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Geochemistry of petroleum systems in the eastern Pearl River Mouth Basin: evidence for mixed oils

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Abstract

Detailed analyses of crude oils and source rock extracts indicate the presence of two effective petroleum source rocks in the eastern Pearl River Mouth Basin of the South China Sea region. Oils derived from the lacustrine source rocks in the Eocene Wenchang Formation are characterized by abundant C₃₀ 4-methyl steranes with relatively few C₁₉ tricyclic terpane and bicadinanes. In contrast, oils from the Eocene-Oligocene Enping Formation source typically contain significant amounts of C_{19} tricyclic terpane and bicadinanes, with relatively few 4-methyl steranes and high pristane/ phytane ratios. However, the chemical compositions of a large number of oils do not conform to those of the unknown source rocks, consistent with mixing of the two sources. Mixed oils occur mainly in the Huizhou Sag and along its south margin, and the highest proportion of the Enping Formation source in the reservoired mixed oils is estimated to be around 80%. Laboratory mixing experiments using selected end-member oils indicate that, even with 50-80% contribution from the Enping Formation source, the mixtures still display sterane biomarker ratio signatures diagnostic of the Wenchang Formation source. Therefore, the presence of abundant 4-methyl steranes is a necessary but not sufficient indicator for the Wenchang Formation source in the eastern Pearl River Mouth Basin. Although our results support the Wenchang Formation as a major source to the known oil discoveries in the study area, the contribution of the Enping Formation source to traps in the Huizhou Sag and surrounding area cannot be ignored. There is clear evidence for the recharge of Enping Formation derived oils into early-biodegraded oil accumulations to form light oil accumulations.

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1. Introduction

It is not uncommon for crude oils accumulated in a single oil reservoir to have originated from more than one source. Mixing of oils from multiple sources potentially creates uncertainties in the oil family classification and complicates oil-source correlation studies. Although few studies on mixed oils can be found in literature, the possibility of mixing mature oils with immature bitumen along migration pathways and/or in reservoirs has been raised in the study of rifted basins in eastern China (Li et al., 1995, 1999, 2003; Wang et al., 1999; Li, 2000; Pang et al., 2001, 2003a,b) and in southeastern Asia (Curiale, 2001), and multiple basins in western China (Li, 2000). Even in the cratonic Williston Basin of North America, mixing is considered to have been responsible for the paradoxic relationships associated with the existing petroleum system classifications (Jiang et al., 2001; Jiang and Li, 2002a,b). Mixed maturity oils are expected to be common products in the narrow, high relief rifted basins (Li et al., 1995, 1999).

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Peters et al. (1989) used the difference in stable carbon isotopic compositions to calculate the contributions of prospective source rocks to the mixed Beatrice oils. A biomarker fingerprinting approach was employed by Bissada (1996) to distinguish oils generated from freshwater and hypersaline lacustrine sources and to repartition artificially the contribution of each source to the mixed oils in Southeast Asian near-shore rift basins. Horstad and Larter (1997) showed that most oils in the Troll field were mixtures of degraded and fresh oils. As the concentrations of biomarker molecules in the C_{15+} saturated and aromatic hydrocarbon fractions vary significantly, the conventional qualitative fingerprinting approaches are generally inadequate in the study of petroleum fluid mixing (Li et al., 1995, 1999, 2003; Jiang et al., 2001; Jiang and Li, 2002a,b; Pang et al., 2003a,b). Combined bulk hydrogen and carbon isotopic analyses appear promising for characterizing mixed oils in the onshore Brazilian Potiguar Basin (Santos Neto and

Hayes, 1999), and the use of hydrogen isotopes of individual alkanes in the oil was recently reported for similar applications (Li et al., 2001). In the study of crude oils from the Cainan oil field of the eastern Junggar Basin, Chen et al. (2003) were able to repartition the mixed oils to multiple source rocks using stable carbon isotopes and quantitative biomarker data.

We report here the geochemical evidence for mixed oils derived from two Tertiary source rocks in the eastern Pearl River Mouth Basin (EPRMB), an area also known as the Zhu-1 depression (Fig. 1). The Pearl River Mouth Basin is located in the northern continental shelf of the South China Sea, and includes the vast area between the Hainan Island and Taiwan Islands, with an area of 175,000 km². The EPRMB covers an area of ~131,000 km² east of 113°10′E. Since the 1980s 10 oil fields have been discovered and put into production. The oils are mainly produced from the sandstone reservoirs of the upper Oligocene Zhuhai Formation, with minor pro-



Fig. 1. Structural units and oilfield distribution of the eastern Pearl River Mouth Basin, together with sampling locations.

duction also from the carbonate reservoirs near the base of the lower Miocene Zhujiang Formation (Fig. 2). The likely source rocks for these oils include the lacustrine shales and mudstones of the Eocene Wenchang Formation and the shallow lacustrine-deltaic coal-bearing sequence of the Eocene-Oligocene Enping Formation.

Limited in-house studies by China National Offshore Oil Corporation (CNOOC) in the 1990s suggest that the oils in the study area were derived from the lacustrine source facies in the Wenchang Formation where the wide occurrence of 4-methyl steranes was taken as the key geochemical evidence. In contrast, oils with mixed sources from both Wenchang and Enping formations were suggested in the Huizhou Sag (Fig. 1). The major evidence cited for a source in the Enping Formation includes the high pristane/phytane ratio and the presence of oleanane and several other un-identified pentacyclic triterpanes (Chen et al., 1991). As oils in PY4-2, an oilfield with large reserves discovered in 1998, were correlated to the source rocks in the Wenchang Formation because of their high relative abundance of 4methyl steranes, petroleum explorationists working in this area were led to believe that the Wenchang Formation was the most important source rock in the EPRMB.



Fig. 2. Generalized stratigraphic column of the Pearl River Mouth Basin. Modified from Chen et al. (1991).

The results of the present study indicate that contribution from the Enping Formation source rocks cannot be ignored in the study area, particularly for reservoirs within the Huizhou Sag and adjacent areas (Fig. 1). As the mixing of significant amounts of Enping Formation-derived oil with that of a Wenchang Formation origin produced oil containing relatively abundant 4-methyl steranes in laboratory mixing experiments, the use of selected geochemical parameters often based on trace molecules in the oil (such as 4-methyl steranes) without considering the bulk oil properties may potentially result in misleading oilsource correlation and hence erroneous exploration decisions.

2. Samples and experimental methods

A total of 365 potential source rocks (mudstones and carbonaceous mudstones) and 47 crude oil samples were provided for this study by CNOOC. The sampling locations are shown in Fig. 1. The rock samples include cores and cuttings collected from the Wenchang, Enping and Zhuhai formations. The oil samples covers all of the discovered oil pools in the study area.

Total organic carbon contents (TOC) and hydrocarbon generative potentials for all of the rock samples were determined using a Rock-Eval/TOC apparatus. Sixty-three rock samples with more than 1% TOC were then selected for solvent extraction (Soxhlet, chloroform, 72 h). A portion of the oil samples were analyzed using a Varian 3700 gas chromatography fitted with a 30 m×0.25 mm i.d. HP-5 capillary column (with a film thickness of 0.25 μ m) and a flame ionization detector. Nitrogen was used as carrier gas. The oil samples were injected when the oven was held at 40 °C. After 4 min, the over was programmed to 310 °C at 8 °C /min.

After asphaltene precipitation, the rocks extracts and crude oils were separated into saturated hydrocarbons, aromatic hydrocarbons and a polar fraction using an aluminum/silica gel column sequentially eluted with hexane, dichloromethane/hexane (2:1) and chloroform/ ethanol (1:1). Gas chromatography-mass spectrometric analyses (GC/MS) of the saturated hydrocarbon fractions were carried out on a Fisons MD800 mass spectrometer coupled to a Carlo-Erba 8000 gas chromatography equipped with a 30 m \times 0.25 mm i.d. DB-5ms capillary column with a film thickness of 0.25 µm. The samples were injected via a splitless injector maintained at 300 °C when the oven temperature was set at 70 °C. After 5 min, the oven was programmed to 300 °C at 2 °C/min, using helium as carrier gas. The temperatures for interface and ion source were maintained at 300 °C and 200 °C, respectively. The mass spectrometer was operated in the mode of multiple ion monitoring at 70 eV, with a scanning rate of 2 s/cycle.

