Article

Differential Thermal Evolution between Oil and Source Rocks in the Carboniferous Shale Reservoir of the Qaidam Basin, NW China

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Abstract: Shale oil and source rock samples of the Carboniferous Keluke Formation from well Chaiye 2 in the Delingha Depression were analyzed by gas chromatography–mass spectrometry. Source rocks were highly mature at the gas generation stage with vitrinite reflectance (Ro) of 1.45–1.88%. However, the oil produced from the shale reservoir was characterized by abundant biomarkers but low abundance of diamondoid hydrocarbons with estimated Ro of ca. 0.78%, indicating hydrocarbons were still at a relatively low thermal maturity level. As the crude oil was generated and accumulated autochthonously, preliminary results indicate that crude oil and source rocks witnessed differential thermal evolution and significant disparity of the current thermal maturity in the shale reservoir due to rapid tectonic subsidence and clay mineral catalysts that accelerated the thermal maturation process. Although tectonic uplifts occurred afterwards, the vitrinite recorded the highest maturity that source rocks have ever reached, whereas the oil has not reached the same maturity level due to less impact from thermal alteration or mineral catalysis than source rocks in the shale reservoir. Such a discovery enlarges the hydrocarbon perseveration of maturity ranges in reservoirs, particularly for the unconventional tight formation, and benefits potential hydrocarbon exploration from highly mature sediments.

Keywords: thermal maturity; differential evolution; biomarkers; diamondoid hydrocarbons; clay catalysis; Qaidam Basin

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1. Introduction

The Qaidam Basin, with an area of 121,000 km², is the largest intermontane basin of the northeastern Tibetan Plateau, and a prolific hydrocarbon production province. Hydrocarbons were considered to be mainly derived from the Jurassic [1,2], Paleogene [3], Neogene [4], and Quaternary [5]. However, the Carboniferous strata were highly mature and eliminated from potential source rocks, as was previously considered well metamorphosed. Since the early 1990s, the Carboniferous strata has gradually received attention in the Qaidam Basin [6–8], and recent research has indicated the Carboniferous rock was formed under warm and humid climatic conditions in the sedimentary environment of a coastal platform facies [7], actually unmetamorphosed [9]. Rapid tectonic subsidence and uplifts occurred in the Carboniferous strata and source rocks have temporarily been at a great burial depth and exposed to high temperatures, but the basin drastically uplifted afterwards [10]. The rapid tectonic subsidence stages were recorded during the periods of Late Devonian–early Carboniferous, Middle Jurassic, and Late Oligocene–Miocene at subsidence rates of 48, 10, and 45 m/Ma, respectively [11]. The reservoir temperature increased dramatically due to the expeditious burial, reaching 160–170 °C in the maximum

burial of the Carboniferous [10,11]. The basin witnessed uplifts during periods of Late Triassic–Jurassic, Late Cenozoic–middle Miocene, and Late Miocene [10].

Carboniferous source rock is mainly composed of dark-colored mudstones, marls, coals, carbonaceous mudstones, and shales and their exploration potential has been gradually revealed [7,12,13]. Carboniferous source rock was at the hydrocarbon generation stage as early as the Late Carboniferous based on the burial history [9]. However, hydrocarbon generation suspended due to the uplift and erosion of the Carboniferous controlled by the Hercynian Movement [9]. During the Indochina period, the Carboniferous witnessed uplift and erosion once again. Tectonic subsidence and burial occurred to the Carboniferous of the Dehaling Depression in the period of late Yanshan orogeny when the source rocks were thermally mature for a new round of hydrocarbon generation. In May 2018, straight-well segmented fracturing gas tests (1081–1061 and 820–800 m) were conducted on the Carboniferous Keluke Formation of well Chaiye 2 by the Institute of Geomechanics, Chinese Academy of Geological Sciences. The maximum gas flow rate was 55.52 m³ per hour with guaranteed yields of 145.32 m³ per day, and shale oil was simultaneously produced at a flow rate of 0.65 m³ per day. Shale gas and shale oil, herein, are first discovered in the Paleozoic of Qinghai Tibet Plateau. Source rocks penetrated by well Chaiye 2 are characterized by type III organic matter and are highly mature, with a vitrinite reflectance (Ro) above 1.45%, suggesting the late gas generation stage. However, the liquid oil from well Chaiye 2 shows a normal maturity level.

