



Research paper

Characteristics and origin of carbon isotopes of n-alkanes in crude oils from the western Pearl River Mouth Basin, South China sea



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ABSTRACT

The quantitative characterization of carbon isotopes of n-alkanes is commonly carried out in organic geochemical studies. Possible controls on carbon isotopes include source organic matter, maturity, fractionation during oil expulsion and migration, and the mixing of different oils. In this study of the origin of crude oils in the western Pearl River Mouth Basin, the influences of all of these factors have been considered in reaching a conclusion. Carbon isotopes of n-alkanes in the crude oils, and the extracts of the two effective source rocks (the Wenchang and Enping formations) in the basin, exhibit clear differences. The Wenchang source rocks have heavy $\delta^{13}\text{C}$ values that remain almost constant or become slightly heavier with increasing carbon number. The Enping source rocks have light $\delta^{13}\text{C}$ values that become lighter with increasing carbon number. Two groups of oils in this area were identified based on the carbon isotopes of the n-alkanes; grouploils are similar to extracts of the Wenchang source rocks. However, the grouploils are different from both the Wenchang and Enping source rocks and the carbon isotopic profiles of their n-alkanes exhibit a “V” feature with increasing carbon number. The results of artificial thermal maturation experiments indicate that, from the early stage to the peak stage of oil generation (with EasyRo between 0.64% and 1.02%), the $\delta^{13}\text{C}$ values of n-alkanes in the pyrolysis oils become heavier by about 3‰ with increasing thermal maturity, but the shape of the carbon isotopic profiles are not significantly changed. Calculated $\delta^{13}\text{C}$ values of n-alkanes in “mixed” artificial pyrolysis oils indicate that the mixture of oils generated from the same source rocks with different maturities could not change the carbon isotopic profile of the n-alkanes, however, a mixing of the Wenchang and Enping oils could give the “V” feature in the profiles, similar to the grouploils in this area. The grouploils appear to be mixed Wenchang and Enping oils, the latter being the dominant component in the mixture. We conclude that the source organic matter and the degree of mixing are the main factors controlling the carbon isotopic characteristics of n-alkanes in crude oils in the western Pearl River Mouth Basin.

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1. Introduction

The values and profiles of carbon isotopes of n-alkanes have been extensively used in oil-source rock correlations (Odden et al., 2002; Li and Guo, 2010), in identifying effective source rocks (Rielely et al., 1991; Murray et al., 1994; Xiong and Geng, 2000) and for paleoenvironment and paleoclimate reconstructions (Sofer, 1984; Schoell et al., 1994; Ruble et al., 1994). However, under geological conditions, there are several factors influencing the carbon isotopic

characteristics of n-alkanes in crude oils, and in the extracts of source rocks, including source organic matter (Sofer, 1984; Boreham et al., 1994; Collister et al., 1994; Murray et al., 1994; Odden et al., 2002), maturity (Bjørøy et al., 1991, 1992; Clayton, 1991; Clayton and Bjørøy, 1994; Tang et al., 2005; Schwab et al., 2005), fractionation in oil expulsion and migration (Xiong et al., 2001; Liao et al., 2004), and the mixture of different oils (Rooney et al., 1998; Li and Guo, 2010). The numerous factors controlling the carbon isotopic characteristics of n-alkanes and the lack of detailed research on mixed oils, including oils generated from the same source rocks with different maturities, and oils contributed from different source organic matter, have restricted the usefulness of this parameter in organic geochemistry.

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The western Pearl River Mouth Basin is a multi-sourced petroleum system with several sedimentary sags and two source rock formations, which have different organic phases and development characteristics in different sags. The groups of oils and the oil-source relationships within this area are complicated due to several episodes of petroleum generation and accumulation (Zhu et al., 1999; Gong and Li, 1997, 2004; Huang et al., 2003, 2007; Cheng et al., 2013a). Biomarkers have been commonly used to identify the source rocks and discriminate groups of different crude oils in the western Pearl River Mouth Basin (Huang et al., 2003, 2007; Cheng et al., 2013a), however, there is a lack of detailed research on carbon isotopes of n-alkanes in the crude oils and source rocks. In this study, carbon isotopic characteristics of n-alkanes in crude oils and extracts from typical source rocks in the western Pearl River Mouth Basin (Fig. 1) were investigated, and in combination with petroleum generation histories in this area, the origin of the carbon isotopic profiles of the n-alkanes in crude oils in this area was identified. This research also provides new evidence for the identification of source rocks, and discrimination of the groups of crude oils, as well as the pool-forming mechanism in the western Pearl River Mouth Basin.

2. Geological background

Several papers have reported on the geology of the western Pearl River Mouth Basin (Zhu et al., 1999; Huang et al., 2003, 2007; Gan et al., 2009a; Cheng et al., 2013a). The main characteristics of this area as related to our research are briefly summarized as follows. The Pearl River Mouth Basin is separated into two sections by longitude E113°10', located at the northern edges of the continental shelf, South China Sea. The western Pearl River Mouth Basin has eight structural divisions (Fig. 1), among which the Wenchang A

and Wenchang B sags are the main hydrocarbon-generating sags. The thicknesses of sedimentary formations are distinctly different in the two sags. The Wenchang A sag has a current burial depth of 7000–9000 m in the centre and 4000–7000 m at the margin, and the Wenchang B sag has current burial depths of 4000–7000 m and 2000–3000 m respectively in the central and marginal areas (Lin and Sun, 1999; Gong and Li, 1997, 2004). The Yangjiang uplift, Qionghai uplift and Shenhu uplift are three sub-uplifts in this area which are the important accumulation areas for oil and gas. Several commercial oil pools have been discovered in the western Pearl River Mouth Basin (Fig. 1).

The dominant depositional environment of the western Pearl River Mouth Basin changed from lacustrine in the Eocene and early Oligocene, through to a bay in the late Oligocene, then to an open marine setting after the Oligocene, during which time the source rocks of the Wenchang and Enping formations, the reservoir sandstones of the Zhuhai and Zhujiang formations, and the seal rocks of the Hanjiang and Yuehai formations were deposited (Zhu et al., 1999; Gong and Li, 1997, 2004). These sedimentary formations comprise a vertical source–reservoir–seal sequence (Fig. 2). There were two tectonic stages in this region, an early rifting stage (before 30 Ma) and a later depression stage (after 30 Ma), and structural activity continued to the end of the middle Miocene, so that most of the structural traps in the western Pearl River Mouth Basin only became established since the late Miocene (Wang and Zhang, 1999; Gong and Li, 2004; Cai, 2005).

3. Samples and methods

3.1. Geological samples

Thirty-two crude oil samples were selected from twenty-one oil pools in different areas of the western Pearl River Mouth Basin

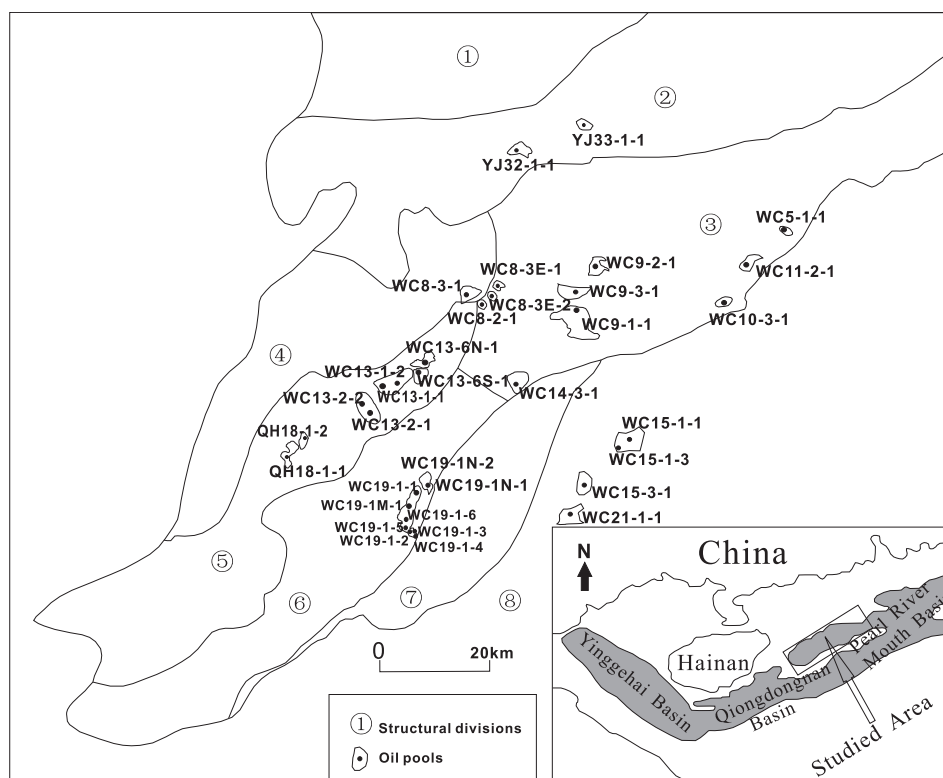


Fig. 1. Map showing the location of the structural divisions of the western Pearl River Mouth Basin: ①Yangjiang Sag; ②Yangjiang Uplift; ③Wenchang A Sag; ④Qionghai Sag; ⑤Qionghai Uplift; ⑥Wenchang B Sag; ⑦Wenchang C Sag; ⑧Shenhu Uplift. Crude oils were selected from the Wenchang A Sag, the Qionghai Uplift, the Wenchang B Sag and the Shenhu Uplift (Modified after Huang et al., 2003).

