

Article

TSR Action and Genesis Mechanism of Antimony Deposit: Evidence from Aromatic Hydrocarbon Geochemistry of Bitumen from Paleo-Oil Reservoir in Qinglong Ore Field, Southwestern Guizhou Depression, China

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Abstract: In Qinglong ore field, the paleo-oil reservoir is found to be associated with antimony deposits, and they have a close genetic relationship. In this study, the aromatics geochemistry of paleo-oil reservoir bitumen was studied to further discuss the thermochemical sulfate reduction (TSR) reaction and the mechanism of antimony mineralization. A total of 124 aromatic compounds were identified by gas chromatography–mass spectrometry (GC–MS) analysis in bitumen samples, including abundant phenanthrene series, dibenzothiophene series, fluoranthene series, chrysene series, and a small number of fluorene series, naphthalene series, dibenzofuran series, biphenyl series, and triaromatic steroid series. Aromatic parameters such as trimethylnaphthalene index (TMNr), methylphenanthrene index (MPI), methylphenanthrene distribution fraction (MPDF, F_1 , and F_2), methyl dibenzothiophene parameter (MDR), $C_{28}TAS-20S/(20R + 20S)$, and benzo[fluoranthene]/benzo[e]pyrene indicate that the Qinglong paleo-oil reservoir is in over maturity level. The abundance of phenanthrene and chrysene aromatic compounds and a small amount of naphthalene series, benzo[fluoranthene], fluoranthene, pyrene, anthracene, retene, perylene, and biphenyl suggest that the organic matter source of the paleo-oil reservoir was mainly low aquatic organisms, mixed with a small amount of higher plant. They detected a certain number of compounds, such as retene, triaromatic steroid series, and perylene, the ternary diagram of DBF–DBT–F and binary plot of Pr/Ph–DBT/P, DBT/(F + DBT)–DBF/(F + DBF), and Pr/Ph–DBT/DBF reveal that the source rock of the paleo-oil reservoir was formed in the marine environment of weak oxidation and weak reduction. The comprehensive analysis shows that the Qinglong paleo-oil reservoir originated from Devonian source rocks, just like other paleo-oil reservoirs and natural gas reservoirs in the Nanpanjiang basin. Abundant dibenzothiophene series were detected, indicating that the paleo-oil reservoir underwent a certain degree of TSR reaction. We believe that the gas reservoir formed by the evolution of the oil reservoir in the ore field participated in antimony mineralization; that is, hydrocarbon organic matter acted as a reducing agent and transformed SO_4^{2-} in oilfield brine into H_2S through TSR, providing reduced sulfur and creating environmental conditions for mineralization.

Keywords: palaeo-oil reservoir; aromatic hydrocarbons; thermochemical sulfate reduction (TSR); Qinglong antimony deposit; Nanpanjiang basin



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1. Introduction

Sedimentary basin is a huge complex system in which a variety of organic and inorganic, metallic and nonmetallic mineral resources, and water resources coexist [1]. As the phenomenon of close paragenesis or associated occurrence between metal deposits and hydrocarbon organic matter has been discovered [2–12], the relationship between

metal mineralization and hydrocarbon accumulation has attracted more and more attention from mineral deposit scholars, and the study of organic–inorganic interactions and mineralization effects in sedimentary basins has been aroused [13–18].

Qinglong antimony ore field is located in the southwest Guizhou depression of the Nanpanjiang basin, and its antimony metal reserves (~0.21 Mt) rank fifth in the south China giant antimony metallogenic belt [19–21] (Figure 1). The characteristics of the deposit, ore-forming materials, ore-forming fluids, and ore-forming age have been studied deeply by predecessors [22–33]. As early as the 1990s, scholars reported that the Qinglong antimony deposit is rich in organic inclusions and speculated that its formation is related to organic matter [34,35]. Since no large-scale organic geological bodies were found, further study on the genetic relationship between organic matter and antimony deposits was limited. Fortunately, in 2012, our team found a paleo-oil reservoir in the Shailing ore block when we were prospecting outside the Qinglong antimony deposit [36,37], which created conditions for further discussion on the relationship between organic matter and antimony mineralization.

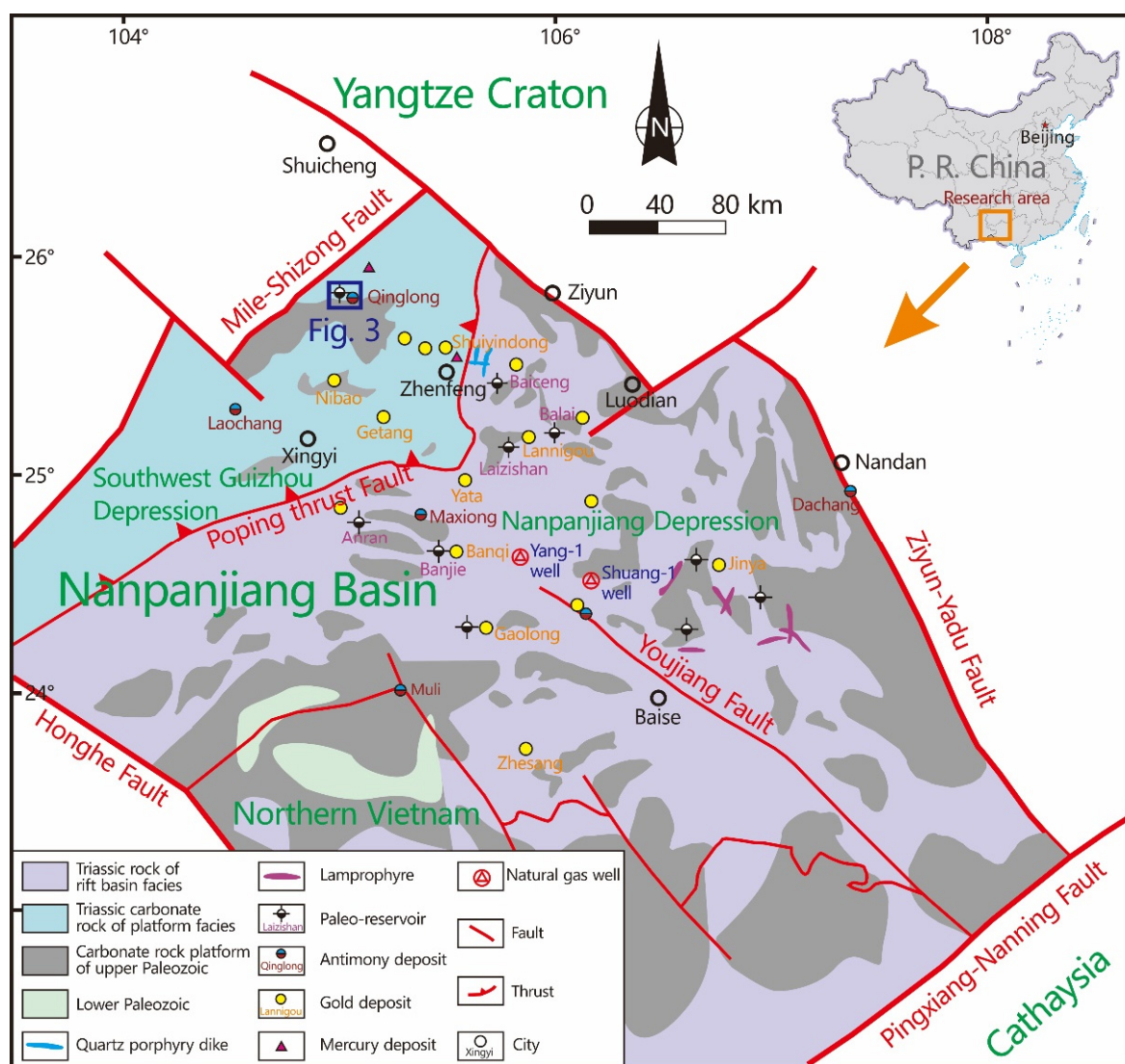


Figure 1. Simplified geologic map showing the distribution of tectonic units and Au-Sb deposits in the Nanpanjiang basin, SW China (modified after [38]).

Our team has carried out research work on paleo-oil reservoir bitumen, including physical characteristics and genesis of bitumen, element geochemistry, organic geochem-

istry, S-C isotope, inclusion, Re-Os isotope dating, and its relationship with antimony deposits [36–40]. Based on the data, we believe that hydrocarbon organic matter is involved in antimony mineralization by contributing a large amount of reduced sulfur [38–40]. However, some scholars hold a different view and believe that S originated from magma [22,27]. The evidence is that the ore stibnite has a narrow $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ range (-2.9‰ to $+6.9\text{‰}$, average 1.3‰), which is similar to the magma sulfur isotope composition ($0 \pm 5\text{‰}$). However, our team used 2D seismic data to reveal that there is no rock mass in the deep part of the basin [41,42]. Moreover, pyrite in paleo-oil reservoir bitumen also has the sulfur isotope range (-1.90‰ to $+3.10\text{‰}$, average $+0.97\text{‰}$) consistent with that of ore sulfide, suggesting that the reduced sulfur required for antimony mineralization may originate from thermochemical sulfate reduction (TSR) reaction of hydrocarbon organic matter [38]. Many studies have shown that dibenzothiophene series compounds in aromatic hydrocarbons are indications of TSR action [43,44]. Therefore, the aromatics geochemistry of paleo-oil reservoir bitumen was studied in this study to further discuss the TSR reaction and the mechanism of antimony mineralization.

2. Geological Background

2.1. Regional Geology

The Nanpanjiang Basin (also referred to as the Youjiang Basin or Nanpanjiang-Youjiang Basin in some references) belongs to the South China fold system, which is located at the southwestern margin of the Yangtze Block and extends from Southwest China to North Vietnam (Figure 1). The Nanpanjiang Basin hosts many Au-Sb-As-Hg deposits, which is an important part of the low-temperature metallogenic domain in southwest China [45]. The basin is significantly influenced by deep-seated faults, and its margins are controlled by three faults and a shear zone, which are the NE-striking Mile-Shizong fault, NW-striking Ziyun-Yadu fault, NE-striking Pingxiang-Nanning fault, and SW Honghe shear zone [41]. There are NW-striking, NE-striking, NEE-striking, and EW-striking faults in the basin, among which NW-striking faults are dominant.

Geophysical data reveal that the Nanpanjiang Basin may have three sets of basements, namely the Paleoproterozoic crystalline basement, Mesoproterozoic shallow metamorphic basement, and early Paleozoic fold basement [46]. The cover of the basin is Devonian to Triassic. Bounded by Poping thrust fault, Nanpanjiang Basin can be divided into the southwest Guizhou depression in the northwest and Nanpanjiang Depression in the southeast [47] (Figure 1). The southwest Guizhou Depression is a platform facies area with shallow platform carbonate rocks and impurity carbonate rocks intercalated with clastic rocks from the Upper Paleozoic to Mesozoic. The Nanpanjiang depression is a basin facies area, which is characterized by the flysch formation clastic rocks of the Triassic. Isolated platform carbonate rocks of Carboniferous and Permian are also distributed sporadically in the basin.

