to exhibit this feature, in which the OEP (1.21–1.33) and CPI (1.13–1.24) of crude oil samples are both less than 1.5 (the identification map is from Li et al., 2017) (Figure 6b) (Table 2).15 C\textsubscript{33} hopane 22S/(22S + 22R) ratios (0.43–1.00) of crude oil samples are consistent with the C\textsubscript{29} sterane maturity parameters mentioned above (Table 2), which have reached the isomerization equilibrium, revealing that crude oils are already mature.49 In addition, the difference in thermal stability between Ts and Tm makes them suitable maturity parameters.48 The Ts/(Ts + Tm) ratio of crude oil samples is greater than 0.5 (0.51–1.00) (Table 2), reflecting a higher maturity condition.44 As the most commonly used maturity parameter of phenanthrene compounds,50 MPI is in high correlation with R\textsubscript{o},64,49 and the R\textsubscript{o} (calculated vitrinite reflectance) of crude oil samples (0.78–1.12%) calculated by MPI is in relatively good agreement with the oil maturity reflected by C\textsubscript{29} sterane (Table 2). On performing the analysis of the above biomarker maturity parameters, Chang 7 crude oils in Longdong area are found to be already mature. This feature is just consistent with the maturity of Chang 7 source rocks proposed by previous research.14,50

4.2. Origin and Forming Environment of Crude Oil. The source and forming environment of organic matter in crude oil are of great significance to trace the formation process and conditions of crude oil and are also critical evidence in the oil–source correlation analysis, especially for the refined correlation of mixed oil sources.6,10 In this study, the source of organic matter in crude oil and the redox condition of the forming environment were evaluated using both biomarkers and trace elements, specifically including the distribution characteristics of n-alkanes and aromatics and several related biomarker parameters, along with V/Ni and Ni/Co ratios.21,25

4.2.1. Organic Matter Source of Crude Oil Based on Biomarkers. Before the interpretation of biomarker parameters, it is necessary to determine the degree of biodegradation, which will lead to changes in the structure of biomarker compounds and thus affect their effectiveness.51 The relatively complete n-alkane sequence (C\textsubscript{10}–C\textsubscript{33}) and the high Sat/Aro ratio (>4.70) of all crude oil samples, as well as the m/z 85
Table 3. REE Contents (ppb) and Related Parameters of Chang 7 and Chang 8 Crude Oil Samples

| sample          | formation | Z120 | B457 | L169 | Z71 | Z52 | L140 | Z87 | X255 | Z24 | L16 | Z233 | X237 | Z182 | X133 | Z172 | L91 | ave |
|-----------------|-----------|------|------|------|-----|-----|------|-----|------|-----|-----|------|------|------|------|------|-----|-----|
| depth (m)       |           | 1715.20 | 1988.20 | 2351.30 | 1852.30 | 1826.10 | 2114.30 | 2004.20 | 1910.40 | 1924.60 | 1879.20 | 1774.60 | 1952.80 | 2079.2 | 1842.3 | 2402.3 |
| La              |           | 32.71 | 25.33 | 17.99 | 9.86 | 33.50 | 9.35 | 26.58 | 34.06 | 59.21 | 122.92 | 140.33 | 10.84 | 173.23 | 47.92 |
| Ce              |           | 60.43 | 52.94 | 33.82 | 24.46 | 56.73 | 24.15 | 38.66 | 61.71 | 17.11 | 54.50 | 55.36 | 144.24 | 292.85 | 279.16 | 22.68 | 277.26 |
| Pr              |           | 7.23 | 4.88 | 3.18 | 2.37 | 5.94 | 5.58 | 2.95 | 6.56 | 1.91 | 5.14 | 6.64 | 11.68 | 25.49 | 25.26 | 2.4  | 32.46 | 9.36 |
| Nd              |           | 24.66 | 15.86 | 10.34 | 8.59 | 19.90 | 20.54 | 10.27 | 21.88 | 6.64 | 15.64 | 22.19 | 45.75 | 86.04 | 80.99 | 8.01 | 110.99 | 31.77 |
| Sm              |           | 4.97 | 3.10 | 1.76 | 1.82 | 4.20 | 3.15 | 1.91 | 3.83 | 1.37 | 3.08 | 3.98 | 7.09 | 17.79 | 15.02 | 1.37 | 21.51 | 6.00 |
| Eu              |           | 1.17 | 0.63 | 0.37 | 0.68 | 1.04 | 1.13 | 0.41 | 1.02 | 0.35 | 0.53 | 0.90 | 1.56 | 5.12 | 2.39 | 0.15 | 5.71 | 1.45 |
| Gd              |           | 4.37 | 2.60 | 1.63 | 1.35 | 3.88 | 2.67 | 1.56 | 3.56 | 1.29 | 2.40 | 3.91 | 6.12 | 14.22 | 12.13 | 0.96 | 19.06 | 5.11 |
| Tb              |           | 0.72 | 0.49 | 0.28 | 0.23 | 0.66 | 0.50 | 0.28 | 0.62 | 0.21 | 0.42 | 0.64 | 1.01 | 2.26 | 2.12 | 0.14 | 2.77 | 0.83 |
| Dy              |           | 3.86 | 2.26 | 1.54 | 1.14 | 3.56 | 1.98 | 1.46 | 3.13 | 1.26 | 2.63 | 4.13 | 6.57 | 12.97 | 12.18 | 0.71 | 15.03 | 4.65 |
| Ho              |           | 0.78 | 0.42 | 0.33 | 0.27 | 0.81 | 0.46 | 0.31 | 0.68 | 0.26 | 0.57 | 0.80 | 1.07 | 3.19 | 2.48 | 0.15 | 3.39 | 1.00 |
| Er              |           | 2.17 | 1.34 | 1.00 | 0.73 | 2.19 | 1.44 | 0.99 | 1.90 | 0.81 | 1.84 | 2.66 | 3.69 | 8.21 | 8.02 | 0.38 | 9.48 | 2.93 |
| Tm              |           | 0.42 | 0.25 | 0.20 | 0.15 | 0.46 | 0.28 | 0.18 | 0.36 | 0.17 | 0.37 | 0.50 | 0.64 | 1.56 | 1.67 | 0.07 | 1.71 | 0.56 |
| Yb              |           | 2.54 | 1.58 | 1.33 | 1.08 | 2.73 | 1.59 | 1.28 | 2.17 | 1.13 | 2.41 | 3.30 | 4.01 | 9.48 | 11.45 | 0.5  | 10.61 | 3.57 |
| Lu              |           | 0.36 | 0.24 | 0.18 | 0.17 | 0.39 | 0.22 | 0.17 | 0.36 | 0.16 | 0.36 | 0.52 | 0.58 | 1.49 | 1.72 | 0.06 | 1.46 | 0.53 |
| ΣREE            |           | 146.37 | 111.92 | 73.95 | 57.26 | 132.04 | 115.48 | 77.96 | 141.30 | 42.02 | 116.47 | 119.39 | 293.12 | 603.59 | 594.92 | 48.4 | 684.66 | 209.93 |
| L/HREE          |           | 8.62 | 11.20 | 10.39 | 10.20 | 8.00 | 11.64 | 11.53 | 10.05 | 6.95 | 9.58 | 6.25 | 11.39 | 10.31 | 10.49 | 15.35 | 9.78 | 10.11 |
| (La/Yb)CN      |           | 9.25 | 11.49 | 9.72 | 6.56 | 7.76 | 10.72 | 9.83 | 11.05 | 5.95 | 7.91 | 7.41 | 10.6 | 9.3 | 8.79 | 15.45 | 11.71 | 9.60 |
| (La/Sm)CN      |           | 4.25 | 5.27 | 6.59 | 3.50 | 4.54 | 4.88 | 5.95 | 4.39 | 4.52 | 5.52 | 4.46 | 6.03 | 5.1 | 5.20 | 5.14 |
| (Gd/Yb)CN      |           | 1.43 | 1.36 | 1.02 | 1.04 | 1.18 | 1.39 | 1.00 | 1.36 | 0.94 | 0.82 | 0.98 | 1.24 | 1.28 | 1.15 | 1.49 | 1.18 |
| δEu            |           | 0.77 | 0.68 | 0.66 | 1.33 | 0.78 | 1.20 | 0.73 | 0.85 | 0.80 | 0.59 | 0.69 | 0.72 | 0.98 | 0.54 | 0.39 | 0.86 | 0.79 |
| δCe            |           | 0.96 | 1.17 | 1.10 | 1.05 | 1.46 | 1.11 | 1.32 | 1.02 | 0.99 | 1.14 | 0.90 | 1.34 | 1.28 | 1.15 | 1.09 | 0.91 | 1.12 |