Few documented studies reported significant discrepancy of thermal maturity between source rocks and liquid hydrocarbons. How can liquid oil be preserved in the highly mature source rocks in the gas generation stage occurring in the Qaidam Basin? Preservation of liquid hydrocarbons in high-maturity source rocks from the Qaidam Basin indicates that source rocks and liquid oil from well Chaiye 2 witnessed differential evolution during thermal maturation. This study was conducted to disclose the preservation of liquid oil in high-maturity source rocks, and to unravel the mechanism of differential evolution between source rocks and expelled hydrocarbons during thermal maturation in the shale reservoir. The present study provides favorable prospects for further hydrocarbon exploration from the highly mature source rocks.

2. Geological Setting

Qaidam Basin is characterized by a rhomb-shaped intermontane basin on the northeastern margin of the Tibetan Plateau, surrounded by the Qilian, Kunlun, Altyn, and Alashan Mountains (Figure 1a). The basin was initially an independent craton during the Paleoproterozoic, with basement consisting of mainly metamorphic rocks and carbonate sedimentation. During the periods of the Paleozoic Carboniferous, Qaidam Basin was merely a simple synclinal depression while compressional uplift and erosion occurred during the Permian and Cretaceous. In the Paleogene, the basin was characterized by strike-slip depressions. Compressional folding and depressions were recorded during the periods of the Neogene and Quaternary, and finally featured intrabasinal deformation and uplift [14].

The Carboniferous succession was characterized by marine-terrestrial transitional facies due to the unique depositional environments [14]. The Carboniferous is subdivided into Lower Carboniferous and Upper Carboniferous, and the Keluke Formation belongs to the Upper Carboniferous. The Keluke Formation, with a thickness of 400–700 m, was the main organic-rich source rock section developed in the Carboniferous. Sediments in the Keluke Formation were highly mature and characterized by dark-colored shale, carbonaceous shale, mudstone, muddy siltstone, mudstone, limestone, and shale. Source rock samples in the present study were collected from the Carboniferous Keluke Formation at a depth range of 842–1063 m from well Chaiye 2 in the Delingha Depression (Figure 1b,c). The source rocks were mainly mudstone, black shale, and coaly mudstone, as is shown in the stratigraphic column in Figure 1c. One oil sample was obtained from the Carboniferous mudstone at a depth range of 800–820 m.

Figure 1. Geological settings: (a) geological map of Qaidam Basin; (b) geological map of Delingha Depression; (c) general stratigraphy of well Chaiye 2 (modified after Wang et al. [10]).

3. Methods

3.1. Vitrinite Reflectance Measurements and Rock-Eval Analyses

The bulk geochemical characteristics of the studied source rock samples were carried out by Rock-Eval pyrolysis and vitrinite reflectance measurement. Mean random vitrinite reflectance of source rocks was measured at 546 nm in oil under the operation of an Opton 20 Microscope and Axioplan-Opton microphotometer in the present study.

Rock-Eval pyrolysis was performed on the crushed samples (80–100 mesh) by a Rock-Eval 6 apparatus equipped with a flame ionization and infrared detectors. Detailed pyrolysis procedures and descriptions can be found in Lafargue et al. [15]. The pyrolysis procedure and experiment settings are the same as described by Li et al. [14]. The free hydrocarbons (S1 peak), hydrocarbons generated from kerogen (S2 peak), and CO₂ from oxygenated compounds (S3 peak) were measured for bulk geochemical characterization in the present study.

3.2. Gas Chromatography–Mass Spectrometry (GC-MS) Analysis

Core samples were pulverized into 80–100 mesh for Soxhlet extraction. Extractable organic matter (EOM) was obtained for hydrocarbon separation in the silica solid phase extraction (SPE) columns. For the purpose of component quantification, internal standards for saturated hydrocarbons (i.e., cholestane-d₄, adamantane-d₁₆, phenyldecane-d₃₀) and aromatic hydrocarbons (i.e., naphthalene-d₈, phenanthrene-d₁₀, and 1,1'-binaphthyl) were also added in the SPE columns. The sample preparation and operation procedures were the same as described by Wang and Huang [16]. GC–MS analyses of saturated and aromatic fractions were performed using an Agilent 7890B gas chromatograph linked to an Agilent 5977A MSD system with detailed settings described by Wang and Huang [16]. The concentration calculation was based on the peak area without response factor calibration.

3.3. X-ray Diffraction Mineralogy

Pulverized samples were analyzed using an X-ray diffraction (XRD) instrument with a CuKα radiation source to measure the relative content of each mineral composition. The

voltage of 30–45 kV, current of 20–100 mA, and scanning between 5 and 45 °C with a speed of 6 dg/min were used on the whole rock. However, the XRD analysis of clay minerals was conducted with scanning of 0.5–30 °C and 6 dg/min.

4. Results

4.1. Bulk Geochemical Characterization

Samples from well Chaiye 2 are rich in organic matters with visually quantified content ranging from 2.6% to 4.9% (Table 1). The maceral composition of organic matter is mainly composed of vitrinite and inertinite in proportions of 38.5–72.7% and 27.3–61.5%, respectively, and the kerogen is dominated by type III from the microscopic examination (Table 1).