The magmatic activity in the Nanpanjiang basin is not particularly developed, and there are multi-stage igneous rocks from the Hercynian period to Yanshan Period [27]. The volcanic activity in the basin is weak, and there are only a few basic-ultrabasic rocks. The volcanic activity in the basin margin is more frequent, and there are many basic rocks and a small number of intermediate-acid and ultra-basic rocks.

Au-Sb deposits occur mainly in the Permian to Middle Triassic impure carbonate rocks and terrigenous fine clastic rocks and often coexist with, or adjacent to, paleo-oil reservoirs, remnant oil and gas, and bitumen in the Permian reef and shoal carbonate rocks in space (Figure 1). The host rocks and ores of these deposits are characterized by rich organic matter, and the hydrothermal minerals of the ore often contain rich bitumen and hydrocarbon organic inclusions, indicating a close genetic relationship between gold and antimony mineralization and oil and gas accumulation [9,39].

2.2. Deposit Geology

The Qinglong antimony ore field is located in the southwest Guizhou Depression (Figure 1). Its tectonic evolution experienced the formation of a basement and palaeohigh in the pre-Devonian, extension structure in the Devonian to Middle Triassic, foreland thrust-fold structure in the late Indosinian, and uplift and denudation stage in the Yanshanian and Himalayan period [42]. The Devonian system is dominated by limestone and dark mudstone, and the lower part of the organic-rich mudstone is a good source rock. The Carboniferous is mainly composed of dolomite, followed by limestone, with localized source rocks in the lower part. The Permian consists of limestone, volcanic rock, coal-bearing strata, and mudstone from bottom to top, with several sets of localized source rocks. The Triassic is carbonate rock and clastic rock (Figure 2).

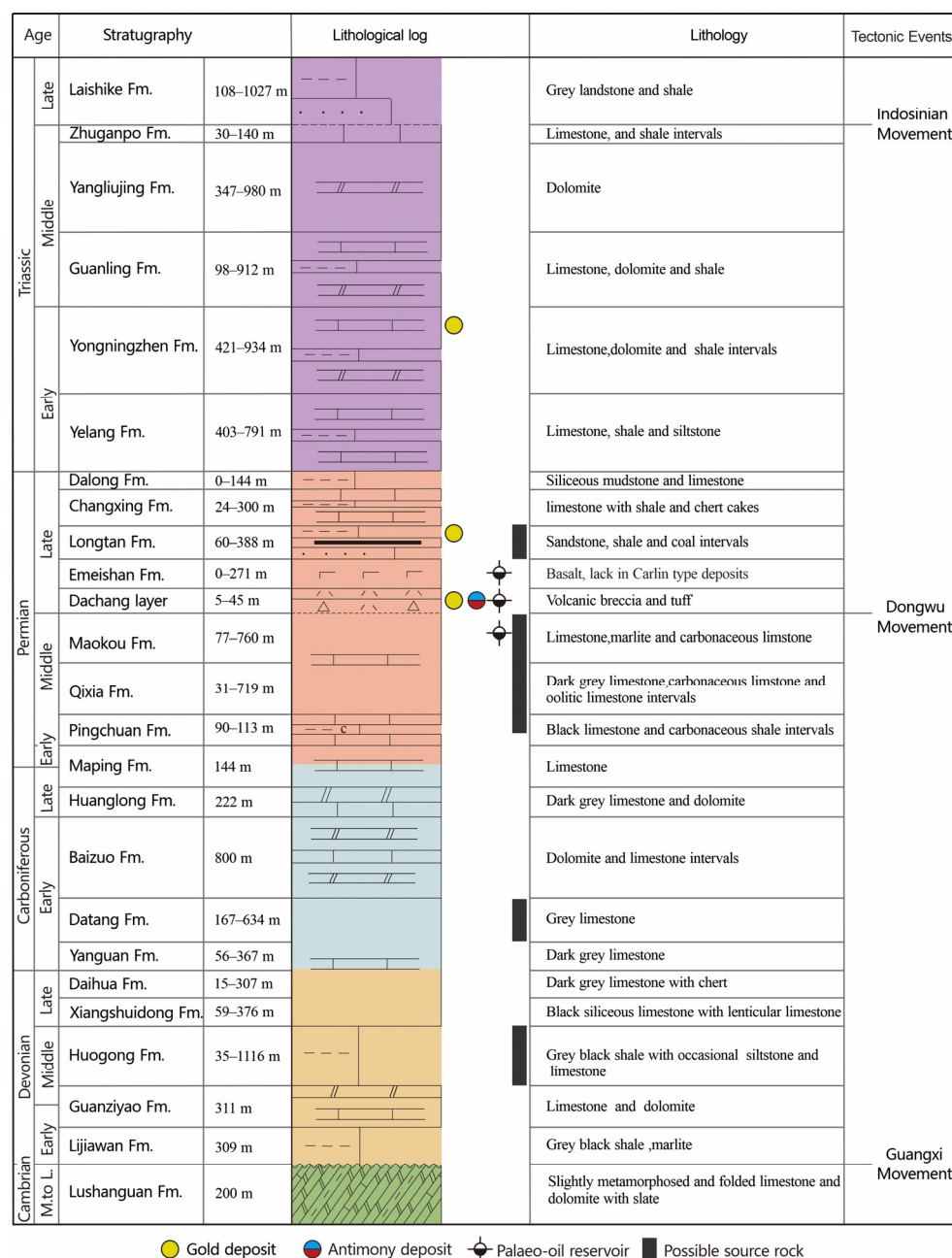


Figure 2. The stratigraphic sequences of central Southwestern Guizhou (modified after [42]).

The strata exposed in the Qinglong antimony ore field are mainly Permian, including middle Permian Maokou Formation limestone (P_2m), “Danchang layer” (P_3d), Upper

Permian Emeishan basalts ($P_3\beta$), and Upper Permian Longtan Formation coal-bearing strata (P_3l) from old to new [39] (Figure 3). The ore field is obviously controlled by the NE-striking structure. The spatial distribution of basalt and antimony deposits in this area is controlled by the high-angle thrust fault of the Huayujing and Qingshanzhen faults [38].

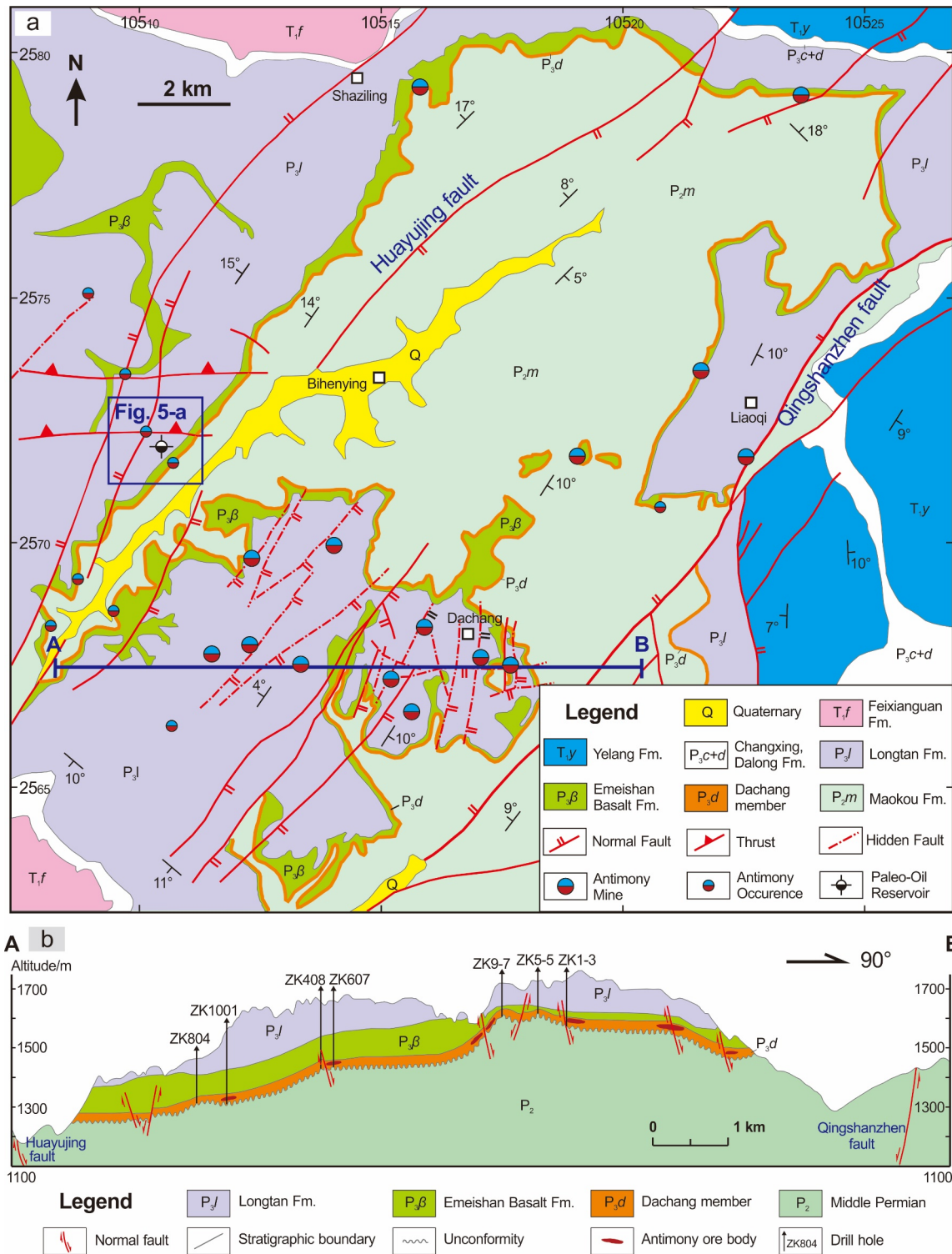


Figure 3. Geological map of Qinglong antimony ore field (a) and geological section map (b) (modified after [38]).

The antimony ore body mainly occurs in the “Dachang layer”, a set of siliceous altered rocks between the Maokou Formation and the Emeishan basalts (Figure 4). The “Dachang layer” is not a formal rock stratigraphic unit in the region, but an important marker bed in the mining area. According to lithology, it can be divided into three units: the lower unit is the strong silicified rock, and the top of the brecciated strong silicified rock is the ore-hosting part of the antimony deposit. The middle unit is composed of a basaltic conglomerate in which the brecciated clay stone with strong silicification is the main ore-hosting site; The upper unit is clay rock, among which alteration basalt is the ore-hosting site [27].

