

A Mathematical Calculation Model Using Biomarkers to Quantitatively Determine the Relative Source Proportion of Mixed Oils

CHEN Jianping^{1,2,*}, DENG Chunping^{1,2}, SONG Fuqing^{1,2} and ZHANG Dajiang^{1,2}

1 *Research Institute of Petroleum Exploration and Development, PetroChina, PO Box 910, Beijing 100083*

2 *Key Laboratory of Petroleum Geochemistry of CNPC, PO Box 910, Beijing 100083*

Abstract: It is difficult to identify the source(s) of mixed oils from multiple source rocks, and in particular the relative contribution of each source rock. Artificial mixing experiments using typical crude oils and ratios of different biomarkers show that the relative contribution changes are non-linear when two oils with different concentrations of biomarkers mix with each other. This may result in an incorrect conclusion if ratios of biomarkers and a simple binary linear equation are used to calculate the contribution proportion of each end-member to the mixed oil. The changes of biomarker ratios with the mixing proportion of end-member oils in the trinal mixing model are more complex than in the binary mixing model. When four or more oils mix, the contribution proportion of each end-member oil to the mixed oil cannot be calculated using biomarker ratios and a simple formula. Artificial mixing experiments on typical oils reveal that the absolute concentrations of biomarkers in the mixed oil cause a linear change with mixing proportion of each end-member. Mathematical inferences verify such linear changes. Some of the mathematical calculation methods using the absolute concentrations or ratios of biomarkers to quantitatively determine the proportion of each end-member in the mixed oils are deduced from the results of artificial experiments and by theoretical inference. Ratio of two biomarker compounds changes as a hyperbola with the mixing proportion in the binary mixing model, as a hyperboloid in the trinal mixing model, and as a hypersurface when mixing more than three end-members. The mixing proportion of each end-member can be quantitatively determined with these mathematical models, using the absolute concentrations and the ratios of biomarkers. The mathematical calculation model is more economical, convenient, accurate and reliable than conventional artificial mixing methods.

Key words: mixed oil, biomarker, oil source correlation, quantitative determination, mathematical model

1 Introduction

The mixing of oil from different sources is quite common in composite stacked basins (Peters and Moldowan, 1993; Szatmari, 2000; Isaksen et al., 2002; Jiang and Li, 2002; Chen et al., 2003a, b; 2004). The source of oil in some oilfields has been debated for a long time, and mixing of oil from multiple sources may be relevant. However, it is rather difficult to identify the source(s) of mixed oil from multiple source rocks, and in particular the relative contribution of each source rock. In terms of reducing hydrocarbon exploration risk, such studies have considerable economic significance in areas such as the

North Sea (Isaksen et al., 2002), the South Atlantic (Szatmari, 2000), Northwest China (Chen et al., 2003a, b), the East Pearl River Mouth Basin in China (Zhang et al., 2003), and the Bohai Bay Basin, East China (Li et al., 2004).

Dzou et al. (1999) concluded that some oils in the Colombian Central Llanos Basin are mixtures of Cretaceous crude oils (the initial oil charging the reservoirs, but subsequently biodegraded) and Tertiary undegraded oils, on the basis of the existence of the Tertiary age-diagnostic diterpanes and oleanane, and a homologous series of 25-norhopanes. Based on the occurrence of biomarkers such as 24-*n*-propylcholestanes, β -carotane, oleanane, 25-norhopanes, and 24- or 27-nordiacholestanes, Peters et al. (1999) proposed that the crude oil in some

* Corresponding author. E-mail: chenjp@petrochina.com.cn.

sandstone clasts from Brora, Scotland is a mixture of crude oils derived from a Devonian lacustrine source rock and from a Cretaceous or younger, paralic marine shale. Moldowan (2004) showed that the concentration of diamondoid biomarkers and stigmastane can recognize the mixing of post-mature and normally matured sources. George et al. (2004) and Ahmed et al. (2004) suggested that solid bitumens in Late Cretaceous sandstone core from the Subu-1 and Subu-2 wells, Aure Scarp, Papua New Guinea, have two sources, using biomarker characteristics such as rearranged hopanes and steranes, 2-methylhopanes, binorhopanes and dibenzothiophenes.

Peters et al. (1989) calculated the approximate contribution of Middle Jurassic and Devonian source rocks to the Beatrice co-sourced oil from the Inner Moray Firth, UK, using widely differing carbon isotopic compositions of oil and bitumens. To emphasize the problems of quantification, subsequent authors have argued for a purely Devonian source for the Beatrice oil, based on stable carbon isotope ratios for oil fractions compared with fractions of the pyrolysates of the two potential source rocks (Bailey et al., 1990). Having eliminated biodegradation effects, van Aarssen et al. (1999) used methyl-naphthalenes to qualitatively demonstrate intra-reservoir mixing of oils from the same source but expelled at different maturities. Based on steroid and hopanoid biomarker concentrations, Jiang and Li (2002) quantified non-linear mixing of two end-member oils (from the Bakken and Lodgepole source rocks) in the Canadian Williston Basin, the non-linearity deriving from different concentrations of biomarkers in the two source rocks. In addition to biomarkers, binary mixing models were developed for trimethyl-aryl isoprenoids, C_{18} *n*-alkylbenzene, dibenzothiophenes and naphthalenes, phenanthrene and methylbiphenyls. Chen et al. (2003a, b) qualitatively determined the proportion of Permian (lacustrine), Triassic (lacustrine) and Jurassic (coal measure) source rocks to the oil in the Cainan Oilfield, the Junggar Basin, Northwest China, based on steroid and hopanoid biomarker absolute concentrations, stable carbon isotopes of whole oils, and artificial mixing experiments of typical oils. Zhang et al. (2003) calculated the approximate contribution of marine source rocks (Eocene Wenchang Formation) and coal measure source rocks (Eocene Enping

Formation) to some oils from the East Pearl River Mouth Basin in China, using the concentration changes of 4-methylsteranes and bicadinane in artificially mixed oils. Wang et al. (1999) and Li et al. (2004) judged a mixing of immature oil and mature oil using biomarkers, and estimated the approximate contribution of the immature oil and mature oil to the mixed oil in the Subei Basin and the Bamiyan Oilfield, Bohai Bay Basin respectively.