aCh-Chang; δEu = EuCN/(SmCN × GdCN)1/2; δCe = CeCN/(LaCN × PrCN)1/2; CN stands for chondrite-normalized values.
mass chromatograms of all samples without an obvious unresolved complex mixture, all indicate the low level or no biodegradation of crude oils and the validity of biomarker parameters (Tables 1 and 2 and Figure 3).\textsuperscript{51,52} The C\textsubscript{main} of crude oil samples (mainly C\textsubscript{15}−C\textsubscript{19}) demonstrates that the organic matter is derived from plankton and/or algae (Table 2 and Figure 3).\textsuperscript{53} Also, the slightly odd carbon advantage (OEP > 1.21) and the absolute short-chain n-alkane advantage (\(\sum nC_{21}^-/\sum nC_{22}^- > 1.69\), \((C_{21} + C_{22})/(C_{28} + C_{29}) > 2.68\)) further proved that the organic matter is mainly of lower aquatic organisms such as algae and micro-organisms (Table 2).\textsuperscript{54}

The relative content of regular sterane is widely used to identify the source of organic matter.\textsuperscript{8,10,14} It is generally believed that C\textsubscript{27} and C\textsubscript{28} steranes are mainly from algae and other lower aquatic organisms, while C\textsubscript{29} steranes are derived from higher plants or algae.\textsuperscript{48,52} According to the ternary diagram of the relative contents of C\textsubscript{27}, C\textsubscript{28}, and C\textsubscript{29} sterane, the data points of crude oil fall in the area of mixed sources (except for one data point at the junction of phytoplankton dominated and mixed sources) (the identification map is from Li et al., 2017; the data of Chang 7 oil shale and mudstone are from Xu et al., 2019) (Figure 7a).\textsuperscript{14,15} Combined with the distribution pattern of m/z 217 (Figure 3), it demonstrates that the phytoplankton mixed with algae is the main source input. Similarly, the cross-plots of Pr/nC\textsubscript{17} versus Ph/nC\textsubscript{18} and C\textsubscript{27}/C\textsubscript{29} regular sterane versus Pr/Ph also reveal this conclusion (the identification maps and the data of Chang 7 oil shale and mudstone are from Xu et al., 2019) (Figure 7b,c).\textsuperscript{14} As an important component of hopane series compounds, tricyclic terpane mainly comes from bacteria, algae, and other lower organisms, and the abundant tricyclic terpanes reflect the input of lower organisms.\textsuperscript{55} The \(\sum\) tricyclic terpene/\(\sum\) hopane ratios of crude oil samples are mostly more than 1, indicating the contribution of bacteria and algae in organic matter (Table 2). Because the regular sterane is mainly derived from algae or higher plants while the hopane comes from bacteria, the \(\sum\) regular sterane/\(\sum 17(\alpha)H\)-hopane ratio can be used to indicate the proportion of different sources.\textsuperscript{16} The \(\sum\) regular sterane/17(\(\alpha\))H-hopane ratios of crude oils
(0.22–6.05) show the same features as mentioned before (Table 2), that is, the organic matter of crude oils is mainly derived from algae, with some contribution of bacteria. This understanding can be compared with previous research conclusions that the organic matter of Chang 7 oil shale and mudstone originated from algae and aquatic micro-organisms, with some contribution of higher plants. 14,15

4.2.2. Redox Conditions of Crude Oil Forming Environment Based on Biomarkers. Several biomarker parameters were also used to evaluate the redox conditions of Chang 7 crude oil formation environment. As a commonly used
depositional redox condition indicator, it is generally considered that the Pr/Ph ratio greater than 1 represents the anoxic environment, while the less than 1 ratio reflects the anoxic conditions or hypersaline depositional environment. The average Pr/Ph ratio of Chang 7 crude oil in the Longdong area is 1.03 (Table 2), which displays the transitional environment average Pr/Ph ratio of Chang 7 crude oil in the Longdong area