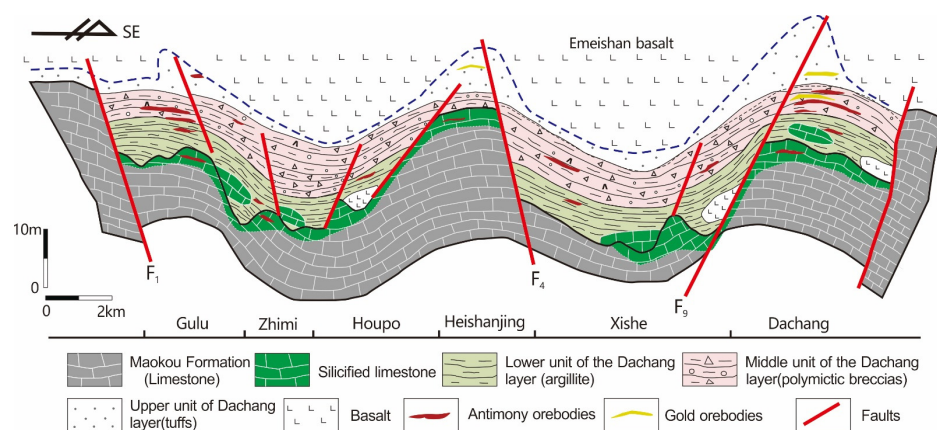


Figure 4. Lithologic variation and orebody occurrence in “Dachang layer” (modified after [27]).

The mineral assemblage of the deposit is relatively simple. The main metallic minerals are stibnite and pyrite, with a small amount of valentinite and chalcopyrite. Gangue minerals mainly include quartz, fluorite, calcite, kaolinite, and a small amount of barite and gypsum. The wall rock alteration includes pyritization, silicification, fluoritization, clayization and a little bituminization, calcilization, baratization, and gypsification.

3. Features of Qinglong Paleo-Oil Reservoir

The paleo-oil reservoir is very close to the antimony deposit in spatial location (Figure 3). A total of fifteen layers of bitumen were found in the five exploration drill holes (ZK3506, ZK2907, ZK2303, ZK2905, ZK3101) (Figure 5). The bitumen layers mainly occur in the Upper Permian Emeishan basalt ($P_3\beta$) and a small amount in the Upper Permian “Dachang layer” volcanic breccia (P_3d) and Middle Permian Maokou formation limestone (P_2m). The thickness of bitumen layers is between 0.20 and 8.39 m, with an average of 3.3 m. The volume percentage of bitumen in the drill core is estimated to be 0.5%–15.0% based on effective thin section porosity, with a weighted average of 4.86%. According to the estimation of experts from Sinopec, the bitumen reserve is 84×10^4 t, and its original oil reserve is about 2000×10^4 t, which is equivalent to the size of a medium-scale oil field in China.

The bitumen is black and brown, hard, brittle, hands-free, with resin luster and conchoidal fracture, and non-combustible (Figure 6a). The bitumen is mainly filled in tuff fractures or pores (Figure 6b), between volcanic breccia (Figure 6c), in the fractures or vesicles of basalt (Figure 6d), in limestone fractures or caves (Figure 6e). The paragenesis of pyrite and bitumen can be seen in hand specimens (Figure 6f). Microscopic observation also shows that bitumen is paragenetic with chalcopyrite, bornite, and calcite.

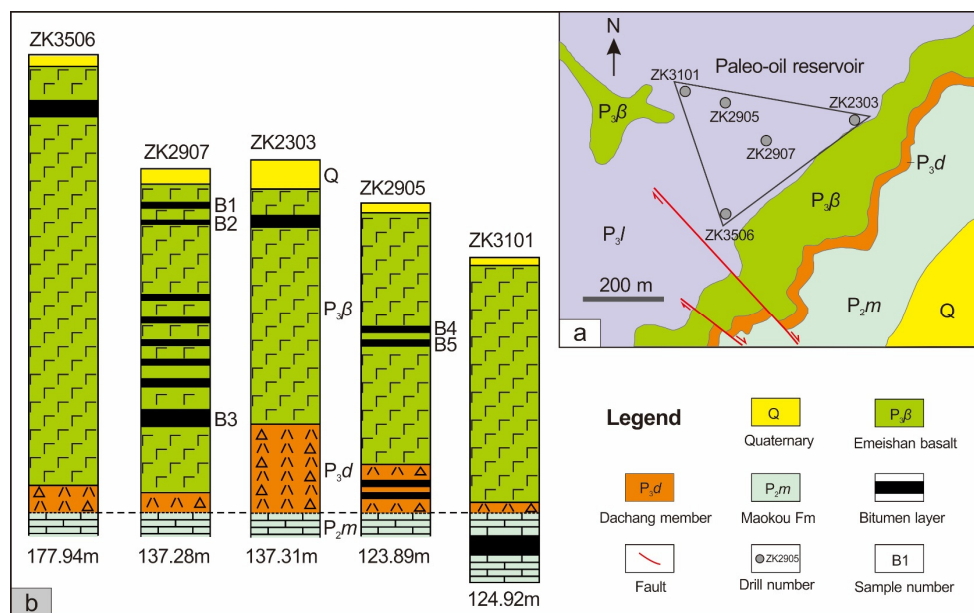


Figure 5. Sketch map of the location of the five boreholes (a) and drill columns (b) in Qinglong antimony ore field (modified after [38]).

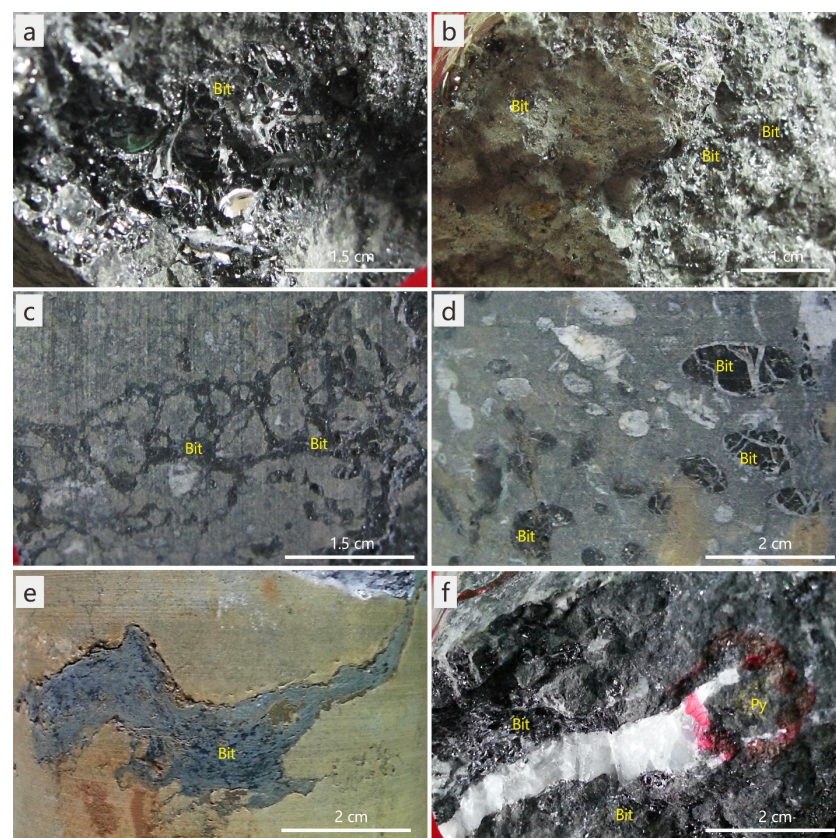


Figure 6. The distribution of bitumen in the paleo-reservoir from Qinglong antimony ore field. (a) Black bitumen hard and brittle, with resinous luster and conchoidal fracture; (b) bitumen in the pores of tuff; (c) bitumen between volcanic breccia; (d) bitumen in the vesicles of basalt; (e) bitumen in the caverns of limestone. (f) The paragenesis of pyrite and bitumen. Abbreviations: Bit = Bitumen; Py = Pyrite.

Fieldwork shows that solid bitumen also exists in the surrounding rock of the deposit (Figure 7). Solid bitumen can be seen in both the unaltered basalt (Figure 7a) and altered basalt (Figure 7b–d) of the “Dachang layer”. The bitumen is a black granular or thin film and paragenetic with quartz, kaolinite, fluorite, and pyrite, but no paragenetic with stibnite. Microscopic observation shows that there are many idiomorphic cubic pyrite particles wrapped in the solid bitumen, which is formed by the combination of H_2S rich in the reducing hydrocarbon fluid and Fe^{2+} in the formation (Figure 7e). There are many oval or round pores in bitumen particles, which are generated after hydrocarbon gas escapes (Figure 7e). Laser Raman spectroscopy showed that bitumen had an obvious D peak (1348.3 cm^{-1}) and G peak (1596.3 cm^{-1}) (Figure 7f).

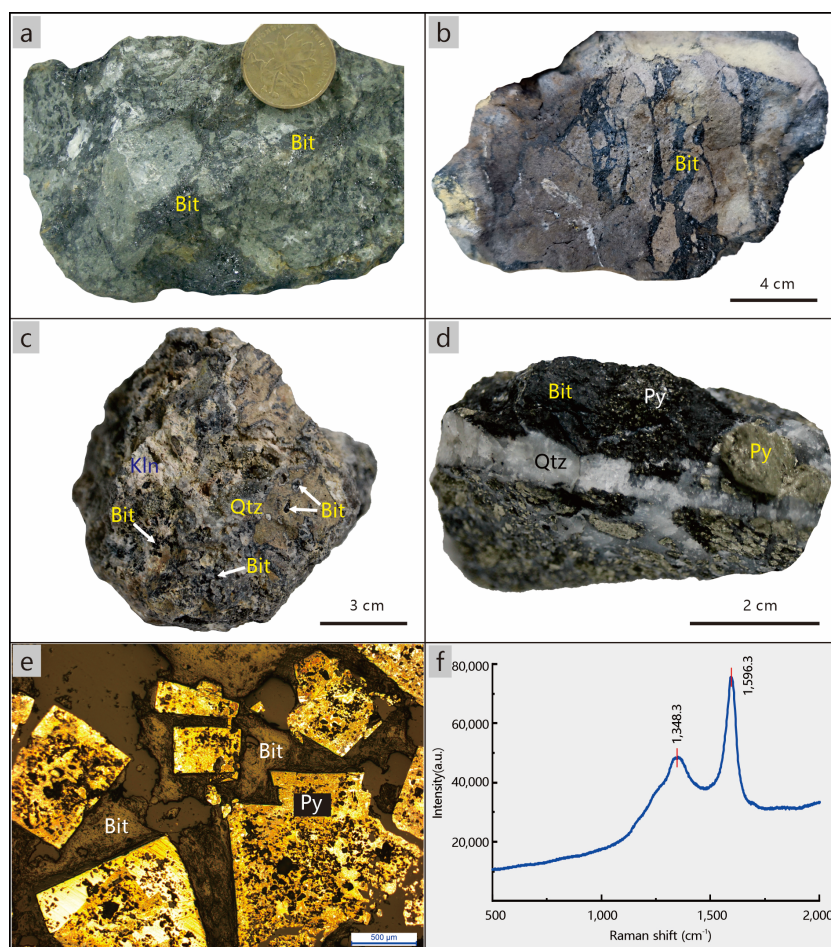


Figure 7. Characteristics of solid bitumen in surrounding rock from Qinglong antimony ore field. (a) Granular bitumen occurs in the pores of unaltered basalt in “Dachang layer”; (b–f) Bitumen in altered basalt of “Dachang layer”; (b) thin film bitumen distributed along basalt fissures; (c) granular bitumen is paragenetic with quartz and kaolinite; (d) lump bitumen is paragenetic with quartz and pyrite; (e) bitumen contains cubic pyrite particles; (f) laser Raman spectroscopy characteristics of bitumen. Abbreviations: Bit = Bitumen; Py = Pyrite; Kln = kaolinite.