Table 1	
The thickness and organic richness in the source rocks of the Wenchang and Enping formations from the eastern Pearl River Mouth B	Basin

Sag	Well	Formation thickness	Thickness of source	Sample*	TOC (%))	S1+S2 (1	mg/g)	HI (mg/g	TOC)	Extract (0%)	Hydrocan in rock (J	rbons ppm)	
		(111)	TOCK(III)		Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	
(a) Wench	hang Formatio	n													
Lufeng	HF33-3-1	430.0	59.5	10 (5)	0.24	0.06-1.05	0.21	0.03-0.95	47.14	9-104	0.0378	0.0159-0.0569	142	53-208	
	LF 1-1-1	416.0	110.0	7	0.11	0.05-0.18	0.11	0.06-0.24	41.60	10-64					t e
Lufeng13	LF13-2-1	140.0		16 (2)	2.77	1.93-4.46	11.48	7.51-28.82	416.70	268-606	0.3151	0.2656-0.3647	1565	1275-1848	N1
	HZ18-1-1	156.0		4	1.29	0.61-1.42	1.94	0.60-2.15	137.68	85-144					Tha
Huizhou	XJ24-1-1X	165.0	45.5	8 (4)	0.96	0.79-1.44	1.18	0.82-1.58	108.48	91-129	0.0984	0.0549-0.5271	420	272-567	рg
Enping	EP17-3-1	294.0	173.5	6 (3)	1.07	0.88-1.45	1.24	0.59-1.42	84.75	50-178	0.0826	0.0625-0.1197	450	355-541	et a
(b) Enping	g Formation														1./0
Hanjiang	HF28-2-1	884.4	156.5	11	0.53	0.14-1.64	0.46	0.13-1.88	63.52	33-105					SLC
Lufeng	HF33-3-1	227.0	65.5	8 (2)	0.88	0.42-1.52	1.37	0.40 - 5.05	123.31	81-318	0.0969	0.0541-0.1398	346	182-510	an
	LF1-1-1	785.0	195.0	16 (1)	0.46	0.10-3.13	0.59	0.04 - 4.78	77.54	8-200	0.0168		39		<i>ic</i> (
Lufeng13	LF13-1-1	373.0	130.0	8 (2)	0.85	0.35-3.00	1.03	0.32-4.80	88.32	44-150	0.0289	0.0192-0.0386	115	80-149	ieo
	LF13-2-1	292.0	139.5	5	2.75	0.78 - 5.52	6.24	0.75-13.57	174.55	86-257					che
	LF14-2-1	714.5	314.0	24 (1)	1.76	0.31-5.48	2.22	0.24-8.90	101.21	52-185	0.0320		80		mi
Huizhou	HZ08-1-1	1412.5	562.0	29 (2)	2.03	0.66-4.48	4.17	1.06-13.06	177.52	82-316	0.2264	0.1625-0.2903	904	800-1007	str
	HZ9-2-1			2 (1)	1.17	0.37-2.33	2.21	0.16-6.65	131.03	32-254	0.1048		529		ч 3
	HZ13-1-1	999.0	417.5	19 (2)	1.95	049-6.05	4.23	0.56-31.13	167.62	94-327	0.3634	0.2043-0.5224	1671	972-2369	4
	HZ21-1-1	810.0	210.0	6(1)	1.01	0.09-2.81	1.26	0.03-4.36	68.45	11-135	0.0502		214		200
	HZ23-2-1	786.0	382.0	40 (9)	1.58	0.62-4.71	2.76	0.81-14.62	122.96	66-285	0.1258	0.0455-0.35271	537	198-1222)3)
	XJ24-3-1	680.0	159.5	4 (2)	2.09	1.00-4.64	2.86	0.27-2.28	115.78	23-208	0.1192	0.0940-0.1444	508	489-527	97
Xijiang	XJ33-2-1	810.0	422.0	2 (2)	1.56	0.75-2.36	1.98	0.59-3.36	92.05	68-116	0.1041	0.0495-0.1587	427	174-680	1-0
	XJ36-3-1			4	1.71	1.39-2.10	1.59	1.07-2.44	81.98	70-107					166
Enping	EP12-1-1	446.0	178.0	1 (1)	0.54	0.54	0.98	0.98	159.26	159.26	0.0464		272		
	EP17-3-1	1136.0	161.0	15 (3)	0.87	0.16-3.39	1.28	0.08-5.10	89.46	25-172	0.1303	0.0275-0.2889	454	94–973	
Panyu	PY15-1-1	515.5	170.0	14 (1)	2.12	0.58-6.01	3.23	0.40-16.09	99.36	3-248	0.0940		352		

* Number of samples used for Rock-Eval analysis (solvent extraction).

Table 2						
Biomarker parameters	of source rock	extracts collected	from the easter	rn Pearl River	Mouth	Basin ^a

Well no.	Depth (m)	Terpane							Sterane						Isopre	noids	
		C19/C23 TT	TT/PT	$C_{24} Tet / \ C_{30}$	T_s/T_m	Ole/C_{30}	T/C ₃₀	Gam/C ₃₀	20 <i>R</i> -C ₂₇	20 <i>R</i> -C ₂₈	20 <i>R</i> -C ₂₉	C ₃₀ / C ₂₉	ββ	20 <i>S</i>	Pr/Ph	Ph/C_{18}	Pr/C ₁₇
Wenchang 1	Fm																
XJ24-1-1X	3642.5-3647.5	2.41	0.11	0.06	0.19	0.08	0.35	0.04	0.19	0.11	0.70	0.12	0.47	0.45	1.88	0.91	1.74
XJ24-1-1X	3680-3687.5	0.89	0.05	0.04	0.33	0.16	0.15	0.05	0.20	0.08	0.73	0.11	0.46	0.44	1.61	0.96	1.54
XJ24-1-1X	3815-3817.5	2.30	0.07	0.04	0.93	0.18	0.16	0.08	0.31	0.13	0.55	0.19	0.48	0.44	1.46	0.86	1.31
XJ24-1-1X	3822.5-3827.5	1.51	0.08	0.05	0.79	0.13	0.23	0.07	0.29	0.14	0.57	0.19	0.45	0.42	3.75	0.43	1.42
EP17-3-1	4680	0.58	0.58	0.16	0.99	0.07	0.99	0.10	0.39	0.25	0.36	0.22	0.47	0.39	1.01	0.79	0.81
EP17-3-1	4755	0.45	1.14	0.12	0.51	0.04	0.49	0.17	0.29	0.33	0.38	0.12	0.37	0.38	0.81	0.62	0.52
EP17-3-1	4780	0.27	1.29	0.13	0.74	0.10	0.24	0.12	0.33	0.32	0.35	0.22	0.52	0.40	1.48	0.38	0.65
HF33-3-1	3203-3209	0.57	0.05	0.03	0.38	0.03	0.01	0.09	0.25	0.17	0.58	0.19	0.42	0.37	4.17	0.40	1.53
HF33-3-1	3224-3230	0.88	0.08	0.04	0.39	0.03	0.04	0.09	0.29	0.19	0.52	0.19	0.43	0.39	5.85	0.39	2.05
HF33-3-1	3254-3257	0.34	0.04	0.03	0.45	0.01	0.02	0.11	0.25	0.23	0.52	0.17	0.44	0.38	2.88	0.38	1.16
HF33-3-1	3279.2	0.27	0.08	0.05	0.79	0.06	0.09	0.06	0.38	0.20	0.42	0.17	0.41	0.35	2.00	0.54	1.50
HF33-3-1	3314-3317	0.83	0.06	0.05	2.65	0.02	0.04	0.06	0.34	0.16	0.50	0.23	0.42	0.35	4.75	2.69	1.88
LF-14-2-1	3590-3600	0.29	0.25	0.10	0.54	0.02	0.13	0.10	0.36	0.21	0.43	0.19	0.40	0.38	4.22	0.14	0.52
LF13-2-1	3142.5	0.48			0.78	0.04	0.04		0.31	0.15	0.54	2.19	0.70	0.58			
LF13-2-1	3150-3160	0.46	0.02		0.82	0.07	0.04		0.39	0.11	0.50	1.28	0.53	0.41	2.08	0.46	0.99
LF13-2-1	3202.5-3207.5	0.31	0.04	0.03	1.02	0.03	0.05	0.06	0.44	0.15	0.41	0.26	0.35	0.49	1.48	0.44	0.81
Enping Fm																	
HF33-3-1	2981-2987	0.36	0.12	0.06	0.19	0.00	0.05	0.07	0.27	0.14	0.59	0.18	0.38	0.28	3.43	0.39	1.44
HF33-3-1	3059-3065	1.31	0.03	0.03	0.33	0.10	0.05	0.05	0.35	0.12	0.53	0.28	0.25	0.28	1.50	0.85	1.27
LF1-1-1	2829-2844	1.62	0.09	0.07	0.12	0.10	0.05	0.07	0.28	0.18	0.54	0.15	0.33	0.27	2.81	0.45	1.43
LF13-1-1	2911.4	1.83	0.08	0.11	0.07	0.00	0.02	0.06	0.35	0.17	0.48	0.12	0.32	0.39	5.17	0.09	0.55
LF13-1-1	3177.5-3185	0.41	0.05	0.05	0.29	0.04	0.03	0.04	0.30	0.15	0.54	0.47	0.34	0.41	7.10	0.59	3.94
LF-14-2-1	3492.5-3500	1.98	0.07	0.15	0.05	0.00	0.16	0.05	0.21	0.15	0.64	0.10	0.28	0.42	6.42	0.39	3.08
HZ23-2-1	3852-3864	5.06	0.21	0.24	0.39	0.10	0.70	0.04	0.17	0.17	0.65	0.13	0.52	0.42	1.92	0.79	1.62
HZ23-2-1	3942-3954	5.72	0.24	0.20	0.47	0.08	1.74	0.06	0.28	0.21	0.50	0.18	0.46	0.37	1.90	0.64	1.30
HZ23-2-1	3975.6	0.69	0.23	0.09	0.95	0.10	2.46	0.16	0.39	0.22	0.40	0.16	0.38	0.31	1.30	0.40	0.47
HZ23-2-1	4062-4068	10.33	0.34	0.21	0.65	0.12	2.06	0.08	0.29	0.23	0.48	0.18	0.44	0.38	1.97	0.63	1.35
HZ23-2-1	4131-4140	3.07	0.30	0.22	0.75	0.13	1.81	0.08	0.31	0.22	0.47	0.20	0.48	0.39	2.18	0.49	1.16
HZ23-2-1	4263-4269	2.55	0.38	0.18	0.64	0.08	1.44	0.07	0.30	0.20	0.50	0.15	0.45	0.39	3.89	0.12	0.53