| sample | formation | depth (m) | V  | Co  | Ni  | V/(V + Ni) | Ni/Co |
|--------|-----------|----------|----|-----|-----|------------|-------|
| Z120   | Chang 71  | 1715.20  | 120.79 | 293.24 | 838.65 | 0.13 | 2.86 |
| B457   | Chang 71  | 1988.20  | 137.49 | 355.81 | 778.28 | 0.15 | 2.19 |
| L169   | Chang 71  | 2351.30  | 70.13 | 150.34 | 357.93 | 0.16 | 2.38 |
| Z71    | Chang 71  | 1852.30  | 60.90 | 168.24 | 394.93 | 0.07 | 4.72 |
| Z52    | Chang 71  | 1826.10  | 220.67 | 294.15 | 361.39 | 0.38 | 1.23 |
| L140   | Chang 71  | 2114.30  | 28.85 | 61.58 | 300.52 | 0.09 | 4.88 |
| Z87    | Chang 71  | 2004.20  | 130.01 | 156.05 | 409.67 | 0.24 | 2.63 |
| X255   | Chang 71  | 1910.40  | 106.98 | 95.88 | 244.91 | 0.30 | 2.60 |
| Z24    | Chang 71  | 1924.60  | 77.31 | 116.27 | 380.35 | 0.17 | 3.27 |
| L16    | Chang 71  | 1879.20  | 158.45 | 293.25 | 1575.75 | 0.09 | 5.37 |
| Z233   | Chang 71  | 1774.60  | 82.83 | 183.24 | 882.99 | 0.09 | 4.82 |
| X237   | Chang 71  | 2017.54  | 1072.26 | 172.24 | 1292.52 | 0.45 | 7.50 |
| Z182   | Chang 71  | 1952.8  | 135.25 | 9.51 | 82.54 | 0.62 | 8.88 |
| X133   | Chang 71  | 2079.2  | 105.24 | 7.61 | 72.64 | 0.59 | 9.55 |
| Z172   | Chang 8   | 1842.3  | 29.81 | 0.44 | 7.26 | 0.80 | 16.58 |
| L91    | Chang 8   | 2402.30  | 109.95 | 6.57 | 65.89 | 0.63 | 10.03 |
| average |          | 165.43  | 147.78 | 528.17 | 0.31 | 5.58 |

some important bio-indicator elements such as V, Ni, and Co; therefore, the concentration of these elements in crude oil will be influenced by the biodegradation, thermal degradation, and migration process in reservoirs. It has been confirmed that the V/Ni and Ni/Co ratios in crude oil incline to be constant, which makes them the most convincing parameters for speculating the redox conditions of the crude oil forming environment and for conducting oil−oil or oil−source correlation analysis. The V/(V + Ni) ratio greater than 0.5 and less than 0.5 indicates that crude oil is formed in anoxic and oxic conditions, respectively. While the Ni/Co ratio greater than 7.0, between 5.0 and 7.0, and less than 5.0 represents the anoxic, dysoxic, and oxic environment, respectively. The V/(V + Ni) ratios of all crude oil samples ranged from 0.07 to 0.80, with a mean of 0.31, displaying a slight oxic condition (Table 4). Ni/Co ratios range from 1.23 to 16.58, averaging at 5.58, showing a dysoxic tendency (Table 4). Yet, specifically, all crude oil samples can be obviously classified into two groups through V/(V + Ni) and Ni/Co ratios. The first group includes all Chang 71 and Chang 72 samples, exhibiting that V/(V + Ni) and Ni/Co ratios are all less than 0.5 and 7.0, respectively (Table 4). While the second group includes all Chang 73 and Chang 8 crude oil samples, their V/(V + Ni) and Ni/Co ratios are greater than 0.5 (except for one sample of X237) and 7.0, respectively (Table 4). The diversity between the two groups of samples reflects their respective different redox conditions of the formation environment, that is, Chang 71 and Chang 72 samples formed under slight oxic conditions, while Chang 73 and Chang 8 samples were from the anoxic environment. This further reveals the internal homology of crude oil samples in each group and different sources between two groups.

### 4.3. Oil−Source Rock Correlation Analysis

It is generally accepted that the Chang 7 section is the thickest and most geographically extensive source rock in Yanchang Formation, which supply hydrocarbons to the adjacent reservoir of top and bottom. Despite being rarely mentioned in previous research works, the Chang 7 crude oil should come from the Chang 7 source rock theoretically. However, there is no literature that refers to the respective contribution and lateral range of Chang 7 mudstone and oil shale to Chang 7 crude oil. Through the distribution pattern of
REE, it can be seen that most of the crude oil samples have comparability with that of Chang 7 oil shale and mudstone, which indicates the same source attribute (Chang 7 oil shale data are from Qiu et al., 2015,19 while Chang 7 mudstone data are from Qiu et al., 2015,20) (Figure 5a,e,f). This feature also emerged in the identification maps of organic matter origin and forming environment redox conditions in crude oil, in particular, the data points of Chang 7 crude oil coincide with those of Chang 7 oil shale and mudstone (Figure 7a–c). The above evidence can directly prove that Chang 7 crude oil comes from Chang 7 mudstone and oil shale, but such relatively traditional qualitative comparison of the REE distribution pattern and the single parameter chart coincidence cannot meet the refined oil–source correlation. The data of Chang 7 source rock in the existing literature may cause unexpected errors in the oil–source correlation analysis.14,19,20 Only data of crude oil samples in this study are used for refined oil–source correlation analysis. Meanwhile, based on the generally accepted viewpoint that the most remarkable difference between Chang 7 oil shale and mudstone is the depositional environment redox condition, of which Chang 7 oil shale is anoxic, while mudstone is sub-oxic,14,18–20,40 we carry out an oil group classification using biomarker parameters and REE of crude oil samples and further discuss the source rock corresponding to each oil group.

4.3.1. Using Biomarker Parameters. Only the most sensitive biomarker parameters (Pr/Ph ratios, C27 steranes, and GI values) to the origin of organic matter and redox conditions were selected as the partition variables for the oil group classification. Hierarchical cluster analysis (HCA) using SPSS 19.0 statistical software is the most suitable method for considering the number of variables and samples. According to the dendrogram of HCA analysis results shown in Figure 8, all samples were divided into two oil families of primary components whose eigenvalues and variances are shown in Table 5, so only these two were applied for further classification, and their component matrix scores are shown in Figure 9.

![Figure 8. Dendrogram result of HCA using biomarker parameters of crude oil samples, showing oil group classification.](Image)

![Figure 9. Component matrix score diagram of REE and related parameters in principal component 1 and principal component 2.](Image)

This group were formed in the anoxic with slightly brackish water conditions, in which Chang 7 crude oil has stronger reducibility and is just similar to that of Chang 7 oil shale. According to the above analysis, the crude oil samples of group I are mainly from Chang 7 mudstone, while group II is principally from Chang 7 oil shale. Specifically, Chang 71 and Chang 72 crude oil come from Chang 7 mudstone, while Chang 73 crude oil originated from Chang 7 oil shale entirely.