Generally, many studies refer to the mixing of oils from different source rocks, but few attempt to quantify the relative contributions. The quantitative calculations mentioned above usually focused on binary mixing and use a simple equation or an artificial mixing experiment. A ubiquitous method to calculate mixing proportions in binary, trinal or more complicated end-member mixing models has not been established. In fact, artificial mixing experiments take a long time and include a series of complex operations, and their validity depends on the accurate representative of end-member oils and also on experimental precision. Mathematical calculation methods may be more accurate, more economical and more convenient. In this paper, a mathematical calculation method is established, based on the binary and trinal artificial mixing experiments.

2 Samples and Experiments

2.1 Samples

For the artificial mixing experiments, typical end-member crude oil samples derived from three source rocks (Permian, Triassic and Jurassic) were selected on the basis of the previous geochemical study (Chen et al., 2003a, b). The typical Permian-sourced oil is from the Dinan-1 well, the typical Triassic-sourced oil is from the Fu-5 well (4640–4645 m), and the typical Jurassic-sourced oil is from the Mu-5 well. Summary geochemical data on these oils are listed in Table 1. The Permian and Triassic oils have similar carbon isotopic values and Pr/Ph, but have very different gross compositions. The Triassic and Jurassic oils have similar gross compositions, but have different stable carbon isotopic values and Pr/Ph. The three typical end-member oils have similar maturities (R_c from MPI = 0.88%±0.02), but have great differences in the absolute concentration and distribution of biomarkers (Chen et al., 2003a, b). These

Table 1 Geochemical data of the typical end-member oils for the artificial mixing experiments

Typical oil	Well	Sat. (%)	Aro. (%)	Resin (%)	Asp. (%)	$\delta^{13}C_{oil}$ (‰)	Pr/Ph	Pr/nC ₁₇	Ph/nC ₁₈	CPI	C ₂₁ /C ₂₂ ⁺	MPI	R_c (%)
Permian oil (A)	Dinan-1	75.0	9.8	12.3	2.9	−30.8	1.74	0.55	0.35	1.18	2.1	0.81	0.88
Triassic oil (B)	Fu-5	81.7	7.8	7.7	2.8	−30.9	1.75	0.44	0.26	1.19	2.1	0.78	0.87
Jurassic oil (C)	Mu-5	82.4	8.2	6.8	2.6	−27.6	4.00	0.48	0.10	1.20	2.6	0.84	0.90

Note: MPI = methylphenanthrene index; $R_c=0.6 \times MPI+0.4$ (Radke and Welte, 1983; Radke, 1987).

Table 2 Absolute concentrations (columns A to J; $\mu\text{g/g}$) and ratios (columns K to O) of biomarkers in the end-member and mixed oils

No.	A (P)	B (T)	C (J)	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Mix-1	0	100	0	20.7	57.5	112.5	83.0	77.0	299.6	154.9	26.1	15.1	34.6	0.36	0.74	0.26	0.17	0.05
Mix-2	20	80	0	26.2	97.0	201.0	82.9	73.3	432.9	196.1	55.5	24.8	45.9	0.27	0.41	0.17	0.28	0.05
Mix-3	40	60	0	27.7	133.2	309.3	82.7	74.6	590.5	247.2	81.7	35.8	58.5	0.21	0.27	0.13	0.33	0.07
Mix-4	60	40	0	32.2	171.6	394.1	80.9	71.3	718.1	291.3	110.5	47.1	69.4	0.19	0.21	0.10	0.38	0.07
Mix-5	80	20	0	35.7	206.5	486.1	77.4	68.6	849.0	341.8	149.6	58.3	78.6	0.17	0.16	0.08	0.44	0.08
Mix-6	100	0	0	40.0	244.9	590.6	76.5	61.3	997.0	379.7	185.5	72.9	90.2	0.16	0.13	0.06	0.49	0.09
Mix-7	80	0	20	39.2	196.9	522.3	71.4	55.1	871.4	343.8	148.9	60.7	80.7	0.20	0.14	0.06	0.43	0.09
Mix-8	60	0	40	37.0	145.2	426.7	55.7	53.3	695.5	292.9	110.4	46.8	66.5	0.25	0.13	0.08	0.38	0.10
Mix-9	40	0	60	35.8	102.4	368.0	50.9	50.0	593.7	269.0	82.4	36.1	59.0	0.35	0.14	0.08	0.31	0.11
Mix-10	20	0	80	38.3	54.6	281.4	42.2	44.7	453.1	231.3	43.5	22.9	47.7	0.70	0.15	0.10	0.19	0.12
Mix-11	0	0	100	37.0	9.2	190.5	27.0	40.1	311.9	192.7	8.5	7.7	37.0	4.02	0.14	0.13	0.04	0.24
Mix-12	0	20	80	34.8	19.4	171.4	36.8	44.2	298.4	182.1	9.2	7.8	35.6	1.79	0.21	0.15	0.05	0.15
Mix-13	0	40	60	28.4	28.2	148.5	45.4	48.2	286.4	164.5	11.3	9.6	34.1	1.01	0.31	0.17	0.07	0.08
Mix-14	0	60	40	26.8	37.3	133.6	57.4	56.6	289.7	160.2	15.2	11.0	34.9	0.72	0.43	0.20	0.09	0.06
Mix-15	0	80	20	21.5	47.0	108.5	62.7	60.8	270.1	144.7	18.0	12.1	33.1	0.46	0.58	0.23	0.12	0.05
Mix-16	20	60	20	29.1	81.3	206.0	63.7	61.9	405.2	187.6	49.3	21.7	44.1	0.36	0.31	0.15	0.26	0.07
Mix-17	40	40	20	29.2	116.5	299.9	67.0	65.7	552.0	237.6	77.9	31.1	56.2	0.25	0.22	0.12	0.33	0.07
Mix-18	60	20	20	35.7	156.1	406.6	68.4	59.0	699.9	287.8	107.9	48.0	67.9	0.23	0.17	0.08	0.37	0.08
Mix-19	40	20	40	36.5	111.2	322.8	53.9	51.6	556.9	247.2	79.5	29.7	56.2	0.33	0.17	0.09	0.32	0.08
Mix-20	20	20	60	35.6	67.1	251.0	47.2	50.5	433.7	214.3	42.0	19.5	46.5	0.53	0.19	0.12	0.20	0.08
Mix-21	20	40	40	32.1	75.3	223.9	57.0	55.3	424.8	204.0	50.2	21.2	46.4	0.43	0.25	0.13	0.25	0.07