Tab	le 2	(continued)
		(,

Well no.	Depth (m)	Terpane							Sterane						Isopre	noids	
		C19/C23 TT	TT/PT	$C_{24} Tet / \ C_{30}$	T_s/T_m	Ole/C ₃₀	T/C_{30}	Gam/C ₃₀	20 <i>R</i> -C ₂₇	20 <i>R</i> -C ₂₈	20 <i>R</i> -C ₂₉	C ₃₀ / C ₂₉	ββ	20 <i>S</i>	Pr/Ph	Ph/C_{18}	Pr/C ₁₇
HZ23-2-1	4338-4344	2.56	0.22	0.20	0.45	0.05	0.83	0.06	0.32	0.21	0.46	0.20	0.46	0.38	3.94	0.24	0.96
HZ23-2-1	4422-4425	0.59	0.37	0.15	0.85	0.06	1.14	0.10	0.35	0.21	0.44	0.20	0.42	0.38	1.19	0.43	0.48
HZ23-2-1	4479-4482	1.06	0.17	0.09	0.53	0.06	0.40	0.10	0.31	0.21	0.48	0.18	0.39	0.35	4.00	0.21	0.85
HZ21-1-1	4680	4.99	0.12	0.09	0.10	0.03	2.28	0.04	0.24	0.21	0.55	0.13	0.35	0.36	3.29	0.19	0.67
HZ9-2-1	3681-3690	57.57	0.49	0.25	0.11	0.07	0.12	0.03	0.24	0.21	0.55	0.12	0.41	0.32			
HZ08-1-1	3436-3439	6.06	0.07	0.15	0.10	0.04	0.20	0.04	0.12	0.12	0.76	0.09	0.33	0.44	2.94	0.62	1.99
HZ08-1-1	3535-3538	9.37	0.12	0.19	0.07	0.04	0.21	0.07	0.13	0.11	0.76	0.09	0.38	0.41	2.75	0.62	1.79
HZ08-1-1	4009	1.09	0.34	0.21	0.30	0.13	0.77	0.04	0.21	0.14	0.65	0.13	0.52	0.45	0.67	0.09	0.05
HZ08-1-1	4321-4324	1.65	0.29	0.20	0.23	0.06	0.62	0.06	0.23	0.16	0.61	0.14	0.48	0.43	4.11	0.26	1.07
HZ13-1-1	3887.5	14.36	0.08	0.05	0.11	0.05	0.05	0.05	0.18	0.09	0.73	0.10	0.35	0.36	4.81	1.14	5.50
HZ13-1-1	4422.5	1.58	0.05	0.06	0.23	0.03	0.06	0.08	0.25	0.12	0.63	0.16	0.45	0.41	4.34	0.34	1.69
HZ13-1-1	4890		0.00	0.08	0.02	0.00	0.08	0.02	0.10	0.10	0.80	0.06	0.24	0.36	8.56	0.90	7.70
XJ24-3-1X	3497.5-3507.5	0.73	0.05	0.06	0.37	0.04	0.03	0.09	0.27	0.12	0.61	0.15	0.40	0.41	3.13	0.53	2.21
XJ24-3-1X	4040-4052.5	2.38	0.10	0.10	0.21	0.07	0.72	0.05	0.23	0.15	0.63	0.14	0.48	0.41	2.08	0.77	1.70
XJ33-2-1	4082.3	3.27	0.09	0.07	0.07	0.16	0.62	0.05	0.21	0.17	0.62	0.08	0.27	0.33	2.50	1.36	4.41
XJ33-2-1	4838.3	1.06	0.21	0.10	0.88	0.10	1.50	0.15	0.37	0.22	0.41	0.18	0.39	0.31	2.09	0.67	1.22
EP12-1-1	3638.35-3639.37	8.22	0.14	0.18	0.15	0.05	2.64	0.07	0.31	0.26	0.43	0.13	0.39	0.36	3.45	0.39	1.41
EP12-1-1	3647.5	1.85	0.10	0.08	0.13	0.23	9.75	0.05	0.24	0.28	0.48	0.00	0.37	0.39	2.03	0.93	2.03
EP17-3-1	3535	2.19	0.11	0.09	0.13	0.04	0.22	0.08	0.20	0.32	0.48	0.08	0.34	0.38	5.07	0.35	1.97
EP17-3-1	3715	0.97	0.18	0.13	0.30	0.05	0.63	0.10	0.23	0.32	0.45	0.12	0.42	0.40	1.85	0.87	1.70
EP17-3-1	4040	0.20	0.09	0.04	0.80	0.05	0.07	0.08	0.33	0.26	0.42	0.41	0.41	0.40	1.19	0.37	0.61
PY15-1-1	4140	0.88	0.07	0.05	0.12	0.05	0.55	0.06	0.28	0.19	0.53	0.14	0.36	0.38	5.85	0.37	2.38
PY27-2-1	4627	0.28	0.08	0.05	0.96	0.07	0.21	0.04	0.35	0.22	0.43	0.17	0.43	0.36	1.74	0.37	0.76
PY33-1-1	4315-4335	1.16	0.54	0.20	0.70	0.13	4.60	0.09	0.41	0.23	0.36	0.16	0.44	0.42			
PY33-1-1	4495-4510	0.32	0.89	0.26	0.99	0.10	5.29	0.12	0.48	0.21	0.31	0.19	0.50	0.46			
PY33-1-1	4610-4615	0.31	0.55	0.19	9.62	0.11	11.25	0.14	0.43	0.24	0.33	0.19	0.43	0.41			