4.3.2. Using REEs. The theoretical basis of the oil group classification by REEs is that the REEs content and distribution pattern of crude oil from the same source should be similar.15,20,26,31,32 Also, δCe, δEu, (La/Yb)CN, (La/Sm)CN, and (Gd/Yb)CN ratios are important feature parameters of REE distribution patterns. Hence, a total of 21 variables including these featured parameters and REE contents were used for oil group classification of Chang 7 and Chang 8 crude oil samples. In order to improve the data discrimination from so many variables, factor analysis and principal component analysis are the most appropriate analysis measurements for data similarity comparison. Using SPSS 19.0 statistical software, the components with eigenvalues greater than 1, total variance greater than 10%, and cumulative variance greater than 70% were selected through the Caesar criterion. Finally, four principal components were extracted from 21 variables, whose eigenvalues and variances are shown in Table 5. It can be seen that the first two principal components account for more than 80% of the total variance (Table 5), so only these two were applied for further classification, and their component matrix scores are shown in Figure 9.

| Case Label | Num | Rescaled Distance Cluster Combine |
|------------|-----|----------------------------------|
| H69 Ch-7   | 3   | 0                                |
| L36 Ch-7   | 8   | 5                                |
| H56 Ch-7   | 2   | 10                               |
| N50 Ch-7   | 4   | 15                               |
| W67 Ch-7   | 5   | 20                               |
| B246 Ch-7  | 1   | 25                               |
| Z45 Ch-7   | 6   |                                  |
| L87 Ch-7   | 7   |                                  |
| N44 Ch-7   | 9   |                                  |
| N45 Ch-7   | 10  |                                  |

![Table 5. Eigenvalues and Variances (%) of Four Principal Components in 21 Variables](Table 5)

| Component | Eigenvalues | Total Variance (%) | Cumulative Variance (%) |
|-----------|-------------|--------------------|-------------------------|
| PC 1      | 14.73       | 70.12              | 70.12                   |
| PC 2      | 2.52        | 12.02              | 82.14                   |
| PC 3      | 1.83        | 8.73               | 90.87                   |
| PC 4      | 1.31        | 6.25               | 97.12                   |

![Figure 9. Component matrix score diagram of REE and related parameters in principal component 1 and principal component 2.](Image)
PC1 (principal component 1) accounts for 70.12% of the total variance and is composed of specific REE content (La to Lu) and \( \sum \)REE, reflecting the content of REE (Table S).

PC2 accounts for 12.02% of the total variance and is composed of L/HREE, \((La/Yb)_{CN}\), \((La/Sm)_{CN}\) and \((Gd/Yb)_{CN}\) ratios, in which the score of \((La/Yb)_{CN}\) ratio is the highest, followed by \(L/HREE\), \((Gd/Yb)_{CN}\) and \((La/Sm)_{CN}\) ratios, respectively (Table S). PC2 mainly represents the REE distribution patterns.

The \( \delta Ce \) and \( \delta Eu \) ratios are negative related to both PC1 and PC2 except for a weak positive of \( \delta Eu \) ratios to PC1, which reflects that these two parameters are not comparable and inheritable in oil group classification. The \( \delta Ce \) ratio can be an indicator for paleoredox conditions in sediments.62–64 Some researchers believe that the \( \delta Ce \) ratio in organic extracts and solid bitumen is inherited from the precursor kerogens.62,64 However, the \( \delta Ce \) ratio will be easily obliterated by diagenetic alterations.65 Eu is the only other REE with many factors and a complex process affecting its content.66 In general, negative Eu anomalies in sediments are indicator of the oxidation environment;62 yet, in a word, there are few studies on the source and impact factors of Ce and Eu anomalies in crude oil. Therefore, the cause of Ce and Eu anomalies in crude oil is not clear. What can be confirmed in this study is that \( \delta Ce \) and \( \delta Eu \) ratios have no obvious comparative fingerprint in the oil—oil correlation, which also proves the complex influencing factors of Ce and Eu anomalies in crude oil.

Based on the fact that the PC1 and PC2 represent the absolute content and distribution pattern of REE in crude oil samples, it can be seen that these two features are key in the oil group classification by REE. The PC1 and PC2 component scores of all crude oil samples are plotted in Figure 10, in which two groups can be discriminated obviously: group A and group B (except for one outlier sample Z172), and group A have two subgroups A1 and A2.

![Figure 10](https://dx.doi.org/10.1021/acsomega.0c02233)

**Figure 10.** Cross-plot of component scores of PC1 and PC2 for all crude oil samples.

Group A includes all Chang 71 and Chang 72 crude oil samples with one Chang 73 sample. Samples of this group are characterized by \( \sum \)REE values <300 ppb, a relatively low PC1 score, and a moderate PC2 score (Table 3 and Figure 9).

Among them, the main distinguishing fact for A2 subgroup from that of A1 subgroup is that the Chang 73 sample X237 has clearly larger \( \sum \)REE value and PC1 score than those of A1 subgroup.

Group B consists of one Chang 8 sample (L91) and two Chang 73 samples (Z182 and X133), featured by \( \sum \)REE values >590 ppb, a moderate PC2 score, and a high PC1 score (Table 3 and Figure 9).

Though the crude oil samples for analysis are different, the results of oil group classification by REE are quite similar to those by biomarker parameters, that is, Chang 71 and Chang 72 crude oils are generally related, whereas Chang 71 and Chang 8 crude oil may have the same source. On the basis of REE classification, combined with the V, Ni, and Co features of all crude oil samples discussed above, it can be found that \( V/(V + Ni) \) and Ni/Co ratios of Chang 71 and Chang 72 crude oil (<0.5 and <7.0, respectively) in subgroup A1 represent the slight oxic forming condition (Table 4), which is consistent with that of Chang 7 mudstone, while \( V/(V + Ni) \) and Ni/Co ratios of three samples in group B reflect the anoxic condition, which are the same as those of Chang 7 oil shale. \( V/(V + Ni) \) and Ni/Co ratios of the Chang 73 sample X237 in subgroup A2 are 0.45 and 7.50, respectively (Table 4), just showing a transitional environment between the forming conditions of Chang 7 mudstone and oil shale. Only one outlier, Chang 8 sample Z172, has an obviously higher Ni/Co ratio than other Chang 8 samples, as well as obviously lower trace element contents and \( \delta Eu \) ratio than those of other samples, which may be caused by the unexpected error in the sample pretreatment and experimental processes. Therefore, from the oil classification results by REE and redox conditions reflected by \( V/(Vi + Ni) \) and Ni/Co ratios, it can be concluded that Chang 71 and Chang 72 crude oil are from Chang 7 mudstone, Chang 71 crude oil has a mixed source of Chang 7 mudstone and oil shale, and part of Chang 8 crude oil is from Chang 7 oil shale.

It can be seen that the absolute content and the distribution pattern of REE in crude oil are two key indexes for oil group division, among which the absolute content of REE represented by PC1 is the most relevant because of its nearly 70% total variance. There are few studies of the source and interfering factors of REE in crude oil.27,67–70 Previous studies on the occurrence of REEs in crude oil suggested the following: REEs occur in clay minerals;27 they are organo-combined;67 they are adsorbed by hydrogen functional groups or directly bonded by carbon;69 they are related to the abundance of different functional groups in crude oil;69 and they do not mainly occur in a certain organic compound.70 Lately, based on the REE data collection and correlation analysis of various types of crude oil and extracts around the world, Gao et al., 2015 pointed out that metal complexes and/or functional groups that provide complexing sites for V could be carriers for REEs; also, the distribution pattern of REE has a certain correlation with the type of organic matter types of source rock.70 There is no direct evidence for the origin of REEs in crude oil in this study. The \( \sum \)REE and the content of V, Ni, and Co show poor to no correlation. In short, it is still controversial whether REEs in crude oil are controlled by organic components or inorganic metal complexes. Thus, more studies on the mechanism of occurrence and transformation of REEs in crude oil are urgently needed to expand the applicability of REEs in oil—oil and oil—source correlations.

