Comprehensive geochemical identification of highly evolved marine hydrocarbon source rocks: Organic matter, paleoenvironment and development of effective hydrocarbon source rocks*

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Abstract This study analyzed the developing environments of hydrocarbon source rocks in the Ordos Basin and evaluated carbonate rocks as hydrocarbon source rocks and their distributions on account of the fact that China's marine carbonate rocks as hydrocarbon source rocks are characterized by the intensive thermal evolution and relatively low abundance of organic matter, by taking the Lower Paleozoic of the Ordos Basin for example and in light of the calculated enrichment coefficients of trace elements, the profile analysis of trace element contents, ratios of relevant elements, and stable isotopic compositions and their three-dimensional diagrammatization in combination with the necessary organic parameters. As for the Ordos Basin, TOC=0.2% is an important boundary value. Studies have shown that in the strata TOC＞0.2%, V/(V+Ni)＞0.50, Zr/Rb＜2, Rb/K(×10^4)＞30, Z＞122, Th/U＞0.80, Zn and Mo are enriched with a positive $\delta^{13}C_{carb}$ excursion. All these indicated a stagnant and stratified sedimentary environment that has low energy, anoxia and high salinity in bottom water. In these strata the geological conditions are good for the preservation of organic matter, hence favoring the development of hydrocarbon source rocks. These strata have $\delta^{13}C_{org}$＜-28‰ (Ⅰ－Ⅱtype) and high hydrocarbon-generated potential. The Klimory and Wulalik formations show certain regularities in those aspects, therefore, they can be regarded as the potential effective hydrocarbon source rocks. In the strata TOC≤0.2%, Zr/Rb＞1, V/(V+Ni)＜0.50, Rb/K＜30, Th/U＜0.80, Cu, Zn, etc are depleted, and $\delta^{13}C_{org}$ values range from -24‰ to -28‰. All these facts showed that most of the carbonate rocks or mudstones were formed in high-energy oxidizing environments, thus unfavorable to the development of hydrocarbon source rocks. It is feasible to make use of the geochemical method to comprehensively assess the highly evolved marine carbonates rocks as potential hydrocarbon source rocks and their distributions.

Key words marine hydrocarbon source rock; paleoenvironment; comprehensive geochemical identification; Ordos Basin

1 Introduction

China's widespread marine carbonate rock series are mostly characterized by intensive thermal evolution and low abundance of organic matter, especially the Lower Paleozoic carbonate rocks have experienced multi-episodes of tectonics and a

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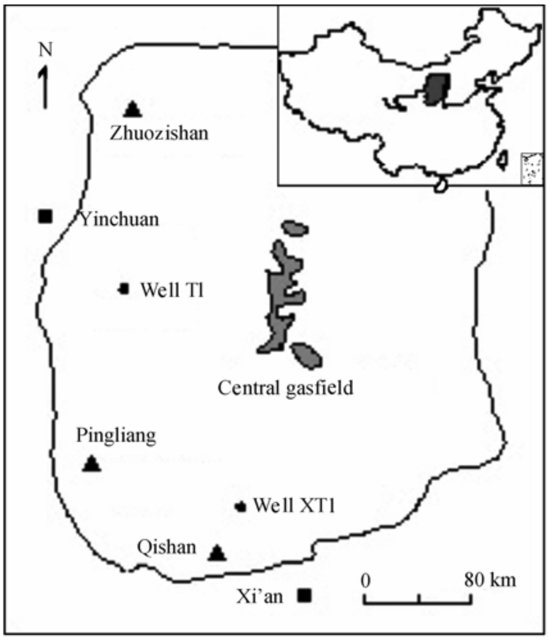

Fig. 1. Location of the sampling profile in the study region.

prolonged history of thermal evolution, thus making it more complicated the development and distribution of hydrocarbon source rocks, as reflected in the sedimentary, biological and geochemical facies. Consequently, it appears much less powerful to assess the highly evolved marine carbonates rocks as effective hydrocarbon source rocks and their distributions merely in light of organically geochemical characteristics of the present strata or some geochemical indices. Particularly in the assessment of hydrocarbon source rocks many important organically geochemical indices such as hydrocarbon-generating potentiality, H/C ratio, etc. seem to be unavailable. Many authors tried to lower the lower limit value of the content of residual organic carbon and restore the primary abundance of organic matter to resolve the problem of effectiveness (Cheng Keming et al., 1996; Hao Shisheng et al., 1996), but they have been puzzled by a lot of difficulties, and there has been still a big controversy (Xia Xinyu, 2000; Zhang Shuichang et al., 2002). Therefore, research on the methods of assessing marine carbonate rocks as hydrocarbon source rocks is still a key problem which needs to be solved urgently and also has been a hot subject of study at present time.