Table 1. Bulk and maceral compositions of source rock samples from well Chaiye 2.

Depth (m)	Total Rock (%)			Organic Composition (%)				Kerogen Type
	Total OM	Pyrite	Other Minerals	Sapropelic OM	Liptinite	Vitrinite	Inertinite	
1009	3.3	4.7	92.0	0.0	0.0	72.7	27.3	III
1020	2.6	2.9	94.5	0.0	0.0	38.5	61.5	III
1027	4.9	3.3	91.8	0.0	0.0	53.1	46.9	III
1033	3.6	2.6	93.8	0.0	0.0	52.8	47.2	III
1053	3.2	2.1	94.7	0.0	0.0	43.8	56.3	III

OM, organic matter.

The total organic carbon (TOC) contents from Rock-Eval pyrolysis have a range of 1.32–31.8 wt% (Table 2). The free hydrocarbons in the source rocks (S1 peak) are fairly low, ranging from 0.04 mg/g rock to 1.01 mg/g rock with an average value of 0.23 mg/g rock. The hydrocarbons generated from kerogen (S2 peak) vary in a range of 0.44–22.7 mg/g rock (averaged at 3.81 mg/g rock). Hence, the total hydrocarbon generation potential, which is represented by (S1 + S2), varies in the range of 0.49–23.7 mg/g rock. The hydrogen index (HI = S2/TOC × 100) of the studied samples ranges from 9–101 mg/g TOC (averaged at 41.8 mg/g TOC) (Table 2), whereas the oxygen index (OI = S3/TOC × 100) varies in the range of 0–10 mg/g TOC (averaged at 4.9 mg/g TOC) (Table 2), also suggesting the source rocks were mainly type III kerogens (Figure 2b). The temperature of maximum generation of pyrolytic hydrocarbons (S2), i.e., Tmax values, range from 486 to 502 °C (Table 2). Solvent extractable organic matter varies from 0.16 to 0.79 mg/g (averaged at 0.37 mg/g) (Table 2). Although the source rocks were dominated by III kerogens (Figure 2b), they were still showed good to excellent potential for hydrocarbon generation (Figure 2a).

Table 2. Results of Rock-Eval pyrolysis and Soxhlet extraction of Chaiye 2 rock samples.

Depth (m)	TOC (wt%)	Tmax (°C)	HI (mg/g)	OI (mg/g)	EOM (mg/g Rock)
1009	1.58	490	30	6	0.25
1020	1.8	486	39	8	0.28
1025	1.32	490	33	9	0.18
1027	3.28	492	34	5	0.21
1033	2.86	488	27	5	0.41
1037	31.8	493	9	0	0.56
1047	7.18	497	51	3	0.79
1053	22.4	500	101	1	0.61
1061	8.61	497	51	2	0.16
1063	2.13	502	43	10	0.25

Vitrinite reflectance is a petrographic method to quantify the percentage of incident light reflected from polished vitrinite particles for thermal maturity assessment [17]. Mean vitrinite reflectance, based on at least 20–100 random measurements in a polished slide of whole rock, is the most common and trustworthy method, which is widely used for

maturity assessment of source rocks. The studied samples have valid measured vitrinite reflectance points of 21–52 (Table 3). The thermal maturity of source rocks can be classified into immature, early mature, mature, and overmature stages. Immature source rocks with vitrinite reflectance usually below 0.6% are too cool or have too short a duration for thermal generation of petroleum, whereas they began to generate small amounts of petroleum in the early mature stage (~ 0.5 – 0.6 %Ro) [17]. When the source rocks are mature, organic matter is in the oil-generation window and vitrinite reflectance herein is in a range of 0.6–1.4%. With increasing thermal maturity, source rocks are overmature and it was previously regarded that further oil generation ceased [17]. The mean Ro values increase from 1.45% to 1.88% (Table 2), indicating that the studied source rock samples were at the thermally mature to overmature stages.

Figure 2. Bulk geochemical data of source rock samples from well Chaiye 2: (a) S1 + S2 vs. TOC; (b) HI vs. OI.

Table 3. Measured Ro values of source rock samples from well Chaiye 2.

