

THE PETROPORPHYRINS IN SEVERAL OIL SHALES, CHINA

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ABSTRACT

A study of petroporphyrins from several oil shales was carried out by using TLC, UV, HPLC and MS. This paper deals with the type and structure of porphyrins, the distribution of carbon numbers and DPEP/ETIO values etc. The results indicate that the porphyrins exist in common oil shales except for the poor oil shale from Shengli Oil Field which was buried under 3000m deep. During the early diagenetic stage, the reaction from DPEP to ETIO is very strong and then slows down with diagenesis. The ratio of DPEP/ETIO was related not only to maturation but also to the Ox-Re condition of the environment. The low DPEP/ETIO value of Maoming oil shale is due to the weaker oxidation environment.

INTRODUCTION

As a kind of potential source of energy, oil shales have been paid more and more attention, thus making the study in the relevant area going deeper and deeper. In order to know composition characteristics and distribution of petroporphyrins in oil shales from different areas of varying ages, several types of oil shales from Xinjiang, Fushun, Maoming, Jianghan and US Green River were analysed together with the determined results of biomarkers such as steranes and terpanes. Afterthen, a systematic study was made on the porphyrins from these samples. The general situation of the samples is in Table 1.

EXPERIMENTAL

The samples(100g) were crushed (less than 200 mesh) and extracted with methanol and dichloromethane (1/2;V/V). The solvent was removed with

Table 1. Age and depth of the samples selected

No.	Area	Well No.	Depth	Age
1	Yaomoshan, Xinjiang		Outcrop	P ₂
2	Sangonghe, Xinjiang	Southern wing of syncline	Outcrop	P ₂
3	Sangonghe, Xinjiang		"	"
4*	Shengli Oil Field	DongFeng-5	3005-3008m	E _{s3}
5**	Jiangnan Oil Field	Ma-5	765.3m	E _{q1}
6	Fushun		Outcrop	E _{2-3fg}
7	Fushun		"	"
8	Maoming		"	E _y
9	Green River, USA		"	E ₂

*poor oil shale

**brown oil shale

rotary evaporator.

After deasphaltene, the soluble fraction was separated by silica gel column chromatography using petroleum ether, toluene, toluene-methylene chloride, methylene chloride and anhydrous ethanol as eluting reagents. After then, the concentrated fraction with crude metalloporphyrins was purified by thin layer chromatography of silica G. The nickel and vanadyl porphyrin fractions were collected separately.

The purified metalloporphyrins were placed in a bottom-flat flask and refluxed at 110°C with a mixture of toluene, hexane and pure methyl sulfuric acid. Cooled, diluted with distilled water, added a little amount of hexane, the solution was transferred into a separating funnel and shaken thoroughly. After separation, the red-colored aqueous phase was washed with the saturated solution of sodium bicarbonate to remove the residual acid and extracted three times with methylene chloride. Finally, anhydrous sodium acetate was used to remove residual water.

Metalloporphyrins appear to form evident absorption peaks in visible range, thus, their contents can be measured quantitatively. UV-3000 type spectrophotometer was used to get porphyrin absorption spectra. The absorption wavelengths of nickel and vanadyl porphyrins are round 552, 515 and 570, 530 nm, while metal-free porphyrins are 618, 565, 535, 500, 400 nm more or less.

High performance liquid chromatographic analysis of metal-free porphyrins was made on a Spectra-Physics Model SP8100 with SP8400 ultra-violet detector. The column was packed with Patisil 5 silica (4.0 mm × 30 cm),

eluted in gradient programme by hexane, acetone, methylene chloride and acetic acid at a flow rate of 2ml/min for 30min and the detected wavelength is 400nm.

Mass spectrometric determination was performed on a Finnigan 4500 mass spectrometer connected to INCOS data system. Samples were directly injected into the ion source through the probe. The running condition was as follows: emission current is 300 μ A; source temperature 150 $^{\circ}$ C; electron energy for vanadyl porphyrin is 35eV and that for nickel and metal-free porphyrins is 30eV. The source was heated rapidly from 150 $^{\circ}$ C to 280 $^{\circ}$ C and the fragments ranging from (M/E) 300-700 were collected.