The development of hydrocarbon source rocks is primarily controlled by sedimentary environment (Hunt, 1979; Demaison and Moor, 1980; Chester, 2003). The thermal evolution degree of organic matter is relatively high in Paleozoic carbonate rocks, but there is a long way to go before the organic matter reaches substantial metamorphism (graphitization) (Li Rongxi, 1996). In addition, hydrocarbon source rocks are a kind of fine-grained sedimentary rocks (Hunt, 1979). Under this condition, most transition elements are usually immobile, even though they show some variations in contents, the ratios of relevant elements and their distribution patterns would still maintain balance (Wang Zhonggang et al., 1989; Zhao Zhenhua, 1997). The maturity level of organic matter has no influence on the distribution of trace metals (Alberdi-Genolet and Tocco, 1999). Only a little variation was noticed in carbon isotopic composition in the process of diagenesis-epigenesis (Zheng Yongfei and Chen Jingfeng, 2000; Galimov, 2002). So in the highly evolved marine strata these inorganic parameters are stable relative to organic matter, and they have a better capacity to bear primary geological information, and a higher reliability with respect to the information they bear on the developing environment of source rocks.

In this work we took the Lower Paleozoic of the Ordos Basin for example and introduced such inorganic parameters as trace elements and carbon and oxygen isotopes, as well as relevant environmental tracing theories into research on hydrocarbon source rocks with an attempt to reconstruct the environment of development of the hydrocarbon source rocks, and, in combination with the necessary organic parameters, to explore the development extent of the hydrocarbon source rocks, so as to establish the effective methods to assess those highly evolved marine carbonates rocks as effective hydrocarbon source rocks.

2 Sample collection & measurement

The study region is located at the western and southern margins of the Ordos Basin, where a total of 78 samples (12 shale samples and 66 carbonate rock samples) were collected. The samples were collected from the Zhuozishan (O_1z), Klimory (O_1k) and Wulalik (O_2w) formations of the Zhuozishan profile; from the 4th to 6th members of the Majiagou Formation (O_1m^{4-6}), and from the 6th member (O_1m^6) of the Majiagou Formation in well XT1 (Fig. 1).

The samples were analyzed for their organic carbon, major and trace elements, and stable isotopic composition, and pyrolysis analysis was also made of the samples mentioned above. Pyrolysis analysis and organic carbon analysis were effected by means of a Rock-Eval pyrolysis instrument and a CS-344 Model C-S analyzer, with a precision of ±0.5%; the major and trace elements were analyzed on a 3080E3X X-ray fluorospectrometer and an inductively coupled plasma spectrometer (ICP) with a precision of ±10%. Kerogen carbon isotopes ($\delta^{13}C_{org}$), carbonate carbon isotopes ($\delta^{13}C_{carb}$) and oxygen isotopes ($\delta^{18}O$) were measured on a MAT-252 spectrometer with a precision of ±0.2‰. ICP analyses were accomplished at Xi'an Institute of Mineral Resources and the rest at the Key

Laboratory of Gas Geochemistry, Chinese Academy of Sciences.

3 Organic geochemical characteristics

The analytical results of TOC, $\delta^{13}C_{org}$, and pyrolytic parameters for all the samples are listed in Table 1. Over 65% of the samples from O_1k and O_1m^6 of well XT1 have TOC > 0.2%, averaging 0.28% (non-shale samples). Most samples in O_2w have TOC ≥ 0.45%. However, all the samples from O_1z、O_1s and $O_1m^{4\text{-}6}$ have TOC < 0.2%. Pyrolysis peak temperatures (T_{max}) for 85% of the samples are higher than 460℃, so high as to be beyond the over-mature stage. Chloroform bitumen A, hydrocarbon-generating potentiality (S_1+S_2), index of hydrogen (I_H) and other pyrolysis parameters are too low to be of indicative significance for hydrocarbon source rocks (with the exception of shale samples from O_2w of the Pingliang profile), this is consistent with previously research results (Hao Shisheng et al., 1996; Xia Xinyu, 2000).

4 Inorganic parameters and their geological significance

4.1 Zr/Rb and hydrodynamic condition

Hydrodynamics is an integrative effect of water depth, wave base and current velocity. The preservative quantity of organic matter in sediments generally increases with decreasing hydroenergy (Hunt, 1979). Zirconium (Zr) is enriched in coarse-grained sediments (in the form of zircon), but depleted in fine-grained sediments. Rubidium (Rb) is basically deposited in low hydroenergy environment and enriched in fine-grained minerals such as clay minerals and mica (Zhao Yiyang and Yan Mingcai, 1994; Liu Zhaoshu et al., 2002). Therefore, the ratio of Zr to Rb (Zr/Rb) can quantitatively reflects hydrodynamic changes as a proxy indication, i.e., a high Zr/Rb value shows a high-hydroenergy environment and vice versa.