^a For terpane parameters, C_{19}/C_{23} TT: C_{19}/C_{23} tricyclic terpane ratio; TT/PT: tricyclic/pentacyclic terpane ratio; C_{24} Tet/ C_{30} : C_{24} tetracyclic/ C_{30} hopane ratio; Ts/Tm: $18\alpha(H)$ -/ $17\alpha(H)$ -trisnorhopane ratio; Ole/ C_{30} : oleanane/ C_{30} hopane ratio; T/ C_{30} : bicadinane-"T"/ C_{30} hopane ratio calculated from *m/z* 412 mass chromatogram; Gam/ C_{30} : gammacerane/ C_{30} hopane ratio. For sterane parameters, 20R- C_{27} , 20R- C_{28} and 20R- C_{29} : relative abundances of 20R- C_{27} , C_{28} and $C_{29} \alpha \alpha \alpha$ steranes; C_{30}/C_{29} : C_{30} 4-methylsterane/ C_{29} sterane ratio; $\beta\beta$: $\beta\beta/(\beta\beta + \alpha\alpha) C_{29}$ sterane ratio; 20S: $20S/(20S + 20R) C_{29}$ sterane ratio. For acyclic isoprenoids, Pr/Ph: pristane/phytane ratio; Pr/C17 and Ph/C18: pristane/*n*- C_{17} and phytane/*n*- C_{18} alkane ratios.

Table 3
Basic geochemical data for the oil samples collected from the eastern Pearl River Mouth Basin

Well no.	Reservoir age	Depth (m)	DST	Density (d ²⁰) (g/ml)	Viscosity (50 °C, cp)	Pour Point (°C)	Wax (%)	S (%)	SAT (%)	ARO (%)	Resin (%)	Asp. (%)	$\begin{array}{c} \delta^{13}C_{oil} \\ (\%) \end{array}$
HZ21-1-1	Zhujiang	2918-2925	DST3						85.22	10.71	2.93	1.14	-27.4
HZ21-1-1	Zhujiang	2874-2885	DST6A	0.7995	3.7	22	12.62	0.09	85.35	12.64	1.17	0.84	-27.1
HZ21-1-1	Zhujiang	2850-2856	DST7	0.7975	2.84	17	18	0.14	81.65	13.87	3.68	0.79	-27.6
HZ27-1-1	Zhujiang	2405-2420	DST2	0.8095					80.18	11.02	2.64	6.15	-27.4
HZ27-1-1	Zhujiang	2230-2240	DST3	0.8280					81.98	5.54	6.45	6.02	-27.0
XJ24-3-1	Zhujiang	2939-2944	DST1						77.02	14.93	2.48	5.56	-26.9
XJ24-3-2	Zhujiang	2333-2337	DST1	0.8254	4.75	34	23.1	0.03	78.22	13.62	4.45	3.69	-28.8
XJ24-3-2	Zhujiang	2102-2111	DST2	0.8638	15.7	39	26	0.06	71.97	18.69	3.69	5.63	-27.6
XJ24-3-2	Zhujiang	2042-2047	DST3	0.8639	17.5	39	27.2	0.06	80.18	7.09	8.32	4.41	-27.6
XJ24-1-1	Zhujiang	2790-2792	DST1A	0.8633	8.27	37.8	28.6	0.04	78.88	15.46	2.21	3.44	-28.3
XJ24-1-1	Zhujiang	2725-2731	DST2	0.8227	3.62	32.2	31	0.04	78.07	17.78	2.73	1.41	-39.0
XJ24-1-1	Zhujiang	2674-2681.5	DST3	0.8368	4.83	35	43.6	0.05	76.16	17.76	2.34	3.73	-28.2
XJ24-1-1	Zhujiang	2543-2546	DST4	0.8348	4.64	35	28.2	0.06	76.08	18.25	3.38	2.27	-28.5
XJ30-2-2X	Zhujiang	2446.5-2449	DST3						63.13	21.72	6.48	8.67	-26.6
XJ30-2-2X	Zhujiang	2688-2693	DST1	0.8762					63.62	19.66	6.81	9.90	-26.4
XJ30-2-2X	Zhujiang	2514.5-2517	DST2A	0.8762					61.44	21.79	7.36	9.41	-26.6
XJ30-2-2X	Hanjiang	1944–1951	DST4	0.8961					65.08	23.73	5.63	5.56	-26.9
HZ26-1-1	Zhujiang	2307-2312	DST4	0.8294	1.83 (109 °C)				75.57	17.93	2.49	4.00	-26.8
HZ26-1-1	Zhujiang	2025-2029.5	DST6	0.8733	4.78 (97 °C)				74.84	15.01	4.41	5.73	-26.8
HZ32-5-1	Zhujiang	2381-2389	DST1	0.8268					74.51	17.55	2.33	5.21	-27.4
HZ32-5-1	Zhujiang	1878-1884.5	DST2	0.8269					75.25	18.69	2.69	3.36	-27.3
HZ32-5-1	Zhujiang	1691-1695	DST3	0.8440					77.74	17.59	2.63	2.04	27.3
HZ33-1-1	Zhujiang	2194-2200	DST4	0.8896	36.1	34	21.3	0.12	51.78	27.60	7.02	13.59	-27.0
HZ33-1-1	Zhujiang	1990-2025	DST8A	0.8900	37.7	34	21	0.12	52.71	30.17	5.45	11.67	-27.8
LF13-1-1	Zhujiang	2505-2516	DST2	0.8751	27.75 (40 °C)				62.08	25.00	4.88	8.03	-29.6
LF15-1-1	Zhujiang	1870-1882	DST1A	0.8833	31				64.78	20.84	4.21	10.17	-28.4
LF15-1-1	Zhujiang	1854-1862	DST2	0.8681	29.6				64.51	23.73	3.29	8.46	-28.5
LF22-1-2E	Zhujiang	1615-1640	DST1	0.8560	4.35				63.38	22.18	4.35	8.07	-28.5
LH11-1-1A	Zhujiang	1197.5-1240	DST1	0.9256	92.7	-10	0.44	0.41	49.11	33.96	6.73	10.18	-26.9
LH4-1-1	Zhujiang	1235.2-1291.7	DST1	0.9372	153.23	-10	2.04	0.28	38.45	40.95	8.81	12.77	-27.0
PY4-2-1	Zhujiang	2155-2161.5	DST1	0.9170					60.81	25.81	6.34	7.03	-27.3
PY4-2-1	Zhujiang	1900-1914	DST2	0.8927					59.33	27.06	5.94	7.67	-26.1
PY4-2-1	Zhujiang	1864–1874	DST2a	0.8980					56.71	26.83	8.81	7.65	-26.4
PY4-2-1	Hanjiang	1768-1777	DST3	0.9280					43.98	33.45	7.46	15.09	-25.9
PY5-1-1	Zhujiang	2136.5-2143.5	DST1						56.52	28.21	6.76	8.52	-26.9
PY5-1-1	Zhujiang	1844.5-1852	DST2						45.31	28.01	10.14	16.54	-27.1
PY5-1-2	Zhujiang	1851-1857	DST1						43.89	32.13	10.07	13.89	-26.9
PY5-1-2	Zhujiang	1851-1860	DST1aR						43.34	37.38	7.37	11.90	-27.0
PY5-1-2	Zhujiang	1565-1568	DST2						34.74	38.33	10.62	16.31	-26.8
XJ34-3-1	Zhuhai	2653-2661	DST3	0.8473	12.9	39	16.7	0.2	69.53	16.71	4.67	9.08	-27.2
HZ9-2-1	Enping	3578-3598	DST2	0.7860	0.16								-28.7

3. Results and discussion

3.1. Geochemistry of potential source rocks

The eastern Pearl River Mouth Basin has been divided into 10 structural units, consisting of five depressions (sags in Chinese literature) and five uplifts (Fig. 1). The regional unconformity that developed during the late Oligocene (corresponding to the T_7 seismic reflector) (Fig. 2) separates the sedimentary column in the study area into two tectono-stratigraphic sequences. Beneath the unconformity, non-marine sediments of the Paleocene to early Oligocene age were deposited during extensive rifting. The sediments consist mainly of the fluvial, variegated sand-containing mudstone and coagulate carbonate interbeds of the Shenhu Formation, the lacustrine mudstones and sandstone interbeds of the Wenchang Formation, and the shallow lacustrine to deltaic coal-bearing clastics of the Enping Formation (Zhao et al., 1992). Organic-rich rocks that have significant petroleum generative potentials have been encountered mainly in the Wenchang and Enping for-



Fig. 3. Rock-Eval pyrolysis data of potential source rocks collected from the wells LF13-2-1 (a) and HZ08-1-1 (b). See Fig. 1 for well locations.

mations. Detailed geochemical parameters for these potential source rocks are summarized in Table 1. Marine sediments were developed above the unconformity when the regional subsidence began to unite the previously separated sag areas into one large depression. The basal marine sequence consists mainly of reef carbonates and deltaic to near-shore sediments, overlaid by marine sandstone and shale interbeds (Zhao et al., 1992). Therefore, the two tectono-stratigraphic sequences vertically form an ideal source, reservoir and caprock combination (Fig. 2).