Depth (m)	%Ro			Valid Measured Points	Standard Deviation (%)
	Minimum	Maximum	Mean		
1009	1.10	1.71	1.48	35	0.139
1020	1.35	1.63	1.48	21	0.100
1027	1.29	1.67	1.45	27	0.112
1033	1.50	2.18	1.88	44	0.167
1053	1.41	2.07	1.76	52	0.174

4.2. Geochemical Characterization of Source Rocks

Two types of *n*-alkanes distributions can be recognized in the source rock extracts. The first type is characterized by a unimodal distribution with low molecular *n*-alkanes and a relatively high abundance in *n*-C₁₄–*n*-C₁₈ (Figure 3a). With increasing thermal maturity, high-molecular-weight *n*-alkanes will encounter thermal cracking to form low-molecular-weight *n*-alkanes [17]. Hence, the relative abundance of high- and low-molecular-weight *n*-alkanes, i.e., $\sum n\text{-C}_{20}^- / \sum n\text{-C}_{21}^+$, can be applied for thermal maturation assessment [18]. The values of $\sum n\text{-C}_{20}^- / \sum n\text{-C}_{21}^+$ range from 8.25–27.3 with an average of 15.7 (Table 4), much higher than those in the other types of extracts. The second type shows a bimodal distribution of *n*-alkanes (Figure 3b), also a relatively high abundance in *n*-C₁₄–*n*-C₁₈, with the other peak in *n*-C₂₃ but less abundant than the dominant peak in *n*-C₁₆. The values of $\sum n\text{-C}_{20}^- / \sum n\text{-C}_{21}^+$ range from 2.60–5.24 (Table 4). Ratios of pristane/phytane (Pr/Ph), Pr/*n*-C₁₇, and Ph/*n*-C₁₈ in the two types have similar ranges, 0.89–1.29, 0.42–0.58, and 0.34–0.64, respectively (Table 4).

Figure 3. Representative chromatograms of m/z 85 showing typical distributions of n -alkanes and isoprenoids: (a) source rock extracts from well Chaiye 2 at a depth of 1009 m; (b) source rock extracts from well Chaiye 2 at a depth of 1033 m; (c) crude oil from well Chaiye 2.

Table 4. Geochemical parameters of oil and source rock samples from well Chaiye 2.

Sample	Depth (m)	$\sum n\text{-C}_{20-} / \sum n\text{-C}_{21+}$	Pr/Ph	Pr/ $n\text{-C}_{17}$	Ph/ $n\text{-C}_{18}$	Ts/(Ts + Tm)	20S/(20S + 20R)	22S/(22S + 22R)	B β ($\alpha\alpha + \beta\beta$)	MNR	DNR	TMNr	MPI-3	MDR	MAI
Oil	800–820	1.35	2.19	0.23	0.11	0.75	0.44	0.57	0.44	1.6	6.08	0.6	0.87	3.65	53
R1	1009	27.3	1.29	0.58	0.64	n/a	n/a	n/a	n/a	3.28	17.6	0.78	3.78	22.7	74.4
R2	1020	11.1	1.04	0.48	0.49	n/a	n/a	n/a	n/a	3.34	20.4	0.85	4.13	32.8	77.7
R3	1025	15.8	1.01	0.46	0.34	n/a	n/a	n/a	n/a	3.91	22.2	0.81	4.18	26.6	72.6
R4	1027	16.8	1.11	0.52	0.53	n/a	n/a	n/a	n/a	3.93	28	0.89	4.62	36.7	73.3
R5	1033	2.6	1.02	0.5	0.35	n/a	n/a	n/a	n/a	4.01	25.3	0.85	4.13	33.1	59.4
R6	1037	4.5	1.16	0.46	0.49	n/a	n/a	n/a	n/a	3.97	36.8	0.94	4.48	47.4	63.7
R7	1047	5.24	0.92	0.44	0.38	n/a	n/a	n/a	n/a	4.12	36.2	0.92	5.28	36.9	63.5
R8	1053	22.5	1.29	0.43	0.43	n/a	n/a	n/a	n/a	3.93	36.4	0.93	4.56	44.9	61.9
R9	1061	8.25	1.24	0.48	0.45	n/a	n/a	n/a	n/a	3	15	0.78	3.39	16.8	78.2
R10	1063	8.34	0.89	0.42	0.43	n/a	n/a	n/a	n/a	3.77	23.8	0.85	4.42	29.4	74.9

Saturated biomarkers, such as steranes and terpanes, were absent in the source rock extracts, indicating the sediments from well Chaiye 2 were at a highly thermal maturity stage. Alternatively, the aromatic hydrocarbons were in relatively high abundance. The naphthalene and methylnaphthalenes of the source rock extracts could reach thousands to tens of thousands $\mu\text{g/g}$ EOM, whereas pentamethylnaphthalenes were below 20 $\mu\text{g/g}$ EOM or even absent, indicating the source rock was at the high maturity stages [19]. Numerous maturity parameters derived from alkyl naphthalenes have been established over the years based on the principle of isomerization that the thermally more stable isomer increases relative to the thermally less stable isomer during thermal maturation processes, such as MNR [=2-MN/1-MN] [20], DNR [= (2,6-DMN + 2,7-DMN)/1,5-DMN] [21], TMNr [=1,3,7-TMN/(1,3,7 + 1,2,5)-TMN] [22], TeMNR [=1,3,6,7-TeMN/(1,3,6,7- + 1,2,5,6- + 1,2,3,5-