4.3.3. Application Comparison of REEs and Biomarkers in Oil—Source Correlation. By using biomarker parameters and REEs for oil—source correlation analysis, the results mutually reinforce the conclusion that Chang 7 mudstone controls the
The oil group classiﬁcation provides additional evidence that Chang 7 crude oil has mixed hydrocarbons from Chang 7 mudstone and Chang 8 crude oil is also from Chang 7 oil shale. Although there is no evidence or discussion on the hydrocarbon accumulation mechanism in this study, previous research works on Chang 7 mudstone and oil shale may give some mechanistic explanation and insight. Although Chang 7 oil shale has a better hydrocarbon generation potential than the mudstone, its expulsion threshold is higher, and the main driving force of hydrocarbon migration from the source to the reservoir is the overpressure in the Chang 7 source rock.\textsuperscript{14,71,72}

In general, Chang 7 mudstone and oil shale are two sets of independent source rocks and nearby reservoir systems. Because oil shale is mainly developed in Chang 7\textsubscript{3} and mudstone is overlapping in Chang 7\textsubscript{1} and Chang 7\textsubscript{2}, mudstone and oil shale mainly control Chang 7\textsubscript{1}−7\textsubscript{2} and Chang 7\textsubscript{3} tight oil pools, respectively. However, the second migration of hydrocarbons started earlier in mudstone because of its lower expulsion threshold, which will partly mix with hydrocarbons from oil shale in the Chang 7\textsubscript{3} reservoir. Of course, more targeted research is needed to conﬁrm this. Nevertheless, the basis and analysis process of the two oil−source correlation methods are quite different. The biomarker-based oil−source correlation method compares the similarity of the related feature parameters ratio of crude oil and source rock samples. The parameters for comparison are selected according to the largest differences between potential source rocks, such as parameters reﬂecting the organic matter origin, redox condition, thermal maturity level, and so forth. The advantage of this method lies in the strong applicability of classiﬁcation, but the related parameter ratio is not accurate enough and has multiple solutions. Whereas the most application limits are that the parameters used for the characterization of crude oil or source rock and oil−source correlation are just the same set of parameters, that is, the evidence is too simple, so relative studies usually add other experimental means (e.g., stable carbon isotope) to verify the analysis results. The REE-based oil−source correlation method in this study just makes up for this weakness: the oil group classiﬁcation is established on the REE contents and REE distribution pattern, and the classiﬁcation results are further veriﬁed and the source rock is determined by speciﬁc trace element ratios. This work can be regarded as a double check by alternate experimental means, which is more efﬁcient and accurate. Although the two experimental methods were not performed on the same samples in this study, there is no doubt that the ﬁnding and understanding have inspiration for the theoretical study of oil−source correlation, especially for the multi-source and complex system and the exploration of Chang 7 tight oil as well as shale oil in the future.

6. SAMPLES AND METHODS

In this study, 26 crude oil samples were systematically collected from 26 wells in Longdong area (Figure 1c), 24 of which were from Chang 7 tight oil reservoir and two from Chang 8 tight oil reservoir. Simultaneously, 10 Chang 7 crude oil samples were used for group component separation and gas chromatography−mass spectrometry (GC−MS) experiments for biomarker characterization, and the other 16 samples were used for elemental analysis. All the samples were ﬁrst stored in brown bottles with glass plugs and then analyzed directly in the laboratory. Moreover, a dataset including the physical properties of Chang 7 crude oil was also collected from the Changqin Oilﬁeld Company to evaluate the comprehensive properties of Chang 7 tight oil.

6.1. Biomarker Characterization. Ten Chang 7 crude oil samples were separated into saturated hydrocarbon, aromatic hydrocarbon, and nonhydrocarbon fractions by liquid column chromatography. The saturated hydrocarbon fraction was collected by \textit{n}-hexane extraction 4 times, the aromatic hydrocarbon fraction was collected by dichloromethane extraction, and the nonhydrocarbon fraction was eluted with a methanol solution. During the experiment, the mixture of standard compounds and samples were fractionated to ensure qualitative and quantitative repeatability. Finally, the saturated hydrocarbon and aromatic hydrocarbon fractions of the crude oil samples were further analyzed by GC−MS.

Geochemical detection of biomarkers in saturated and aromatic hydrocarbon fractions of Chang 7 crude oil was carried out on an Agilent 7890 GC system coupled with an Agilent 5975c mass spectrometer. The HP-5MS elastic quartz capillary column (60 m × 0.25 mm × 0.25 μm) is used as the chromatographic column and helium gas with a ﬂow rate of 1 mL/min as the carrier gas. The temperature of the column oven is programmed as follows: the initial temperature 50 °C is kept for 1 min, followed by an increase to 250 °C at 4 °C/min, and ultimately to 310 °C at 3 °C/min, with an isothermal time
of 30 min. The temperatures of the sample inlet and the transmission line are both 300 °C. Electron ionization is adopted for MS, with the ionization voltage of 70 eV, the electron multiplier voltage of 1200 V, and the filament current of 100 A. According to the retention time of the analytical results and comparison with the literature data, the types of biomarkers were determined.\textsuperscript{3,7,4} The saturated hydrocarbon ratio, the relative abundance of steranes and terpanes, and the aromatic hydrocarbon ratio were calculated from the comprehensive peak area of the related ion chromatography.\textsuperscript{3,11,7,5,76}

6.2. Trace and REEs Analyses. Trace and REE contents of 16 crude oil samples were carried out on a Nu Attom Inductively Coupled Plasma Mass Spectrometry (ICP–MS) instrument at the IGGCAS, Lanzhou, China. In consideration of the previous successful determination on REEs in crude oil,\textsuperscript{69,70,77} an acid digestion method is also used in this study for sample pretreatment. The specific steps are as follows: about 1 g of crude oil was decomposed by heating (at ca. 180 °C) for a week in 68 wt % HNO\textsubscript{3} solution in a Teflon vessel with a screw cap. After evaporation of the solution, the organic matter was thoroughly digested by drying in H\textsubscript{2}SO\textsubscript{4} (at ca. 230 °C). After the solution was evaporated again, the sample was ultimately dissolved in 2 wt % HNO\textsubscript{3} for measurement. Selective trace elements (V, Ni, and Co) and REEs of crude oil samples were determined by ICP–MS. The measurement accuracy of all trace elements is better than 2%. In order to dispel the abundance difference between odd and even atomic number elements and to facilitate the comparison with the related source rock REE concentration distribution pattern, the chondrite data from Sun and McDonough, 1989\textsuperscript{44} were used as a reference to normalize the REE concentration in crude oil samples.