The Wenchang Formation is interpreted to occur widely in the eastern Pearl River Mouth Basin according to seismic data, and reasonable source rocks have



Fig. 4. Correlation of potential source intervals in different localities of the eastern Pearl River Mouth Basin and characteristic sterane and terpane distributions for source rocks in the Wenchang and Enping formations.

been found by drilling in the LF13 region, Huizhou and Enping sags (Fig. 1, Table 1). The average TOC content, Rock-Eval $S_1 + S_2$ value and hydrogen index of these rocks are 2.23%, 8.65 mg/g Rock and 329 mg/g TOC, respectively. The highest solvent extract yield, hydrocarbon yield and Hydrogen Index reach 2149 ppm, 1051 ppm, and 600 mg/g TOC, respectively, from samples collected from the LF 13-2-1 well. These characteristics indicate that these rocks contain mostly mixed sapropelic/humic organic matter or "type II₁" according to the classification scheme of Huang and Li (1982) (Fig. 3a). In contrast, fine-grained clastic rocks of the Enping Formation have been penetrated mainly in the Huizhou sag and LF13 region. The average TOC, S1+S2, extract yield and hydrocarbon content are 1.78%, 3.2 mg/g Rock, 1559 ppm and 686 ppm, respectively. Thus, the Enping Formation source rocks contain more humic organic matter (mostly type II₂, and to a lesser extent types II_1 and III, according to Huang and Li (1982) (Fig. 3b).

As shown by the examples in Fig. 4 and Table 2, source rocks in the Wenchang and Enping formations display distinctly different distributions of solvent soluble terpanes and steranes independent of the source rock maturity, reflecting the difference in their organic input and depositional environment. Source rocks in the Wenchang Formation are enriched in 4-methyl steranes relative to regular steranes. The absence or low abundance of oleananes and other pentacyclic terpanes and low pristane/phytane ratios (<2) in these rocks indicate euxinic, anoxic depositional environment with only minor angiosperm plant inputs. On the other hand,

source rocks in the Enping Formation contain relatively abundant bicadinanes, C_{19} -tricyclic and C_{24} -tetracyclic terpanes. For example, a mudstone sample collected from the HZ9-2-1 well at the interval of 3681–3690 m has unusually high C_{19} tricyclic terpane relative to other tricyclic terpanes, with the C_{19}/C_{23} tricyclic terpane ratio as high as 57. These characteristics, together with the relatively low abundance of 4-methyl steranes and high pristane/phytane ratios in these rocks, are consistent with their coal-forming marsh environment.

3.2. Classification of crude oils

The physical properties of crude oils produced from the eastern Pearl River Mouth Basin (Table 3) vary significantly, with 0.787–0.959 in specific density, 3–411 centipoises in viscosity (at 50 °C), and -17 to -44 °C in pour point. These oils are generally low in sulfur (<0.5%) and high in wax, with 2–27% of non-hydrocarbons (asphaltene and polar fractions) and a V/Ni ratio of 0.094–0.267.

Based on the specific gravity of the oils, the oils can be divided into two broad groups: (1) Group I oils, with specific gravity > 0.88, occur in the margins of the Huizhou sag, LH11-1-1 and LH4-1-1 oil fields in the Dongsa swell, PY4-2-1 field in the Panyu swell, and EP18 structure in the Enping sag. These oils are generally heavy and sometimes biodegraded. (2) Group II oils, with specific gravity < 0.88, generally occur in reservoirs with greater depth (> 2000 m) and are laterally distributed within the Huizhou Sag and its southern margin (adjacent to the Xihui low swell area).

Well	Depth (m)	DST	Terpane							Sterane						Isopre	noids		
			C19/C23 TT	TT/PT	C24Tet/C30	T_s/T_m	Ole/C ₃₀	T/C ₃₀	Gam/C ₃₀	20 <i>R</i> -C ₂₇	20 <i>R</i> -C ₂₉	20 <i>R</i> -C ₂₈	C ₃₀ /C ₂₉	ββ	205	Pr/Ph	Ph/C18	Pr/C17	
LF13-1-1	2505-2516	DST2	0.18	0.15	0.04	1.46	0.08	0.09	0.03	0.39	0.44	0.17	0.75	0.53	0.50	2.34	0.28	0.59	
LF15-1-1	1854-1862	DST2	0.66	0.10	0.02	1.65	0.11	0.15	0.02	0.35	0.48	0.17	1.18	0.47	0.61	2.65	0.31	0.74	
LF15-1-1	1870-1882	DST1A	0.66	0.10	0.03	1.64	0.13	0.13	0.03	0.39	0.46	0.15	1.51	0.48	0.61	2.43	0.29	0.68	F .
LF22-1-2	1615-1640	DST1	0.19	0.23	0.07	1.21	0.08	0.10	0.06	0.38	0.42	0.20	0.63	0.56	0.46	2.65	0.27	0.56	S
HZ 9-2-1	3453	DST2	17.79	0.26	0.15	0.27	0.05	0.87	0.04	0.29	0.59	0.12	0.22	0.51	0.46	7.37	0.11	0.78	Zhc
HZ19-2-1	3453	MDT	2.14	0.32	0.08	1.92	0.35	2.61	0.06	0.21	0.72	0.06	0.70	0.52	0.49	2.96	0.09	0.27	ng
HZ19-2-1	3477.1	MDT	2.39	0.25	0.09	1.71	0.39	1.37	0.07	0.17	0.54	0.28	0.63	0.54	0.47	3.14	0.16	0.47	et
HZ19-2-1	3511.4	MDT	2.20	0.30	0.08	2.26	0.40	15.72	0.05	0.70	0.16	0.15	0.54	0.57	0.56	2.61	0.09	0.23	al.
HZ19-2-1	3622.4-3632.4	DST1	1.15	0.32	0.06	1.95	0.52	4.11	0.06	0.15	0.45	0.39	0.69	0.61	0.47	2.92	0.09	0.23	0
HZ19-3-1	2611-2630	DST3	1.02	0.18	0.05	1.88	0.26	2.37	0.04	0.24	0.45	0.32	1.32	0.51	0.61	2.76	0.10	0.26	rga
HZ19-3-1	2826-2834	DST2	1.02	0.17	0.04	2.12	0.26	1.09	0.05	0.21	0.48	0.31	1.25	0.51	0.61	2.83	0.09	0.26	inic
HZ19-3-1	3160-3165	DST1	0.56	0.08	0.03	1.20	0.15	0.48	0.03	0.24	0.57	0.19	1.92	0.45	0.58	3.43	0.19	0.62	ŝ
HZ21-1-1	2850-2856	DST7	7.69	0.38	0.08	1.55	0.16	1.16	0.04	0.31	0.41	0.28	1.35	0.54	0.55	4.66	0.15	0.66	200
HZ21-1-1	2874-2885	DST6A	2.96	0.44	0.08	1.86	0.18	1.94	0.05	0.37	0.30	0.33	1.36	0.56	0.57	3.40	0.15	0.46	hen
HZ21-1-1	2918-2980	DST3	1.97	0.32	0.05	1.61	0.14	1.28	0.03	0.33	0.36	0.31	1.57	0.55	0.55	3.55	0.14	0.42	nist
HZ26-1-1	2025-2029.5	DST6	0.45	0.11	0.03	1.32	0.10	0.32	0.02	0.37	0.45	0.18	2.23	0.45	0.57	3.16	0.23	0.62	ïy
HZ26-1-1	2307-2312	DST4	0.85	0.17	0.03	1.56	0.13	0.88	0.03	0.38	0.42	0.20	2.13	0.51	0.64	2.83	0.21	0.52	34
HZ27-1-1	2230-2240	DST3	0.13	0.22	0.08	1.17	0.05	0.18	0.07	0.54	0.32	0.14	0.38	0.51	0.39	3.19	0.16	0.44	(2)
HZ27-1-1	2405-2420	DST2	3.99	0.66	0.11	1.26	0.14	0.65	0.05	0.41	0.33	0.27	0.99	0.55	0.59	1.95	0.35	0.64	203
HZ32-5-1	2381-2389	DST1	1.22	0.17	0.03	1.58	0.14	1.24	0.03	0.36	0.35	0.29	2.22	0.50	0.65	3.25	0.13	0.47	5
HZ32-5-1	1878-1884.5	DST2	1.44	0.14	0.03	1.84	0.11	0.82	0.03	0.35	0.42	0.23	1.75	0.49	0.55	3.11	0.16	0.46	77-
HZ32-5-1	1691-1695	DST3	1.38	0.19	0.04	2.07	0.11	0.78	0.03	0.37	0.37	0.26	1.57	0.45	0.58	3.41	0.14	0.42	26-
HZ33-1-1	1990-2025	DST8A	0.35	0.14	0.04	1.11	0.10	0.20	0.02	0.43	0.38	0.20	1.76	0.51	0.55	2.91	0.34	0.93	1
HZ33-1-1	2194-2200	DST4	0.44	0.07	0.02	1.18	0.08	0.18	0.02	0.41	0.44	0.15	2.65	0.40	0.59	3.10	0.36	1.08	
XJ24-1-1	2543-2558	DST4	0.88	0.31	0.08	1.65	0.14	1.27	0.05	0.31	0.42	0.26	0.78	0.56	0.45	3.09	0.17	0.49	