RESULTS AND DISCUSSION

1. The contents of metalloporphyrins

The content calculation of petroporphyrin in samples is based on the data from its absorption spectra. The weighted average of metalloporphyrin molecular weight was used so as to eliminate the effect of adopted porphyrin molecular weight on its calculated content. Table 2 shows the analytic results of porphyrins in oil shale samples.

Table 2. Results of Porphyrin Analyses

No.	\bar{M}	Metalloporphyrin type	Porphyrin/ C_{org} . (ppm)	Carbon number distribution	Majority	$\frac{DPEP}{ETIO}$
1	509.6	Nickel porphyrin	0.235	C ₂₆ -C ₃₄	C ₃₂ D	1.12
2	516.5	" "	26.193	C ₂₇ -C ₃₆	C ₃₁ D	3.29
2	523.0	Vanadyl "	3.643	C ₂₇ -C ₃₆	C ₃₂ D	0.97
3	500.7	Nickel "	98.677	C ₂₅ -C ₃₅	C ₃₁ D	0.94
4		Unfound				
5	530.7	Nickel porphyrin	15.644	C ₂₇ -C ₃₇	C ₃₂ D, C ₃₁ D	1.16
6	529.3	" "	11.176	C ₂₉ -C ₃₃	C ₃₂ D	6.53
7	525.9	" "	115.476	C ₂₉ -C ₃₅	C ₃₂ D	2.51
8	516.7	" "	2.337	C ₂₇ -C ₃₅	C ₃₂ E	0.65
9	540.5	" "	9.997	C ₂₈ -C ₃₆	C ₃₂ D	2.13

It is indicated by Table 2 that there exist porphyrins in common oil shales with different contents except for the poor oil shale from Shengli Oil Field which was buried under 3000m deep. Samples can be divided into four grades by means of the porphyrin contents: (1) Highly contained: including Sangonghe oil shale, Xinjiang(No.3) and Fushun oil shale(No.7),

their porphyrin/ C_{org} ratios account for 98.68 and 115.48ppm respectively. (2)Middlely contained: the sample from the south wing of Sangonghe syncline (No.2, the ratio is 29.84ppm), for instance, and the brown oil shale from Well Ma-5, Jiangnan Oil Field(No.5, the ratio is 15.64ppm). (3)Lowly contained: such as Yaomoshan and Maoming oil shales (No.1 and No.8, the ratios are 0.24 and 2.34ppm separately). (4)Non-contained: such an example found in the poor oil shale from Shengli Oil Field.

Judged by the distribution of porphyrin contents, the samples with highly contained porphyrins are generally parallel to sapropelic(or good) source material with low maturity. The above mentioned Sangonghe and Fushun oil shales (No.3 and No.7), whose porphyrin contents are high, are quite low in maturity, in addition, their R_o values are 0.59 and 0.40 respectively, still in immature stage. Their initial type of the source material belongs to kerogen type "I" in accordance with the concerned information, for instance, their H/C atomic ratios, one is 1.65, the other is 1.38. Ofcourse, the porphyrin content is closely related to the abundance of organic carbon, too. But the organic carbon in our samples selected has quite high values, therefore, it is not so obvious for the organic carbon richness to effect the porphyrin contents.

The reasons that porphyrins are absent in some samples might be in many aspects. It is obvious,however, that high maturity and poor source material are two of the most important factors.

Viewed from Table 2, it is also clear that the porphyrins detected are mainly complexed with nickel. Only in Sangonghe oil shale did vanadyl porphyrin be found, but nickel porphyrin was still a predominant member with a ratio of nickel to vanadyl porphyrins around 7/1. Figs 1 and 2 illustrate the HPLC and MS spectrograms for metal-free porphyrins occurring in Sangonghe sample.

As shown in the figures, the distribution of the two metalloporphyrins differ from each other evidently. The distribution pattern given by nickel porphyrin is much complicated. In this sample, DPEP/ETIO ratio is 1.03 for vanadyl porphyrin, dominated by C_{32} DPEP; while for nickel porphyrin, its DPEP/ETIO amounts to 3.31, predominated by C_{31} DPEP. Therefore, the above stated difference in the same sample is considered to be the fact that the stability of the two kinds of metalloporphyrins are different.