Series		Age (Ma)	Formation	Thickness (m)	Lithology	Sedimentary facies	Essential elements	Tectonic stage
Period	Epoch							
Quaternary	Pleistocene							
Neogene	Pliocene	1.9	Wanshan	800–1200		Open shallow marine	Seal	Depression
		5						
	Miocene	10.5	Yuehai	300–350				
		16.5	Hanjiang	300–350				
		21	Zhujiang	1000–1200				
Palaeogene	Oligocene	21	Zhuhai	1200–1600		Bay	Reservoir	
		30	Enping	1000–2100		Lacustrine	Source rocks	Rifting
	Eocene	35	Wenchang	300–1000				
		49.5	Shenhu	800–1500				

Salt Mudstone	Mudstone	Conglomeratic sandstone	sandstone	Bioclast

Fig. 2. Schematic stratigraphic column of the western Pearl River Mouth Basin, showing lithology, sedimentary faces and petroleum system contains (modified after Gan et al., 2009b).

(Table 1). Fifteen dark mudstones were sampled from the Enping Formation in the Wenchang A and Wenchang B sags, and ten dark mudstones of the Wenchang Formation were selected from the Wenchang B sag, the Wenchang Formation have not been presently drilled in the Wenchang A sag (Gong and Li, 2004; Gan et al., 2009b; Xiao et al., 2009). The mudstones were first analyzed with a Rock-Eval II instrument. Sixteen mudstone samples were selected for their higher TOC (>0.5%) content (Table 2) and extracted using dichloromethane and methanol (DCM:MeOH, 93:7 v:v) in a Soxhlet apparatus for 72 h. After precipitation of asphaltene from the crude oils and rock extracts, the saturated hydrocarbon fractions were obtained using column chromatography.

3.2. Artificial thermal maturation experiments

Two source rock samples were selected, WC19-1-3 (1823–1832m) from the Wenchang Formation and WC8-2-1 (2623–2626 m) from the Enping Formation, representing the two effective source rocks in the western Pearl River Mouth Basin. Both samples have high TOC contents and low thermal maturities and their basic geochemical data are given in Table 3. The experimental procedures were as follows. Firstly, each of the samples was ground

into powder and Soxhlet extracted with dichloromethane and methanol (DCM:MeOH, 93:7 v:v) for 72 h. After drying at 45 °C, the samples were sealed under vacuum into different quartz tubes and heated rapidly in a muffle furnace to specific temperatures where they were held isothermally for 24 h. The list of temperatures together with their calculated corresponding EasyRo values is listed in Table 4. Finally, the samples were extracted again with dichloromethane and methanol (DCM:MeOH, 93:7 v:v) for 72 h to obtain the artificial pyrolysis oils. After precipitation of asphaltene, the saturated hydrocarbon fractions and the n-alkanes were obtained by column chromatography and urea adduction, respectively.

3.3. Urea adduction

The individual n-alkanes were obtained by urea adduction from the saturated hydrocarbon fractions. The method and procedure was described by Ellis and Fincannon (1998) and is briefly summarized here. Firstly, a saturated solution of urea in methanol was added to the saturated hydrocarbon fractions dissolved in a toluene-methanol solvent mixture and held overnight for complete adduction. Then, the solvent was pipetted from the urea

Table 1
Carbon isotopic characteristics of individual n-alkanes in crude oils in different areas of the western Pearl River Mouth Basin.

Areas	Wenchang B sag					Shenhu uplift					The central areas of the Wenchang A sag							
Sample	WC19-1-2	WC19-1N-1	WC19-1-4	WC19-1-5	Average values	WC15-1-1	WC15-1-1	WC15-1-3	WC21-1-1	WC21-1-1	Average values	WC9-1-1	WC9-1-1	WC9-1-1	WC9-2-1	WC9-3-1	WC14-3-1	Average values
Depth (m)	1759-1771	2019-2045	2276-2315	1381.2		1250-1257	DST1	1266.5	1143.5	1144.1		3490-3525	3390-3415	3230-3250	3661-3699	3828-3903	2223-2240	
Group	I					IIa					IIb							
C12	–	–	–	–	–	–28.29	–27.99	–28.26	–28.47	–28.65	–28.33	–	–29.33	–29.19	–	–28.66	–29.55	–29.18
C13	–24.45	–22.87	–23.66	–24.62	–23.90	–28.58	–28.48	–28.57	–28.55	–28.73	–28.58	–29.55	–29.19	–29.85	–29.51	–29.49	–29.53	–29.52
C14	–24.47	–23.05	–23.76	–23.50	–23.69	–28.86	–28.75	–28.92	–28.86	–28.73	–28.82	–29.91	–29.81	–30.03	–29.90	–29.83	–30.20	–29.95
C15	–24.45	–23.23	–23.84	–23.58	–23.78	–29.11	–29.10	–29.03	–29.13	–29.04	–29.08	–30.12	–30.11	–30.37	–30.43	–30.23	–30.05	–30.22
C16	–24.52	–23.28	–23.90	–23.51	–23.80	–29.36	–29.33	–29.35	–29.54	–29.37	–29.39	–30.38	–30.52	–30.68	–30.41	–30.50	–30.56	–30.51
C17	–24.85	–23.48	–24.17	–23.61	–24.03	–29.69	–29.61	–29.69	–29.67	–29.79	–29.69	–30.80	–30.89	–30.97	–30.91	–30.85	–30.99	–30.90
C18	–24.92	–23.39	–24.15	–23.72	–24.05	–30.06	–29.84	–29.95	–30.05	–29.87	–29.95	–31.11	–31.21	–31.22	–30.88	–31.19	–31.26	–31.14
C19	–25.08	–23.60	–24.34	–23.92	–24.24	–30.17	–30.11	–30.21	–30.18	–30.27	–30.19	–31.19	–31.33	–31.53	–31.11	–31.24	–31.57	–31.33
C20	–24.88	–23.61	–24.24	–23.84	–24.14	–30.24	–30.19	–30.34	–30.35	–30.38	–30.30	–31.40	–31.34	–31.47	–31.06	–31.36	–31.66	–31.38
C21	–24.97	–23.75	–24.36	–24.01	–24.27	–30.31	–30.37	–30.37	–30.31	–30.32	–30.34	–31.33	–31.38	–31.51	–31.11	–31.49	–31.84	–31.44
C22	–24.43	–23.61	–24.02	–23.84	–23.97	–29.74	–29.74	–29.73	–29.85	–29.70	–29.75	–30.73	–30.48	–30.68	–30.38	–30.53	–30.94	–30.62
C23	–24.04	–23.54	–23.79	–23.75	–23.78	–29.50	–29.55	–29.62	–29.61	–29.46	–29.55	–30.25	–30.32	–30.37	–29.86	–30.24	–30.44	–30.24
C24	–23.95	–23.48	–23.71	–23.70	–23.71	–29.18	–29.04	–29.18	–28.98	–29.06	–29.09	–29.89	–29.86	–29.78	–29.50	–29.64	–29.96	–29.77
C25	–23.92	–23.50	–23.71	–23.49	–23.66	–29.03	–28.92	–29.07	–29.02	–29.04	–29.02	–29.66	–29.61	–29.67	–29.40	–29.40	–29.71	–29.57
C26	–23.95	–23.51	–23.73	–23.79	–23.74	–29.15	–29.06	–29.35	–29.21	–29.47	–29.25	–30.39	–29.70	–29.75	–29.62	–29.54	–30.12	–29.85
C27	–23.61	–23.28	–23.44	–23.36	–23.42	–28.62	–28.83	–28.86	–28.83	–28.85	–28.80	–29.58	–29.51	–29.57	–29.20	–29.28	–29.62	–29.46
C28	–23.56	–23.29	–23.42	–23.34	–23.40	–28.59	–28.50	–28.62	–28.68	–28.72	–28.62	–29.39	–29.32	–29.25	–29.21	–29.09	–29.43	–29.28
C29	–23.53	–23.27	–23.40	–23.22	–23.35	–28.59	–28.61	–28.70	–28.83	–28.64	–28.68	–29.43	–29.42	–29.36	–28.78	–28.95	–29.39	–29.22
C30	–23.40	–23.38	–23.39	–23.22	–23.35	–28.17	–28.47	–28.92	–28.86	–28.00	–28.48	–29.26	–28.93	–29.05	–28.88	–29.24	–29.73	–29.18
C31	–23.68	–	–24.11	–24.23	–24.01	–29.50	–29.30	–29.33	–	–	–29.38	–29.14	–29.41	–29.19	–	–	–29.70	–29.36
C32	–23.47	–	–	–	–23.47	–	–	–	–	–	–	–	–	–28.97	–	–	–28.57	–28.77