 Table 4

 Biomarker parameters of the oil samples collected from the eastern Pearl River Mouth Basin^a

Table 4 (continued)

Well	Depth (m)	DST	Terpane							Sterane						Isopre	noids	
			C19/C23 TT	TT/PT	C24Tet/C30	T_s/T_m	Ole/C_{30}	T/C ₃₀	Gam/C ₃₀	20 <i>R</i> -C ₂₇	20 <i>R</i> -C ₂₉	20 <i>R</i> -C ₂₈	C ₃₀ /C ₂₉	ββ	20 <i>S</i>	Pr/Ph	Ph/C18	Pr/C17
XJ24-1-1	2674-2681.5	DST3	1.01	0.38	0.11	1.86	0.16	1.73	0.03	0.33	0.46	0.21	1.30	0.53	0.50	3.44	0.13	0.43
XJ24-1-1	2790-2792	DST1A	1.57	0.16	0.04	2.12	0.14	1.10	0.03	0.38	0.35	0.26	1.61	0.49	0.56	3.05	0.17	0.49
XJ24-3-1	2939-2963	DST1	1.75	0.18	0.08	1.12	0.12	0.35	0.03	0.39	0.37	0.24	1.01	0.51	0.60	3.46	0.13	0.42
XJ24-3-2	2042-2047	DST3	0.81	0.12	0.03	1.63	0.13	0.77	0.03	0.38	0.38	0.24	2.31	0.52	0.62	3.18	0.36	1.50
XJ24-3-2	2102-2111	DST2	0.66	0.13	0.03	1.72	0.12	0.69	0.03	0.41	0.33	0.26	2.09	0.51	0.62	3.08	0.37	1.23
XJ24-3-2	2333-2346	DST1	1.10	0.16	0.04	1.71	0.13	1.02	0.03	0.42	0.31	0.27	1.85	0.52	0.60	3.24	0.14	0.42
XJ30-2-2x	1944–1951	DST4	0.77	0.12	0.03	1.68	0.07	0.98	0.03	0.37	0.40	0.22	2.35	0.47	0.63	2.87	1.58	4.93
XJ30-2-2x	2446.5-2449	DST3	0.59	0.09	0.02	1.42	0.10	0.33	0.02	0.40	0.39	0.22	2.71	0.43	0.65	3.23	0.24	0.67
XJ30-2-2x	2514.5-2517	DST2A	0.53	0.08	0.02	1.31	0.08	0.20	0.02	0.42	0.44	0.14	2.70	0.41	0.62	3.10	0.26	0.74
XJ30-2-2x	2688-2693	DST1	0.51	0.09	0.02	1.30	0.12	0.26	0.02	0.41	0.42	0.17	3.03	0.42	0.63	3.32	0.24	0.71
XJ34-3-1	2653-2661	DST3	1.84	0.27	0.08	1.00	0.14	0.42	0.04	0.32	0.51	0.17	0.99	0.43	0.57	3.75	0.11	0.42
LH11-1-1A	1197.5-1305	DST1	0.18	0.27	0.07	1.17	0.08	0.30	0.04	0.41	0.45	0.14	0.93	0.56	0.43	2.64	1.30	3.09
LH4-1-1	1235.2-1291.7	DST1	0.22	0.26	0.06	1.20	0.08	0.32	0.03	0.37	0.45	0.18	1.05	0.59	0.44			
EP11-1-1	1879–1880	5, 6	0.37	0.06	0.02	2.67	0.31	0.24	0.03	0.25	0.68	0.08	2.39	0.49	0.61			
EP11-1-1	1923-1924.5	18, 19, 20	0.65	0.04	0.02	1.73	0.21	0.19	0.03	0.84	0.13	0.04	2.06	0.48	0.60			
EP11-1-1	2077.5		0.26	0.02	0.01	2.59	0.16	0.09	0.02	0.32	0.57	0.11	2.59	0.41	0.55			
PY4-2-1	2155-2206	DST1	0.37	0.31	0.02	1.94	0.10	0.04	0.02	0.33	0.47	0.21	1.41	0.47	0.67	2.41	0.34	0.85
PY4-2-1	1900-1914	DST2	0.16	0.31	0.07	1.36	0.11	0.06	0.04	0.39	0.41	0.19	0.93	0.57	0.43	2.72	0.77	1.91
PY4-2-1	1864–1944	DST2a	0.54	0.14	0.03	1.77	0.11	0.08	0.03	0.33	0.47	0.20	1.36	0.50	0.61	2.30	0.87	1.63
PY4-2-1	1768-1777	DST3	0.21	0.22	0.04	1.31	0.10	0.05	0.03	0.34	0.43	0.23	1.22	0.52	0.51			
PY5-1-1	2136.5-2143.5	DST1	0.22	0.16	0.04	0.98	0.10	0.02	0.02	0.34	0.42	0.24	4.21	0.50	0.44	2.51	0.42	0.97
PY5-1-1	1844.5-1852	DST2	0.29	0.08	0.02	0.88	0.10	0.03	0.02	0.33	0.43	0.25	1.63	0.45	0.47	2.53	1.58	4.35
PY5-1-2	1851-1857	DST1	0.45	0.08	0.02	0.93	0.10	0.03	0.02	0.32	0.43	0.25	1.81	0.43	0.50	2.08	2.12	5.05
PY5-1-2	1851-1860	DST1aR	0.44	0.07	0.02	0.92	0.10	0.03	0.02	0.32	0.43	0.25	1.73	0.45	0.50	2.01	2.56	5.09
PY5-1-2	1565-1682.5	DST2	0.30	0.12	0.03	0.92	0.11	0.03	0.02	0.34	0.40	0.26	1.49	0.49	0.48			

^a See Table 2 for abbreviations.