Note: A (P) = Proportion of the Permian oil (%); B (T) = Proportion of the Triassic oil (%); C (J) = Proportion of the Jurassic oil (%); A = C_{19} tricyclic terpane; B = C_{21} tricyclic terpane; C = $17(\alpha)\text{-C}_{29}$ hopane; D = C_{29}Ts ; E = C_{30} diahopane; F = $17(\alpha)\text{-C}_{30}$ hopane; G = $17(\alpha)\text{-C}_{31}$ hopane; H = Gammacerane; I = $aaa\text{-C}_{28}$ sterane 20R; J = $aaa\text{-C}_{29}$ sterane 20R; K = C_{19} tricyclic / C_{21} tricyclic; L = $\text{C}_{29}\text{Ts} / 17(\alpha)\text{-C}_{29}$ hopane; M = C_{30} diahopane / C_{30} hopane; N = Gammacerane / $17(\alpha)\text{-C}_{31}$ hopanes (20S+20R); O = $aaa\text{-C}_{28}$ sterane 20R / $aaa\text{-C}_{29}$ sterane 20R.

oils provide a firm base for us to observe the trends of biomarker changes with changes in the mixing proportions of the mixed oils.

2.2 Experiments

These oils were used as the end-member for producing 18 different mixtures (mixed oils). The mixing proportions and numbering system are listed in Fig. 1 and Table 2. Crude oils were measured by weight (about 500 mg). The three end-member crude oils and the 18 mixtures were analyzed for whole-oil carbon isotopic compositions, and by gas chromatography (GC: whole oil and saturated hydrocarbons) and gas chromatography–mass spectrometry (GC–MS: saturated and aromatic hydrocarbons) (Table 2). The instrumentation, analytical conditions and quantification methods have been described in the previous paper (Chen et al., 2003a, b, 2004).

3 Experimental Results and Discussion

Taking the artificial mixing of the Permian oil and the Jurassic oil as an example, with an increasing proportion of the Jurassic oil the absolute concentrations of various biomarkers in the mixed oils show linear changes with

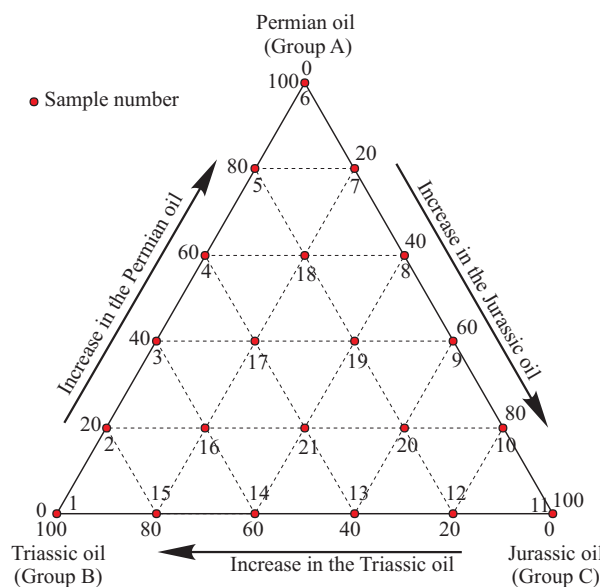


Fig. 1. Ternary diagram showing the proportion and location of the artificially mixed oil samples.

different slopes (Fig. 2a and b). The larger the absolute concentration difference of biomarkers in the two end-member oils, the steeper the slope of the lines. For example, the absolute concentration of C_{21} tricyclic terpane is 245