4. Samples and Experimental Methods

Five samples of bitumen were obtained from drilling cores of the paleo-oil reservoir in the Emeishan basalt. The chloroform bitumen A and its family components analysis show that the aromatic fraction of bitumen samples accounts for 20.51%–25.00% of soluble components, with an average of 23.09% [38] (Figure 8).

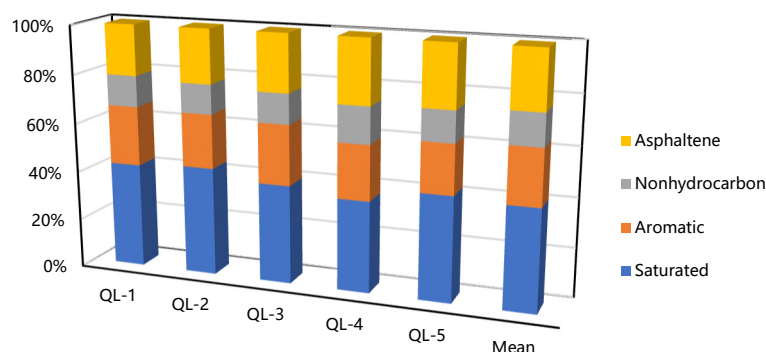


Figure 8. Group components in bitumen samples from Qinglong paleo-oil reservoir (Data from [38]).

The aromatic compounds were analyzed by gas chromatography–mass spectrometry (GC–MS) in the Experimental Center of Exploration and Development Research Institute of Henan Oilfield Company, Sinopec. The experiment was performed on Agilent 5973 N/US55142165 GC–MS instrument equipped with an SE-54 capillary column (30 m × 0.25 mm × 0.5 μm). The injector temperature for gas chromatography (GC) analysis was 300 °C, and helium was used as the carrier gas at a flow rate of 1.0 mL/min. The initial temperature of the test program was 80 °C and was held constant for 1 min. Then, the temperature was raised to 310 °C at a rate of 3 °C/min and again held constant for 20 min. The mass spectrometry (MS) was operated in electron ionization (EI+) mode with an ionization energy of 70 eV and an ion source temperature of 200 °C. Data were obtained by full scan and ion selection at the same time.

5. Results

Aromatic hydrocarbons are composed of hundreds of compounds and contain rich geochemical information. A total of 124 aromatic compounds were identified by GC–MS analysis in bitumen samples from Qinglong paleo-oil reservoir (Figure 9). It mainly consists of phenanthrene series (m/z 178, 192, 206, 220, 234), dibenzothiophene series (m/z 184, 198, 212), fluoranthene series (m/z 202, 216), and chrysene series (m/z 228, 242, 252). There is also a small amount of the fluorene series (m/z 166, 180, 194), naphthalene series (m/z 128, 142, 156, 170, 184, 198), dibenzofuran series (m/z 168, 182, 196), biphenyl series (m/z 154, 168, 182, 196), and triaromatic steroid series (m/z 231, 245).

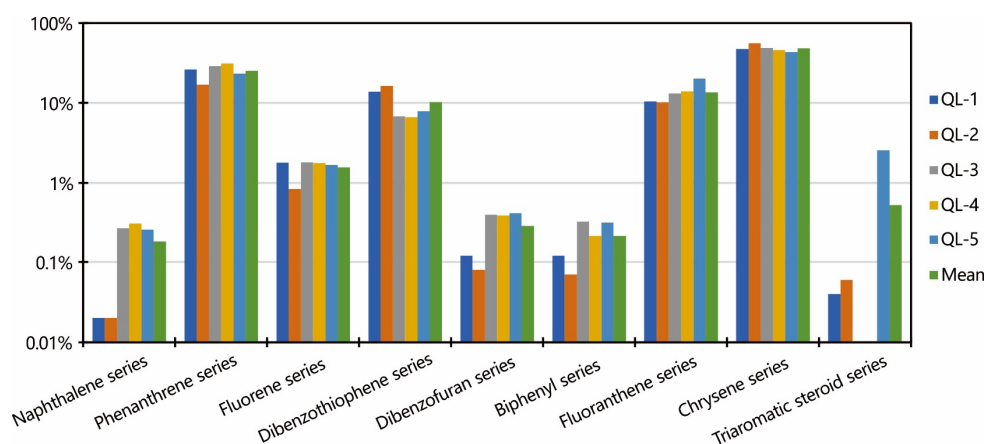


Figure 9. Composition of aromatic compounds in bitumen samples from Qinglong paleo-oil reservoir.

Compared with saturated hydrocarbons, aromatic compounds have a wider range of chemical kinetics [48], which can be better used to indicate maturity, trace the source of organic matter, judge the sedimentary environment, and discuss the TSR reaction. It is

helpful to further study the characteristics and evolution of a paleo-oil reservoir and its significance to antimony mineralization.

6. Discussion

6.1. Maturity and Source Rock of Paleo-Oil Reservoir Bitumen

6.1.1. Maturity

Parameters such as the dimethylnaphthalene ratio (DNR) and its equivalent vitrinite reflectance (R_{C1}), trimethylnaphthalene ratio (TNR) and its equivalent vitrinite reflectance (R_{C2}) are often used to characterize the maturity of organic matter [49,50]. As dimethylnaphthalene and trimethylnaphthalene were not detected in some samples, these indexes were of poor significance to indicate the maturity of the bitumen from the Qinglong paleo-oil reservoir (Table 1). In addition, the trimethylnaphthalene index (TMNr) and tetramethylnaphthalene index (TeMNR) increase gradually with the evolution of organic matter, which are more sensitive and can be used to characterize the maturity of crude oil and source rock. In general, Both TMNr and TeMNR values are >0.5 in high mature crude oil and source rock, $0.4\text{--}0.6$ in mature crude oil and source rock, $0.3\text{--}0.5$ in low mature crude oil, and <0.4 in immature to low mature source rock [51]. Tetramethylnaphthalene (TeMN) was not detected in the bitumen samples from the Qinglong paleo-oil reservoir, and the calculated TMNr value ranged from 0.66 to 0.67 (Table 1), indicating a high degree of thermal evolution.

During the thermal evolution of organic matter, the methylation, methyl rearrangement, and demethylation of phenanthrene series compounds were mainly controlled by thermodynamics and migrated from thermodynamically unstable α substituents to more stable β sites with the increase of thermal evolution degree [52]. With the increase in thermal evolution, the relative contents of 2-MP and 3-MP with good thermal stability will increase, while the relative contents of 1-MP and 9-MP with poor thermal stability will decrease. Therefore, the methylphenanthrene index (MPI, including three indices MPI_1 , MPI_2 , and MPI_3) [53] and the methylphenanthrene ratio (MPR) [54] are often used to study the maturity of source rocks and crude oils, and the values of these two parameters increase with the increase of maturity. In addition, the relative abundance of phenanthrene is not strongly related to maturity, so the methylphenanthrene distribution fraction (MPDF, i.e., the two fractions F_1 and F_2 calculated from methylphenanthrene only) was also proposed by some scholars [55], which had a good indicator effect on samples at various maturity stages and could distinguish mature oil from highly mature oil better than MPI parameters [52]. In general, $F_1 < 0.4$ and $F_2 < 0.27$ in low maturity stage, F_1 is $0.40\text{--}0.55$ and F_2 is $0.27\text{--}0.35$ in maturity stage, $F_1 > 0.55$ and $F_2 > 0.35$ in over maturity stage [56]. The calculated results showed that the values of MPI_1 , MPI_2 , MPI_3 , and MPR were $19.30\text{--}52.04$ (average 36.13), $0.08\text{--}6.35$ (average 4.00), $1.79\text{--}3.50$ (average 2.73), and $0.52\text{--}4.95$ (average 3.12), respectively. MPI_1 showed a good positive correlation with MPI_2 , MPI_3 , and MPR (Figure 10a–c), indicating that these maturity indicators of methylphenanthrene can effectively indicate the maturity of bitumen from Qinglong paleo-oil reservoir. The F_1 and F_2 values of bitumen samples range from 0.64 to 0.78 (average 0.72) and from 0.02 to 0.49 (average 0.36), respectively, suggesting that the paleo-oil reservoir is in the over-mature stage (Figure 10d).

Table 1. The maturity parameters of aromatic compounds in bitumen samples from Qinglong paleo-oil reservoir.

Sample ID	QL-1	QL-2	QL-3	QL-4	QL-5	Mean
DNR	1.64	10.00	3.74	-	-	5.13
Rc ₁	0.64	1.39	0.83	-	-	0.95
TNR	1.17	1.16	-	-	-	1.16
Rc ₂	1.10	1.10	-	-	-	1.10
TMNr	0.67	0.66	-	-	-	0.66
MPI ₁	52.04	50.26	32.81	26.22	19.30	36.13
MPI ₂	6.25	6.35	4.02	3.28	0.08	4.00
MPI ₃	3.50	3.36	2.29	1.79	2.70	2.73
MPR	4.66	4.95	3.08	2.42	0.52	3.12
F ₁	0.78	0.77	0.70	0.64	0.73	0.72
F ₂	0.47	0.49	0.43	0.40	0.02	0.36
MDR	26.23	24.14	14.45	11.69	15.48	18.40
Rc ₃	1.11	0.77	17.16	29.54	17.49	13.21
Rc ₄	1.21	0.46	1.88	40.72	22.11	13.28
a	0.60	0.61	-	-	0.67	0.63
b	0.08	1.09	0.67	0.48	0.82	0.63
c	0.99	-	181.03	138.47	473.36	198.46
d	1.03	-	184.64	141.57	481.68	202.23
e	0.08	-	121.71	67.13	385.88	143.70
R _b	2.10	2.40	2.43	2.46	2.51	2.38

Note: DNR = [(2,6-DMN + 2,7-DMN)/1,5-DMN]; Rc₁ = 0.09 DNR + 0.49; TNR = [(1,3,7-TMN + 2,3,6-TMN)/(1,3,5-TMN + 1,3,6-TMN + 1,4,6-TMN)]; Rc₂ = 0.6 TNR + 0.4; TMNr = 2,3,6-TMN/(2,3,6 + 1,2,5)-TMN]; MPI₁ = 1.5·(3-MP + 2-MP)/(P + 9-MP + 1-MP); MPI₂ = 3·(2-MP)/(P + 9-MP + 1-MP); MPI₃ = (3-MP + 2-MP)/(9-MP + 1-MP); TeMNR = 1,3,6,7-TeMN/(1,3,6,7 + 1,2,5,7)-TeMN; MPR = 2-MP/1-MP; MDR = 4-MDBT/1-MDBT; F₁ = (3-MP + 2-MP)/(1-MP + 2-MP P + 3-MP + 9-MP); F₂ = 2-MP/(1-MP + 2-MP P + 3-MP + 9-MP); Rc₃ (%) = 0.14 × (4,6-DMDBT/1,4-DMDBT) + 0.57; Rc₄ (%) = 0.35 × (2,4-DMDBT/1,4-DMDBT) + 0.46; a = C₂₈TAS-20S/(20R + 20S); b = benzo[fluoranthrene]/benzo[e]pyrene; c = benzo[e]pyrene/perylene; d = (benzo[e]pyrene + benzo[a]pyrene)/perylene; e = benzo[fluoranthrene]/perylene; R_b quoted from [38].