Areas	Qionghai uplift																	
Sample	WC13-1-1	WC13-1-1	WC13-1-1	WC13-1-1	WC13-1-2	WC13-1-2	WC13-2-1	WC13-2-1	WC13-2-2	WC13-2-2	WC13-6N-1	WC8-3-1	WC8-3E-1	WC8-3E-2	QH18-1-1	QH18-1-2	QH18-1-2	Average values
Depth (m)	1301	1412-1420	1385-1402	1296-1303	1400-1410	1230-1250	1087-1105	997-1004	1106-1124	1024-1029	1283-1350	2614-2635	1699-1700	1666-1694	1197.5	1205.4	1292-1202	
Group	IIc																	
C12	–	–29.17	–	–29.99	–29.36	–29.57	–29.42	–29.39	–29.24	–29.25	–29.09	–28.39	–29.80	–29.17	–28.67	–27.44	–28.90	–29.12
C13	–	–29.40	–29.35	–30.05	–29.65	–29.29	–29.78	–29.74	–29.78	–29.73	–29.81	–28.75	–29.80	–29.85	–29.45	–28.59	–29.13	–29.51
C14	–29.64	–29.67	–29.76	–30.03	–29.59	–29.85	–29.99	–29.94	–29.89	–29.93	–30.06	–28.96	–30.04	–30.12	–28.98	–28.66	–29.04	–29.66
C15	–30.17	–29.89	–29.91	–30.30	–29.89	–30.20	–30.04	–30.31	–30.15	–30.08	–30.20	–29.25	–30.33	–30.35	–29.13	–28.86	–29.47	–29.91
C16	–30.34	–30.18	–30.53	–30.59	–30.29	–30.41	–30.42	–30.55	–30.48	–30.60	–30.55	–29.51	–30.82	–30.60	–29.27	–29.25	–29.49	–30.23
C17	–30.79	–30.48	–30.76	–30.89	–30.64	–30.87	–30.92	–31.05	–30.96	–30.99	–30.87	–29.66	–31.09	–31.05	–29.76	–29.82	–30.08	–30.63
C18	–31.07	–30.88	–30.95	–31.12	–31.01	–31.11	–31.25	–31.33	–31.24	–31.12	–31.12	–30.09	–31.30	–31.26	–30.40	–30.23	–30.20	–30.92
C19	–31.35	–31.15	–31.26	–31.52	–31.16	–31.40	–31.42	–31.51	–31.46	–31.40	–31.29	–30.13	–31.53	–31.45	–30.80	–30.61	–30.93	–31.20
C20	–31.44	–31.13	–31.38	–31.50	–31.38	–31.54	–31.50	–31.57	–31.36	–31.48	–31.39	–30.28	–31.65	–31.58	–30.97	–30.93	–30.81	–31.29
C21	–31.44	–31.21	–31.55	–31.58	–31.21	–31.50	–31.49	–31.62	–31.52	–31.55	–31.48	–30.34	–31.63	–31.58	–31.23	–31.20	–31.17	–31.37
C22	–30.51	–30.42	–31.08	–30.67	–30.49	–30.64	–30.60	–30.65	–30.59	–30.69	–30.51	–29.66	–30.82	–30.56	–30.57	–30.34	–30.27	–30.53
C23	–30.27	–30.01	–30.11	–30.29	–30.24	–30.30	–30.33	–30.37	–30.14	–30.30	–30.14	–29.56	–30.36	–30.20	–30.36	–30.07	–29.83	–30.17
C24	–29.73	–29.60	–29.55	–29.82	–29.54	–29.74	–29.67	–29.75	–29.61	–29.80	–29.67	–29.10	–29.79	–29.80	–29.87	–29.74	–29.56	–29.67
C25	–29.64	–29.39	–29.36	–29.56	–29.42	–29.68	–29.49	–29.50	–29.50	–29.55	–29.48	–29.03	–29.66	–29.44	–29.61	–29.51	–29.43	–29.49
C26	–29.68	–29.32	–30.45	–29.75	–29.62	–29.62	–29.55	–29.67	–29.54	–29.53	–29.76	–29.02	–30.04	–29.64	–29.71	–29.64	–29.54	–29.65
C27	–29.32	–29.06	–29.13	–29.36	–29.23	–29.27	–29.39	–29.51	–29.31	–29.46	–29.50	–28.89	–29.28	–29.18	–29.40	–29.44	–29.22	–29.29
C28	–28.88	–28.88	–29.23	–29.27	–28.91	–28.99	–29.25	–29.14	–29.13	–29.22	–29.26	–28.52	–29.35	–29.39	–28.88	–29.35	–28.87	–29.09
C29	–29.07	–29.01	–28.82	–29.42	–29.15	–29.25	–29.27	–29.34	–29.31	–29.37	–29.55	–28.65	–29.15	–29.53	–29.45	–29.73	–29.33	–29.26
C30	–29.28	–28.65	–29.08	–29.12	–29.22	–29.13	–29.22	–29.31	–28.74	–28.98	–29.18	–28.83	–29.13	–29.17	–29.26	–29.31	–28.67	–29.08
C31	–29.90	–29.13	–29.26	–28.77	–	–29.82	–28.78	–	–29.25	–29.50	–	–28.79	–27.93	–	–	–29.59	–29.44	–29.18
C32	–	–29.21	–27.80	–28.29	–	–	–27.98	–	–28.24	–27.72	–	–	–28.03	–	–	–	–28.14	–28.18

“–” Data unavailable.

Table 2

Geochemical data of typical Wenchang and Enping source rocks and the carbon isotopic characteristics of individual n-alkanes in the extracts obtained from them.

Sample	WC19-1-2	WC19-1-2	WC19-1M-1	WC19-1M-1	WC19-1-1	WC5-1-1	WC5-1-1	WC11-2-1	WC11-2-1	WC11-2-1	Average values
Formation	EP										
Depth (m)	2550-2559	2562-2565	2590-2594	2626-2630	3630-3633	3778-3788	3852-3866	4372-4376	4432	4610	
TOC (%)	0.79	0.88	0.59	–	3.64	3.93	3.61	2.31	1.11	–	2.11
HI (mg/g.TOC)	184	128	192	198	217	175	321	266	279	–	218
C13	–	–27.65	–	–	–26.72	–29.07	–28.91	–29.53	–28.61	–26.19	–28.10
C14	–28.04	–27.22	–27.54	–28.41	–27.63	–29.56	–29.61	–29.43	–28.75	–26.99	–28.32
C15	–29.66	–29.46	–29.66	–29.04	–29.03	–29.96	–29.83	–29.79	–29.19	–27.43	–29.31
C16	–30.49	–29.20	–29.61	–28.61	–29.00	–30.24	–29.85	–30.03	–29.56	–27.75	–29.43
C17	–30.62	–29.50	–30.68	–29.92	–29.15	–30.52	–30.19	–30.17	–30.08	–27.98	–29.88
C18	–30.82	–28.70	–30.58	–29.49	–28.25	–30.16	–30.09	–30.21	–29.98	–28.22	–29.65
C19	–31.60	–29.81	–31.55	–30.52	–29.27	–30.18	–30.22	–30.50	–29.97	–28.32	–30.19
C20	–31.15	–29.87	–31.56	–30.28	–29.29	–30.03	–30.26	–30.60	–29.91	–28.35	–30.13
C21	–31.49	–30.76	–31.83	–30.72	–29.74	–30.08	–30.37	–30.60	–29.97	–28.46	–30.40
C22	–31.19	–30.83	–31.70	–30.81	–29.89	–30.14	–30.30	–30.43	–29.53	–28.02	–30.28
C23	–31.38	–31.10	–31.87	–31.00	–30.04	–30.18	–30.33	–30.56	–29.44	–28.11	–30.40
C24	–31.47	–31.15	–31.77	–30.98	–30.15	–30.26	–30.48	–30.63	–29.20	–27.93	–30.40
C25	–31.26	–31.25	–31.95	–30.93	–30.26	–30.46	–30.59	–30.78	–29.30	–28.12	–30.49
C26	–31.94	–31.97	–32.16	–31.70	–30.87	–30.56	–30.59	–30.67	–29.49	–28.66	–30.86
C27	–31.77	–31.80	–32.03	–31.01	–30.37	–30.32	–30.42	–30.60	–29.42	–27.95	–30.57
C28	–32.03	–32.04	–32.39	–31.46	–30.59	–30.17	–30.50	–30.57	–29.16	–28.29	–30.72
C29	–32.08	–32.19	–32.50	–31.73	–30.98	–30.34	–30.82	–30.86	–29.56	–28.23	–30.93
C30	–32.44	–32.35	–32.98	–31.77	–	–30.28	–30.87	–30.34	–29.40	–	–31.30
C31	–32.91	–32.95	–33.53	–32.81	–	–31.44	–31.48	–	–29.39	–	–32.07
C32	–33.38	–32.66	–	–	–	–	–	–	–	–	–33.02

Sample	WC19-1M-1	WC19-1M-1	WC19-1M-1	WC19-1M-1	WC19-1M-1	WC19-1M-1	Average values
Formation	WC						
Depth (m)	3254-3256	3256-3258	3304-3310	3334-3342	3368-3376	3392-3394	
TOC (%)	2.6	2.66	2.79	1.63	2.96	4.68	2.89
HI (mg/g.TOC)	521	422	462	452	431	478	461
C13	–25.12	–25.80	–	–	–	–	–25.46
C14	–25.51	–25.56	–24.74	–24.47	–25.07	–23.10	–24.74
C15	–25.39	–25.35	–23.62	–24.12	–24.64	–23.22	–24.39
C16	–25.17	–24.92	–23.75	–23.67	–24.36	–22.85	–24.12
C17	–25.20	–25.09	–23.96	–23.73	–24.41	–22.91	–24.22
C18	–25.27	–25.47	–24.14	–23.77	–24.64	–22.77	–24.34
C19	–25.59	–25.71	–24.30	–23.83	–24.73	–22.67	–24.47
C20	–25.74	–25.86	–24.34	–23.74	–25.26	–22.75	–24.62
C21	–25.97	–26.01	–24.36	–23.97	–25.22	–22.87	–24.74
C22	–25.85	–25.90	–24.49	–23.87	–25.18	–22.75	–24.67
C23	–25.63	–25.59	–24.17	–23.89	–24.91	–22.54	–24.45
C24	–25.34	–25.49	–24.01	–23.63	–24.69	–22.49	–24.28
C25	–25.68	–25.40	–23.90	–23.49	–24.55	–22.36	–24.23
C26	–25.88	–25.22	–23.93	–23.85	–24.65	–22.55	–24.34
C27	–25.19	–24.97	–23.48	–23.44	–24.26	–21.87	–23.87
C28	–24.93	–25.00	–23.79	–23.66	–24.25	–22.33	–23.99
C29	–25.42	–25.33	–23.84	–23.56	–24.45	–22.41	–24.17
C30	–24.54	–25.11	–23.59	–23.55	–24.04	–22.03	–23.81
C31	–24.66	–24.93	–23.40	–24.31	–24.73	–23.04	–24.18
C32	–	–24.16	–22.88	–	–23.31	–21.47	–22.95
C33	–	–24.11	–24.19	–	–23.38	–20.93	–23.15
C34	–	–	–23.01	–	–	–	–23.01

"–"Data unavailable.

precipitate, after which, the precipitate was dried under nitrogen and repeatedly rinsed with solvent to ensure complete removal of the non-adducted fractions. Finally, the n-alkanes were recovered by the addition of hexane after dissolution of the urea crystals in distilled water.