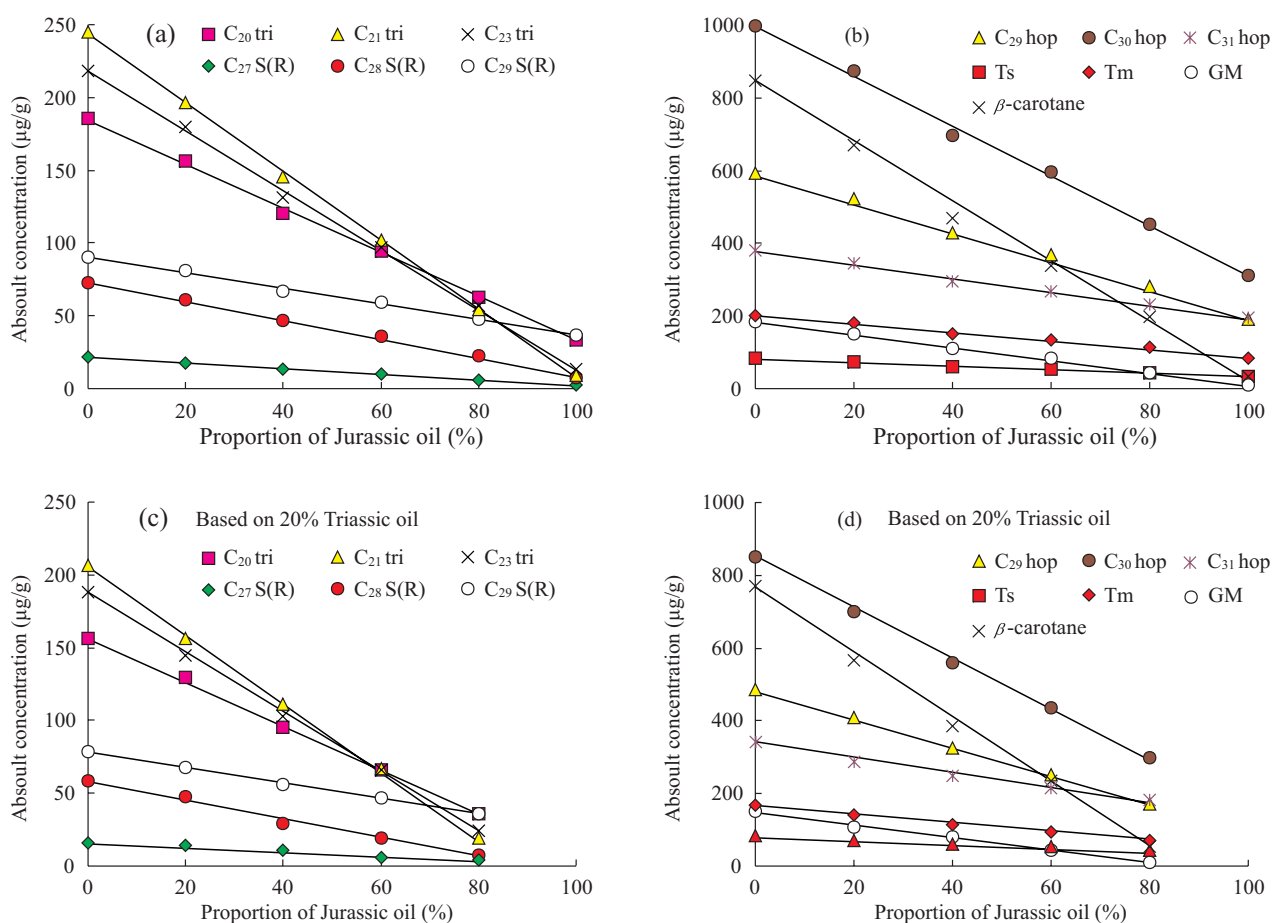


Fig. 2. Trends of absolute concentration of some biomarkers with the mixing proportion of oils. (a) and (b): Binary mixing of the Permian and Jurassic oils; (c) and (d): Trinal mixing of Permian oil and Jurassic oil based on 20% Triassic oil.

C₂₀ tri — C₂₀ tricyclic terpene; C₂₁ tri — C₂₁ tricyclic terpene; C₂₃ tri — C₂₃ tricyclic terpene; C₂₇ S(R) — *aaa*-C₂₇ sterane 20R; C₂₈ S(R) — *aaa*-C₂₈ sterane 20R; C₂₉ S(R) — *aaa*-C₂₉ sterane 20R; C₂₉ hop — $\alpha\beta$ -C₂₉ hopane; C₃₀ hop — $\alpha\beta$ -C₃₀ hopane; C₃₁ hop — $\alpha\beta$ -C₃₁ hopanes; GM — gammacerane.

μg/g in the Permian oil and 9 μg/g in the Jurassic oil, and it rapidly drops to 145 μg/g when 40% of the Jurassic oil is mixed with 60% of the Permian oil. In contrast, the absolute concentration of *aaa*-C₂₉ sterane 20R is about 90 μg/g in the Permian oil and 37 μg/g in the Jurassic oil, and it slowly reduces to 66.5 μg/g when 40% of Jurassic oil is mixed into the Permian oil. The change in the absolute concentration of the former is obviously greater than that in the latter. In fact, the concentration changes of the biomarkers obey the basic chemical principle of consistency, when two oils with different biomarker contents mix. Therefore, when three or more oils mix, the absolute concentration of biomarkers in the mixed oil has a linear relationship with the proportion of each end-member oil. For instance, if 20% of the Triassic oil is kept constantly, the absolute concentration of biomarkers in the mixed oils still changes linearly when a proportion of the Jurassic oil is mixed into the Permian oil (Fig. 2c and d).

On the other hand, the ratio of two different biomarkers changes in a non-linear fashion with the proportion of each end-member, and different ratios show different extended

trends (Fig. 3). For instance, when the Jurassic oil is mixed with the Permian oil, the C₁₉ tricyclic terpene/C₂₁ tricyclic terpene ratio of the mixed oil initially increases slowly with increasing proportion of the Jurassic oil, but then increases rapidly when the proportion of the Jurassic oil exceeds 80% in the mixed oil (Fig. 3a). The ratio shows a similar trend but with different slope when the Jurassic oil is mixed into the Triassic oil. Some ratios, for example, C₃₀ dihopane/C₃₀ hopane (Fig. 3b), show completely different trends when the Jurassic oil is mixed into (1) the Permian oil and (2) the Triassic oil. Therefore, we can conclude that extended trends of different biomarker ratios in mixed oils are strongly controlled by the absolute concentration of the related biomarkers in the end-member oils. Furthermore, changes of biomarker ratios in mixed oils will be very complex when three or more crude oils mix.

Commonly, biomarker ratios and not absolute concentrations are used to judge the sedimentary environments of source rocks, to determine the maturity of oils or source rocks, and to make oil-oil or oil-source rock correlations. However, it is very difficult to use a simple