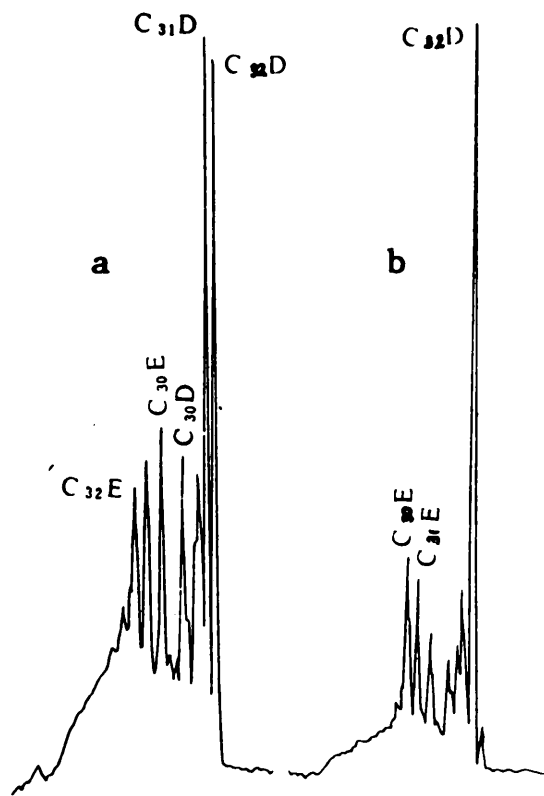


Fig.1 HPLC chromatograms showing two kinds of metal-free porphyrins in Sangonghe oil shale, Xinjiang. (a.Ni-porphyrin; b.V-porphyrin)

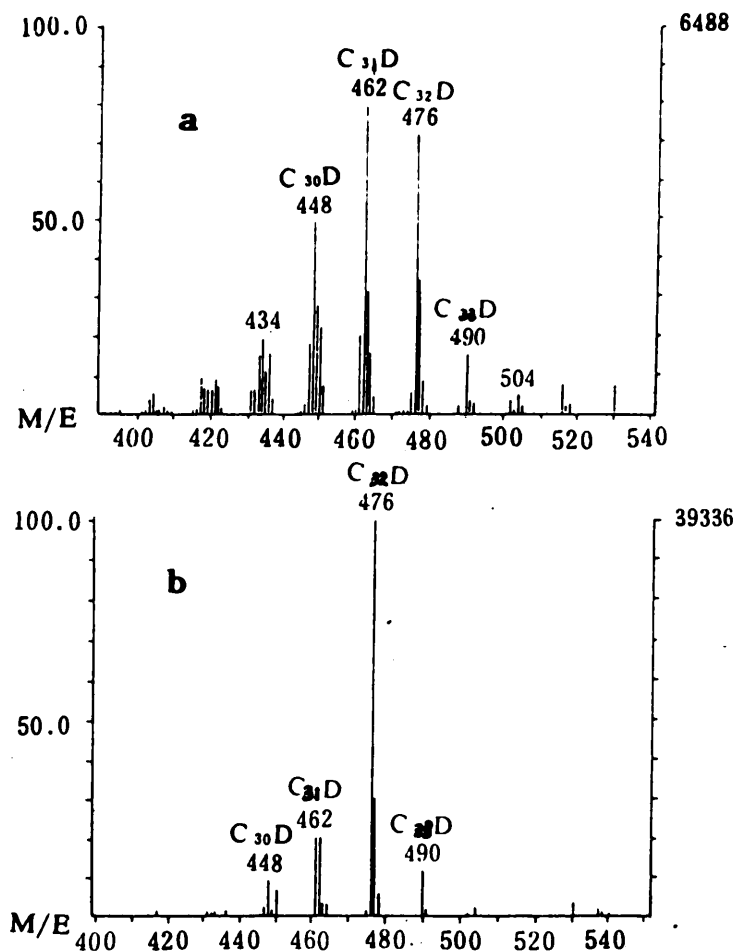


Fig.2 MS spectrograms indicating two kinds of metal-free porphyrins in Sangonghe oil shale, Xinjiang. (a.Ni-porphyrin; b.V-porphyrin)

2. Porphyrins and maturity

Porphyrins are generally used maturity-measured compounds. Generally speaking, with increasing maturation, porphyrin content decreases accompanied with decreasing of porphyrin/ C_{org} and DPEP/ETIO ratios. In the meantime, heavy carbon-numbered porphyrins are converted into light ones, thus resulting the major peak shifting towards lower carbon-numbered direction.