With the thermal evolution of organic matter, the relative contents of 4,6-dimethyldibenzothiothiophene (4,6-DMDBT) and 2,4-dimethyldibenzothiothiophene (2,4-DMDBT) increased, while the relative contents of 1,4-dimethyldibenzothiothiophene (1,4-DMDBT) decreased [57]. Accordingly, the equivalent vitrinite reflectance parameters Rc₃ and Rc₄ of dibenzothiothiophene were established [58]. The results of this study show that Rc₃ and Rc₄ vary widely and are of poor significance for indicating the thermal evolution degree of the paleo-oil reservoir (Table 1). In addition, the methyldibenzothiothiophene parameter (MDR) is commonly used to indicate maturity. The MDR parameter increases slightly with the increase of maturity when Ro is 0.53%–1.1% but increases rapidly with the increase of maturity when Ro > 1.1%, and the MDR value can even reach more than 30 [59]. Therefore, MDR parameters show great potential in the maturity assessment of higher mature samples. In this study, the MDR values of the paleo-oil reservoir bitumen are relatively high, ranging from 11.69 to 26.23, with an average of 18.40 (Table 1), indicating a high degree of thermal evolution.

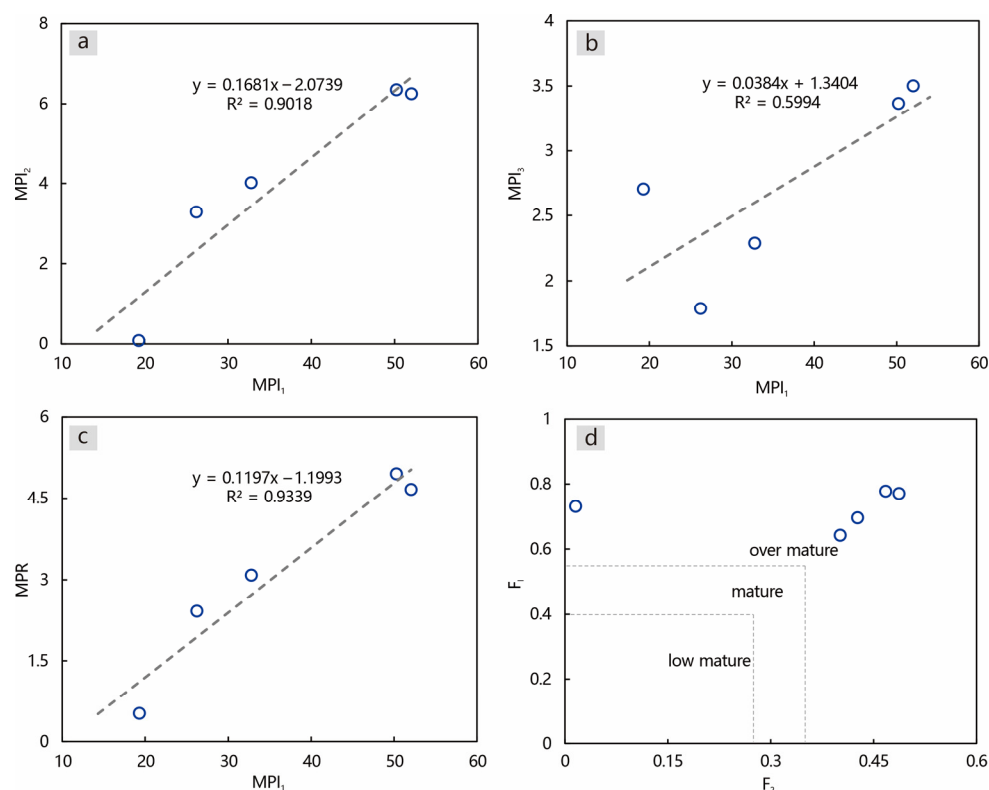


Figure 10. (a–d) Correlation diagram of maturity parameters of alkyl phenanthrene in bitumen from Qinglong paleo-oil reservoir.

Triaromatic steranes (TAS) are the aromatization products of monaryl steranes after heating. The content of TAS in samples increases with maturity, and TAS has strong biodegradation resistance. Previous studies have shown that the $C_{28}TAS-20S/(20R + 20S)$ value can be used for maturity evaluation [60]. TAS was detected in three samples in this study, and the $C_{28}TAS-20S/(20R + 20S)$ values were 0.60–0.67 (average 0.63), significantly higher than those of mature source rocks (0.48–0.59, average 0.56), indicating high maturity.

In addition, Benzo[fluoranthene] and benzo[e]pyrene are both 5-ring dense aromatic hydrocarbons, and the latter is more stable. With the increase of maturity, the ratio of benzo[fluoranthene]/benzo[e]pyrene decreases, so the ratio can be used as an indicator of maturity [51]. In addition, the ratios of benzo[e]pyrene/perylene, (benzo[e]pyrene + benzo[a]pyrene)/perylene, and benzo[fluoranthene]/perylene are also used to study the maturity of oil source rocks and reach their peak values when the organic matter generates large amounts of hydrocarbons [61]. In this study, the values of benzo[e]pyrene/perylene, (benzo[e]pyrene + benzo[a]pyrene)/perylene, and benzo[fluoranthene]/perylene are 198.46, 202.23, and 143.70, respectively, which were poor indicators of maturity. Benzo[fluoranthene]/benzo[e]pyrene values are relatively low, ranging from 0.08 to 1.09 (average 0.63), suggesting a high degree of thermal evolution.

6.1.2. Organic Matter Source and Source Rock

Previous studies have shown that there is a close relationship between the organic matter source of crude oil and the relative content of some aromatic compounds. Aromatic compounds such as the naphthalene series (1,2,5-trimethylnaphthalene (1,2,5-TMN), 1,2,5,6-tetramethylnaphthalene (1,2,5,6-TeMN), benzo[fluoranthene], fluoranthene, retene, cadalene, pyrene, anthracene, perylene and biphenyl, etc., are biomarkers reflecting terrigenous organic matter inputs [48,62–65]. Chrysene and phenanthrene series compounds are closely related to the input of lower aquatic organisms [62]. The ratio of (1,2,5-TMN)/(1,3,6-TMN) is used to distinguish marine and continental crude oil, and this ratio is <0.3 in

marine crude oil, >0.3 in terrestrial crude oil, and 0.71–1.48 in oil derived coals [64]. These aromatic compounds, such as naphthalene series, benzofluoranthene, fluoranthene, pyrene, anthracene, retene, perylene, and biphenyl, were detected in the bitumen samples, but most of them had low content (Figure 1), indicating that the Qinglong paleo-oil reservoir had a small amount of higher plant input. At the same time, the concentrations of phenanthrene and chrysene in aromatic compounds were both very high, ranging from 16.86%–30.90% (average 24.79%) and 12.29%–23.28% (average 18.53%), respectively (Table 1), indicating that the organic matter source of the paleo-oil reservoir was mainly from low aquatic organisms. This is consistent with a mixed source dominated by lower organisms, as revealed by the Pr/nC₁₇–Ph/nC₁₈ plot [38].

Some studies have detected retene in the fraction produced by pyrolysis of green algae and cyanobacteria, and it is believed that the formation of retene is related to the reducing environment [66]. The triaromatic steroid series compounds are thought to be associated with the saltwater environment or low maturity of organic matter [67], and the relative content of the triaromatic steroid series in marine crude oil and oil-derived coals is generally <3% [48]. In addition, the formation of perylene requires a strongly reduced deposition environment [68]. A certain amount of retene, triaromatic steroid series, and perylene were detected in this study, which indicated that the source rock of the paleo-oil reservoir was formed in a relatively reductive sedimentary environment.

In the Pr/Ph–DBT/P binary plot [69,70] (Figure 11a), the bitumen samples from the Qinglong paleo-oil reservoir plot into the field of a sulfur-poor lacustrine environment. In the ternary diagram of DBF–DBT–F [71,72] (Figure 11b) and binary plot of DBT/(F + DBT)–DBF/(F + DBF) [73,74] (Figure 11c), the bitumen samples from the Qinglong paleo-oil reservoir all related to the swamp environment. In the binary plot of Pr/Ph versus DBT/DBF [75] (Figure 11d), all the studied samples plot into the field of weak oxidation to weak reduction environment, which is consistent with the above analysis. In addition, the dibenzothiophene series compounds are abundant in the Qinglong paleo-oil reservoir, with a relative content of 6.63%–16.26% (average 10.28%), which is much higher than that of lacustrine oil and coal-formed oil (average 2.5% and 3.2%, respectively), and close to that of marine facies oil (average 7.7%–42.5%, average 20.6%) [69]. In a word, the comprehensive analysis shows that the source rock of the Qinglong paleo-oil reservoir was formed in the marine environment of weak oxidation and weak reduction, in which the organic matter source was mainly from low aquatic organisms mixed with a small amount of higher plant.

The source rocks developed in the southwest Guizhou depression of Nanpanjiang Basin include Middle Devonian Huohang Formation (D_{2h}), Lower Carboniferous Jiusi Formation (C_{1j}), Middle Permian Liangshan Formation (P_{2l}), and Upper Permian Longtan Formation (P_{3l}), which are also the target beds for shale gas exploration in this area [76] (Figure 2). Previous studies have shown that the main source rocks in the Nanpanjiang Depression are black mudstones deposited in the middle Devonian basin facies, such as Huohong Formation (D_{2h}), Luofu Formation (D_{2l}), and Nabiao Formation (D_{2n}), which are characterized by huge thickness, high organic carbon content, and mainly sapropelic organic matter (Type I–II₁, mainly lower aquatic organisms) [77]. In addition, Carboniferous and Permian source rocks belong to the secondary source rocks with limited distribution, which are mainly humic organic matter (type II₂–III, mainly terrestrial higher plants) [77,78]. The above aromatic biomarkers revealed that the organic matter source was dominated by lower aquatic organisms, which proved that the source rock of the paleo-oil reservoir was Devonian source rock.