TeMn)] [22]), and PMNr [=1,2,4,6,7-PMN/(1,2,4,6,7- + 1,2,3,5,6-PMN)] [22]. As risks arise in the highly mature sediments ($R_o > 1.0\%$) when TeMnR and PMNr parameters are used for maturity assessment [19], parameters derived from methyl-, dimethyl-, and trimethyl-substituted homologues of naphthalene are accepted as valid thermal maturity parameters for the studied samples ($R_o > 1.45\%$). The values of MNR, DNR, and TMNr are in the ranges of 3.00–4.12, 15.0–36.8, and 0.78–0.94, respectively (Figure 4a–c, Table 4).

Figure 4. Distribution of thermal maturity parameters derived from aromatic hydrocarbons of the source rock extracts and crude oil. The oil sample is at a depth of 800–820 m. (a) methylnaphthalene ratio ($MNR = 2\text{-MN}/1\text{-MN}$); (b) dimethylnaphthalene ratio [$DNR = (2,6\text{-DMN} + 2,7\text{-DMN})/1,5\text{-DMN}$]; (c) trimethylnaphthalene ratio [$TMNr = 1,3,7\text{-TMN}/(1,3,7 + 1,2,5)\text{-TMN}$]; (d) methylphenanthrene index [$MPI\text{-}3 = (2\text{-MP} + 3\text{-MP})/(1\text{-MP} + 9\text{-MP})$]; (e) methyldibenzothiophene index ($MDR = 4\text{-MDBT}/1\text{-MDBT}$).

The methylphenanthrene index [$MPI\text{-}1 = 1.5 \times (2\text{-MP} + 3\text{-MP})/(P + 1\text{-MP} + 9\text{-MP})$] proposed by Radke and Welte [23] is one of the most widely used maturity parameters. However, previous study has shown that MPI-1 is invalid in the studied samples due to the involvement of phenanthrene in the maturity parameter formula [24,25]. Instead, MPI-3 [$= (2\text{-MP} + 3\text{-MP})/(1\text{-MP} + 9\text{-MP})$] was still valid in assessing the maturity and therefore was applied in the studied samples. This parameter rests on the β -substituent isomers, which are more thermally stable than the α -substituent counterparts. The MPI-3 values of the source rock extracts range from 3.39 to 5.28 (Figure 4d, Table 4).

As 4-methyldibenzothiophene (4-MDBT) is more thermally stable than 1-MDBT, the methyldibenzothiophene index ($MDR = 4\text{-MDBT}/1\text{-MDBT}$) was hence proposed for thermal maturity assessment [26]. The MDR appears to be very sensitive to thermal maturity due to its excellent correlations with vitrinite reflectance [14]. The source rock extracts have MDR values ranging from 16.8–47.4 (Figure 4e, Table 4).

4.3. Geochemical Characterization of Crude Oil

The alkane distribution of crude oil is dominated by full series of *n*-alkanes ($n\text{-C}_{10}\text{--}n\text{-C}_{35}$) (Figure 3c). The dominant *n*-alkane ($n\text{-C}_{17}$) concentration can reach up to 10,364 $\mu\text{g/g}$ oil. The $\sum n\text{-C}_{20}^-/\sum n\text{-C}_{21}^+$ ratio is 1.35 (Table 4), typical of light oil. There is no odd over even predominance of *n*-alkanes in the crude oil. Isoprenoid alkanes are in much lower abundance than adjacent *n*-alkanes with Pr/Ph, Pr/ $n\text{-C}_{17}$, and Ph/ $n\text{-C}_{18}$ ratios of 2.19, 0.23, and 0.11, respectively (Table 4).