As listed in Table 2 and shown in Fig. 2, at the Zhuozishan profile, the average Zr/Rb value in O_1z is up to 6.02, but Zr/Rb values in O_1k and O_2w are both less than 2 (averaging 0.92). This fact suggests a deeper water and lower hydroenergy environment, in consistency with their geological characteristics, i.e., O_1k and O_2w are composed of dark-colored laminal micrite, pelmicrite, marlite, and graptolite shale; O_1z, of light-colored massive limestone and has strong biologic perturbation. "Calcium pellets" were contained within laminal limestones from O_1k, which also suggests a deep, still water environment (Feng Zengzhao et al., 1998).

At the Pingliang profile, the average Zr/Rb value in O_1s is 5.09, and lithologically the profile is composed of slab-massive limestones, with no muddy deposits (Table 2). At the Qishan profile, the average Zr/Rb values in $O_1m^{4\text{-}6}$ generally range from 5.25 to 6.47, which are higher than those in the contemporaneous strata at the western margin (Table 2). These characteristics indicate an adlittoral, roily environment. The average Zr/Rb value in O_1m^6 of well XT1 is 0.45, similar to that in O_1k, suggesting a

Table 1. Organic geochemical characteristics of the Ordovician at the southwestern margin of the Ordos Basin

Profile	Lithology	Formation	TOC (%)	"A" (×10⁻⁶)	S_1+S_2 (mg/g)	I_H	I_O	$\delta^{13}C_{org}$ (‰)	T_{max} (℃)
Zhuozishan	Shale	O_2w	0.53−0.88 / 0.70 (7)	42.7(1)	0.02−0.06 / 0.04 (3)	2−5 (3)	46−79 (3)	-29.6−-30.4 / -30.1 (3)	507−514 / 511 (3)
		O_1k	0.17−1.25 / 0.71 (2)	20.7(1)	0.02−0.05 / 0.035 (2)	3−6(2)	54−135 (2)	-30.0 (1)	480−513 / 497 (2)
	Carbonate rock	O_2w	0.18−0.21 / 0.195 (2)	28.7(1)	0.09 (1)	24(1)	133 (1)	-29.1 (1)	500 (1)
		O_1k	0.11−0.74 / 0.28 (28)	23.3−26.8 / 25.1 (2)	0.02−0.16 / 0.06 (13)	2−50(13)	24−128(13)	-28.1−-29.6 / -28.7 (13)	478−504 / 488 (9)
		O_1z	0.13−0.17 / 0.15 (6)	15.6−25.9 / 20.9 (3)	0.01−0.05 / 0.04 (6)	6−31(6)	77−292(6)	-27.8−-29.7 / -28.5 (3)	414−497 / 471 (6)
Pingliang	Shale	O_2w	0.45−0.85 / 0.60 (3)	183−851 / 499 (2)	0.67−3.07 / 1.63 (3)	140−342(3)	19−104(3)	-30.8−-31.7 / -31.2 (3)	439−443 / 440 (3)
	Carbonate rock	O_2w	0.09−0.11 / 0.10 (3)		0.06−0.12 / 0.083 (3)	10−91(3)	150−327(3)	-26.7−-26.8 / -26.75 (2)	433−468 / 447 (3)
		O_1s	0.10−0.15 / 0.12 (6)	48(1)	0.05−0.09 / 0.07 (6)	31−60(6)	92−160(6)	-29.4(1)	452−483 / 466 (6)
Qishan	Carbonate rock	O_1m^6	0.1−0.18 / 0.14 (8)	8(1)	0.05−0.07 / 0.06 (8)	28−55(8)	86−285(8)	24.1–24.2(2)	480−498 / 492 (8)
		O_1m^5	0.07−0.14 / 0.11 (3)		0.05−0.07 / 0.06 (3)	29−42(3)	100−183(3)	-25.1(1)	478−485 / 482 (3)
		O_1m^4	0.15−0.18 / 0.17 (2)	21.8(1)	0.06−0.07 / 0.065 (2)	28−33(2)	80−89(2)	-25.7(1)	477−480 / 479 (2)
Well XT1	Carbonate rock	O_1m^6	0.14−0.58 / 0.28 (8)	21.8−34 / 26 (4)	0.02−0.17 / 0.06 (8)	6−15(8)	40−93(8)	-27.3−-28.8 / -28.1 (3)	416−524 / 500 (8)

* Maximum value–minimum value/average (No. of samples).

localized basin where water was deeper and hydroenergy was relatively low in the Majiagou (O_1m) period. The existence of a sub-depression was evidenced by the petrography and paleogeography data presented by Feng Zengzhao et al. (1998).