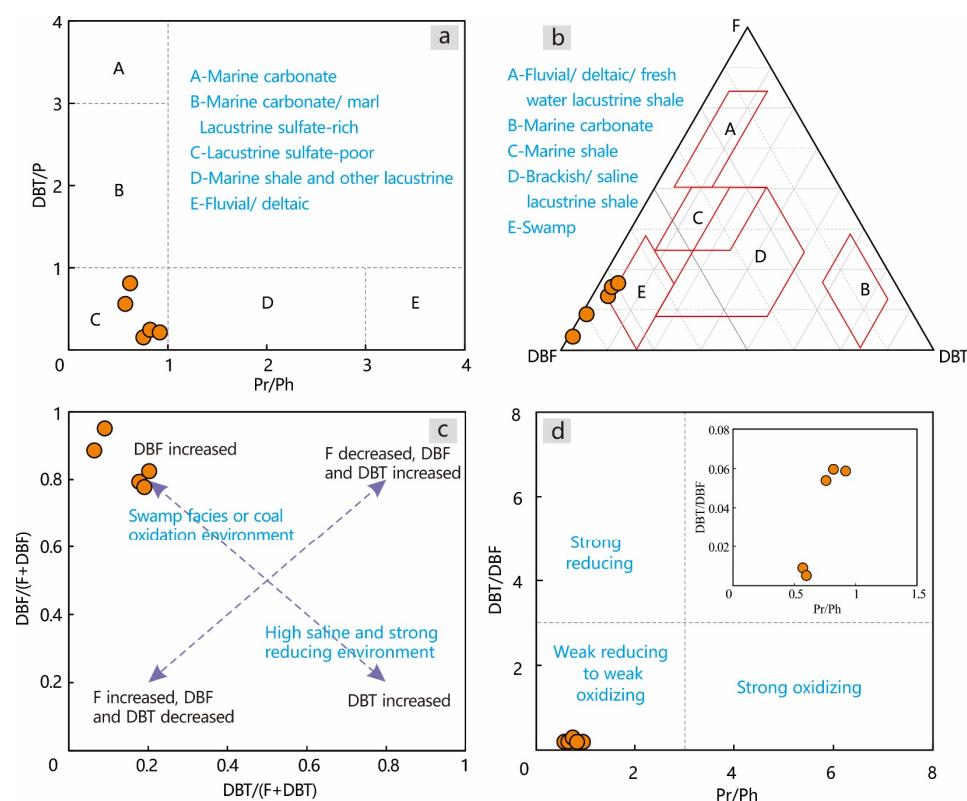


Figure 11. Discrimination diagram of sedimentary environment. (a) Crossplot of Pr/Ph versus DBT/P ; (b) ternary diagram of DBF – DBT – F ; (c) binary plot of $DBT/(F + DBT)$ versus $DBF/(F + DBF)$; (d) crossplot of Pr/Ph – DBT/DBF .

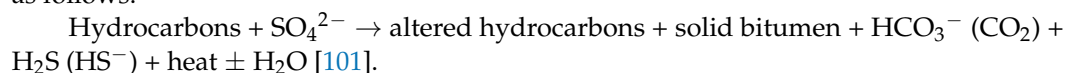
The study shows that there are many reef limestone paleo-oil reservoirs (D_2 – P_3) and some high N_2 gas reservoirs (such as Shuang1 well and Yang1 well) distributed in the Nanpanjiang Depression (Figure 1), which are all derived from the Devonian source rocks; Paleo-oil reservoir bitumen is considered as the pyrobitumen produced in the process of oil cracking into gas under the action of high temperature and pressure, and high N_2 natural gas is derived from the gas generated by the kerogen cracking of the Middle Devonian source rocks [79–81]. The physical characteristics and geochemical analysis of bitumen in this study show that it is also the pyrobitumen formed by the thermal cracking of early paleo-oil reservoirs due to the rise of paleo-geothermal temperature [37]. Previous studies on saturated hydrocarbon biomarkers, carbon isotopes, and rare earth elements [38], as well as the evidence of aromatic hydrocarbon biomarkers in this paper, all indicate that Qinglong paleo-oil reservoir originated from Devonian source rocks, just like other paleo-oil reservoirs and natural gas reservoirs in the Nanpanjiang basin.

6.2. Indication of the TSR Reaction

Thermochemical sulfate reduction (TSR) refers to the chemical reaction of sulfate with organic matter or hydrocarbons to reduce sulfate minerals and generate hydrogen sulfide (H_2S) and carbon dioxide (CO_2). The concept of TSR was first proposed by Orr (1974) to explain the presence of large amounts of H_2S in natural gas in the Big Horn Basin [82]. In fact, oil and gas reservoirs with high H_2S content are widely distributed around the world and reach the scale of industrial oil and gas flows [83,84]. These reservoirs are mainly located in Canada [85–87], the United States [82,88], and Mexico in North America; Iran [89], Iraq, Saudi Arabia [90], and the United Arab Emirates [91] in the Middle East; the Amu Darya River, North Caspian Sea, Volga-Urals, Siberia, and the Timan-Pechora in the former Soviet Union [85]; Croatia [92], Germany, and France in Europe; and China's Sichuan and Tarim Basin [93,94] and India [85] in Asia. The buried depth of these reservoirs

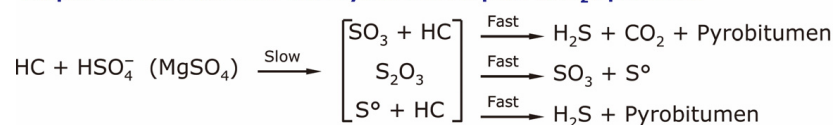
ranges from 500 m to 6000 m, and the reservoir strata are Sinian to Tertiary [83,84]. Among them, the South Texas gas reservoir has the highest H₂S content of 98%. The H₂S content in the world-class Lacq gas field in France and the Puguang and Dukouhe giant gas fields in Sichuan Basin, China, all exceeded 15% [95,96].

As a reducing agent, the organic matter of oil and gas produces a large amount of reduced sulfur through the TSR reaction, which is the only way to form high concentration H₂S oil and gas reservoirs. TSR reaction is also an important formation mechanism of reduced sulfur in many metal deposits [6,7,9,39,97–100]. The TSR total reaction equation is as follows:



TSR is considered to be an autocatalytic process, and thiols and other sulfides are intermediate transition products. The specific reaction process can be roughly divided into three steps (Figure 12) [102].

Step 1: Sulfate reduction with hydrocarbons prior to H₂S presence



Step 2: Sulfur incorporation to hydrocarbons by reacting with H₂S



Step 3: Sulfate reduction by reactive labile sulfur compounds oxidation

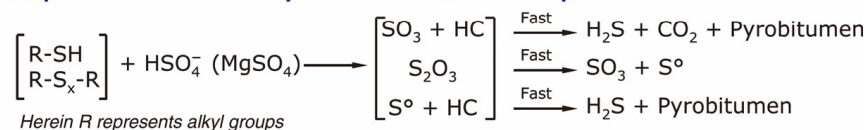


Figure 12. TSR reaction mechanism (after [102]).

Many studies have shown that H₂S produced in the TSR reaction process reacts with hydrocarbon compounds to form new sulfur-containing compounds, such as thiophene (TP), tetrahydrothiophene (THTP), benzothiophene (BP), dibenzothiophene (DBT), thiadiazomondoid (TA), etc. [43,44,103–106], which leads to an increase in sulfur content, a decrease in saturated hydrocarbon/aromatic ratio, and an increase in non-hydrocarbon and asphaltene content of crude oil [107]. Wang et al. (2013) believed that the TSR reaction occurred in Majjiang large paleo-oil reservoir in Guizhou Province, and in this process, biphenyl (BP) was transformed into dibenzothiophene (DBT), methylbiphenyl (MBP) was transformed into methyl dibenzothiophene (MDBT), and dimethylbiphenyl (DMBP) was transformed into dimethyl dibenzothiophene (DMDBT) [108].

The formation order of sulfur compounds is thiophene, tetrahydrothiophene, benzothiophene, dibenzothiophene, and thiadiazomondoid, which is related to its own stability [109]. Tetrahydrothiophene and benzothiophene compounds with poor thermal stability were formed earlier and faster in the TSR reaction, while dibenzothiophene and thiadiazomondoid compounds with relatively high stability were formed more slowly, and it was difficult to take further reaction once formed. Although a small amount of dibenzothiophene and thiadiazomondoid can be inherited from source rocks, TSR can produce a large amount of dibenzothiophene and thiadiazomondoid with a high degree of modification, which is much more than that from kerogen sources. Therefore, higher concentrations of dibenzothiophene and thiadiazomondoid are considered to be marker compounds for the TSR reaction [43,44].

In general, dibenzothiophene series compounds are not very abundant in the aromatic components of source rocks or crude oils. For example, its relative content is 1.29% on average in the source rocks from the Jurassic Haifanggou Formation in Niuyingzi Depression of Lingyuan-Ningcheng Basin [48], <2.5% in the Paleogene source rock in Miaoxibei Sag

of Bohai Sea area [110], 2.67% on average in the crude oil from Chi'an Oilfield in Gaoyou Sag [111], and <4% in Light Oils from Xihu Sag in East China Sea Basin [112].

The bitumen samples of the Qinglong paleo-oil reservoir contain abundant dibenzothiophene series compounds; the relative content ranges from 6.63 to 16.26%, with an average of 10.28% (Figure 13). Dibenzothiophene (DBT) and methylthiophene (MDBT) were the main compounds in the dibenzothiophene series, and their relative contents are 1.09%–6.63% (average 3.37%) and 1.95–7.53 (average 4.08%), respectively (Figure 14). A small amount of dimethylthiophene (DMDBT) is also included, with a relative content of 0.06%–0.28% and an average of 0.18%. While the biphenyl series (including BP, MBP, and DMBP) in the ancient reservoir is very small, with the relative content ranging from 0.07 to 0.33%, with an average of 0.21% (Figures 13 and 14). Therefore, we believe that the Qinglong paleo-oil reservoir underwent a certain degree of TSR alternation, during which some biphenyl series compounds were converted into dibenzothiophene series compounds, and a large amount of H_2S was generated.