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End- member B/A ratio	% B in mixture by volume	Terpa	nes							Steranes				
	-,	T_s/T_m	"T"/C ₃₀ H	C_{19}/C_{23}	TT/H	C_{19-22}/C_{23-26}	$C_{24}Tet/C_{26}TT$	C_{31}/C_{30}	$C_{29}Ts/C_{29}H$	C_{30}/C_{29}	C_{27}/C_{29}	C ₂₉ dia./reg.		
0:1	0	1.14	0.17	0.35	0.09	0.76	0.51	0.37	0.38	2.38	0.73	0.29		
1:1	50	0.93	0.36	1.19	0.14	1.11	0.72	0.39	3.71	1.95	0.75	0.32		
3:1	75	0.80	0.34	3.70	0.13	1.96	1.12	0.52	0.32	1.72	0.70	0.30		
5:1	83	0.74	0.38	4.25	0.13	2.32	1.33	0.54	0.30	1.54	0.68	0.38		
1:0	100	0.27	0.87	17.79	0.26	9.95	7.33	1.10	0.12	0.22	0.70	0.39		

Table 5	
Biomarker parameters for the two end-member oils and their binary mixtures ^{a,b}	

^a End-member A, representing the Wenchang Formation-derived oils, was taken from the Zhujiang Formation reservoir of the HZ33-1-1 well (at the depth of 2194–2200 m). End-member B, representing the Enping Formation-derived oils, was taken from the Enping Formation reservoir of the HZ9-2-1 well (at the depth of 3681–3690 m).

^b "T"/ C_{30} H: bicadinane "T"/ C_{30} hopane ratio (m/z 412); C_{19}/C_{23} : C_{19}/C_{23} tricyclic terpane ratio; TT/H: total tricyclic terpane/total hopane ratio; C_{19-22}/C_{23-26} : C_{19-22}/C_{23-26} tricyclic terpane ratio; C_{24} Tet/ C_{26} TT: C_{24} tetracyclic terpane/ C_{26} tricyclic terpane ratio; C_{31}/C_{30} : C_{31}/C_{30} ; C_{31}/C_{30} ; C_{30}/C_{29} : C_{29} Ts/ C_{29} H: C_{29} Ts/ C_{29} hopane ratio; C_{30}/C_{29} : C_{30} 4-methyl/ C_{29} sterane ratio; C_{27}/C_{29} : C_{27}/C_{29} sterane ratio; C_{29} dia. /reg.: C_{29} diasterane /regular sterane ratio.

In order to determine if the oil groupings described above on the basis of physical properties were source, maturity or biodegradation related, several classes of biomarker compounds in the oils were investigated, including bicyclic drimanes, bicadinanes, tricyclic terpanes, oleananes, hopanes, regular steranes and 4methyl steranes (Table 4).

Although drimane homologs of a prokaryotic origin (Alexander et al., 1983; Volkman, 1988) are abundant in both groups of oils, there are sufficient differences in the relative abundances of various isomeric drimanes and homodrimanes that can be used to differentiate between the two groups of oils (Fig. 5a). For example, cross plotting of two selected ratios in Fig. 6a clearly separate the two groups of oils, even though the underlying reason for the separation remains to be determined.

Cadinane, bicadinanes and tricadinanes identified in Southeastern Asian oils and sediments are believed to originate from the angiosperm Dammar resin (van Aarssen and de Leeuw, 1989; van Aarssen et al., 1990). Such compounds were detected in relatively high abundance from the marine mudstones of the Miocene Meisan Formation and condensate oils from the Yacheng 13-1 gas field of the adjacent Ying-Qiong basins (Zhang and Zhang, 1993). Bicadinanes also occur in the oils produced from the eastern Pearl River Mouth Basin, although their abundances are generally lower than those in the Ying-Qiong basins. The Group II oils are differentiated from the Group I oils by their high abundance of bicadinanes (labeled as "T" and "W" in Fig. 5b) relative to C_{30} hopane on the m/z 412 mass chromatogram, thus the bicadinane-T/C₃₀-hopane ratio can be used as an effective molecular parameter for classifying the oils in the study area (Fig. 6b).

Tricyclic terpanes are common constituents in crude oil, with a possible origin from prokaryotic cell membranes (Ourisson et al., 1982). While the C_{23} member is

often the dominant homolog in crude oils of a marine or lacustrine source (Connan et al., 1980; Aquino Neto et al., 1983), the dominance of a lower-molecular-weight homolog such as the C₁₉ has been related to the possible input from higher plants associated with coal-bearing depositional settings (Peters and Moldowan, 1993). As the C₁₉-C₂₆ tricyclic terpanes displayed different distribution patterns for the two groups of oils studied (Fig. 5c), the C₁₉/C₂₃ tricyclic terpane ratio (abbreviated to "C₁₉/C₂₃ TT") was also used here as a molecular parameter in classifying the oils.

Oleananes are well known markers for angiosperm plant input to sedimentary organic matter since the late Cretaceous time (Peters and Moldowan, 1993; Moldowan et al., 1994). The abundances of oleananes relative to C_{30} hopane in the studied oils are generally lower than those reported from the Tertiary Niger Delta (Ekweozor et al., 1979). Both groups of the oils contain detectable amounts of oleananes (Fig. 5b), and the average oleanane/C₃₀-hopane ratios are slightly different.

 4α -Methyl steranes can be formed from dehydration and hydrogenation of 4α -methyl sterols in dinoflagellates, prymnesiophyte microalgae, or even bacteria (Wolff et al., 1986; Volkman et al., 1990). 4α -Methyl-24-ethylcholestanes often occur in relatively high abundance in the Tertiary source rocks and related oils from China (Fu et al., 1992). As almost all of the oils from the eastern Pearl River Mouth Basin contain significant amounts of 4-methyl steranes (Fig. 5d), it is difficult to use these compounds in the differentiation of the two oil groups. The only exception is the oil newly discovered from the HZ9-2-1 structure (Fig. 1), which contains little 4-methyl steranes.

Therefore, the oil grouping based on physical properties appears to be supported by the molecular indices. To the best of our knowledge, almost all of these indices



Fig. 5. Biomarker distributions for the two end-member oils in the eastern Pearl River Mouth Basin.



Fig. 6. Classification of crude oils produced from the eastern Pearl River Mouth Basin using selected molecular parameters. See Fig. 5 for the identifications of compounds used in the calculation of the parameters.

do not appear to be affected significantly by thermal maturation or biodegradation. Thus, the most likely cause for the variation of oil compositions in the study area was source related.

3.3. Oil-source rock correlation

As indicated in Figs. 7 and 8, end members of the Groups I and II oils correlate well with the source rocks in the Wenchang and Enping formations, respectively. However, cross-plots of a number of biomarker ratios suggest that the correlative relationships are far more complicated when all of the oils are considered (Figs. 9 and 10). On the basis of the C_{19}/C_{23} tricyclic terpane and bicadinane-T/C₃₀ hopane ratios, a tight cluster of the Group I oils and Wenchang Formation source rocks

(Fig. 9) indicates a possible genetic relationship. However, correlation for most of the Group II oils with the two known source rocks appears more problematic. The relatively high C_{30} 4-methylsterane/ C_{29} sterane ratios of these oils (Fig. 10) may be opportunistically interpreted as a Wenchang Formation source, as suggested by previous CNOOC in-house studies (Keqiang Wu, personal communications). This interpretation is not supported by the relatively high bicadinane-"T"/ C_{30} hopane ratios of these oils, which are generally characteristic of the Enping Formation source rocks.

We attribute this apparent contradiction to petroleum fluid mixing, thus each of the Group II oils may have received different proportion of Enping Formation-derived oils relative to those of a source in the Wenchang Formation. In order to determine if this hypothesis is plausible, mixing experiments were conducted in the laboratory. Here we selected the HZ33-1-1 (DST8a) and HZ9-2-1 (DST2) oils as the potential end members derived from the Wenchang and Enping formations respectively. The oils, collected after gas separation, were mixed in different proportions. The saturated hydrocarbon fractions of the resultant mixtures were then analyzed by GC/MS. As shown in Fig. 11 and Table 5, an increase in the proportion of Enping Formation-derived oil in the mixture would lead to (1) an increase in the bicadinane-"T"/ C_{30} hopane and C_{19}/C_{23} tricyclic terpane ratios, (2) a decrease in the C_{30} 4-methyl sterane/ C_{29} regular sterane ratio in the mixture. However, these variations are not significant until the proportion of Enping Formationderived oil in the mixture is over 80% (Fig. 11). Oils generated from the coaly source rocks in the Enping Formation generally contain lower concentrations of high molecular-weight biomarkers such as terpanes and steranes than those from a lacustrine source in the Wenchang Formation. Thus, the results of these artificial experiments illustrate that the contribution of the Enping Formation-derived oil in the mixture would not be recognized using these biomarker parameters unless the contribution was more than 80%. As a consequence, the contribution of the Wenchang Formation source to known oil reserves in the eastern Pearl River Mouth Basin may have potentially been greatly overestimated. Therefore, the presence of relatively high abundance of 4-methylsteranes is a necessary, but not sufficient, molecular criterion for identifying the Wenchang Formation-derived oils in the study area.