DPEP/ETIO ratio for different samples change a lot (Tab.2). Maoming oil shale got the lowest value, which is 0.65. The highest is 6.55, found in Fushun oil shale. It is recognized that the maturation degree of a sample is a dominant factor which gives effect on DPEP/ETIO ratio. Meanwhile, this ratio is also effected by the Ox-Re condition of the environment. A reduction condition is available for DPEP to be preserved.

Moreover, on the basis of porphyrin analyses, kerogen vitrinite reflectance, saturated hydrocarbon CPI and cyclic biomarkers such as steranes and terpanes were determined altogether so as to check the inter-

relation among them. In the ensuing paragraphs, we take $20S/(20R+20S)$ ratio of $5\alpha,14\alpha,17\alpha-C_{29}$ steranes and R_o as maturity indicators to discuss the effect of maturation on the distribution pattern of porphyrins.

The ratio $20S/(20R+20S)$, which is increased regularly with increasing maturity, is a function of the thermodynamics of the sedimentary surroundings concerned. The relation between the two ratios mentioned, that is, $20S/(20R+20S)$ and $DPEP/ETIO$, plotted in Fig.3.

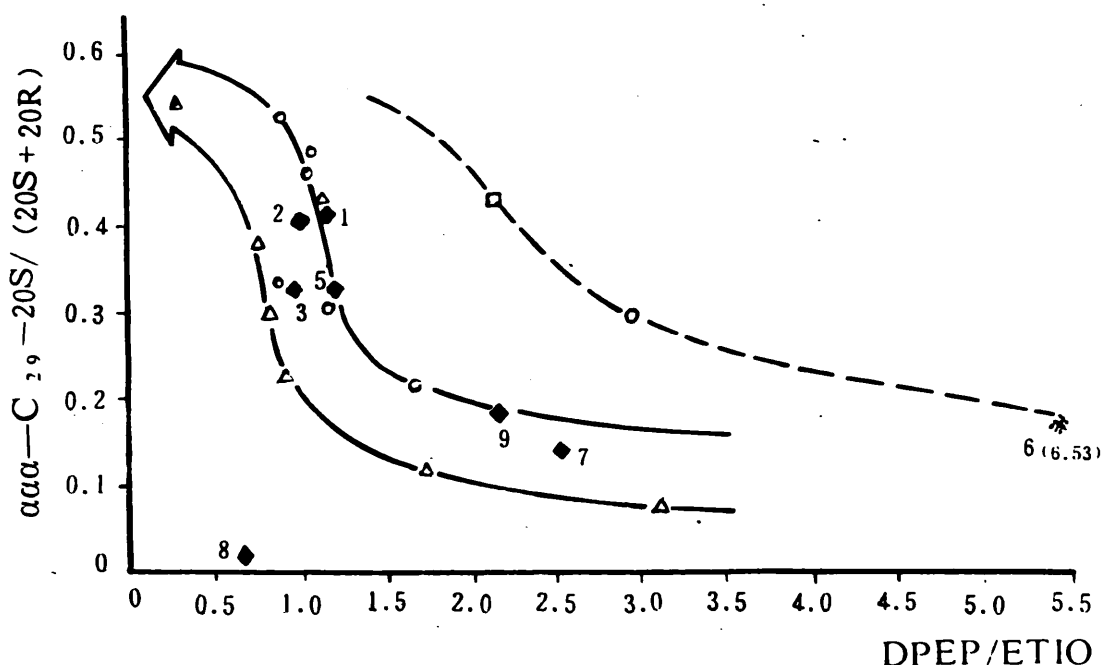


Fig.3 Relationship between $DPEP/ETIO$ and $20S/(20R+20S)$

Note: The samples marked with symbol \blacklozenge are oil shales, and the remainders are source rocks and crude oils.