Biomarkers, such as terpanes and steranes, were discovered to decrease in abundance with increasing thermal maturity, reaching equilibrium at the early oil generation stage (before 0.8 %Ro) [27,28]. Hence, most parameters derived from steranes and hopanes are only valid at low thermal maturity levels ($\sim 0.6\%$ Ro) [29]. Steranes and terpanes were abundant in the crude oil sample. The biologically produced $17\alpha(\text{H})$ -trishnorhopane (Tm) was believed to be less stable than $18\alpha(\text{H})$ -trishnorhopane (Ts) and Ts/(Ts + Tm) is

commonly used as the thermal maturity indicator [17]. The $T_s/(T_s + T_m)$ ratio of the crude oil sample is 0.75 (Table 1). Isomerization at C-22 in C_{31} 17 α (H),21 β (H)-homohopanes can be also used for thermal maturity assessment by calculating the 22S/(22S + 22R) ratio, as those with a 22R configuration are gradually converted to a mixture of 22R and 22S diastereomers with increasing thermal maturity [17]. The ratio of C_{31} 22S/(22S + 22R) homohopanes is 0.57 (Table 4), approaching the equilibrium value of 0.6 within the oil generation window. The ratios of C_{29} 20S/(20S + 20R) and C_{29} $\beta\beta$ ($\alpha\alpha + \beta\beta$) steranes were approved to be reliable biomarkers for indicating thermal maturity [30,31]. The ratios of C_{29} 20S (20S + 20R) and C_{29} $\beta\beta$ ($\alpha\alpha + \beta\beta$) steranes of the oil sample are both 0.44 (Table 4), suggesting the oil was approaching thermally mature.

Diamondoid hydrocarbons are a class of petroleum compounds with unique thermal stability. Adamantane and diamantane are well-known diamondoid hydrocarbons with adamantane consisting of cyclohexane rings in ‘chair’ conformation (the diamond subunit) and diamantane containing two subunits. The methyladamantane index [MAI = 1-MA/(1-MA + 2-MA)] was proposed as a thermal maturity indicator by Chen et al. [32]. The MAI ratios increase from initial values of about 50% with increasing thermal maturity. In the studied samples, the liquid oil has an MAI value of 53% while those derived from source rock extracts range from 59% to 78% (Table 4), suggesting the source rocks were much more thermally mature than the liquid oil.

Diamondoid hydrocarbons are neither destroyed nor created with progressive concentrations during thermal cracking, and hence were regarded as a naturally occurring “internal standard” to estimate the extent of oil cracking [33]. Unlike diamondoid hydrocarbons, the biomarkers that were synthesized by oil precursor organisms, such as bacteria and algae, can be easily cracked. The biomarker concentrations decrease with increasing thermal maturity, and some biomarkers were even eliminated before cracking of the major oil components. For example, the concentration of C_{29} 5 α (H),14 α (H),17 α (H)-24-ethylcholestane 20R sterane drops to near zero at about the point where diamondoid hydrocarbon concentrations begin to rise [33], and hence, was used to distinguish low-maturity oils derived from biomarker-rich sources from those of high-maturity, highly cracked, and diamondoid-rich sources. The steranes were quite abundant in the liquid oil whereas they were absent in the source rock extracts due to highly thermal maturation. On the contrary, diamondoid hydrocarbons were highly concentrated in the source rock extracts. The summed concentrations of methyladamantanes (MDs), including 4-MD, 1-MD and 3-MD, range from 33 to 252 $\mu\text{g/g}$ EOM and one sample ($R_o = 1.88\%$) with an abnormal high value of 2419 $\mu\text{g/g}$ EOM. The summed C_{29} steranes in the liquid oil, including C_{29} 5 α (H),14 α (H),17 α (H) 20S sterane, C_{29} 5 α (H),14 β (H),17 β (H) 20R sterane, C_{29} 5 α (H),14 β (H),17 β (H) 20S sterane, and C_{29} 5 α (H),14 α (H),17 α (H) 20R sterane, is 209 $\mu\text{g/g}$ oil in concentration. As is illustrated in Figure 5, the liquid oil was not cracked; however, the source rocks fell into the intense thermal cracking zone with concentrated methyladamantanes.

All the parameters derived from alkylnaphthalenes, including MNR, DNR, and TMNr of the crude oil, have lower values than those of the source rock extracts. The MNR value of the crude oil is 1.60 whereas those in the source rock extracts range from 3.00–4.12 (Figure 4a). Large discrepancy occurs for the DNR ratio where the value of the crude oil is barely 6.08 but ranges from 15.0–36.8 in the source rock extracts (Figure 4b, Table 4), indicating that the crude oil is less thermally mature than the source rocks. The MPI-3 and MDR values of the crude oil are 0.87 and 3.65, respectively, while those from the source rock extracts range from 3.39–5.28 and 16.8–47.4, respectively, inferring the source rocks from well Chaiye 2 are more thermally mature than the crude oil. As verified of type III kerogen of the studied samples (Figure 2b), the equivalent vitrinite reflectance value ($R_c = 0.51 + 0.073 \times \text{MDR}$) derived from MDR is 0.78 % R_o . The existence of abundant biomarkers, together with the very low diamondoid hydrocarbon concentration in oil, further verifies that the equivalent maturity level in oil is much lower than the measured vitrinite reflectance of the source rocks.