3.4. Instrumental analysis

The n-alkanes obtained from both crude oils and rock extracts were analyzed by gas chromatography (GC) and gas chromatography-isotope ratio mass spectrometry (GC-IRMS).

Table 3

Geochemical data of selected dark mudstones for artificial thermal pyrolysis experiments from the western Pearl River Mouth Basin.

Sample	Depth (m)	Formation	Sedimentary facies	Type of kerogen	Ro (%)	Rock-Eval		
						TOC (%)	Tmax (°C)	HI (mg/g.TOC)
S1913	1823–1832	WC	medium-deep lacustrine	II	0.45 ^a	2.7	434	444 ^a
S821	2623–2626	EP	shallow lacustrine	III	0.59 ^a	5.1	448	245 ^a

^a Data from Xiao et al. (2009).

Table 4
EasyRo values, the yield and relative yield of the pyrolysis oil and saturated hydrocarbon of the Wenchang and Enping samples in the artificial pyrolysis experiment.

Sample	EasyRo (%)	S821 (Enping formation)						S1913 (Wenchang formation)				
		Pyrolysis oils		Saturated hydrocarbon		Saturated hydrocarbon content (%)	Pyrolysis oils		Saturated hydrocarbon		Saturated hydrocarbon content (%)	
		Yield (mg/g.TOC)	Relative yield (%) [*]	Yield (mg/g.TOC)	Relative yield (%) [#]		Yield (mg/g.TOC)	Relative yield (%) [*]	Yield (mg/g.TOC)	Relative yield (%) [#]		
300	0.64	6.11	17.56	0.62	5.91	10.215	34.39	45.79	5.10	22.22	14.838	
330 (A)	0.79	18.54	53.26	4.41	41.78	23.794	66.11	88.02	18.90	82.30	28.592	
360 (B)	1.02	34.81	100.00	10.56	100.00	30.334	75.11	100.00	22.97	100.00	30.579	
380 (C)	1.24	23.08	66.29	2.41	22.79	10.427	34.26	45.62	4.82	21.00	14.076	
400	1.49	9.86	28.33	0.05	0.47	0.500	4.47	5.95	<0.05	–	–	
420	1.79	4.64	13.31	<0.05	–	–	4.10	5.45	<0.05	–	–	

EasyRo was calculated using the software GOR-Isotope (GeolsoChem Corporation, 2003) based on the given temperature and corresponding isothermal time in the artificial thermal pyrolysis experiments. A, B and C are the end-member oils for mixture; “*” the ratio of pyrolysis oil at each temperature compared with the pyrolysis oil at 360 °C; “#” the ratio of saturated hydrocarbons at each temperature compared with the saturated hydrocarbon at 360 °C; “–” Data unavailable.

A Trace GC (Thermo Scientific Ultra) equipped with a TG-5MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used to carry out the gas chromatography. Samples were injected using the splitless injector mode, maintained at 290 °C and carried by nitrogen at a flow rate of 1.5 ml/min into the oven. The GC oven temperature was held for 4 min at 100 °C and ramped to 210 °C at 4 °C/min, then to 305 °C at 1.7 °C/min and held for 15 min isothermally. Compounds were quantified by relative integral areas.

The gas chromatography-isotope ratio mass spectrometry (GC-IRMS) analyses were performed on a VG Isochrom II instrument. The GC was equipped with a HP-5 fused silica capillary column (50 m × 0.32 mm i.d., 0.25 μm film thickness). Helium was used as the carrier gas. The GC oven temperature was held for 4 min at 70 °C and ramped to 300 °C at 3 °C/min and held isothermally at this temperature for 15 min. A standard mixture of individual n-alkanes (nC₁₂, nC₁₆, nC₂₀, nC₂₂, nC₂₄, nC₂₇ and nC₃₂) with known isotopic composition was used daily to test the performance of the instrument. Each sample was analyzed twice with an analytical precision of ±0.3‰ and the values averaged to give final results.

4. Results and discussion

4.1. Carbon isotopic characteristics of n-alkanes in the extracts of source rocks

Though δ¹³C values of individual n-alkanes in both the Wenchang and Enping source rocks become heavier (about 3‰–4‰) with increasing thermal maturity, there are still clear differences between the two source rocks (Table 2, Fig. 3). The former have relatively heavy δ¹³C values, ranging from –26‰ to –21‰, the values keeping almost constant or becoming slightly heavier with increasing carbon number. The latter have light δ¹³C values, ranging from –33‰ to –27‰, and the values become lighter with increasing carbon number.

Previous research has indicated that the δ¹³C values of n-alkanes sourced from terrestrial source organic matter are heavier than the n-alkanes sourced from aquatic source organic matter (Clayton, 1991; Chung et al., 1994). For example, in offshore mid-Norway, the δ¹³C values of n-alkanes in the Åre source rocks, which are mainly derived from terrestrial organic matter, range from –24‰ to –27‰, whereas the values in the Spekk source rocks derived mainly from aquatic organic matter range from –29‰ to –33‰ (Odden et al., 2002). In the western Pearl River Mouth Basin, however, the δ¹³C values of n-alkanes in the Wenchang source rocks, which based on other evidences (Gong and Li, 1997, 2004;

Huang et al., 2003, 2007; Cheng et al., 2013b) are mainly contributed from aquatic organic matter, are much heavier than the Enping source rocks (Fig. 3), which are derived mainly from terrestrial organic matter (Gong and Li, 1997, 2004; Huang et al., 2003, 2007; Cheng et al., 2013b).

4.2. Carbon isotopic characteristics of n-alkanes in crude oils

Two groups of oils in the western Pearl River Mouth Basin were identified based on the carbon isotopic characteristics of n-alkanes (Table 1, Fig. 4). The group I oils are mainly located in the Wenchang B sag, such as from the WC19-1-2 and WC19-1N-1 wells. The δ¹³C values of n-alkanes in these oils are isotopically heavy, ranging from –25‰ to –22‰, and the values are almost constant or become slightly heavier with increasing carbon number, matching well with the Wenchang source rocks. The group II oils are extensively distributed in and around the Wenchang A sag, such as the WC9 wells in the central area of the Wenchang A sag and the WC13 (Qionghai uplift) and WC15 (Shenhu uplift) wells in the margins of the sag. δ¹³C values of the group II n-alkanes are light, ranging from –32‰ to –28‰, and at first become lighter with increasing carbon number and then become heavier after the C₂₁-alkane, resulting in a “V” feature in the profile (Fig. 4). In addition, the δ¹³C values of n-alkanes in group I oils are slightly different according to location. Oils in the wells located in the marginal areas of the Wenchang A sag, such as the WC13 wells in the Qionghai uplift (IIc) and the WC15 wells in the Shenhu uplift (IIb), have heavier δ¹³C values compared with the oils in the WC9 wells located in the central area of the sag (IIa) (Fig. 4). However, the carbon isotopic characteristics of n-alkanes in group I oils differ from both the Wenchang and Enping source rock extracts.

4.3. Factors influencing the carbon isotopic characteristics of n-alkanes in crude oils

There are several influences on the carbon isotopic characteristics of n-alkanes in crude oils, the main factors being as follows:

- (1) Source organic matter. This is one of the main factors controlling the carbon isotopic characteristics of individual n-alkanes in oils (Rieley et al., 1991; Collister et al., 1994; Murray et al., 1994; Boreham et al., 1994). Generally, the characteristics of n-alkanes in oils and their correlated source rocks are similar both in the δ¹³C values and profiles (Murray et al., 1994; Xiong et al., 2001; Odden et al., 2002). However, a

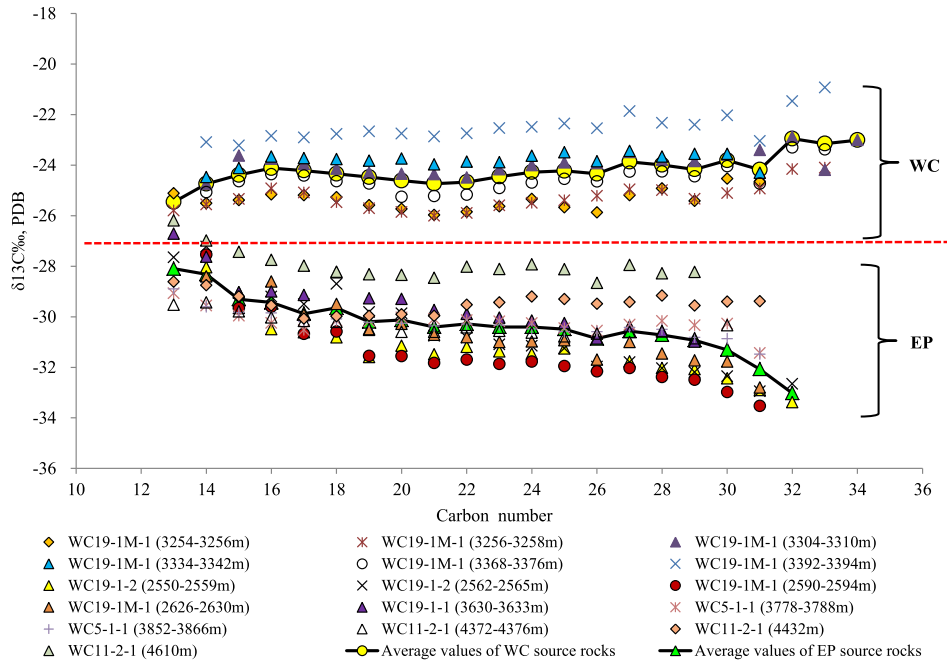


Fig. 3. Carbon isotopic characteristics of n-alkanes in the extracts of the Wenchang and Enping source rocks. (WC: Wenchang Formation; EP: Enping Formation).

specific source rock corresponding to the grouploils in the western Pearl River Mouth Basin has not been found.