It is worth notice from Fig.3, that the ratio $DPEP/ETIO$ reduces regularly with raising $20S/(20R+20S)$ value. Another point which should be noticed is that the data dots in the diagram are not centralized, most of them are distributed in a ribbon zone. In addition, the slope of the ribbon changes greatly with a turning point of $20S/(20R+20S)$ ratio around 0.25. In the stage where $20S/(20R+20S)$ ratio is less than 0.25, $DPEP/ETIO$ value reduces abruptly with increasing maturation degree, which indicates that $DPEP$ was converted into $ETIO$ rapidly in the early process of diagenesis. After crossing this turning point, however, the conversion of $DPEP$ to $ETIO$ was subsided gradually. Finally, when steranes reached their end point of isomerization, $DPEP/ETIO$ ratio got its minimum value.

Surely, $DPEP/ETIO$ ratio is connected not only with the maturity of samples, but influenced by the $Ox-Re$ conditions of the environment. The abnormal point in Fig.3, which is Maoming oil shale (No.8), is such an

example and will be discussed afterwards.

As illustrated in Fig.4, which describes kerogen R_o versus porphyrin DPEP/ETIO relation, it is evident that DPEP/ETIO value decreases with increasing R_o . But thermodynamic effect is not the only factor to influence DPEP/ETIO value, so, for a given R_o , the ratio is not an exact value, but having a changing ridge.

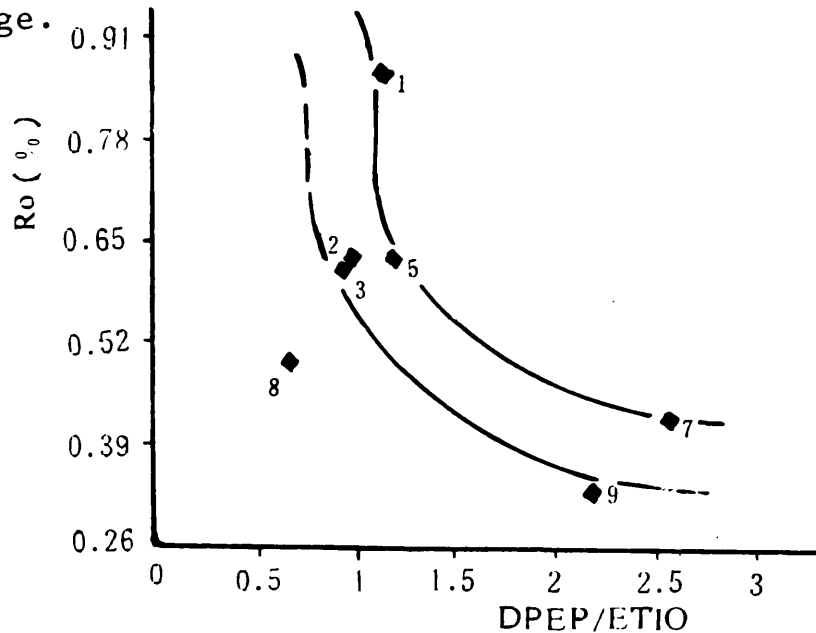


Fig.4 Relationship between DPEP/ETIO and vitrinite reflectance R_o .

It is a general tendency for DPEP/ETIO ratio to reduce with increasing maturation degree of the samples. The conversion of DPEP to ETIO is much faster at the beginning of the diagenesis, and then slowed down after the turning point. There is another that should be noticed that, when using DPEP/ETIO ratio as a maturation parameter, especially used in different basins and sedimentary facies zones, other factors should also be considered. Usually, if maturity is a predominant factor, the distribution pattern of the porphyrins will be changed from heavy carbon-numbered preference to lower ones.

3. Porphyrin and the environment

Porphyrins are generated under reduction condition. An oxidation environment appears to destroy them. So the environment nature is another factor which influences porphyrin contents, distribution pattern and even their structures.