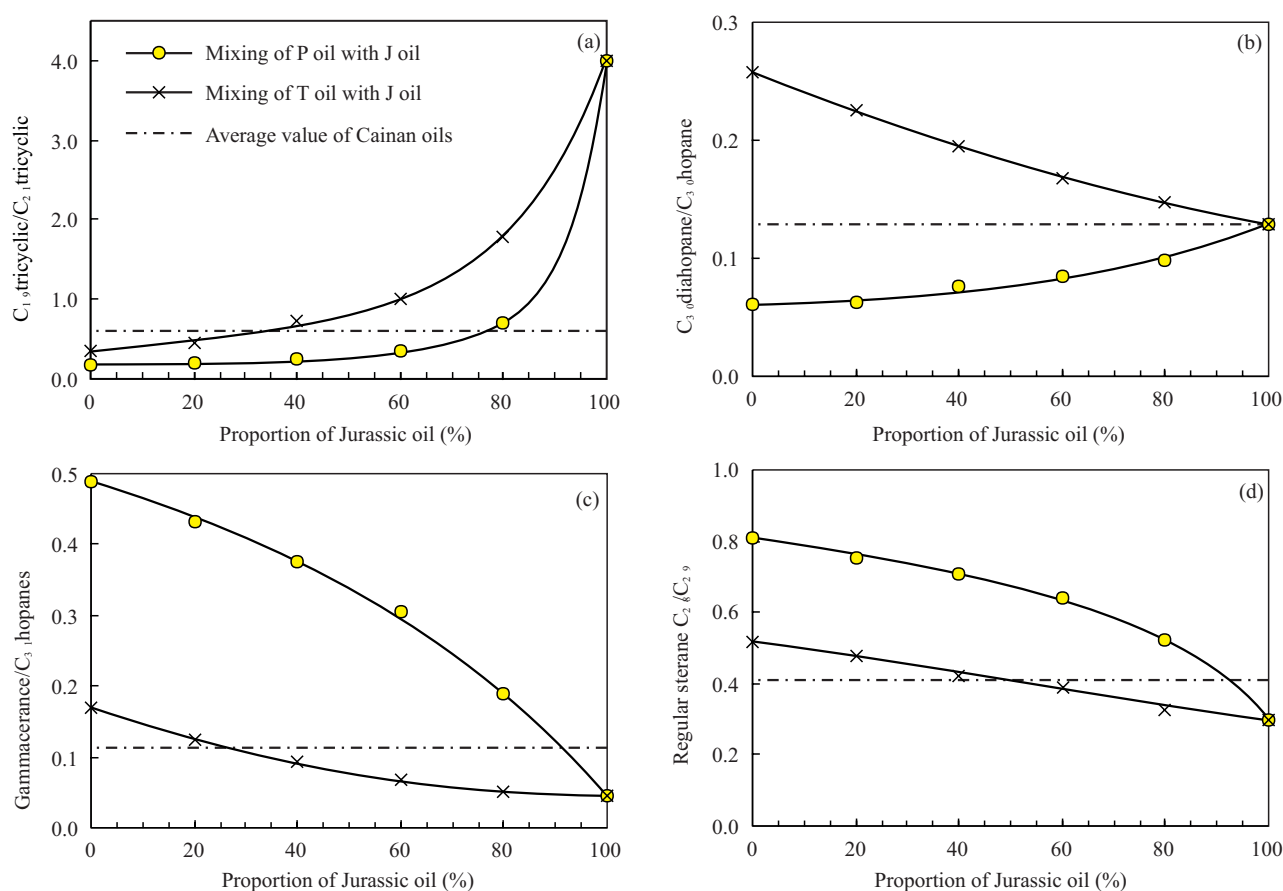


Fig. 3. Trends of some biomarker ratios with the mixing proportion of oils. (a) C_{19} tricyclic terpene/ C_{21} tricyclic terpene; (b) C_{30} diahopane/ C_{30} hopane; (c) Gammacerane/ C_{31} hopanes; (d) C_{28}/C_{29} regular steranes.

linear formula and biomarker ratio to calculate the contribution proportion of each end-member oil to a binary mixed oil. It will be much more difficult and complex to quantitatively determine the contribution proportion of each end-member oil to the mixed oil produced by three or more end-member oils.

4 Mathematical Calculation Model

From the observation of the artificial mixing experiments and by mathematical inference, it can be shown that the absolute concentration of biomarkers in a mixed oil has a linear relation with the mixing proportion of each end-member oil. A mathematical calculation model can be developed for binary mixing, trinal mixing and the mixing of more end-member oils.

4.1 Binary mixing model

The basis of the mathematical calculation model of binary mixing of end-member oils is shown in Fig. 4. The two end-member oils are Oil 1 and Oil 2, and a_1 , a_2 , and C represent the absolute concentration of a biomarker in the two oils and their mixed oil, respectively. Theoretically, the

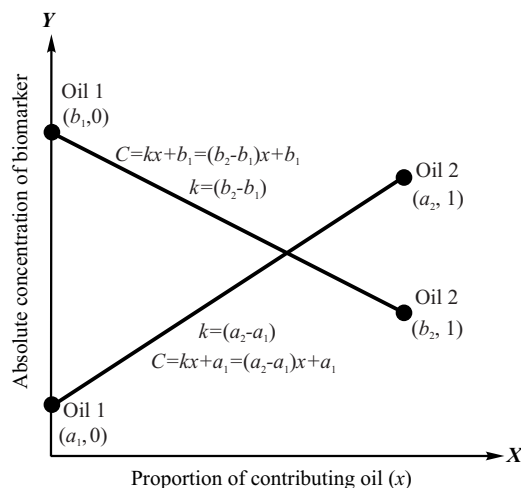


Fig. 4. Mathematical model for binary mixing.

absolute concentration (C) of the biomarker in the mixed oil is positively proportional to the absolute concentrations (a_1 , a_2) of the biomarker in the two oils and the proportion of Oil 1 ($1-x$) and the proportion of Oil 2 (x), that is:

$$C = a_1(1-x) + a_2x \quad (0 \leq x \leq 1) \quad (1)$$

Transforming the above formula, we can get the following:

$$C = (a_2 - a_1)x + a_1 \quad (0 \leq x \leq 1) \quad (2)$$

where $(a_2 - a_1)$ is the slope of the line.

Therefore, the formula to calculate the mixing proportion (x) of Oil 2 is:

$$x = (C - a_1) / (a_2 - a_1) \quad (3)$$

Nevertheless, biomarker ratios are usually obtained from routine GC-MS analysis, and ratios are used to interpret the sedimentary environments of source rocks, to make oil-source correlations, and so on. Therefore, biomarker ratios and the above formula cannot be directly used to calculate the contribution proportion of each end-member oils to their mixed oil.