### AUTHOR INFORMATION

**Corresponding Author**

Yande Zhao — Peli Petroleum Engineering College, Lanzhou City University, Lanzhou 730000, China; Email: zydlyzcui@163.com

**Authors**

Ruiliang Guo — Shaanxi Key Laboratory of Petroleum Accumulation Geology and School of Earth Sciences and Engineering, Xi’an Shiyu University, Xi’an 710065, China; Key Laboratory of Petroleum Resources, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, Gansu Province, China; University of Chinese Academy of Sciences, Beijing 100049, China; [orcid.org/0000-0002-5339-4571]

Weibin Wang — Peli Petroleum Engineering College, Lanzhou City University, Lanzhou 730000, China

Xinyou Hu — PetroChina Changqing Oil Field Company, Xi’an 710018, China

Xinping Zhou — PetroChina Changqing Oil Field Company, Xi’an 710018, China

Lewei Hao — Key Laboratory of Petroleum Resources, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, Gansu Province, China

Xiaofang Ma — Key Laboratory of Petroleum Resources, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, Gansu Province, China

Dongzhu Ma — Peli Petroleum Engineering College, Lanzhou City University, Lanzhou 730000, China

---

**Shutong Li** — Key Laboratory of Petroleum Resources, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, Gansu Province, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02233

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This study was jointly supported by funds from the National Natural Science Foundation of China (grant nos. 41772142 and 41802160) and the Lanzhou City University Doctoral Research Initiation Fund (grant no. LZCU-BS2018-12).

**REFERENCES**

(1) Zou, C.; Zhu, R.; Wu, S.; Yang, Z.; Tao, S.; Yuan, X.; Hou, L.; Yang, H.; Xu, C.; Li, D.; Bai, B.; Wang, L. Types, characteristics, genesis and prospects of conventional and unconventional hydrocarbon accumulations: taking tight oil and tight gas in China as an instance. Acta Pet. Sin. 2012, 33, 173–187.

(2) Yang, H.; Li, S.; Liu, X. Characteristics and resource prospects of tight oil and shale oil in Ordos Basin. Acta Pet. Sin. 2013, 34, 1–11.

(3) Yao, J.; Deng, X.; Zhao, Y.; Han, T.; Chu, M.; Pang, J. Characteristics of tight oil in Triassic Yanchang Formation, Ordos Basin. Pet. Explor. Dev. 2013, 40, 161–169.

(4) Zou, C.; Zhang, G.; Yang, Z.; Tao, S.; Hou, L.; Zhu, R.; Yuan, X.; Ren, Q.; Li, D.; Wang, Z. Geological concepts, characteristics, resource potential and key techniques of unconventional hydrocarbon: On unconventional petroleum geology. Pet. Explor. Dev. 2013, 40, 385.

(5) Jia, C.; Zou, C.; Li, J.; Li, D.; Zheng, M. Assessment criteria, main types, basic features and resource prospects of the tight oil in China. Acta Pet. Sin. 2012, 33, 343–350.

(6) Jia, C.; Zheng, M.; Zhang, Y. Unconventional hydrocarbon resources in China and the prospect of exploration and development. Pet. Explor. Dev. 2012, 39, 139–146.

(7) Zou, C.; Tao, S.; Yang, Z.; Yuan, X.; Zhu, R.; Hou, L.; Jia, J.; Wang, L.; Wu, S.; Bai, B.; Gao, X.; Yang, C. New Advance in Unconventional Petroleum Exploration and Research in China. Bull. Mineral., Petrol. Geochim. 2012, 31, 312–322.

(8) Duan, Y.; Wang, C. Y.; Zheng, C. Y.; Wu, B. X.; Zheng, G. D. Geochemical study of crude oils from the Xiaren oilfield of the Ordos basin, China. J. Asian Earth Sci. 2008, 31, 341–356.

(9) Zhang, W. Z.; Yang, H.; Yang, Y. H. Petrology and element geochemistry and development environment of Yanchang Formation Chang-7 high quality source rocks in Ordos Basin. Geochimica 2008, 37, 59.

(10) Duan, Y. Geochemical characteristics of crude oil in fluvial deposits from Maling oilfield of Ordos Basin, China. Org. Geochem. 2012, 52, 35–43.

(11) Zou, C.; Yang, Z.; Cui, J.; Zhu, R.; Hou, L.; Tao, S.; Yuan, X.; Wu, S.; Lin, S.; Wang, L.; Bai, B.; Yao, J. Formation mechanism, geological characteristics and development strategy of nonmarine shale oil in China. Pet. Explor. Dev. 2013, 40, 15–27.

(12) Fu, J. H.; Deng, X. Q.; Chu, M. J.; Zhang, H.; Li, S. Features of Deepwater Lithofacies, Yanchang Formation in Ordos Basin and Its Petroleum Significance. Acta Sedimentol. Sin. 2013, 31, 928–938.

(13) Guo, R.; Chen, X.; Ma, X.; Ma, J.; Wang, Q.; Chen, L. Analysis of the characteristics and its influencing factors of horizontal movable fluid in the Chang 7 tight reservoir in Longdong area,Ordos Basin. Nat. Gas Geosci. 2018, 29, 665–674.

(14) Xu, Z.; Liu, L.; Liu, B.; Wang, T.; Zhang, Z.; Wu, K.; Feng, C.; Dou, W.; Wang, Y.; Shu, Y. Geochemical characteristics of the Triassic Chang 7 lacustrine source rocks, Ordos Basin, China: Implications for paleoenvironment, petroleum potential and tight oil occurrence. J. Asian Earth Sci. 2019, 178, 112–138.
(15) Li, D.; Li, R.; Zhu, Z.; Wu, X.; Cheng, J.; Liu, F.; Zhao, B. Origin of organic matter and paleo-sedimentary environment reconstruction of the Triassic oil shale in Tongchuan City, southern Ordos Basin (China). *Fuel* 2017, 208, 223–235.

(16) Zhang, X.; He, J.; Zhao, Y.; Wu, H.; Ren, Z. Geochemical Characteristics and Origins of the Crude Oil of Triassic Yanchang Formation in Southwestern Yishan Slope, Ordos Basin. *Int. J. Anal. Chem.* 2017, 1–12.

(17) Yang, W.; Liu, G.; Feng, Y. Geochemical significance of 17 alpha(H)-diahopane and its application in oil-source correlation of Yanchang formation in Longdong area, Ordos basin, China. *Mar. Pet. Geol.* 2016, 71, 238–249.

(18) Liu, G. D.; Yang, W. W.; Feng, Y.; Ma, H. Y.; Du, Y. G. Geochemical characteristics and genetic types of crude oil from Yanchang Formation in Longdong Area, Ordos Basin. *Earth Sci. Front.* 2013, 20, 108–115.