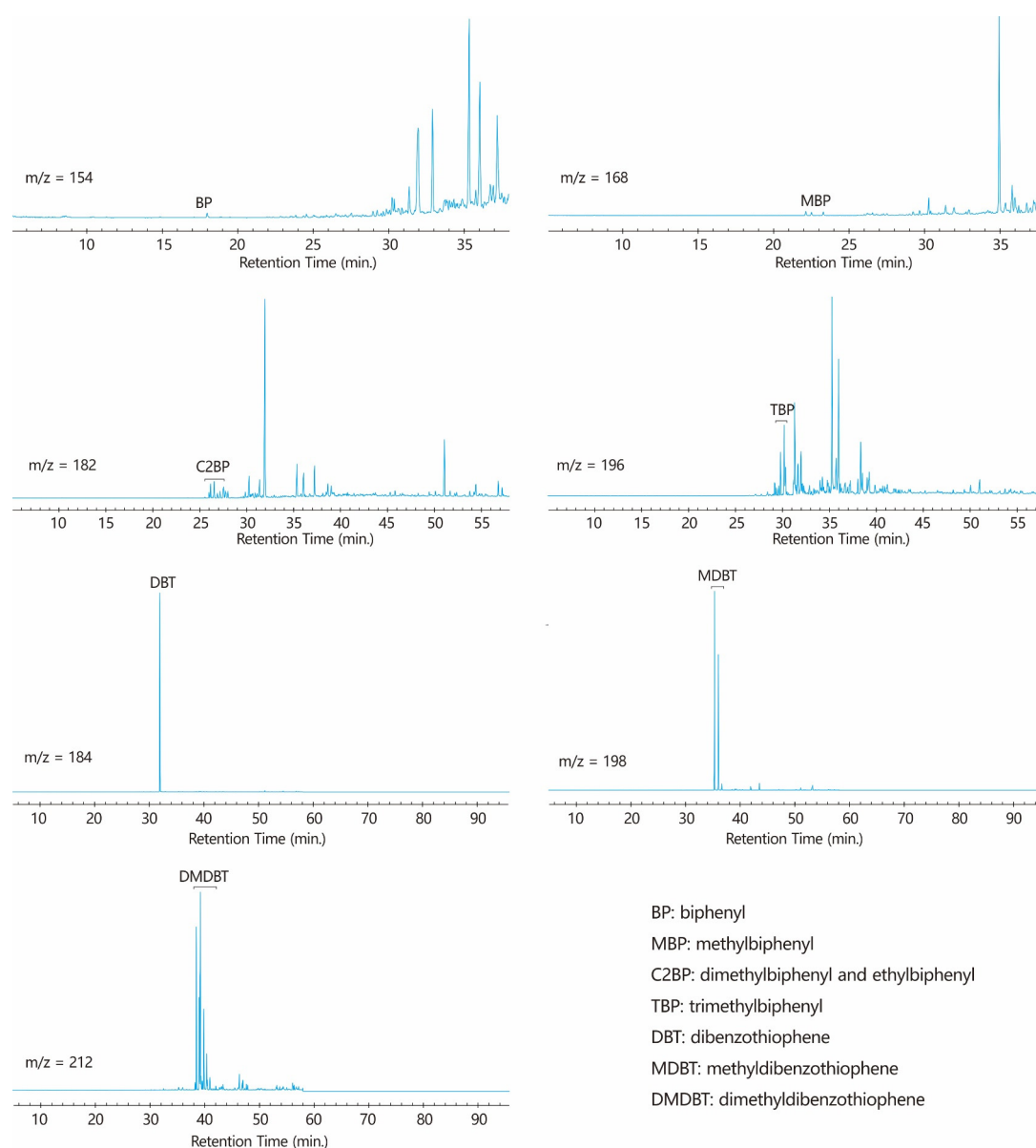


Figure 13. Mass chromatograms of the biphenyl series and dibenzothiophene series (QL-1).

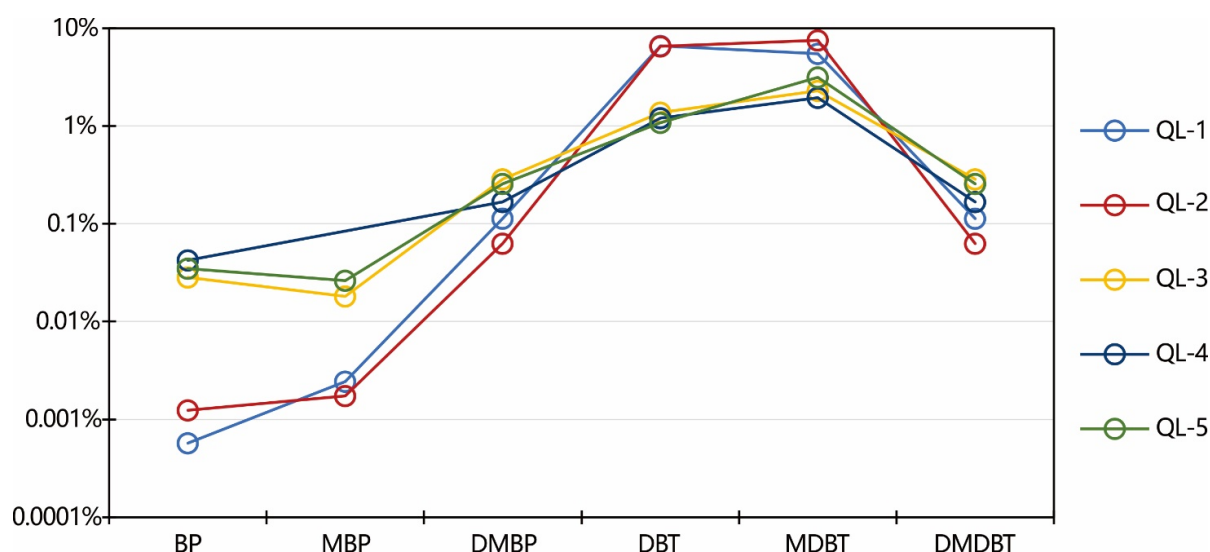


Figure 14. Relative percentage of the biphenyl series and dibenzothiophene series.

6.3. Genetic Relationship between Paleo-Oil Reservoir and Antimony Deposits

6.3.1. Spatial-Temporal Relationship between Hydrocarbon Accumulation and Antimony Mineralization

The spatial relationship between the paleo-oil reservoir and the Qinglong antimony ore field is very close (Figure 3). The antimony body is close to the core of the Dachang anticline and is distributed in the Upper Permian “Dachang layer” (P_3d) between the Huyujing fault and Qingshanzhen fault, which is obviously controlled by the NE trending fault. The paleo-oil reservoir is located in the northwest wing of the Dachang anticline, and its reservoirs are mainly Emeishan basalt ($P_3\beta$), “Dachang layer” (P_3d), and Maokou Formation (P_2m). The paleo-oil reservoir is closely associated with the antimony deposits, which are about 2.5 km apart in the plane, and the vertical hosting horizon is also consistent.

According to the parameters of strata, lithology, and geochemistry, the Basin Model software is used to simulate the burial history, thermal history, and maturation history of the paleo-oil reservoir (Figure 15). The exponential compaction model, instantaneous heat flow model, and Easy Ro model are used to simulate the burial history, thermal history, and maturation history, respectively. The results show that rapid burial occurred during the Permian to Early Jurassic, during which the paleo-oil reservoir strata (Middle Permian) were rapidly buried below 5500 m. Although slow uplift occurred in the late Early Jurassic to Early Cretaceous, the buried depth of the paleo-oil reservoir strata was always below 4000 m. Rapid uplift occurred since the Late Cretaceous, and the paleo-reservoir strata were exposed to the surface and eroded by weathering since the Eocene.

The previous bitumen Re-Os isotopic chronology indicates that the age of the oil generation peak of the Devonian source rock is 254 Ma (early Late Permian) [39]. The basin simulation in this study indicates that the oil reservoir formed in the early to middle Triassic (~235 Ma). With the burial of strata, the geothermal temperature continued to rise, and the oil reservoir was thermally cracked to generate a large amount of solid bitumen and gaseous hydrocarbons, which accumulated into the Dachang dome and formed gas reservoirs at the end of the Late Triassic (~210 Ma). The paleo-oil reservoir bitumen experienced high temperatures above 200 °C and has a high degree of thermal evolution, which is consistent with the aromatic maturity parameters and the measured R_b data (Table 1) [40]. The Sm-Nd isotopic isochron ages of calcite and fluorite in the Qinglong antimony ore field indicate that the metallogenic epoch is the late Jurassic (142–148 Ma) [24,29]. Therefore, in terms of time relationship, oil and gas accumulation was earlier than metal antimony mineralization, and the oil reservoir had already been thermally cracked to become the gas reservoir.

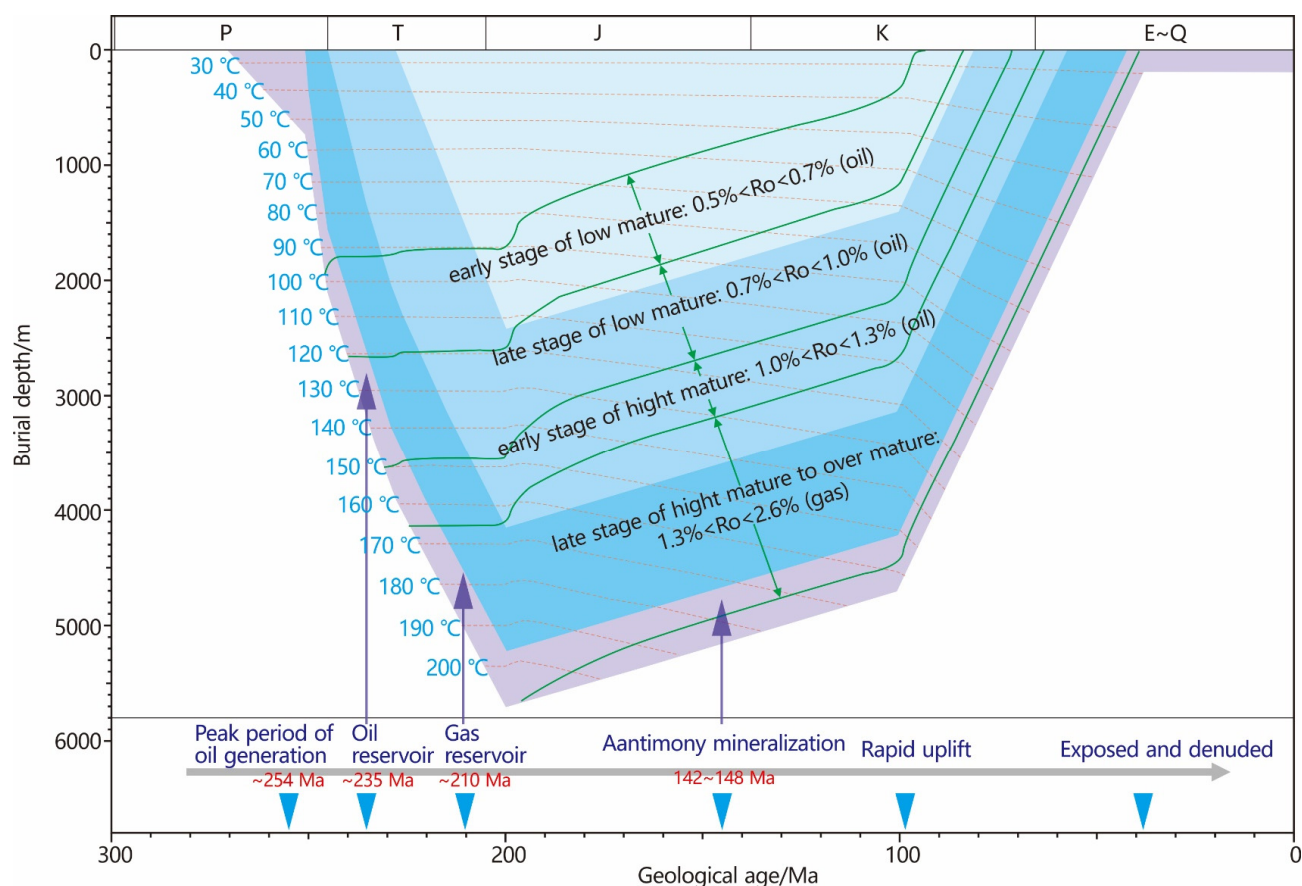


Figure 15. Simulation results of burial history, thermal history, and maturation history of Qinglong Paleo-oil reservoir show the time relationship between hydrocarbon evolution and antimony mineralization.