(2) Thermal maturity. Due to the lower energy required to crack the ^{12}C – ^{12}C bond compared with the ^{13}C – ^{12}C bond, the ^{12}C – ^{12}C bond is preferentially cracked in the process of kerogen maturation, leading to enrichment of the light isotope (^{12}C) in early-generated oils and concentration of the heavier isotope (^{13}C) in the residue (Clayton, 1991; Tang et al., 2005; Schwab et al., 2005). However, thermal maturity has a limited effect on the shape of the carbon isotopic profiles of n-alkanes in oils (Xiong et al., 2001; Liao et al., 2012).

(3) Fractionation during oil expulsion and migration. Isotopic fractionation during oil expulsion and migration could have had a slight influence on the $\delta^{13}\text{C}$ values of n-alkanes in oils. Because the ^{12}C -rich n-alkanes having slightly lighter molecular mass than the ^{13}C -rich n-alkanes, they preferentially expulse and migrate to reservoirs during oil generation, which resulting in the n-alkanes in early-accumulated oils having lighter $\delta^{13}\text{C}$ values compared with the later-charged oils (Xiong et al., 2001; Liao et al., 2004). However, the effect could have a significant influence on the relative contents of individual n-alkanes of low-carbon number ($<C_{21}$)

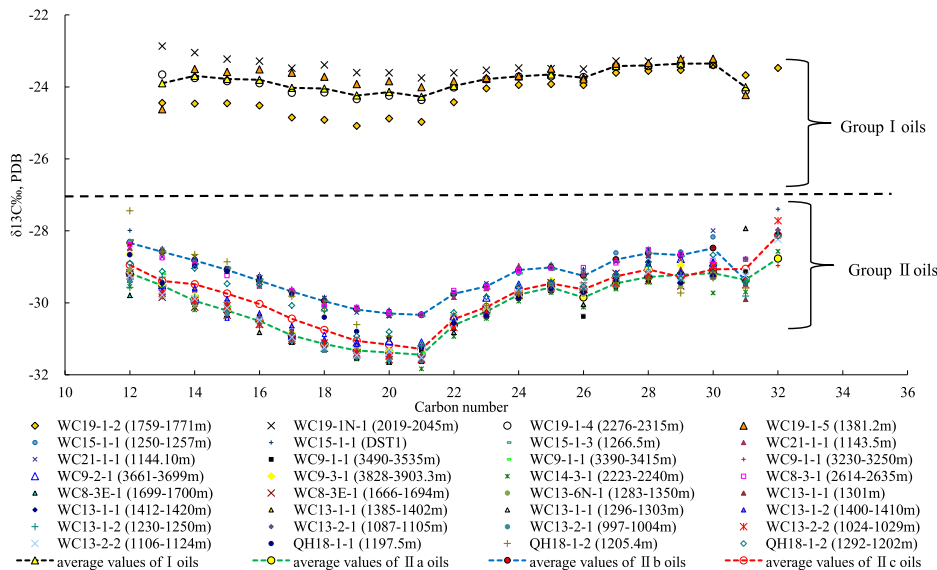


Fig. 4. Carbon isotopic characteristics of n-alkanes in the groups of crude oils from different locations in the western Pearl River Mouth Basin. (WC: Wenchang Formation; EP: Enping Formation; QH: Qionghai Formation; SH: Shenhu Formation).

Table 5
Carbon isotopic characteristics of individual n-alkanes in the pyrolysis oils, the “mixed” oils with different maturities and material sources, and the maximum changed $\delta^{13}\text{C}$ values ($\Delta\delta^{13}\text{C}\text{‰}$, PDB) of n-alkanes in the artificial pyrolysis experiment.

Sample	S821 (Enping formation)								Max, $\Delta\delta^{13}\text{C}$ (‰, PDB) ^a	Mixed oil ^a , $\delta^{13}\text{C}$ (‰, PDB)
	/		A		B		C			
EasyRo (%)	0.64		0.79		1.02		1.24			
Mixed ration [#]	/		$P_A = 41.78\%$		$P_B = 100\%$		$P_C = 22.79\%$			
Carbon number	Relative content (%)	$\delta^{13}\text{C}$ (‰, PDB)	Relative content (%)	$\delta^{13}\text{C}$ (‰, PDB)	Relative content (%)	$\delta^{13}\text{C}$ (‰, PDB)	Relative content (%)	$\delta^{13}\text{C}$ (‰, PDB)		
C13	0.00	–	0.49	–	0.65	–	–	–	–	–
C14	0.16	–	2.93	–29.49	3.78	–28.73	3.21	–27.06	–	–28.68
C15	1.54	–29.52	5.72	–29.46	6.84	–29.00	11.50	–27.45	2.07	–28.75
C16	3.60	–29.61	7.48	–29.79	9.20	–29.15	16.17	–27.33	2.28	–28.86
C17	4.94	–30.12	8.04	–30.09	10.13	–29.42	16.99	–27.52	2.61	–29.12
C18	6.15	–29.83	8.48	–30.06	10.85	–29.34	16.38	–27.36	2.48	–29.07
C19	7.00	–30.11	8.25	–30.21	10.90	–29.43	13.80	–27.06	3.06	–29.15
C20	7.69	–30.30	8.08	–30.32	10.31	–29.41	9.95	–26.76	3.53	–29.22
C21	8.18	–30.36	7.72	–30.32	9.27	–29.36	6.23	–26.45	3.92	–29.28
C22	8.36	–30.30	7.19	–30.19	7.77	–29.16	3.36	–26.32	3.98	–29.24
C23	8.29	–30.31	6.56	–30.15	6.18	–28.94	1.61	–25.61	4.70	–29.16
C24	7.95	–30.58	5.87	–30.39	4.67	–29.05	0.68	–25.36	5.21	–29.43
C25	7.49	–30.43	5.20	–30.23	3.36	–29.05	0.12	–	–	–29.37
C26	6.79	–30.42	4.46	–30.23	2.34	–29.13	–	–	–	–29.62
C27	6.06	–30.46	3.80	–30.21	1.57	–28.83	–	–	–	–29.52
C28	5.03	–30.85	3.03	–30.70	0.97	–29.13	–	–	–	–30.02
C29	4.12	–30.92	2.38	–30.67	0.59	–29.32	–	–	–	–30.17
C30	3.08	–31.29	1.75	–30.97	0.35	–29.33	–	–	–	–30.44
C31	2.06	–31.23	1.16	–31.14	0.18	–	–	–	–	–31.14
C32	1.21	–31.35	0.74	–31.04	0.09	–	–	–	–	–31.04
C33	0.31	–32.06	0.42	–	0.00	–	–	–	–	–
C34	0.00	–	0.19	–	0.00	–	–	–	–	–

The relative content is the ratio of an individual n-alkane versus the whole n-alkanes (C_{12} – C_{34}) in each pyrolysis oil based on the integral areas in chromatograms; A, B and C are the end-member oils for mixture; “#” the relative content of saturated hydrocarbon of each end-member oil in the “mixed” oil; “*” the maximum changed $\delta^{13}\text{C}$ value ($\Delta\delta^{13}\text{C}\text{‰}$, PDB) of an individual n-alkane between the two pyrolysis oils with EasyRo = 0.64% and 1.24%, respectively; “a” the calculated $\delta^{13}\text{C}$ value of an individual n-alkane in the “mixed” oils with different maturities; “b” the calculated $\delta^{13}\text{C}$ value of an individual n-alkane in the “mixed” oils with different material sources, the mixed ration of the end-member oils based on their mass (m:m); “–” Data unavailable.

compared with those of high-carbon number ($\geq\text{C}_{21}$) (Leythaeuser et al., 1984; Brothers et al., 1991; Chen and Zha, 2006), causing a change in the carbon isotopic characteristics of n-alkanes in the mixed oils.

- (4) Mixing of different oils. Under geological conditions, oils in reservoirs may have contributions from oils generated from the same source rocks with different thermal maturities (Mackenzie et al., 1988), or the oils may have been generated from different source organic matter (Xiong and Geng, 2000; Rooney et al., 1998; Li and Guo, 2010). This factor may also have a significant influence on the carbon isotopic characteristics of n-alkanes in oils.

In summary, no source rocks have been found in the western Pearl River Mouth Basin that could match well with the group II oils, and neither the thermal maturity nor the effects of isotopic fractionation in oil expulsion and migration could change the carbon isotopic profile of the n-alkanes. This focuses attention on the mixing of oils generated either from the same source rocks with different thermal maturities or from different source organic matter.

4.4. Artificial thermal maturation experiments

To investigate whether under geological conditions, reservoir oils may have mixed with oils with different thermal maturities or source organic matter (Mackenzie et al., 1988; Rooney et al., 1998), artificial thermal maturation of the Wenchang and Enping source rocks were performed to identify the character of oils generated from these source rocks at different thermal maturities. Mixtures of

these end member oils can be simulated to investigate whether this could account for the group II oils. The results of the experiments (Table 4) indicate that the main stage of oil generation of the two source rocks ranges from EasyRo = 0.64%–1.24%, with the peak stage of hydrocarbon generation at EasyRo = 1.02%.