(19) Qiu, X.; Liu, C.; Mao, G.; Deng, Y.; Wang, F.; Wang, J. Major, trace and platinum-group element geochemistry of the Upper Triassic nonmarine hot shales in the Ordos basin, Central China. *Appl. Geochem.* 2015, 53, 42–52.

(20) Qiu, X.-W.; Liu, C.-Y.; Wang, F.-F.; Deng, Y.; Mao, G.-Z. Trace and rare earth element geochemistry of the Upper Triassic mudstones in the southern Ordos basin, Central China. *Geol. J.* 2015, 50, 399–413.

(21) Peters, K.; Walters, C.; Moldowan, J. *The Biomarker Guide*; Cambridge University Press, 2005.

(22) Liang, D.-G.; Chen, J.-P. Oil-source correlations for high and over matured marine source rocks in South China. *Pet. Explor. Dev.* 2005, 32, 8–14.

(23) Peters, K. E.; Scott Ramos, L.; Zumberge, J. E.; Valin, Z. C.; Peters, K. E.; Cassa, M. R.; Welte, D. H.; Wilk, J. H. Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. *Org. Geochem.* 1986, 10, 51–63.

(24) Sun, S.-S.; McDonough, W. F. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geol. Soc. 1989, 42, 313–345.

(25) Taylor, S. R.; McLennan, S. M. *The Continental crust: Its composition and evolution*. Blackwell Scientific Publications, 1985.

(26) Huang, D. F.; Li, J. C.; Zhang, D. J.; Huang, X. M.; Zhou, Z. H. Comparative study on lacustrine formation, diagenesis and its effects on reservoir porosity: A case study of Upper Triassic Chang 7 Member tight sandstone in Ordos Basin, NW China. *Pet. Explor. Dev.* 2015, 42, 56–65.

(27) Li, S.; He, S. Geochemical characteristics of dibenzothiophene, dibenzofuran and fluorene and their homologues and their environmental indication. *Geochemica 2008, 37, 45–50.

(28) Radke, M.; Welte, D. H.; Wilk, J. H. Alkanes as geochemical fossils indicators of geological environments; Its Significance In Petroleum Resource Assessment; Pergamon Press Ltd: Oxford, 1991; pp 359–366.

(29) Hanson, A. D.; Ritts, B. D.; Moldowan, J. *Advances in Organic Geochemistry of Oil and Source Rock Strata of the Ordos Basin, northwestern China*. Oxford, 1983; Vol. 1, 74.

(30) Hakimi, M. H.; Abdullah, W. H. Geochemical characteristics of some crude oils from Alif Field in the Marib-Shabowah Basin, and their source input in the Lower Toarcian of SW-Germany. *Org. Geochem.* 1986, 10, 915–926.

(31) Rodriguez-Caro, D. Rare Earth Elements (REE) as Geochemical Clues to Reconstruct Hydrocarbon Generation History; Kansas State University, 2013.

(32) Jiao, W.; Yang, H.; Zhao, Y.; Zhang, H.; Zhou, Y.; Zhang, J.; Xie, Q. Application of trace elements in the study of oil-source correlation and hydrocarbon migration in the Tarim Basin, China. *Energy Explor. Exploit.* 2010, 28, 451–466.

(33) Yang, Y.; Li, W.; Ma, L. Tectonic and stratigraphic controls of hydrocarbon systems in the Ordos basin: A multicycle cratonic basin in central China. *AAPG Bull.* 2005, 89, 255–269.

(34) Guo, R.; Xie, Q.; Qu, X.; Chu, M.; Li, S.; Ma, D.; Ma, X. Fractal characteristics of pore-throat structure and permeability estimation of tight sandstone reservoirs: A case study of Chang 7 of the Upper Triassic Yanchang Formation in Longdong area, Ordos Basin, China. *J. Pet. Sci. Eng.* 2020, 184, 106555.

(35) Xie, X. Provenance and sediment dispersal of the Triassic Yanchang Formation, southwest Ordos Basin, China, and its implications. *Sediment Geol.* 2016, 335, 1–16.

(36) Yao, S.; Zhang, K.; Hu, W.; Fang, H.; Jiao, K. Sedimentary facies of the Triassic Yanchang Formation in the Ordos Basin. *Oil Gas Geol.* 2009, 30, 74.

(37) Pang, Z.; Zou, C.; Tao, S.; Zhi, Y.; Wu, S. Formation, distribution and resource evaluation of tight oil in China. *Eng. Sci.* 2012, 14, 60.

(38) Huang, F. X.; Yang, T.; Yan, W.; Guo, B.; Tang, H.; Li, X.; Ma, H. Analysis of dominant factors affecting tight oil reservoir properties of China. *J. Chengdu Univ. Technol.* 2014, 41, 538–547.

(39) Zhu, H.; Zhong, D.; Yao, J.; Sun, H.; Niu, X.; Liang, X.; You, Y.; Li, X. Alkaline diagenesis and its effects on reservoir porosity: A case study of Upper Triassic Chang 7 Member tight sandstone in Ordos Basin, NW China. *Pet. Explor. Dev.* 2015, 42, 56–65.

(40) Sin, S. H.; Yuan, X.; Yang, Z. Comparative study on lacustrine shale and mudstone and its significance: a case from the 7th member of Yanchang Formation in the Ordos Basin. *Oil Gas Geol.* 2017, 38, 517–523.

(41) Peters, K. E.; Cassa, M. R.; Magoon, L.; Dow, W. The petroleum system—From source to trap. *AAPG Mem.* 1994, 60, 93–120.

(42) Li, S.; He, S. Geochemical characteristics of dibenzothiophene, dibenzofuran and fluorene and their homologues and their environmental indication. *Geochemica 2008, 37, 45–50.

(43) Radke, M.; Welte, D. H.; Wilk, J. H. Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. *Org. Geochem.* 1986, 10, 51–63.

(44) Sun, S.-S.; McDonough, W. F. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geol. Soc. 1989, 42, 313–345.

(45) Marchitto, T. P.; Ritts, B. D.; Moldowan, J. *The Continental crust: Its Composition and Evolution*. Blackwell Scientific Publications, 1985.

(46) Huang, D. F.; Li, J. C.; Zhang, D. J.; Huang, X. M.; Zhou, Z. H. Maturation Sequence of Tertiary Crude Oils In The Qaidam Basin and Its Significance In Petroleum Resource Assessment; Pergamon Press Ltd: Oxford, 1991; pp 359–366.

(47) Peters, K. E. *Biomarkers in Sediments and Petroleum*; Springer, 2017.

(48) Moldowan, J. M.; Sundararaman, P.; Schoell, M. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany. *Org. Geochem.* 1986, 10, 915–926.

(49) Radke, M. The methylphenanthrene index (MPI): a maturity parameter based on aromatic hydrocarbons. *Adv. Org. Geochem.* 1981, 1983, 504–512.