4.2 Transition elements and redox condition

Anoxic condition is one of the key factors leading to the enrichment of sedimentary organic matter; under this condition, there is generally a high preservative ratio of organic matter (Hunt, 1979; Demaison and Moor, 1980). But the abundance of organic matter and its hydrocarbon generating potential are low under oxidation condition (Hunt, 1979; Demaison and Moor, 1980; Cheng Keming et

Table 2. Organic carbon contents of and inorganic parameters for carbonate rock samples

Section	Formation	Sample No.	TOC (%)	Cu ($\times10^{-6}$)	Zn ($\times10^{-6}$)	Mo ($\times10^{-6}$)	Zr/Rb	V/(V+Ni)	Rb/K ($\times10^{4}$)	Th/U	$\delta^{13}C_{carb}$ (‰)	$\delta^{18}O$ (‰)	Z
Zhuozi-shan	O_2w	w3-10	0.21	3.4	15.7		3.00	0.28	23		-1.3	-9.6	120
		w3-5	0.18	5.6	7.9	0.8	0.68	0.31	44	0.87	-1.0	-6.2	122
	O_1k	w2-31	0.23	4.4	9.7		1.38	0.41	43		0.2	-6.2	125
		w2-30	0.11	4.3	10.0		0.96	0.40	44				
		w2-29	0.11	4.3	14.7		2.50	0.29	18				
		w2-28	0.11	4.3	15.1	0.5	2.68	0.35	28	0.93	0.1	-7.1	124
		w2-27	0.24	7.7	7.8		0.69	0.65	33		0.4	-7.0	125
		w2-26	0.25	8.0	12.3		0.69	0.59	38				
		w2-25	0.58	16.8	26.6	2.7	0.57	0.82	39	1.50	0.5	-6.4	125
		w2-24	0.15	5.4	19.1		12.20	0.44	8				
		w2-23	0.23	8.0	14.6		1.28	0.54	35		0.0	-7.2	124
		w2-22	0.42	10.6	18.4		0.60	0.72	41		-0.3	-3.1	125
		w2-21	0.40	10.1	14.2	1.8	0.71	0.52	41	1.19	0.2	-6.6	124
		w2-20	0.15	4.5	11.9		0.98	0.49	34				
		w2-19	0.19	7.8	23.3		0.93	0.30	37				
		w2-18	0.27	3.8	12.7	0.5	1.07	0.50	38	0.84	0.1	-6.6	124
		w2-17	0.16	3.9	12.9		1.35	0.41	31				
		w2-16	0.31	8.4	19.5		0.75	0.61	35		0.4	-6.2	125
		w2-15	0.68	19.4	65.7		0.48	0.80	41		0.4	-6.5	125
		w2-14	0.23	7.0	18.3		0.58	0.70	36				
		w2-13	0.18	6.5	14.9		1.77	0.44	29				
		w2-12	0.22	6.5	10.7		1.14	0.44	32		0.4	-6.3	125
		w2-11	0.19	8.4	12.2		0.82	0.38	30				
		w2-10	0.60	15.1	32.2		0.62	0.66	38				
		w2-9	0.74	19.3	35.2	1.4	0.66	0.77	39	1.61	0.4	-7.9	124
		w2-8	0.26	8.4	13.6		0.68	0.40	37				
		w2-7	0.25	7.0	12.3		0.71	0.44	35				
		w2-6	0.25	6.0	12.3	0.6	1.08	0.42	33	0.82	0.5	-7.5	125
		w2-5	0.21	6.5	9.1		1.01	0.40	33				
		w2-4	0.17	7.5	9.2		1.64	0.45	26				
	O_1z	w2-2	0.15	4.3	10.1	2.6	3.50	0.41	9	0.61	0.1	-7.6	124
		w2-1	0.15	4.5	10.5		7.60	0.35	4				
		w2-2-1	0.13	4.1	8.9		5.89	0.44	11		0.1	-7.9	124
		w1-3	0.16	5.1	9.1		12.08	0.38	3				
		w1-2	0.17	4.5	17.3	0.9	3.43	0.36	8	0.41	-1.5	-9.2	120
		w1-1	0.13	3.7	7.7		3.63	0.32	29		-1.0	-10.3	120
Ping-liang	O_2w	P2-8	0.11	2.2	6.4		2.41	0.35	28		-0.3	-5.7	124
		P2-4	0.09	1.7	1.5	0.5	3.60	0.26	36	1.03	0.1	-6.6	124
	O_1s	P1-2	0.12	2.6	1.8		6.04	0.32	19		-0.2	-7.5	123
		P1-3	0.13	2.9	7.3		4.72	0.33	7		0.2	-6.6	124
		P1-4	0.15	2.4	8.1	0.5	4.51	0.47	10	0.89	-0.1	-6.4	124
Qi-shan	O_1m^6	Q2-12	0.13	1.2	12.1		0.40	0.39	31		-0.6	-3.8	124
		Q2-11	0.10	1.5	5.9	0.4	9.40	0.37	25	0.48	-0.1	-7.6	123
		Q2-9	0.18	5.7	9.6	0.8	9.60	0.49	33	0.42	0.3	-4.2	126
	O_1m^5	Q1-6	0.07	1.8	1.5	0.5	7.57	0.41	35	0.63	-0.5	-5.8	123
	O_1m^4	Q1-5	0.18	2.6	7.9	0.5	2.92	0.42	36	0.74	-0.1	-3.8	125
Well XT1	O_1m^6	X1-6	0.58	1.7	15.6		0.26	0.39	42		1.5	-8.6	126
		X1-9	0.30	3.4	15.1	1.4	0.66	0.34	31	1.51	2.1	-5.8	129
		X1-13	0.14	3.2	35.2	0.8	0.39	0.37	34	0.51	0.3	-7.3	124
Average content in carbonate rock (Turekian et al., 1961)				4.0	20.0	0.4							