During the process of the experiment, the author found that some samples were predominated by ETIO rather than DPEP even though their maturity is quite low. In this case, it is not reasonable to explain this

situation from the viewpoint of maturity. The Maoming oil shale mentioned before, for example, is relatively high in the contents of isoprenoids, steranes and terpanes. Its n-alkanes are still dominated by odd carbon-numbered ones (Zhang Dajiang et al., 1985). The maturity indicator, i.e., the ratio $20S/(20R+20S)$ of $\alpha\alpha\alpha$ - C_{29} steranes, is far away from equilibrium value. Therefore, it is safe to say that this sample is immature. However, viewed from the analyzed results of porphyrins, it is clear that ETIO occupies a preferential position with a DPEP/ETIO ratio equal to 0.65. The environment parameters for the samples give an explanation on this situation. For instance, its Fe^{2+}/Fe^{3+} is equal to 0.91, Pr/Ph up to 1.69. This means the surroundings is weakly oxidized. So the above stated appears to be the main reason that the sample is dominated by ETIO. Fig.5 shows the spectrograms for the metal-free porphyrins from this sample.

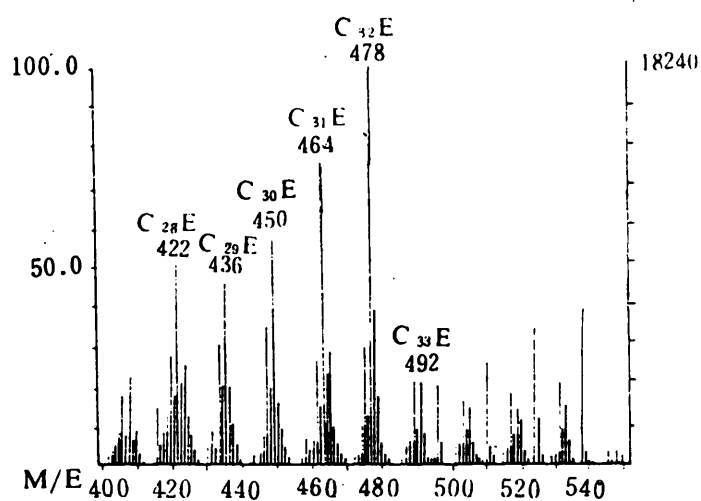


Fig.5 Spectrograms for metal-free porphyrins derived from Maoming oil shale.

The porphyrins in geological samples were generated from a series of reactions occurred in the pigments from living organisms particularly from plant bodies. So when a sample is in the low maturation stage, its porphyrin distribution is dominated by C_{32} DPEP. Meanwhile, with the variation of maturation degree and environment condition, the fingerprint pattern of porphyrin changes regularly. As shown in Fig.5, a C_{32} ETIO major peak is emerged. This means that while the heavy carbon-numbered porphyrins were degraded to light ones, the conversion of DPEP to ETIO did not happen because the ETIO predominance in the sample is mainly caused by a weaker oxidation condition of the surroundings, rather than the maturation degree of the sample.

CONCLUSION

- (1) There exist porphyrins commonly in oil shales. Porphyrin contents differ from each other greatly in different samples. In general, the samples with high content in porphyrins are low in maturity and good in source material.
- (2) The conversion of DPEP to ETIO is rather strong during the early diagenetic stage, and then slowed down with increasing diagenesis. Finally, when C_{29} steranes reach their equilibrium values of the isomerization, DPEP/ETIO gets its minimum.
- (3) The environment nature is also an important factor which gives effect upon porphyrin content, distribution pattern and even its molecular structure.

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REFERENCES

- Baker, E.W. et al., *Adv. Org. Geochem.*, 1981, pp.401-421.
- Barwise, A.J.G. et al., *Org. Geochem.*, 6(1984), pp.167-176.
- Eglinton, G. et al., *Adv. Org. Geochem.*, 1979, pp.193-208.
- Shi jiyang, *Scientia Sinica (Series B)*, 26(1983), No.8, pp.865-875.
- Xu Lian et al., *Acta Sedimentologica Sinica.* 2(1984), No.1, pp.29-42 (in Chinese).
- Zhang Dajiang et al., *Petroleum Geology and Oilfield Development in Daqing*, 4(1985), No.2, pp.1-18 (in Chinese).