6.3.2. The Role of Paleo-Oil Reservoir in Antimony Mineralization

Many studies have shown that hydrocarbon organic matter at different stages of thermal evolution can be involved in metal mineralization in sedimentary basins, and organic hydrocarbon gases in ore-forming fluids are often captured by precipitated hydrothermal minerals to form hydrocarbon gas (mainly CH_4 and C_2H_6) inclusions. When liquid hydrocarbons (oil reservoir) are involved in metal mineralization, solid bitumen is often associated with minerals at the mineralization stage, and bitumen inclusions (generated by pyrolysis of petroleum inclusions) are common in ores, such as the Mayyuan Pb-Zn [7] and Jinding Pb-Zn deposits [8]. While gas hydrocarbons (gas reservoir) are involved in metal mineralization, the phenomenon of association of solid bitumen and minerals formed in the ore-forming period is almost not seen in the ore, such as the Carlin-type gold deposit in southwest Guizhou [6,9].

In terms of material connection, although the Devonian source rock is enriched in Sb (11 times that of the upper crust on average), the paleo-oil reservoir bitumen is deficient in Sb (unpublished data), suggesting that the source rock may be a source of metallic Sb but are unlikely to be transported by hydrocarbon fluids. Although there is no phenomenon of mineral paragenesis of solid bitumen and stibnite in the ore, the composition of organic inclusions in the deposit is similar to that of natural gas reservoirs in Nanpanjiang Basin, indicating that the ore-forming fluid is rich in hydrocarbon gases, and these hydrocarbon gases are captured by precipitated hydrothermal minerals. In addition, ore stibnite has the sulfur isotopes ($\delta^{34}\text{S}$) range (-2.9‰ to $+6.9\text{‰}$, average $+1.3\text{‰}$) consistent with that of pyrite in paleo-oil reservoir bitumen (-1.90‰ to $+3.10\text{‰}$, average $+0.97\text{‰}$) consistent with that of ore sulfide, suggesting that hydrocarbon organic matter contributed to reducing sulfur to antimony mineralization [38]. Therefore, we believe that the gas reservoir formed by the

evolution of the oil reservoir participated in Sb mineralization; that is, hydrocarbon organic matter acted as a reducing agent and transformed SO_4^{2-} in oilfield brine into H_2S through TSR, providing reduced sulfur and creating environmental conditions for mineralization. Since the gaseous hydrocarbon rather than liquid hydrocarbon is involved in antimony mineralization, no solid bitumen was found in the ore, but organic gas components are common in the ore inclusions.

Because the sulfur isotopes range of stibnite in the ore is similar to that of magmatic sulfur isotopes composition ($0 \pm 5\text{‰}$), some scholars hold different views that the Qinglong antimony deposit S originated from magma [22,27]. However, 2D seismic data with higher detection accuracy reveal that there is no hidden rock mass in Nanpanjiang Basin [41,42]. The hidden magmatic rock mass previously inferred from gravity and aeromagnetic anomalies is actually a palaeohigh above the basement, which controls the distribution of Au-Sb deposits [42].

It has been confirmed that Sb mainly originated from the “Dachang layer”, and the ore-forming fluid is mainly basin fluid [38]. Therefore, on the basis of previous studies and combined with the understanding obtained in this study, we proposed a model diagram of the involvement of gaseous hydrocarbon organic matter formed by the pyrolysis of the oil reservoir in Sb mineralization (Figure 16).

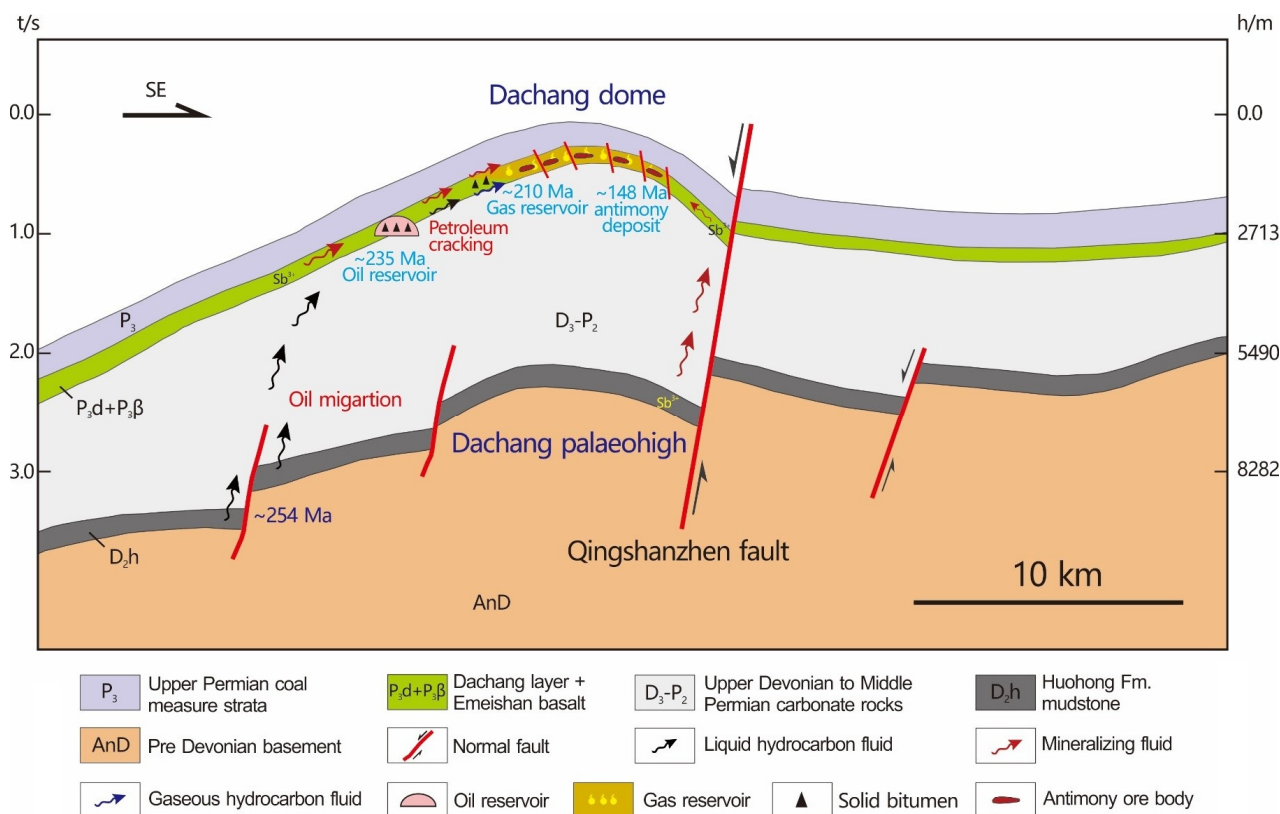


Figure 16. Schematic metallogenic model for the Qinglong antimony deposit, showing the genetic relationship between oil and gas accumulation and antimony mineralization. The stratum, structure, and depth of the figure are based on 2D seismic profile interpretation, which is NW-SE striking and adjacent to the northern area of Figure 2 (modified from [38]).

With the rapid burial of the strata, the Devonian source rock matured in the early Late Permian (~254 Ma) and a large amount of oil was generated. Liquid hydrocarbon fluids migrated upward and gradually accumulated under the shielding effect of tuff in the third member of the “Dachang layer”, and then the oil reservoir was formed during the early to middle Triassic (~235 Ma). After that, the heated basin fluid continuously extracted metal Sb in the Devonian source rock and the “Dachang layer”, and gradually

formed Sb-rich ore-forming fluid. On the other hand, with burial heating, the oil reservoir gradually underwent thermal cracking to produce large quantities of solid bitumen and gaseous hydrocarbons, and the gaseous hydrocarbons accumulated in the Dachang dome at the end of the Late Triassic (~210 Ma) to form the gas reservoir. In these processes, oil and gas organic matter act as a reducing agent to reduce SO_4^{2-} in oilfield brine to H_2S through the TSR reaction.

In the late Jurassic (142–148 Ma), Sb-rich ore-forming fluids gradually accumulated in the Dachang palaeohigh. Due to the change in physical and chemical conditions, the metal Sb combines with H_2S in the gas reservoir and precipitates to form the antimony deposits at the appropriate position. Since the late Cretaceous, with the rapid uplift of the crust, the antimony deposits were lifted to the near-surface position for exploration and utilization, while the gas reservoir was destroyed by denudation, and a large amount of solid bitumen remained in the adjacent positions. Therefore, the antimony deposits and the paleo-oil reservoir were produced in the same stratum adjacent to each other.

7. Conclusions

Various aromatic compounds have been detected in the Qinglong paleoreservoir bitumen, including abundant phenanthrene series, dibenzothiophene series, fluoranthene series, chrysene series, and a small number of fluorene series, naphthalene series, dibenzofuran series, biphenyl series, and triaromatic steroid series.

Aromatic compounds and their related parameters indicate that the paleo-oil reservoir is in over mature level, and the organic matter source of the paleo-oil reservoir was mainly low aquatic organisms mixed with a small amount of higher plant. The paleo-oil reservoir was derived from the Devonian source rock, which was formed in the marine environment of weak oxidation to weak reduction.

Abundant dibenzothiophene series and less biphenyl series were detected, indicating that the oil reservoir underwent a certain degree of TSR reaction. We believe that the gas reservoir formed by the evolution of the oil reservoir participated in antimony mineralization; that is, hydrocarbon organic matter acted as a reducing agent and transformed SO_4^{2-} in oilfield brine into H_2S through TSR, providing reduced sulfur and creating environmental conditions for mineralization.

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