al., 1996; Hao Shisheng et al., 1996).

Transition metals such as vanadium (V), zinc (Zn), copper (Cu), molybdenum (Mo) and uranium (U), are widely used as redox tracers in the fields of oceanography and environmental science. Variations in abundance and/or ratio of the trace metals can reflect the absence of dissolved O_2 (the presence of H_2S) and the stratification degree of water columns. Vanadium, Mo and U with low electrovalences (V^{3+}, Mo^{4+}, U^{4+}) were deposited under anoxic condition. Copper and Zn in the form of Cu^{2+} and Zn^{2+} were deposited in an anoxic environment in the case of the existence of H_2S. Generally, high V, Mo, U, Zn, Cu and S abundances, high degree of pyritization (DOP) ($\geqslant 0.67$), and high V/(V+Ni) ratios ($\geqslant 0.54$) all indicate an anoxic environment where H_2S was present in stratified bottom waters (Hatch, 1992; Wang Jizhong et al., 2005). The applications of the above indices basically are not restricted by lithology (Yan Jiaxin et al., 1998). Uranium/Th ratios (in mudstones) generally increase with increasing reduction, and U/Th $\geqslant$ 0.75 indicates an anoxic environment (Jones and Manning, 1994). However, U/Th ratios in microfossils decrease with increasing reduction, which can directly reflect the redox status of sea water (Zhao Zhenhua, 1997).

In Fig. 2 and Table 3, the abundances of V, Zn and TOC from O_1k and O_2w are much higher than those from O_1z, trace metal abundances of the samples with TOC>0.2% that have a positive correlation with TOC are several-fold higher than those of the samples with TOC<0.2%.

The concentrations of authigenic elements in marine sediments can reflect the change of marine environment (Zhao Yiyang and Yan Mingcai, 1994; Chester, 2003). In order to quantitatively describe the extent of concentration-dispersion of elements and eliminate the influence of terrestrial components, the authors, on the basis of the concept of contrast grade in geochemical exploration anomalies, tried to work out the enrichment coefficient (EC) with the average content of elements in sedimentary rocks presented by Turekian et al. (1961) as the background value after the contents of elements in the samples were normalized by the terrestrial component index—Al_2O_3, i.e., EC=[(element content/Al content)$_{test}$/(element content /Al content)$_{background}$]. In the case of EC>1 the elements are indicated to be of primary enrichment. Studies have shown that Mo and Cu are strongly enriched in O_1k, O_2w and O_1m^6 of well XT1, and TOC is higher than 0.2%. The EC of Mo is greater than 2, and that of Cu is 1.5−4.9 for about 70% of the samples. About 20% of the samples from O_1k are enriched in Zn, with EC ranging from 1.2 to 3.3, and in well XT1 Zn concentrations are high as well (EC = 2). Reversely, in the samples with TOC<0.2% from O_1z, O_1s and $O_1m^{4\text{-}6}$, Cu, Zn and other elements are depleted.