If selecting two different biomarker compounds, A and B, in the end-member oils, we can get two formulae as the following:

$$C_A = (a_2 - a_1)x + a_1 \quad \text{and} \quad C_B = (b_2 - b_1)x + b_1$$

In the above formulae, a_1 , a_2 , b_1 , and b_2 represent the absolute concentration of two biomarkers in the two end-member oils, Oil 1 and Oil 2, respectively. C_A and C_B represent the absolute concentrations of the compounds A and B in the mixed oil. The ratio (R) of compound A to compound B in the mixed oil is:

$$R = \frac{C_A}{C_B}, \text{ that is, } R = \frac{(a_2 - a_1)x + a_1}{(b_2 - b_1)x + b_1} \quad (4)$$

The above formula (4) represents a hyperbola between the ratio R and the mixing proportion x , and it describes the result of the artificial mixing experiment very well.

Transforming the form of the formula (4), the following formula is obtained:

$$x = \frac{a_1 - b_1 R}{(b_2 - b_1)R - (a_2 - a_1)} \quad (5)$$

For a basin or an area, the average concentration of many biomarkers in various oils can be obtained by analysis of several oil samples. Then, the proportion (x) of the end-member oil in the binary mixed oil can easily be calculated with biomarker ratios, using the above formula (5). Furthermore, many biomarker ratios can be used, so as to better constrain the proportion of two end-member oils to the mixed oil.

For example, the absolute concentration of compound A (a_1 , a_2) is 21 $\mu\text{g/g}$ and 39 $\mu\text{g/g}$ in the end-member Oil 1 and Oil 2 (Fig. 5a), and the absolute concentration of compound B (b_1 , b_2) is 57 $\mu\text{g/g}$ and 9 $\mu\text{g/g}$, respectively. From the above formula (4) or (5), the function of mixing proportion (x) and the ratio of the compound A to compound B (R) can be obtained, that is:

$$R = (6x + 7) / (19 - 16x)$$

or,

$$x = (19R - 7) / (16R + 6)$$

The extended trend drawn by the above formula completely fits the results of the artificial experiment (Fig. 5).

4.2 Trinal mixing model

For the trinal mixing model, the three end-member oils are Oil 1, Oil 2 and Oil 3, and the absolute concentrations of the biomarker compound A are a_1 , a_2 and a_3 respectively. The function of the concentration (C) of compound A and the mixing proportion (x , y , z) of each end-member oil in their mixed oil can be described as the following:

$$\begin{cases} C = a_1x + a_2y + a_3z \\ x + y + z = 1 \end{cases} \quad (0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 1) \quad (6)$$

Transforming the formula (6), the follow formula group is obtained:

$$\begin{cases} C = (a_1 - a_3)x + (a_2 - a_3)y + a_3 \\ C = (a_1 - a_2)x + (a_3 - a_2)z + a_2 \\ C = (a_2 - a_1)y + (a_3 - a_1)z + a_1 \end{cases} \quad (7)$$

Figure 6 demonstrates the above two formula groups very well. The concentration (C) of a compound in the mixed oil is bounded within the triangle plane (a_1 , a_2 , a_3). The three dashed lines present the three formulae in the above formula group (7), respectively. Clearly, the mixing of three oils is much more complex than the binary mixing.

From the formula group (6) or (7), we cannot calculate the contribution proportion of each end-member oil to the mixed oil. Fortunately, there are many different biomarkers and these have different absolute concentrations in crude oils. If selecting two biomarker compounds A and B with different concentrations, the following equation groups can be written:

$$\begin{cases} C_A = a_1x + a_2y + a_3z \\ C_B = b_1x + b_2y + b_3z \\ x + y + z = 1 \end{cases} \quad (8)$$

or,

$$\begin{cases} C_A = (a_1 - a_3)x + (a_2 - a_3)y + a_3 \\ C_B = (b_1 - b_3)x + (b_2 - b_3)y + b_3 \end{cases} \quad (9)$$

where C_A and C_B are the absolute concentrations of the two biomarkers in the mixed oil. The mixing proportion of each end-member oil can be calculated by resolving the above formula groups with two biomarkers.

Thus, from the equation group (8), the ratio of the two compounds can be calculated:

$$R = \frac{a_1x + a_2y + a_3z}{b_1x + b_2y + b_3z} \quad (0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 1; x + y + z = 1) \quad (10)$$

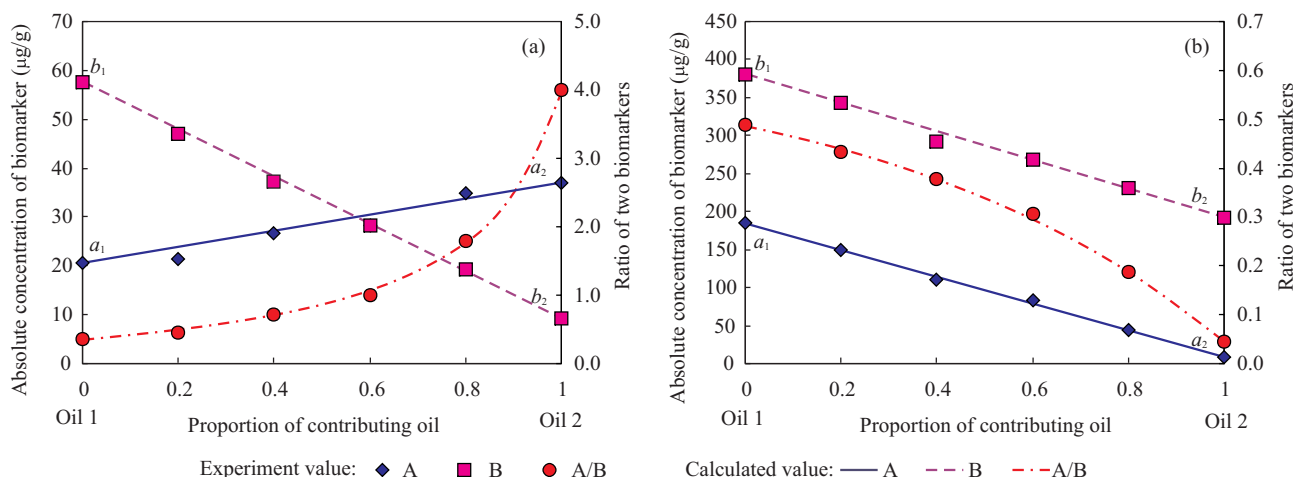


Fig. 5. Comparison of absolute concentrations ($\mu\text{g/g}$) and biomarker ratios for calculated values and experimental values, and variation of different biomarker ratios with the mixing proportion in the mixed oils.