4.4.1. Carbon isotopic characteristics of n-alkanes in the pyrolysis oils at different thermal maturities

From the early stage to the peak stage of oil generation (EasyRo between 0.64% and 1.02%), the n-alkane content in the pyrolysis oils is mainly controlled by n-alkane generation from kerogen pyrolysis, because there is no cracking of the n-alkanes at this stage (Tang et al., 2005). Because of the preferential cracking of the ^{12}C – ^{12}C bond, the early-generated n-alkanes from kerogen pyrolysis have lighter $\delta^{13}\text{C}$ values compared with the later-generated n-alkanes. The $\delta^{13}\text{C}$ values of individual n-alkanes in the pyrolysis oils could increase by about 3‰ with higher thermal maturity. For example, in this experiment, the average $\delta^{13}\text{C}$ value of individual n-alkanes in the Wenchang and Enping pyrolysis oils changed from –24‰ to –21‰ and from –31‰ to –28‰, respectively (Table 5). Nevertheless, the carbon isotopic profiles of n-alkanes in the pyrolysis oils of different maturity have similar characteristics (Fig. 5). The $\delta^{13}\text{C}$ values of individual n-alkanes in the Wenchang Formation pyrolysis oils remain constant or become slightly heavier with increasing carbon number, and become slightly lighter in the Enping Formation pyrolysis oils. Therefore, the effect of thermal maturity has no significant influence on the carbon isotopic profiles of n-alkanes in the pyrolysis oils with different maturities up to the peak of oil generation.

S1913 (Wenchang formation)								Mixed oils ^b (B-WC: B-EP, m: m)				
/		A		B		C		Max, $\Delta\delta^{13}\text{C}$ (‰, PDB)*	Mixed oil ^a , $\delta^{13}\text{C}$ C (‰, PDB)			
0.64		0.79		1.02		1.24				3:1	1:1	1:3
/		$P_A = 82.3\%$		$P_B = 100\%$		$P_C = 21\%$		$\delta^{13}\text{C}$ (‰, PDB)				
Relative content (%)	$\delta^{13}\text{C}$ (‰, PDB)	Relative content (%)	$\delta^{13}\text{C}$ (‰, PDB)	Relative content (%)	$\delta^{13}\text{C}$ (‰, PDB)	Relative content (%)	$\delta^{13}\text{C}$ (‰, PDB)					
0.00	–	0.59	–	1.22	–	1.68	–	–	–	–	–	
0.97	–	2.65	–23.52	3.86	–21.86	8.74	–19.80	–	–21.84	–23.54	–25.24	–26.97
2.63	–23.90	4.87	–23.37	6.39	–21.59	14.09	–19.58	4.32	–21.68	–23.53	–25.41	–27.23
4.79	–23.58	6.87	–23.39	8.31	–21.78	16.42	–19.48	4.10	–21.85	–23.76	–25.64	–27.43
6.18	–23.97	7.60	–23.15	9.63	–21.43	16.40	–19.34	4.63	–21.62	–23.49	–25.51	–27.48
7.62	–23.65	8.05	–22.75	10.41	–21.52	14.67	–18.85	4.80	–21.52	–23.52	–25.49	–27.43
7.17	–24.19	7.44	–23.07	10.13	–21.46	11.17	–18.67	5.52	–21.64	–23.55	–25.57	–27.53
7.98	–24.36	7.39	–23.04	9.59	–21.42	7.71	–18.35	6.01	–21.70	–23.51	–25.54	–27.50
8.17	–24.34	7.14	–23.13	8.63	–21.28	4.72	–17.94	6.39	–21.77	–23.40	–25.45	–27.43
8.36	–24.41	6.99	–23.45	7.64	–21.40	2.57	–17.56	6.85	–22.09	–23.35	–25.29	–27.23
8.01	–24.62	6.56	–23.29	6.45	–21.49	1.22	–17.44	7.18	–22.20	–23.28	–25.12	–27.00
8.33	–24.45	6.36	–23.20	5.43	–21.01	0.49	–17.20	7.25	–22.04	–22.79	–24.71	–26.79
7.53	–23.77	5.78	–22.98	4.25	–20.79	0.11	–	–	–21.89	–22.50	–24.42	–26.59
7.47	–23.62	5.48	–22.83	3.34	–20.90	0.00	–	–	–22.01	–22.45	–24.28	–26.46
6.07	–23.70	4.65	–22.80	2.39	–20.97	0.00	–	–	–22.09	–22.37	–24.07	–26.17
5.52	–23.66	4.19	–22.71	1.63	–20.62	0.00	–	–	–22.04	–22.02	–23.78	–26.06
2.49	–23.78	2.89	–22.65	0.69	–20.89	0.00	–	–	–22.25	–	–	–
0.71	–	2.19	–22.99	0.00	–	0.00	–	–	–22.99	–	–	–
0.00	–	1.26	–23.11	0.00	–	0.00	–	–	–23.11	–	–	–
0.00	–	0.79	–23.73	0.00	–	0.00	–	–	–23.73	–	–	–
0.00	–	0.26	–	0.00	–	0.00	–	–	–	–	–	–
0.00	–	0.00	–	0.00	–	0.00	–	–	–	–	–	–

After the peak stage of oil generation (EasyRo > 1.02%), the $\delta^{13}\text{C}$ values of the individual n-alkanes both in the Wenchang and Enping Formation pyrolysis oils become significantly heavier, increasing 2‰–7‰ compared with the pyrolysis oils with low thermal maturity (EasyRo = 0.64%), with a greater increase for the higher carbon number n-alkanes (Table 5, Fig. 6), similar to previous results on the profile of carbon and hydrogen isotopes of individual n-alkanes in pyrolysis oils (Bjorøy et al., 1992; Tang et al., 2005). The changes can be explained as follows. In the high thermal maturity stage, the n-alkane content in the pyrolysis oil is mainly controlled by the degree of secondary cracking of the n-alkanes. The ^{12}C – ^{12}C bond has lower thermostability and cracks preferentially compared with the ^{13}C – ^{12}C bond, resulting in heavier $\delta^{13}\text{C}$ values of the residual n-alkanes (Clayton, 1991; Clayton and Bjorøy, 1994; Tang et al., 2005). The higher carbon number n-alkanes have weaker thermostability, for example the n-alkanes ($C_n > C_{24}$) have already cracked at the high thermal maturity of EasyRo = 1.24% in this experiment (Fig. 5). Therefore, higher-carbon number n-alkanes have a greater extent of isotopic fractionation than the lower-carbon number n-alkanes (Fig. 6) resulting in the carbon isotopic becomes heavier with increasing carbon number in the pyrolysis oils with higher thermal maturity (Fig. 5).

Although the $\delta^{13}\text{C}$ values of n-alkanes in both the Wenchang and Enping pyrolysis oils become heavier with thermal maturity, there are still clear differences in the $\delta^{13}\text{C}$ values of the two suites of pyrolysis oils in the main stage of oil generation (EasyRo = 0.64%–1.24%). This indicates a modest influence of maturity, whereas different sources can have a more significant effect on $\delta^{13}\text{C}$ n-alkane values.

4.4.2. Carbon isotopic characteristics of mixtures of oils with different maturities

The influence of mixing of oils derived from the same type of source rock at different maturity stages on the carbon isotopic values of n-alkanes was simulated by “mixing” the artificially-generated oils from the pyrolysis experiments. The data from Table 4 indicate significant quantities of oils were collected when the Wenchang and Enping samples were matured to EasyRo values of 0.79%, 1.02% and 1.24%. The lesser amount of oils at EasyRo = 1.24% compared with the oils at EasyRo = 1.02% is attributed to part of the generated oil being cracked under higher thermal stress, resulting in the formation of light oils. This type of light oil occurs widely in the Wenchang A sag (Huang et al., 2003, 2007; Cheng et al., 2013a). Three oils with different thermal maturity, called oils A, B and C, respectively, were selected as the end-members for this “mixture”. Combining the relative contents of individual n-alkanes in each end-member oil (C_{An} , C_{Bn} and C_{Cn}) and their $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}_{An}$, $\delta^{13}\text{C}_{Bn}$ and $\delta^{13}\text{C}_{Cn}$) with the “mixed” ratios of the saturated hydrocarbon of the three end-member oils in the “mixed” oil (P_A , P_B and P_C), the carbon isotopic value of an individual n-alkane ($\delta^{13}\text{C}_n$, n ranging from 12 to 32) in a “mixed” oil was obtained by the formula:

$$\delta^{13}\text{C}_n = \left(C_{An} \times \delta^{13}\text{C}_{An} \times P_A + C_{Bn} \times \delta^{13}\text{C}_{Bn} \times P_B + C_{Cn} \times \delta^{13}\text{C}_{Cn} \times P_C \right) / \left(C_{An} \times P_A + C_{Bn} \times P_B + C_{Cn} \times P_C \right)$$

where C_{An} , C_{Bn} and C_{Cn} represent the relative content of an individual n-alkane in the whole content of n-alkanes (C_{12} – C_{32}) in oils