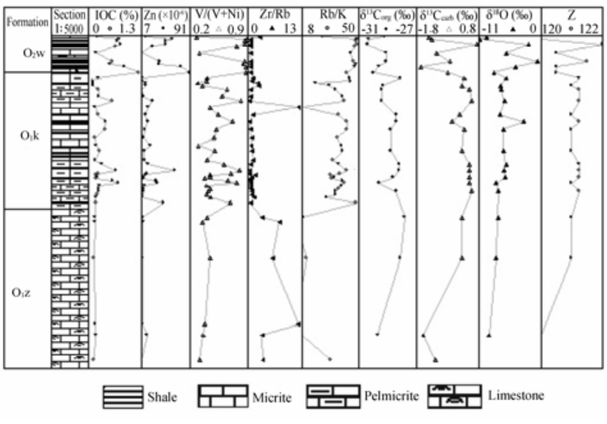

Fig. 2. Vertical variation trends of TOC and inorganic parameters in the Zhuozishan profile.

As shown in Fig. 2 and presented in Table 2, about 60% of the samples from O_1k and O_2w have V/(V+Ni) >0.46 and V/(V+Ni), Zn and TOC show the same tendency of variation, as is observed in the Zhuozishan profile. Th/U ratios in carbonate rock samples from O_1k and O_2w are all higher than 0.8, showing a good corresponding relation with TOC. In the Pingliang profile, the V/(V+Ni) and Th/U values of shale samples from O_2w are 0.58−0.68 and 0.89, respectively; the Th/U value of carbonate rock samples is 1.03. Th/U ratios in O_1m^6 of well XT1 are high (1.51), whereas samples from O_1z, O_1s and $O_1m^{4\text{-}6}$ all are characterized by V/(V+Ni)<0.46 and Th/U<0.80.

The above values suggest that the O_1k, O_2w and O_1m^6 of well XT1 were mainly deposited under anoxic conditions. The results are in line with those of enriched pyrites (Feng Zengzhao et al., 1998) and carbonate rocks have a higher value of Fe^{2+}/Fe^{3+} of 0.78 (Xia Xinyu, 2000). But a sustained oxidative environment in O_1z, O_1s and $O_1m^{4\text{-}6}$ is indicated. These strata are composed mainly of light-colored, slab-massive carbonate rocks and have abundant benthos traces (Feng Zengzhao et al., 1998), also indicating such an environment. In addition, Th/U ratios in carbonate rocks can directly reflect the redox status of marine environment. Under anoxic conditions, the ion U^{6+} will be reduced to U^{4+}, and then U^{4+} will be separated from sea water. Accordingly, the Th/U ratios will increase. In this study area, Th/U > 0.80 suggests an anoxic sedimentary environment.

4.3 Rb/K, carbon and oxygen isotopes and paleosalinity

Salinity is one of the major factors affecting the development of hydrocarbon source rocks. High salinity at the sediment-water interface is favorable to

Table 3. The abundances of transition elements and their correlation coefficients

TOC(%)	Element	V	Cr	Co	Ni	Cu	Zn	Mo	Cd	U
TOC>0.2	Content range ($\times10^{-6}$)	2.5−77	1.5−66	6.7−37	3.6−20	3.4−19	7.8−66	0.5−2.7	0.1−0.2	0.7−3.6
	Average content($\times10^{-6}$)	15.9	10.9	9.9	8.1	8.4	18.6	1.4	0.2	1.9
	Correlative coeffecient	0.8	0.76	0.14	0.78	0.76	0.77	0.60	0.61	0.96
	Sample amount	23	23	23	23	23	23	6	6	6
TOC≤0.2	Content range ($\times10^{-6}$)	2.5−5.4	1.5−3.6	1.5−30	2.0−8.7	1.5−8.4	1.5−35	0.4−2.6	0.1−0.3	0.7−1.8
	Average content($\times10^{-6}$)	3.2	2.0	7.5	5.1	4.1	11.1	0.8	0.2	1.1
	Correlative coeffecient	0.45	0.27	0.24	0.08	0.40	0.44	0.59	0.65	0.53
	Sample amount	31	31	31	31	31	31	10	10	10
Average content in carbonate rock (Turekian et al., 1961)		20	11	0.1	20	4	20	0.4	0.035	2.2

the preservation of organic matter (Li Renwei, 1993). Rubidium/K (Rb/K) are positively correlated to paleosalinity as a primary index. $\delta^{13}C_{carb}$ and $\delta^{18}O$ values generally tend to increase with increasing salinity (Lu Wuchang, 1986; You Haitao et al., 2002; Wang Fushun et al., 2002). Their relations were interpreted Lu Wuchang (1986) in terms of the following formula:

$$Z=2.048\ (\delta^{13}C+50) + 0.498\ (\delta^{18}O+50)$$

where Z is widely used as a trace index for estimating paleosalinity on a quantitative basis. It is suggested that $Z > 120$ is indicative of a marine facies (limestone), $Z<120$ is indicative of a freshwater facies, and Z=120 is indicative of an amorphyous limestone (Chen Rongkun, 1994; Lu Wuchang, 1986; You Haitao et al., 2002). In high-salinity seawaters or salt seawaters in which $Z>122$, $\delta^{13}C_{carb}>0$ and $\delta^{18}O$ values show positive excursions (Chen Rongkun, 1994). Essentially, such isotopic excursion is primarily correlative with the stratification of seawaters and burial rates of organic carbon.