or,

$$R = \frac{(a_1 - a_3)x + (a_2 - a_3)y + a_3}{(b_1 - b_3)x + (b_2 - b_3)y + b_3} \quad (11)$$

The above formulae (10) and (11) demonstrate that the ratio of biomarkers presents a very complex non-linear curve, with the mixing proportion of each end-member oil in the trinal-mixed oil. The mixing proportion cannot be calculated by only using a biomarker ratio. If three or four biomarker compounds are selected, two ratios can be written as follows:

$$\begin{cases} R_1 = \frac{(a_1 - a_3)x + (a_2 - a_3)y + a_3}{(b_1 - b_3)x + (b_2 - b_3)y + b_3} \\ R_2 = \frac{(c_1 - c_3)x + (c_2 - c_3)y + c_3}{(d_1 - d_3)x + (d_2 - d_3)y + d_3} \end{cases} \quad (12)$$

In the above equation groups, a , b , c and d represent the absolute concentrations of four biomarkers in the three end-member oils, respectively. R_1 and R_2 are the ratios of the four biomarkers in the mixed oil. The mixing proportion x , y and z can be calculated by any of the above two equation groups (9) and (12).

4.3 The mixing model for multiple end-member oils

For a mixing model of four or more end-member oils (n), the equation to calculate the mixing proportion x_i is:

$$\begin{cases} C = a_1x_1 + a_2x_2 + \cdots + a_ix_i + \cdots + a_nx_n \\ x_1 + x_2 + \cdots + x_i + \cdots + x_n = 1 \end{cases} \quad (0 \leq x_i \leq 1) \quad (13)$$

Selecting m biomarkers ($m = n-1$) with different concentrations allows the following equation group to be written:

$$\begin{cases} C_1 = a_{11}x_1 + a_{12}x_2 + \cdots + a_{1i}x_i + \cdots + a_{1n}x_n \\ C_2 = a_{21}x_1 + a_{22}x_2 + \cdots + a_{2i}x_i + \cdots + a_{2n}x_n \\ \vdots \\ C_j = a_{j1}x_1 + a_{j2}x_2 + \cdots + a_{ji}x_i + \cdots + a_{jn}x_n \\ \vdots \\ C_m = a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mi}x_i + \cdots + a_{mn}x_n \\ x_1 + x_2 + \cdots + x_i + \cdots + x_n = 1 \end{cases} \quad (14)$$

In the above equation group, a_i or a_{ji} represents the absolute concentration of the selected biomarker in the n end-member oil. C_j is the absolute concentration of the selected biomarker in the mixed oil. The mixing proportion x_i can be calculated by the above equation group.

If selecting m biomarkers ($m=n$) with different concentrations, the following matrix can be written and the mixing proportion can be easily calculated:

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{j1} & a_{j2} & a_{j3} & \cdots & a_{jn} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{m1} & a_{m2} & a_{m3} & \cdots & a_{mn} \end{bmatrix} \times \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_i \\ \vdots \\ x_n \end{bmatrix} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_j \\ \vdots \\ C_m \end{bmatrix} \quad (15)$$

5 Case Studies of Applications of the Mathematical Calculation Method

5.1 Case 1: binary mixing, the PL19-3 Oilfield, Bohai Bay Basin

The PL19-3 Oilfield is located at the Bonan uplift, the Bohai Bay Basin. According to Deng (2002) and Song et al.

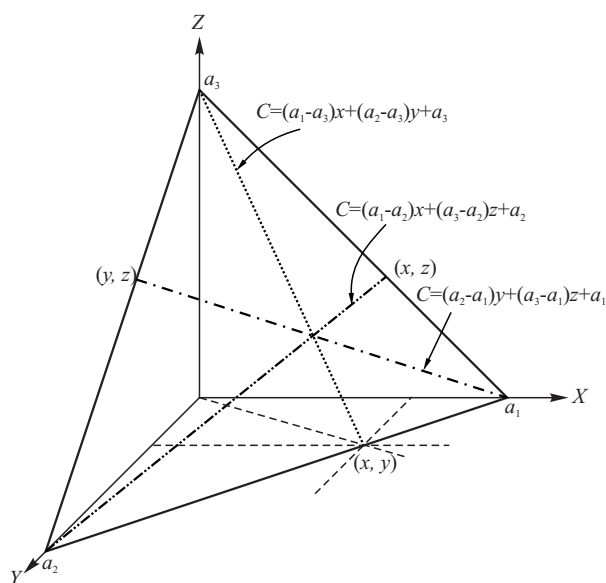


Fig. 6. Mathematical model for trinal mixing.

(2004), possible oil-source rocks of the oilfield are the Eocene Dongying Formation and Shahejie Formation. The study of source rocks and oils in the area indicates that triaromatic steroids and triaromatic dinosteroids can distinguish the Dongying source rocks from the Shahejie source rocks (Song et al., 2004; Wang et al., 2004). However, the oils in the PL19-3 Oilfield are a mixture of oils from the Dongying and the Shahejie source rocks (Song et al., 2004; Wang et al., 2004). GC and GC-MS analyses of five oils from the four wells at the oilfield indicate that these oils all contain significant amounts of 25-norhopane (25-norhopane/ C_{29} hopane ratio ranging from 0.1–0.5) and are biodegraded oils, but aromatic steroids are not biodegraded (Song et al., 2004).

The concentrations of triaromatic steroids and triaromatic dinosteroids are respectively 234 $\mu\text{g/g}$ and 40 $\mu\text{g/g}$ in the typical oils from the Dongying source rocks, and 21 $\mu\text{g/g}$ and 18 $\mu\text{g/g}$ in the typical oils from the Shahejie source rocks. The ratio of triaromatic steroids to triaromatic dinosteroids of the oils from the PL19-3 Oilfield is 3.2. Using the formula (5), the proportion of the Shahejie source rocks that contributed to the PL19-3 mixed oils is 75%, and the other 25% of the mixed oils is derived from the Dongying source rocks. This calculated conclusion fits very well with the result obtained by the artificial mixing experiment (Song et al., 2004).