Figure 5. Correlation between the concentrations of methyl-diamantanes and C_{29} steranes in liquid oil and source rock extracts from well Chaiye 2 showing the degree of thermal cracking.

4.4. Mineralogy

The mineralogical results (Table 5) show that samples are mainly composed of quartz, calcite, and clay minerals with trace amounts of feldspar, siderite, pyrite, hematite, anatase, or ankerite. Clay minerals and quartz are the predominant compositions in the sedimentary rocks at a depth range of 844.75–1021.7 m from well Chaiye 2, accounting for 20.6–39.0% and 47.6–55.9%, respectively (Table 5). However, samples at the depth of 842.25 and 1031.7 m have trace amounts of quartz and an absence of clay minerals with an overwhelming predominance of calcite (>90%) (Table 5).

Table 5. Quantitative X-ray diffraction analysis of sedimentary rocks from well Chaiye 2.

Depth (m)	Mineral (wt.%)									
	Quartz	Potassium Feldspar	Plagioclase Feldspar	Calcite	Siderite	Pyrite	Hematite	Anatase	Ankerite	Clay Minerals
842.25	1.3	n.d.	n.d.	95.9	n.d.	n.d.	2.8	n.d.	n.d.	n.d.
844.75	50.8	n.d.	3.9	1.9	n.d.	4.4	n.d.	n.d.	n.d.	39.0
905.31	52.1	n.d.	2.0	3.2	2.4	n.d.	n.d.	2.0	n.d.	38.3
927.65	47.6	n.d.	1.2	19.3	n.d.	n.d.	n.d.	n.d.	11.3	20.6
1002.5	55.9	n.d.	1.2	1.9	4.9	n.d.	n.d.	1.7	n.d.	34.4
1021.7	50.1	1.3	5.6	1.3	4.0	2.1	n.d.	n.d.	n.d.	35.6
1031.7	1.5	n.d.	n.d.	91.8	n.d.	n.d.	n.d.	n.d.	6.7	n.d.

n.d., not detected.

The clay minerals of the samples at a depth range of 844.75–1021.7 m mainly consist of illite, kaolinite, and illite-montmorillonite mixed layers (Table 6). Mixed illite-montmorillonite clay is the predominant composition among the clay minerals, ranging from 41% to 73% (Table 6). The montmorillonite content among mixed illite-montmorillonite clay is ranges from 15–30%. Illite and kaolinite account for 15–33% and 6–41%, respectively (Table 6). Neither smectite nor chlorite were detected in the samples.

Table 6. Quantitative X-ray diffraction analysis of clay minerals.

Depth (m)	Clay Mineral (wt.%)					Montmorillonite Clay (wt.%)
	Smectite	I/S	Illite	Kaolinite	Chlorite	I/S
844.75	n.d.	41	18	41	n.d.	30
927.65	n.d.	57	27	16	n.d.	30
905.31	n.d.	73	15	12	n.d.	20
1002.5	n.d.	61	33	6	n.d.	15
1021.7	n.d.	56	19	25	n.d.	25

n.d., not detected. I/S, mixed illite-montmorillonite clay.

5. Discussion

Significant maturity inconsistency occurred amongst source rocks and liquid oil from well Chaiye 2. Source rocks from well Chaiye 2 are characterized by high thermal maturity of 1.45–1.88 %Ro. However, the crude oil is at the normal maturity level with calculated vitrinite reflectance of ca. 0.78%. As the source rocks from well Chaiye 2 were deposited as tight mudstone and shale, it is impossible for petroleum and gas to immigrate, and is probably generated and accumulated autochthonously with a short distance of primary migration.

Generally speaking, the crude oil will encounter thermal cracking at reservoir temperatures above 160 °C (ca. 1.4 %Ro) [34]. How could the liquid oil from well Chaiye 2 be preserved in source rocks of extremely high thermal maturity levels? A reasonable explanation is that liquid oil from well Chaiye 2 was generated at the relatively early thermal maturation stage. However, the thermal evolutions of crude oils and source rocks afterwards were not synchronized due to distinctive impacts of temperature and catalysis on oils and sediments in the shale reservoir.

The thermal maturation of source rocks from well Chaiye 2 has a close relationship with rapid tectonic subsidence and uplifts in the study area [9–11]. Carboniferous source rock was at the hydrocarbon generation stage as early as the Late Carboniferous [9]. Source rocks from well Chaiye 2 were temporarily at a great burial depth in the Carboniferous and herein exposed to high temperatures reaching 160–170 °C in the maximum burial of the Carboniferous (Figure 6). The basin drastically uplifted afterwards (Figure 6) [10] and hydrocarbon generation suspended due to the uplift and erosion of the Carboniferous controlled by the Hercynian and Indochina movements [9]. Hence, the tectonic subsidence exerted a nonnegligible impact on the thermal maturation of the source rocks, timewise [9,35]. The recorded vitrinite was the highest maturity that source rocks had experienced.