At the Zhuozishan profile (Fig. 2), Rb/K ($\times10^4$), $\delta^{13}C_{carb}$, $\delta^{18}O$ and Z values all tend to increase from the bottom to the top. This variation trend is particularly obvious at the O_1z-O_1k boundary, suggesting the presence of a high-salinity and anoxic sedimentary environment during the Kelimory (O_1k) and Wulalik (O_2w) periods. The result has also been approved by the above trace element and geological characteristics. Moreover, the $\delta^{13}C_{org}$ values tend to decrease gradually from the upper part of O_1z (-27.8‰) to the upper part of O_2w (-30.4‰), with a range of 2.6‰. This variation trend is opposite to that of V/(V+Ni), Rb/K, $\delta^{18}O$ and Z (Fig. 2). The decrease of $\delta^{13}C_{org}$ in sediments is due to the increase of ^{12}C-rich microbial biomass (e.g. lipoid) and the preferential degradation of ^{13}C-rich organic compounds under anoxic condition (Gong and David, 1997; Galimov, 2002; Lehmann et al., 2002). Therefore, these facts indicate the optimization of organic quality, which is ascribed to the increased productivity and improved preservation of organic matter.

At the Pingliang profile, Rb/K ratios in O_1s are lower than those in O_1K, averaging 12. The $\delta^{18}O$ values decrease from the bottom (-6.4‰) to the top (-7.5‰), which is opposite to the variation trend of $\delta^{18}O$ in O_1k, too. These are due to the restricted circulation of seawater between the Pingliang and Zhuozishan areas during the Kelimory period, and their different sedimentary environments. The fact is consilient with geological characteristics of the region studied. In O_2w, Rb/K ratios range from 28 to 45, averaging 39, the average $\delta^{13}C_{carb}$ is 0.1‰, and Z values vary from 124 to 125. These values reflect that the bottom water was of high paleosalinity during the Wulalik period.

At the Qishan profile, Rb/K ratios in $O_1m^{4\text{-}6}$ range from 25 to 35, $\delta^{18}O$ values are within the range of -3.8‰ — -7.6‰, $\delta^{13}C_{carb}$ values vary between -0.6‰ and 0.3‰, averaging -0.4‰, and Z values lie between 124 and 129, averaging 126. It is reputed that high Z values are correlative with dolomitization in the Qishan area.

In O_1m^6 of well XT1, the average Rb/K ratio is 36, $\delta^{18}O$ is -7.2‰, $\delta^{13}C_{carb}$ values are within the range of 0.3‰—2.1‰, averaging 1.3‰, representing the maximal values in the study area. These values are well corresponding to high TOC. Z values range from 124 to 129, averaging 126. These characteristics further indicate a high-salinity, anoxic and stagnant sedimentary environment.

5 Restoration of the environment in which hydrocarbon source rocks developed

The above discussions showed that the redox, saline and hydrodynamic conditions are the main environmental factors controlling the formation of hydrocarbon source rocks, and can be reliably reflected by inorganic parameters such as Zr/Rb, V/(V+Ni), Rb/K, trace element contents, stable isotopic compositions, etc. Sedimentary organic matter increases in quantity and becomes better in quality with increasing reduction and salinity and decreasing hydrodynamic level.

Figure 3 shows variations in quantity and quality of organic matter under different sedimentary conditions, as reflected by the indices Zr/Rb, V/(V+Ni) and Rb/K. When TOC＞0.2％ (samples from O_1k, O_2w and O_1m^6), about 70％ of the samples have Zr/Rb＜1, V/(V+Ni)＞0.50 and Rb/K＞30 (Fig. 3a). The variation range reflects a low-hydroenergy, anoxic and high- salinity sedimentary environment where the conditions are suitable for the accumulation and preservation of organic matter in large amounts. $\delta^{13}C_{org}$＜-28‰ is indicative of a good type of organic matter (types Ⅰ－Ⅱ, Huang Difan et al., 1984) and a high hydrocarbon-generating potential (Fig. 3b). On the contrary , the samples with TOC＜0.2％ from O_1z、O_1s and $O_1m^{4\text{-}6}$ are have Zr/Rb＞1, V/(V+Ni) ＜ 0.50 and Rb/K＜30 (Fig. 3a). $\delta^{13}C_{org}$ values vary between -24‰ and -28‰, suggesting organic matter of the typesⅡ－Ⅲ (Fig. 3b). This variation range shows a roily, toxic sedimentary environment with a low hydrocarbon-generating potential.