5.2 Case 2: trinal mixing, Cainan Oilfield, eastern Junggar Basin

According to the previous study (Chen et al., 2003a, b, 2004), there are four generative hydrocarbon source rocks of Carboniferous, Permian, Triassic, and Jurassic ages in

the east of the Junggar Basin. The previous geochemical study has shown that these source rocks have generated five groups of oil. The first group of crude oils is derived from the Permian, the second group from the Triassic, the third group from the Jurassic source rocks, and the fifth group from the Carboniferous. The geochemical properties of the fourth group of oils are intermediate between those of typical Permian, Triassic and Jurassic oils, and are thought to be mixed oils derived from multiple source rocks, including the Permian, Triassic and Jurassic. The oils in the Cainan Oilfield belong to this fourth group.

Permian oils have low Pr/Ph ratios, and are rich in β -carotane, tricyclic terpanes, gammacerane and C_{28} and C_{29} steranes. They contain almost no diasteranes and have a low content of C_{27} steranes, Ts and C_{29} Ts (Chen et al., 2003a, b, 2004). Triassic oils are characteristically rich in Ts, C_{29} Ts and diahopanes, and have low gammacerane contents. Jurassic oils have Pr/Ph ratios generally > 3.0 , and are rich in pentacyclic hopanes, C_{19} and C_{20} tricyclic terpanes, and C_{29} steranes, but poor in tricyclic terpanes above C_{21} , gammacerane, and C_{27} and C_{28} steranes (Chen et al., 2003a, b, 2004). Therefore, by selecting any two ratios from C_{19} tricyclic/ C_{21} tricyclic, C_{29} Ts/ C_{29} hopane, to gammacerane/ C_{31} hopane, the proportionate contribution of the Permian, Triassic and Jurassic source rocks to the mixed oils in the Cainan Oilfield can be calculated.

The average absolute concentrations of biomarkers such as C_{19} tricyclic terpane, C_{21} tricyclic terpane, C_{29} hopane and C_{29} Ts in the Permian, Triassic and Jurassic oils are listed in Table 3. The ratios of C_{19} tricyclic/ C_{21} tricyclic and C_{29} Ts/ C_{29} hopane are 0.58 and 0.19 in the Cainan oils, respectively. By calculating using these data and the formula group (12), 64% of the oil in the Cainan Oilfield is from a Jurassic source, 16% is derived from the Triassic source rocks, and 20% is derived from the Permian source rocks. The results conform very well with those (65%, 15% and 20%) obtained by the artificial mixing experiment (Chen et al., 2003a, b, 2004).

6 Advantages of the Mathematical Calculation Model and Its Application Prospect

The following are the advantages of using the mathematical calculation method for determining the proportion of each end-member oil to the mixed oil, and

Table 3 Average absolute concentrations ($\mu\text{g/g}$) of some biomarkers in the oils of the eastern Junggar Basin

Oil group	C_{19} tricyclic terpane	C_{21} tricyclic terpane	C_{29} hopane	C_{29} Ts
Permian oil	22	148	424	63
Triassic oil	19	62	110	68
Jurassic oil	33	12	201	32

exhibit a wide application prospect.

(1) It is a theoretical calculating method, and is available without any of complex artificial mixing experiment, which must run a series of complex experimental processes with a large number of oil samples and depends on the accuracy of the experiment. It is difficult to chart the relation between mixing proportions and biomarker ratios for the mixing of more than two end-member oils. The mathematical calculation model can be applied for resolving the complicated problems of multi-source mixing, and is more economical, convenient and accurate than conventional artificial mixing methods.

(2) The key whether or not the plates or charts created by the artificial mixing experiment data are applicable and reliable depends on the representativeness of the selected typical oil. Although an oil family have similar biomarker characteristics, when an oil sample is selected as the typical end-member oil, it is still difficult to ensure that the selected oil can well represent the absolute concentrations of the oil family, by reason of their different maturity and a relatively wide range of absolute concentrations of biomarkers in the oil family. The mathematical calculation model can take the average concentration of oils in an area as the typical value of the end-member oil family, which is more representative and reliable.

(3) It is very easy to create suitable calculating formula or charts for different areas or basins, based on analyses of the absolute concentrations of biomarkers of oils in reservoirs of an area or a basin.

(4) It is not only suitable for calculating the contributions of non-biodegraded oil to a mixed oil, but is also suitable for calculating the contributions of biodegraded oil in which biomarkers are not degraded.

(5) It can also apply to determining the product proportion of each oil layer in a reservoir with multiple oil layers during oilfield development, in terms of absolute concentrations of distinctive compounds contained in oils of each oil layer.

7 Conclusion

Artificial mixing experiments using typical crude oils show that the absolute concentrations of biomarkers in the mixed oil change linearly with the mixing proportion, but the ratios of different biomarkers vary non-linearly when two oils with different concentrations of biomarkers mix with each other. This may result in an incorrect conclusion if using biomarker ratios and simple binary linear equations to calculate the contribution proportion of each end-member to the mixed oil. The function of biomarker ratios to the mixing proportion of end-member oils is a hyperbola in the binary mixing model, a hyperboloid in the trinal

mixing model, and a hypersurface in the mixing of more than three end-members. Using the absolute concentration or the biomarker ratio, the mixing proportion of each end-member oil can be quantitatively determined by these mathematical models. The mathematical calculation model is more economical, convenient, accurate and reliable than conventional artificial mixing methods.

In the PL19-3 Oilfield in the Bohai Bay Basin, the proportion of the Shahejie source rocks to the PL19-3 mixed oils is 75%, and that of the Dongying source rocks is 25%. In the Cainan Oilfield in the eastern Junggar Basin, 64% of the mixed oil is derived from Jurassic source rocks, 16% from Triassic source rocks, and 20% from Permian source rocks.

Manuscript received Jan. 20, 2006

accepted March 14, 2006

edited by Zhu Xiling

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