Figure 6. Burial and thermal history of well Chaiye 2 (modified after Wang et al. [10]).

When sediment with dispersed organic matter is exposed to high temperatures during burial in a subsiding basin, the organic matter is altered continuously. Thermal maturation of petroleum was the transformation from precursor oil to the more thermodynamically stable products of the gas phase and pyrobitumen [36]. High temperatures contribute to thermal cracking of both crude oils and source rocks. Numerous studies have confirmed that oil is stable to 200 °C [37] given the evidence from field research, laboratory simulations, and theoretical calculations [38–46]. However, the cracking thresholds of source rocks were typically less than 140 °C, much lower than crude oils. Hence, source rock and crude oil in the study area were asynchronous during the thermal maturation, and the source rock was much more thermally mature than crude oil.

Clay catalysis also exerts a significant impact on the differential thermal evolution between oil and source rocks. The kerogen is finely dispersed within the clay matrix of sediments and converted into liquid petroleum hydrocarbons and natural gas with an increasing geothermal gradient during subsequent burial [47–49]. The initial temperature of the liquid petroleum window was recorded as 65 °C [50], at which significant hydrocarbon generation proceeded, and catalysts in petroleum generation therefrom were disclosed. Grim [51] suggested that the clay minerals in shales concentrate organic constituents by absorption, and later act as catalysts in petroleum conversions. The catalyst clay minerals could be montmorillonite [52,53] and smectite (bentonite) [54,55], which promote carbonium ion reactions [56,57], forming free radicals for further rearrangement and hydrocarbon cracking [58–60]. Hence, clay catalysts play a significant role in hydrocarbon generation from kerogen [61]. Clay minerals and quartz predominated in the compositions in the sedimentary rocks of well Chaiye 2 (Table 5). Clay minerals accounted for 20.6–39.0% at a depth range of 844.75–1021.7 m, which consisted of illite, kaolinite, and illite-montmorillonite mixed layers (Table 6). A large amount of clay minerals effectively contributed to hydrocarbon cracking in the sedimentary rocks from well Chaiye 2.

However, hydrocarbons are concentrated in crude oils with minor clay minerals. Catalysis of clay minerals exerted a much lesser impact on the thermal cracking of the crude oils than the sediments where clay catalysts are enriched and dispersed. The clay catalysis probably lowered the activation energies for cracking the hydrocarbon in the sediments [62], and therefore proceeded the thermal maturation process in comparison with crude oils. During the long-term geological history, the thermal maturity disparity of petroleum and source rocks enlarged due to the differential thermal evolution. Liquid hydrocarbons, therefore, were preserved in high-maturity source rocks as disclosed in the Qaidam Basin, NW China. The discovery enlarges the hydrocarbon perseverance of maturity ranges in reservoirs, particularly for the unconventional tight formation, which would benefit potential hydrocarbon exploration of highly mature sediments.

6. Conclusions

Significant maturity inconsistency occurred amongst source rocks and crude oil from well Chaiye 2. Source rocks from well Chaiye 2 are highly thermally mature with measured Ro values of 1.45–1.88%. Source rock extracts are characterized by low-molecular *n*-alkanes and concentrated diamondoid hydrocarbons due to intense thermal cracking but saturated biomarkers including steranes and terpanes were eliminated. However, crude oil, with a full series of *n*-alkanes (*n*-C₁₀–*n*-C₃₅) and abundant steranes and terpanes, was at a normal maturity level with an estimated vitrinite reflectance of ca. 0.78%. As the crude oil was generated and accumulated autochthonously, the source rocks and crude oil encountered differential thermal evolution based on the preliminary results. The source rocks were exposed to high temperatures and accelerated the thermal maturation due to rapid tectonic subsidence. The vitrinite recorded the highest maturity that source rocks have experienced. Meanwhile, the clay minerals in shales concentrate organic constituents by absorption, and the latter act as catalysts in petroleum conversions. However, hydrocarbons are concentrated in crude oils with minor clay minerals. Crude oil has a lower temperature threshold for thermal cracking than source rocks, causing the disparity of the thermal

maturity with source rocks in the Qaidam Basin. Differential thermal evolution between crude oil and source rocks enlarges the hydrocarbon perseverance of maturity ranges in reservoirs, particularly for the unconventional tight formation, which provides favorable prospects for further hydrocarbon exploration of highly mature sediments.

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