From the above discussions it can be seen that samples from the area of research significance, with TOC=0.2% as the boundary, show significant differe-nces in geological and geochemical characteristics. This is not only the response to the nature of sedimentary environment and its evolution, but also a qualitative description of the hydrocarbon source rocks.

At present time, Lower Paleozoic contributions to the central gas field in the Ordos Basin have been known by most researchers (Yang Junjie and Pei Xigu, 1996; Chen Anding, 2002; Xie Zengye et al., 2002; Liu Dehan et al., 2004). In combination with previous modeling of hydrocarbon generation and expelling in the Majiagou carbonate hydrocarbon source rocks (Xie Zengye et al., 2002; Chen Yicai et al., 2002) and the results of research on primary bitumen (Xie Zengye et al., 2002; Liu Dehan et al., 2000, 2004), in regard to the Lower Paleozoic carbonate hydrocarbon source rocks in the Ordos Basin, it can be considered that TOC=0.2% is an important boundary value, the environment where the strata with TOC＞0.2％ were deposited may be the favorite environment for the development of hydrocarbon source rocks, and also a locus where potential effective hydrocarbon source rocks were formed and distributed both in space and in time.

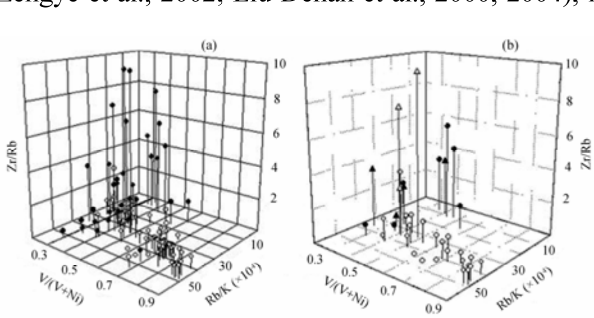

Fig. 3. Variation in quantity and quality of organic matter in different environments. (a) Variation trend of organic matter quantity (TOC). ○ TOC＞0.2％; ● TOC⩽0.2％. (b) Variation trend of organic matter quality ($\delta^{13}C_{org}$). ○ TOC＞0.2％, $\delta^{13}C_{org}$＜-28‰ (type Ⅰ); ● TOC⩽0.2％, $\delta^{13}C_{org}$＜-28‰ (type Ⅰ); ▲ TOC ⩽0.2％, $\delta^{13}C_{org}$ are -26‰–-28‰ (type Ⅱ); △ TOC⩽0.2％, $\delta^{13}C_{org}$＞-26‰ (type III).

6 Conclusions

(1) In the Lower Paleozoic hydrocarbon source carbonate rocks in the Ordos Basin, the contents of residual organic carbon are equal to 0.2%, which is taken as the boundary value. In the strata including O_1k and O_2w, and O_1m^6 of well XT1, the residual organic carbon contents are higher than 0.2%, and the paleoproductivity and burial amounts of organic matter are high, the type of organic matter is good, and there exist two kinds of environments which are favorable to the development of hydrocarbon source carbonate rocks, i.e., 1) deep-water, high-energy, anaerobic slope environment; and 2) vaporized, stagnant lagoon or limited basin. And the distribution of O_1k and O_2w shows some regularities, and those strata can be regarded as the potential effective hydrocarbon source rocks. The strata including O_1z and O_1s, and $O_1m^{4\text{-}6}$, whose residual organic carbon contents are lower than 0.2%, have relatively low burial amounts and infavorite types of organic matter, suggesting that they were deposited in the high-energy, oxidizing environment that is unfavorable to the development of hydrocarbon source rocks.

(2) Zr/Rb ratios can quantitatively reflect the hydrodynamic conditions as a proxy indicator, high Zr/Rb ratios are indicative of a high-energy environment. Th/U ratios in carbonate rocks can directly record the redox status of marine environment: Th/U＞0.80 suggests an anoxic sedimentary environ-ment.

(3) The development of marine hydrocarbon source rocks is mainly attributed to the integrative effect of all environmental factors including paleo-productivity, bottom-water redox, salinity, sediment-tation rate, hydrodynamic condition, etc. Inorganic parameters such as trace metals and stable isotope composition are powerful enough to constrain the physical and chemical variations of sedimentary organic matter and the developing environment of marine hydrocarbon source rocks. And in combination with some necessary organic parameters, it is needed to further identify potential effective hydrocarbon source rocks and their distribution so as to provide new clues to the evaluation of highly evolved marine hydrocarbon source rocks in China.

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