In order to achieve more realistic petroleum resource assessment, it would be highly desirable if the percentage contributions from the two potential sources to each of the discovered oils can be somehow estimated on live oils. This task is inheritably difficult, as the end member oils selected from the samples available to us may not truly represent the oils derived from the two source rocks. The subtle difference in source maturity



Fig. 7. Correlation of an end-member oil with a potential source rock in the Wenchang Formation using biomarker distributions.

and organic facies may potentially create uncertainties in the estimated results, as indicated by the large scatter in the source rock data (e.g. Figs. 9 and 10). Keeping these uncertainties in mind and assuming that the selected end members represent the general characters of the two source rocks, we compared the compositional data observed for the Group II oils with those of mixing experiments to estimate the relative contributions of the two potential source rocks. Most of the oil pools in the Huizhou Sag and along its southern margin appear to contain some proportions of Enping Formation-derived oil, with the highest amounts (up to 80%) in the HZ21-1-1, HZ27-1-1 and HZ9-2-1 oils, and the lowest in the XJ30-2 oil. Oils from the XJ24-3-1, XJ24-1-1, HZ26-1-1 and HZ32-5-1 pools may contain intermediate amounts of Enping Formation-derived oil. While this general mixing trend can be easily observed, the exact percentages of mixing for each of the oils are more difficult to be determined.

3.4. Models for petroleum generation, migration and entrapment

Results of basin modeling (Fig. 12) indicate that peak oil generation from the Wenchang Formation source rocks in the Huizhou Sag occurred during the early to middle Miocene (24–10 Ma b.p.) when the Pearl River and Hanjiang formations were deposited (Gong, 2002). During that period, most of the Enping Formation was immature with respect to oil generation. Oils generated from the Wenchang Formation migrated through faults along both sides of the Huizhou SW graben. As faults were open in the HZ20 area, no oils were accumulated there. In contrast, several traps were already formed along the Dongsa uplift, thus the oils migrated upwards along faults to gain access to the sandstone reservoirs of the Zhuhai Formation. Some of these oils continued to travel considerable distances southeasterly, and eventually accumulated in the carbonate reservoirs of the Zhujiang Formation (Fig. 13). Because of the shallow burial, the oils in the Liuhua and Panyu-4 areas were biodegraded (Fig. 14).

During the deposition of the Yuehai Formation (after 10 Ma b.p.), most of the Enping Formation began to enter the conventional oil window (>0.75%Ro; Keqiang Wu, unpublished results). Reactivation of the old faults created numerous vertical conduits for the Enping Formation-sourced oils to charge reservoirs in the overlying marine strata. Because over 2000 m of marine sediments have acted as regional seals, these oils may have been accumulated much more efficiently than the Wenchang Formation-derived oils. In many of the discovered oil pools such as XJ24 and HZ27, recharging of Enping Formation-sourced oils to reservoirs containing earlier emplaced, biodegraded, oils is clearly indicated by the co-occurrence of abundant *n*-alkanes and 25-norhopane in the oils (Fig. 14).

Consequently, the difference in the locations of effective petroleum source kitchens and the timings of peak oil generation led to the distribution of Group I and II oils at different geographic locations (Fig. 13). The source rocks in the Wenchang Formation within and



Fig. 8. Correlation of an end-member oil with a potential source rock in the Enping Formation using biomarker distributions.

beyond the Huizhou Sag entered conventional oil window. Thus, the Group I oils derived mainly from this source occur in the Huizhou Sag as well as the Dongsa uplift, Huilu and Enxi low swells. In contrast, the source rocks in the Enping Formation are mature only in the Huizhou Sag. As a result, the Group II oils, with different proportions of Enping and Wenchang formationderived oils, occur dominantly in the Huizhou Sag and Xihui low swell area. The latter includes the XJ24-2, XJ24-1, HZ19-3, HZ26-1, HZ32-5, HZ21, HZ27 and HZ9-2-1 structures. Such a distribution pattern can be observed clearly from several structural cross sections in the study area. On the cross section as shown in Fig. 15, for example, oils discovered in the Huizhou Sag (HZ21-1) and Xihui low swell area (XJ24-3 and XJ24-1) display biomarker ratios characteristic of mixed Wenchang/



Fig. 9. Cross plot of C_{19}/C_{23} tricyclic terpane versus bicadinane-"T"/C30 hopane ratios for oils and rock extracts from the eastern Pearl River Mouth Basin, showing oil–rock correlation.



Fig. 10. Cross plot of C_{30} 4-methyl-/ C_{29} sterane versus bicadinane "T"/ C_{30} hopane ratios for oils and rock extracts from the eastern Pearl River Mouth Basin, showing oil–rock correlation and occurrence of mixed oils.



Fig. 11. Change of biomarker parameter values with the mixing proportion, showing dramatic variety of mixed oils when the percentage of the Enping oil increases above 80%.

Enping formation sources. However, the chemical compositions of the oils in the Dongsa uplift indicate that Enping Formation-derived oils did not reach the location represented by the HZ33-1-1 well, thus these oils may have accumulated only in the area northwest of this well. Another point worth to mention is the strong control of local subsidence centers (i.e. individual source kitchens) on the chemical compositions of oils in the Huizhou Sag and Xihui low swell area. For example, oils produced from the XJ30-2 field appear to have derived from a Wenchang Formation source, whereas oils in the adjacent XJ24-1 and XJ24-3 fields display geochemical characteristics of mixed sources. This indicates that oil generated from the Enping Formation within the XJ24 fault block did not migrate across the boundary faults into the XJ30 fault block (Fig. 13).



Fig. 12. The history of burial and hydrocarbon generation in the Huizhou sag.



Fig. 13. Proposed migration fairways for the oils in the eastern Pearl River Mouth Basin.



Fig. 14. Cross plot of density versus 25-norhopane/ C_{30} hopane ratios for oils in the eastern Pearl River Mouth Basin. Arrows denote the processes associated with biodegradation and recharging.

4. Conclusions

This study demonstrates that crude oils discovered in the eastern Pearl River Mouth Basin belong to genetic groups derived from a lacustrine source rock in the Eocene Wenchang Formation and a lacustrine-deltaic, coal-bearing source rock in the Eocene-Oligocene Enping Formation. Crude oils derived from source rocks in the Wenchang Formation are characterized by a high abundance of C_{30} 4-methyl steranes and represent one of the major contributors to known petroleum resources in the study area. Because of the shallow reservoir depth in the Dongsa uplift, many of these oils were altered by in-reservoir biodegradation. In contrast, crude oils derived from a source in the Enping Formation are characterized by high pristane/phytane ratios and abundant bicadinanes and C_{19} tricyclic terpanes. Laboratory binary mixing experiments demonstrate that the contribution of the Enping Formation source rocks to the discovered oils may have been underestimated



Fig. 15. Cross section from the Huizhou sag to Dongsha uplift showing the different biomarker assemblages in the petroleum in the different structural units.

using the conventional biomarker fingerprinting approach, as light oils derived from this source often contain much less abundant C15+ biomarkers than the Wenchang Formation-derived oils. Because the occurrence of the Enping Formation-derived oils was dominantly controlled by short distance migration generally within the individual source kitchens, the focus for further petroleum exploration should be on the subtle structures and stratigraphic traps within the sags and in adjacent low swell areas. It is also possible to find additional oils along the Dongsa uplift and Panyu low swell area, where the oils were generated early from the Wenchang Formation and accumulated after relatively long distance migration (a few tens of kilometers). However, this type of reservoir (above the depth of 2000m) often bears a relatively high risk of encountering biodegraded oils.

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