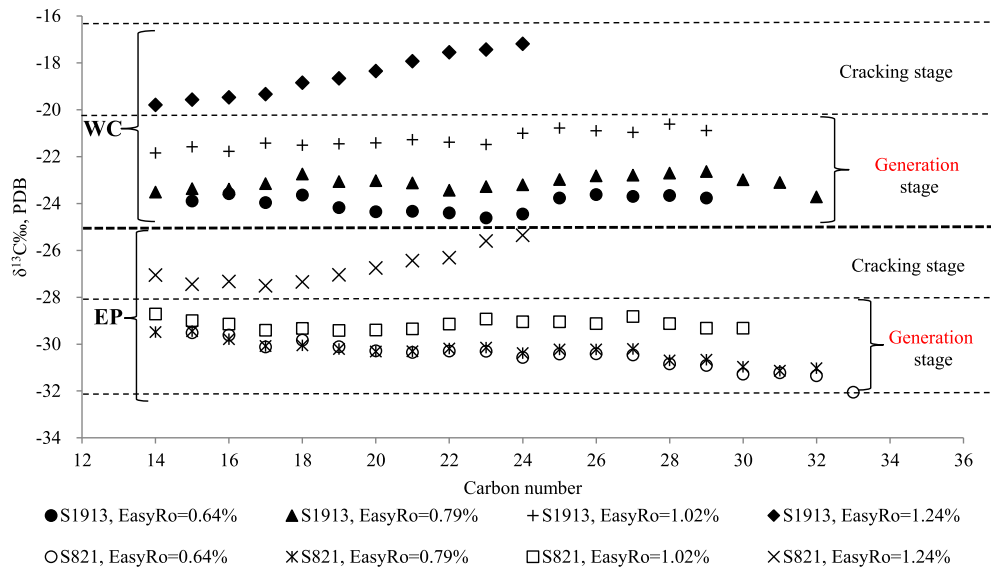


Fig. 5. Carbon isotopic characteristics of n-alkanes in the pyrolysis oils generated from the pyrolysis of the Wenchang and Enping source rocks at different thermal maturities, showing the changes of the carbon isotopic characteristics along with the increase of maturity.

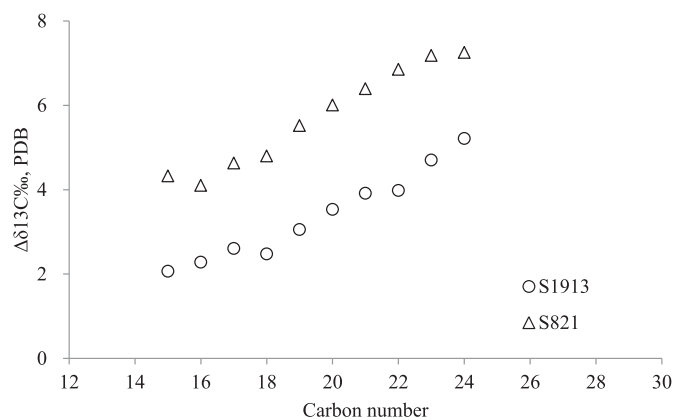


Fig. 6. Changes in $\delta^{13}\text{C}$ values ($\Delta\delta^{13}\text{C}\%$, PDB) of individual n-alkanes in pyrolysis oils generated from the pyrolysis of the Wenchang and Enping source rocks at high maturity (EasyRo = 1.24%) compared to low maturity stages (EasyRo = 0.64%), showing the different isotopic fractionations in the high-carbon number and the low-carbon number n-alkanes.

A, B and C, respectively; $\delta^{13}\text{C}_{\text{An}}$, $\delta^{13}\text{C}_{\text{Bn}}$ and $\delta^{13}\text{C}_{\text{Cn}}$ represent the carbon isotopic values of the corresponding individual n-alkanes in the oils A, B and C, respectively; P_A , P_B and P_C represent the relative contents of the saturated hydrocarbons of each end-member oil in the “mixed” oil, based on the relative yield of the saturated hydrocarbon of pyrolysis oil at different maturity stages.

Both of the Wenchang and Enping “mixed” oils were processed by this expression. The results indicate that the $\delta^{13}\text{C}$ values of n-alkanes of the two “mixed” oils are between their A oil and B oil, but distinct from their C oil (Fig. 7). This is owing to the lower relative content of the saturated hydrocarbon of the C oil in the “mixed” oil (Table 4). The $\delta^{13}\text{C}$ values of the low-carbon number n-alkanes ($<C_{21}$) and the high-carbon number n-alkanes ($\geq C_{21}$) of the two “mixed” oils trend to their B and A end-member oil, respectively (Fig. 7), but it is also in part caused by the different contributions to these n-alkanes from their end-member oils (Table 5). As a whole, for the two “mixed” oils, the carbon isotopic characteristics of n-alkanes are more closely similar to their B oil rather than their A oil, and without the “V” feature in the carbon isotopic profiles of n-

alkanes, differing from the grouploils in the western Pearl River Mouth Basin. Therefore, it is concluded that a mixture of oils derived from the same type of source rock at different maturity stages cannot form the “V” feature in the carbon isotopic profiles of n-alkanes in oils.

4.4.3. Carbon isotopic characteristics of mixtures of oils derived from different source organic matter

The B oils, as defined in Section 4.4.2, from the Wenchang and Enping samples were selected as the two end-members to simulate the “mixture” of oils derived from the two different source rocks, because both of them were obtained at the peak stage of oil generation (Table 4). The carbon isotopic value of an individual n-alkane ($\delta^{13}\text{C}_n$, n ranging from 12 to 32) in a “mixed” oil was obtained by the formula:

$$\delta^{13}\text{C}_n = \frac{(C_{\text{wcn}} \times \delta^{13}\text{C}_{\text{wcn}} \times \alpha + C_{\text{epn}} \times \delta^{13}\text{C}_{\text{epn}} \times \beta)}{(C_{\text{wcn}} \times \alpha + C_{\text{epn}} \times \beta)}$$

where C_{wcn} and C_{epn} represent the relative content of an individual n-alkane in the whole series of n-alkanes (C_{12} – C_{32}) in the Wenchang B oil and the Enping B oil, respectively; $\delta^{13}\text{C}_{\text{wcn}}$ and $\delta^{13}\text{C}_{\text{epn}}$ represent the $\delta^{13}\text{C}$ value of the corresponding individual n-alkane in the Wenchang B oil and Enping B oil, respectively; α and β are defined as the relative content of the Wenchang B oil and Enping B oil in the “mixed” oil, respectively.

The results indicate that the $\delta^{13}\text{C}$ values of n-alkanes in the “mixed” oils vary, depending on the relative contents of the Wenchang oil and the Enping oil in the mixture between the two end-member oils. Table 5 presents the data with ratios of Wenchang oil to Enping oil ($\alpha : \beta$) being 3:1, 1:1 and 1:3. For the 3:1 ratio, the $\delta^{13}\text{C}$ values of n-alkanes in the “mixed” oil have a similar trend as the Wenchang oil with increasing carbon numbers, but are lighter than the Wenchang oil. When the ratio is 1:1, the $\delta^{13}\text{C}$ values of n-alkanes in the “mixed” oil are in the middle of the two end-member oils, remaining almost constant with increasing carbon number in the low-carbon number n-alkanes ($<C_{21}$) and elevated in the high-carbon number n-alkanes ($\geq C_{21}$). For the 1:3 ratio, the $\delta^{13}\text{C}$ values of n-alkanes in the “mixed” oil are close to the Enping oil, the

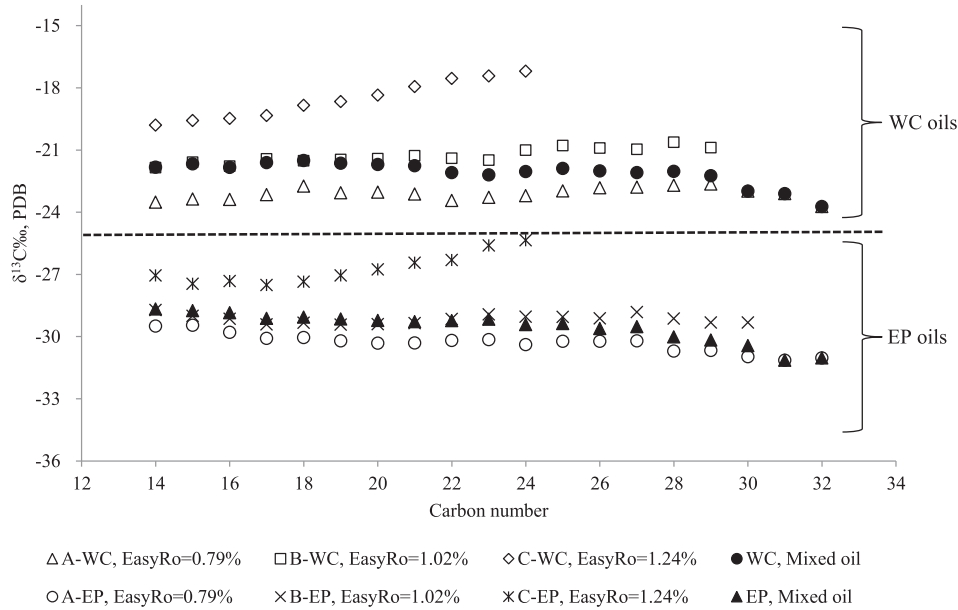


Fig. 7. Carbon isotopic characteristics of individual n-alkanes in the Wenchang and Enping “mixed” pyrolysis oils with different maturities. (WC: Wenchang Formation; EP: Enping Formation). For details see the text.

carbon isotopic profile of the n-alkanes exhibiting a typical “V” feature, which is similar to the group I oils in the western Pearl River Mouth Basin (Figs. 4 and 8).