(50) Hanson, A. D.; Ritts, B. D.; Moldowan, J. M. Organic geochemistry of oil and source rock strata of the Ordos Basin, north-central China. *AAPG Bull.* 2007, 91, 1273–1293.

(51) Hakimi, M. H.; Abdullah, W. H. Geochemical characteristics of some crude oils from Alif Field in the Marib-Shabowah Basin, and source-related types. *Mar. Pet. Geol.* 2013, 45, 304–314.

(52) Volkman, J. Sterols in microorganisms. *Appl. Microbiol. Biotechnol.* 2003, 60, 495–506.

(53) Fu, X.; Yang, J.; Zeng, Y.; Li, Z.; Wang, Z. Geochemical and palynological investigation of the Shengli River marine oil shale (China): Implications for paleoenvironment and paleoclimate. *Int. J. Coal Geol.* 2009, 78, 217–224.

(54) Tissot, B.; Pelet, R.; Rouache, J.; Comba, A.; Alkannas as geochemical fossils indicators of geological environments; *Advances in Organic Geochemistry*; Campos, R., Goni, J., Eds.; Empresa Nacional de Investigaciones Mineras: Santiago, Chile, 1975; pp 117–154.

(55) Aquino Neto, F. d. Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleum. *Advances in Organic Geochemistry*; Wiley, 1983; Vol. 1981, pp 659–667.
(56) Peters, K. E.; Moldowan, J. M. Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of homohopanes in petroleum. Org. Geochem. 1991, 17, 47–61.
(57) Ten Haven, H. L.; De Leeuw, J. W.; Rullkötter, J.; Damsté, J. S. S. Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. Nature 1987, 330, 641.
(58) Yandoka, B. M. S.; Abdullah, W. H.; Abubakar, M.; Hakimi, M. H.; Adgeoke, A. K. Geochemical characterisation of Early Cretaceous lacustrine sediments of Bima Formation, Yola Sub-basin, Northern Benue Trough, NE Nigeria: Organic matter input, preservation, paleoenvironment and palaeoclimatic conditions. Mar. Pet. Geol. 2015, 61, 82–94.
(59) Philp, R. P.; Fan, P.; Lewis, C. A.; Zhu, H.; Wang, H. Geochemical characteristics of oils from Chaidamu, Shanganning and Jianghan basins, China. J. Southeast Asian Earth Sci. 1991, 5, 351–358.
(60) Abanda, P. A.; Hannigan, R. E. Effect of diagenesis on trace element partitioning in shales. Chem. Geol. 2006, 230, 42–59.
(61) Jones, C.; Manning, D. A. C. Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. Chem. Geol. 1994, 111, 111–129.
(62) Gao, P.; Liu, G.; Wang, Z.; Jia, C.; Wang, T.; Zhang, P. Rare earth elements (REEs) geochemistry of Sinian–Cambrian reservoir solid bitumens in Sichuan Basin, SW China: potential application to petroleum exploration. Geol. J. 2017, 52, 298–316.
(63) Liu, Y.-G.; Miah, M. R. U.; Schmitt, R. A. Cerium: a chemical tracer for paleo-oceanic redox conditions. Geochim. Cosmochim. Acta 1988, 52, 1361–1371.
(64) Pi, D.-H.; Liu, C.-Q.; Shields-Zhou, G. A.; Jiang, S.-Y. Trace and rare earth element geochemistry of black shale and kerogen in the early Cambrian Niutitang Formation in Guizhou province, South China: Constraints for redox environments and origin of metal enrichments. Precambrian Res. 2013, 225, 218–229.
(65) Shields, G.; Stille, P. Diagenetic constraints on the use of cerium anomalies as palaeoseawater redox proxies: an isotopic and RIE study of Cambrian phosphorites. Chem. Geol. 2001, 175, 29–48.
(66) Brookins, G. Aqueous Geochemistry of Rare Earth Elements. Geochemistry and Mineralogy of Rare Earth Elements; De Gruyter, 1989; pp 221–225.
(67) Manning, L. K.; Frost, C. D.; Branthaver, J. F. A neodymium isotopic study of crude oils and source rocks: potential applications for petroleum exploration. Chem. Geol. 1991, 91, 125–138.
(68) Wang, W.; Qin, Y.; Sang, S.; Zhu, Y.; Wang, C.; Weiss, D. J. Geochemistry of rare earth elements in a marine influenced coal and its organic solvent extracts from the Antaibao mining district, Shanxi, China. Int. J. Coal Geol. 2008, 76, 309–317.
(69) Nakada, R.; Takahashi, Y.; Zheng, G.; Yamamoto, Y.; Shimizu, H. Abundances of rare earth elements in crude oils and their partitions in water. Geochim. J. 2010, 44, 411–418.
(70) Gao, P.; Liu, G.; Jia, C.; Ding, X.; Chen, Z.; Dong, Y.; Zhao, X.; Jiao, W. Evaluating rare earth elements as a proxy for oil–source correlation. A case study from Aer Sag, Erlbian Basin, northern China. Org. Geochem. 2015, 87, 35–54.
(71) Yang, H.; Niu, X.; Xu, L.; Feng, S.; You, Y.; Liang, X.; Wang, F.; Zhang, D. Exploration potential of shale oil in Chang7 member, upper Triassic Yanchang formation, Ordos Basin, NW China. Pet. Explor. Dev. 2016, 43, 560–569.
(72) Li, Q.; Yang, Z.; Zou, C. Shale Oil Geological Characteristics and Resource Potential of Mesozoic Yanchang Formation in Ordos Basin, North-Central China, International Conference and Exhibition, Melbourne, Australia 13–16 September 2015; Society of Exploration Geophysicists and American Association of Petroleum, 2015; p 333.
(73) Amijaya, H.; Schwarzbauer, J.; Litke, R. Organic geochemistry of the Lower Suban coal seam, South Sumatra Basin, Indonesia: paleoecological and thermal metamorphism implications. Org. Geochem. 2006, 37, 261–279.
(74) Kitson, F. G.; Larsen, B. S.; McEwen, C. N. Gas Chromatography and Mass Spectrometry: A Practical Guide; Academic Press, 1996.
(75) Philp, R. P. Biological markers in fossil fuel production. Mass Spectrom. Rev. 1985, 4, 1–54.
(76) van Aarssen, B. G. K.; Bastow, T. P.; Alexander, R.; Kagi, R. I. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. Org. Geochem. 1999, 30, 1213–1227.
(77) Zhao, Y.; Liu, C.-Y.; Niu, H.-Q.; Zhao, X.-C.; Zhang, D.-D.; Yang, D.; Deng, H. Trace and rare earth element geochemistry of crude oils and their coexisting water from the Jiyuan Area of the Ordos Basin, N China: Crude Oils and Coexisting Water in the Ordos Basin, N China. Geol. J. 2018, 53, 336.