4.5. The origin of the carbon isotopic characteristics of n-alkanes in the crude oils

The carbon isotopic characteristics of n-alkanes in the group I oils match well with the Wenchang source rocks (Figs. 3 and 4) in the

Wenchang B sag in which only the Wenchang source rocks have reached the stage of oil generation (Gong and Li, 1997, 2004; Huang et al., 2003, 2007). The molecular compositions of the group I oils also show a clear correlation with the Wenchang source rocks (Huang et al., 2003, 2007; Cheng et al., 2013a, 2013b). The group I oils have low pristane/phytane (Pr/Ph) and 17 α (H) rearrangement C₃₀-hopane/17 α (H)21 β (H) C₃₀-hopane (DiaC₃₀/C₃₀) values and are rich in C₃₀ 4-methylsteranes, but the lack of bicadinane “T” and oleanane indicates they were typically generated from mainly

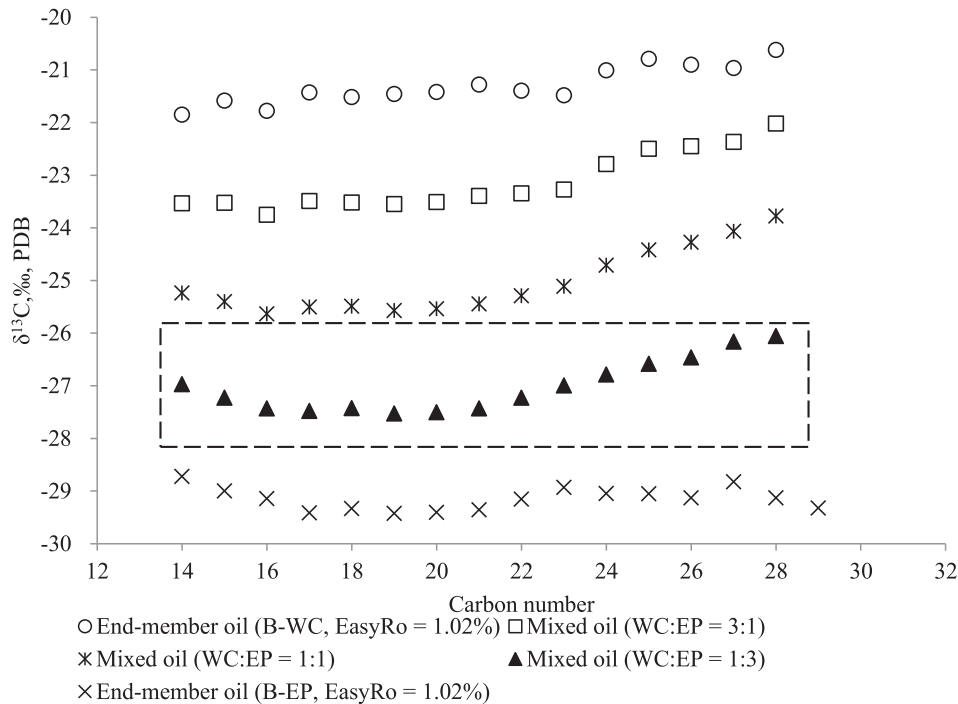


Fig. 8. Carbon isotopic characteristics of individual n-alkanes in the “mixed” pyrolysis oils with different source organic matter. The two end-member oils are the pyrolysis oils generated at the peak stage of oil generation. For details see the text. (WC: Wenchang Formation; EP: Enping Formation).

aquatic organic matter deposited in a weakly reducing sedimentary environment.

However, as noted above, source rocks have not been found that correspond well with the grouploils in the western Pearl River Mouth Basin. The artificial thermal maturation experiments and the calculations of $\delta^{13}\text{C}$ values of n-alkanes in “mixed” oils indicate that both thermal maturity and the mixing of oils with different thermal maturities has no significant effect on the carbon isotopic profile of n-alkanes in the main stage of oil generation (Figs. 5 and 7). However, the mixing of oils with different source organic matter could certainly change the profile (Fig. 8). Therefore, the grouploils probably received contributions from both the Wenchang and Enping Formation source rocks. In combination with information on the time of formation of oil pools in this area, the origin of grouploils can be readily explained.

The grouploils are mainly distributed in and around the Wenchang A sag where the potential source rocks of the Wenchang and Enping formations are both developed. For different burial depths, the two source rocks had different hydrocarbon generation histories (Lin and Sun, 1999; Gong and Li, 1997, 2004; Huang et al., 2007; Xiao et al., 2009). Because the Wenchang oils were generated earlier than the formation time of most structural traps, most of the early-formed Wenchang oils have been lost from the reservoir of the petroleum system (Gan et al., 2009a; Xiao et al., 2009; Cheng et al., 2013b). The residual Wenchang oils are rich in high-carbon number n-alkanes ($\geq C_{21}$) because of the preferential expulsion and migration of low-carbon number n-alkanes ($< C_{21}$) (Leythaeuser et al., 1984; Brothers et al., 1991; Chen and Zha, 2006). In contrast, the generation time of the Enping oils was later than the formation of the traps and the oils were rich in low-carbon number n-alkanes because of the fractionation effect during oil expulsion and migration. These oils accumulated in the traps and mixed with the residual Wenchang oils. Because most of the high-carbon number n-alkanes ($\geq C_{21}$) came from the Wenchang oils with heavy $\delta^{13}\text{C}$ values, and most of the low-carbon number n-alkanes ($< C_{21}$) contributed from the Enping oils had light $\delta^{13}\text{C}$ values, in the mixed oils the $\delta^{13}\text{C}$ values of low-carbon number and high-number n-alkanes were respectively similar to the Enping and Wenchang oils, resulting in a “V” feature in the carbon isotopic profile of n-alkanes. The molecular compositions of the group II oils also indicate they were contributed by both the Wenchang and Enping source rocks. The grouploils have high Pr/Ph and Dia C_{30}/C_{30} values, and have moderate contents of the bicadinane “T”, oleanane and C_{30} 4-methylsteranes, indicating they were generated both from terrigenous and aquatic organic matter (Huang et al., 2003, 2007; Cheng et al., 2013a, 2013b). The $\delta^{13}\text{C}$ values of the n-alkanes in the grouploils are more like the Enping oils (Tables 1 and 2), and the carbon isotopic profile of n-alkanes reveals the “V” feature only when the Enping oils are dominant in the “mixed” oils (the ratio of Wenchang to Enping oils is 1:3). Therefore, there is a greater proportion of Enping oils than Wenchang oils in grouploils.

However, the $\delta^{13}\text{C}$ values of n-alkanes in the grouploils are slightly different according to location (Fig. 4). The oils in the central areas of the Wenchang A sag (such as from the WC9 wells) have lighter $\delta^{13}\text{C}$ values of n-alkanes than the oils in the marginal areas (such as from the WC13 wells in the Qionghai uplift and the WC15 wells in the Shenhu uplift), but their thermal maturities appear lower (Huang et al., 2003, 2007; Cheng et al., 2013b), which is contradictory to research findings (Clayton, 1991; Tang et al., 2005; Schwab et al., 2005) that the $\delta^{13}\text{C}$ values of the n-alkanes become heavier with higher maturity (Fig. 5). This case probably to be attributed to the different relative contents of Wenchang and Enping Formation derived oils in the mixed oils at the different locations. For the deeper burial depths in the central area of the Wenchang A sag compared with the marginal areas of the sag, the

time of generation of the Wenchang oils in the former area is much earlier than in the latter area, resulting in fewer Wenchang oils preserved in the former area. Therefore, the grouploils in the marginal areas of the Wenchang A sag have a higher relative content of Wenchang oils, resulting in the heavier $\delta^{13}\text{C}$ values of n-alkanes in these oils. Compared with the oils in the central areas of the Wenchang A sag, the mixed oils in the marginal areas of the sag have a higher content of C_{30} 4-methylsteranes, a lower content of bicadinane “T” and oleanane (Cheng et al., 2013b), indicating the higher relative content of Wenchang oils in the mixed oils of the latter areas.

5. Conclusions

Based on the carbon isotopic characteristics of n-alkanes in crude oils and extracts of typical source rocks in the western Pearl River Mouth Basin, the main conclusions are as follows:

- (1) The carbon isotopic characteristics of n-alkanes in the extracts of the Wenchang source rocks are significantly different to the extracts from the Enping source rocks. The n-alkanes in the Wenchang source rocks have heavy $\delta^{13}\text{C}$ values (-26‰ to -21‰) which remain almost constant or become slightly heavier with increasing carbon number, whereas the Enping source rocks have light $\delta^{13}\text{C}$ values (-33‰ to -27‰), which become lighter with increasing carbon number.
- (2) Two groups of oils in this area were identified based on the carbon isotopic characteristics of the n-alkanes. The grouploils distributed in the Wenchang B sag have $\delta^{13}\text{C}$ values that are heavy (-25‰ to -22‰) and similar to the Wenchang source rocks. Grouploils are mainly distributed in and around the Wenchang A sag; their $\delta^{13}\text{C}$ values are light (-32‰ to -28‰) and reveal a “V” feature in the carbon isotopic profile of n-alkanes, and are different from typical extracts of both the Wenchang and Enping source rocks.
- (3) The results of artificial thermal maturation experiments indicate that from the early stage to the peak stage of oil generation (with the EasyRo range between 0.64% and 1.02%), the $\delta^{13}\text{C}$ values of n-alkanes in the pyrolysis oils increase by about 3‰ with increase thermal maturity, but the carbon isotopic profiles of n-alkanes are not significantly affected by thermal maturity. In the main stage of oil generation, the carbon isotopic characteristics of n-alkanes of the Wenchang and Enping source rocks as well as their pyrolysis or geological oils, are still clearly distinct.
- (4) The mixing of oils with different thermal maturities from the same source rock has no significant influence on the carbon isotopic profile of n-alkanes in the mixed oils. However, the mixing of oils with different source organic matter is capable of producing the “V” feature in the carbon isotopic profile of n-alkanes. Therefore, based on both the experimental and geological samples, the grouploils are explained to be mixtures of Wenchang and Enping oils in which the latter was the dominant component.

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