# THE PARAMAGNETIC RESONANCE AND CARBON ISOTOPE FEATURES OF THE CRUDE OIL AND SOURCE ROCKS IN ZHUNGEER BASIN

**Fan Pu　Zhang Qian**

(Lanzhou Institute of Geology, Academia Sinica)

## PREFACE

The sedimentary area of Zhungeer Basin is about 130,000 km$^2$ and its sedimentary rocks from Carboniferous till Latter Tertiary are 2,000m in maximum thickness. Owing to the long-term and stable sinking dominating over the basin and the influence of the rift-differential movement in the basin, different oil-forming depressions were formed in different geological periods. With the development of geological history the oil-forming depressions were transferred. Six oil-forming depressions (Fig.1) used to be developed in Zhungeer Basin during its geological history. They are the

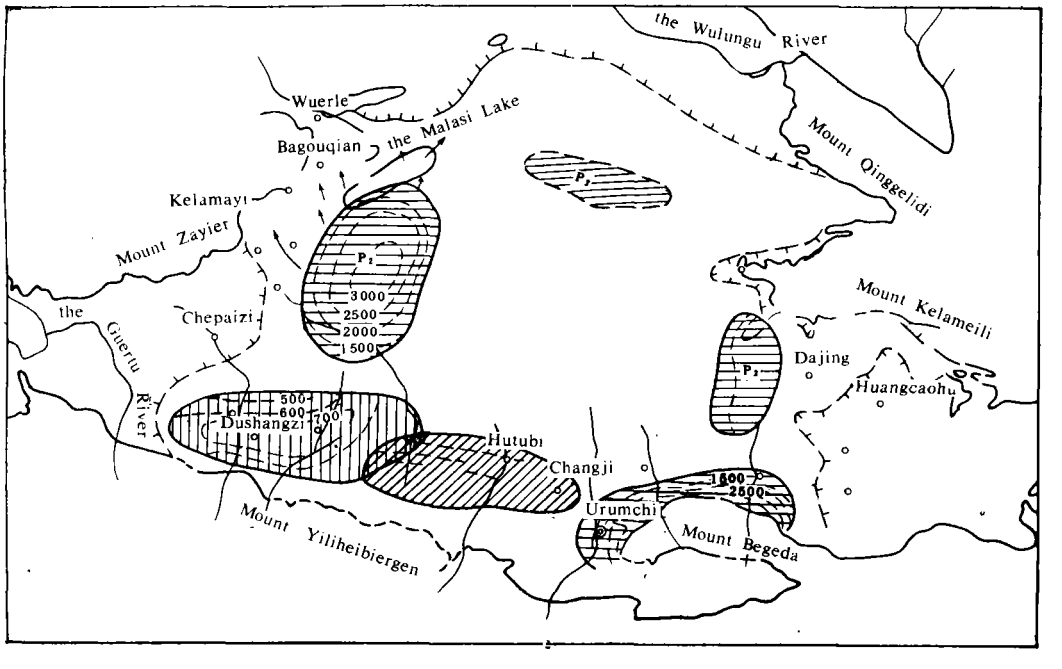


Fig. 1　Distribution of oil-forming depressions in Zungeer Basin

Upper Permian oil-forming depression east of the Malasi Lake, the Wudong-Dalongkou oil-forming depression, the Wucaiwan-Dajing oil-forming depression, the Wulonggu oil-forming depression, the Middle Jurassic Fukang-Tuositai oil-forming depression and the Lower Tertiary Dushanzi oil-forming depression. These oil-forming depressions provide Zhungeer Basin with rich oil and gas resources and dominate the distribution of oil-gas fields.

Based on studying the free radical of crude oil and source rocks as well as their carbon isotopes and combining our geological observation in fieldwork, the paper deals with the oil source of oil-forming depressions in the basin, the oil-gas evolution and so on.

## FEATURES OF FREE RADICAL OF CRUDE OIL AND SOURCE ROCKS

It is getting more important day by day to study the free radical of the organic matter in crude oil and source rocks by applying the electronic paramagnetic resonance (EPR, ESR) in order to solve some problems of oil

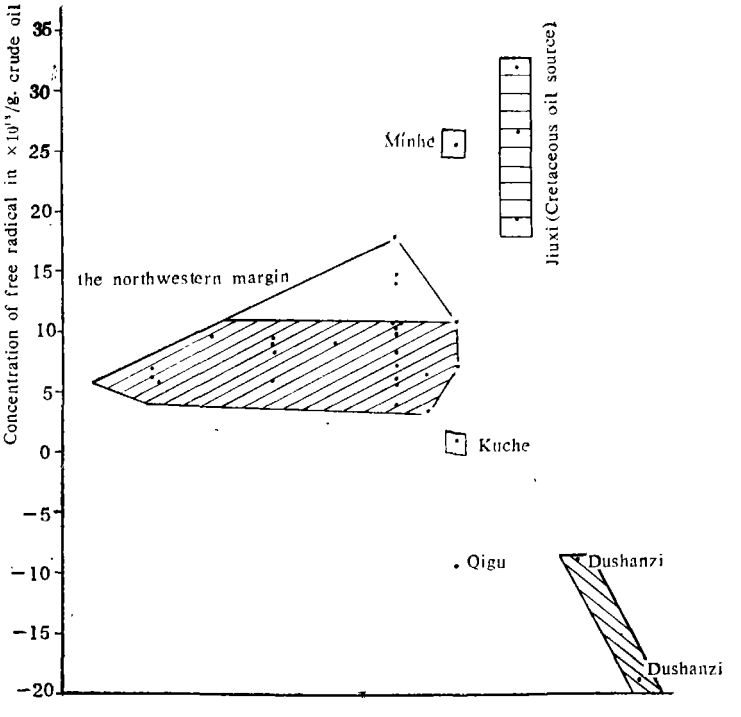


Fig. 2 Distribution of concentration of free redicals in crude oil different ages in Zungeer Basin

geology, such as oil sources, level of oil evolution etc. Generally speaking,

organic compounds, e. g. coal, oil, asphalt, kerogen and so on, contain the free radical (i. e. unpaired electrons). The free radical formed by the compound of solid carbon or with aromatic structure is usually stable. The simulated test of organic matters has proved that the concentration of the free radical increases with the increase of heating temperature, and when the temperature reaches to 500—700°C, the concentration of the free radical goes up to the highest point($10^{19}$—$10^{20}$/g organic matter), then it falls down.[1][2][3]

1 The Free Radical of Crude Oil

The concentration of the free radical of the crude oil in Zhungeer Basin varies within the range of $0.5\times10^{16}$—$18.1\times10^{18}$/g. The distribution of the free radical of crude oil in different ages is shown in Fig. 2. According to the division of different areas, Fig. 2 shows that the crude oil in the northwest of Zhungeer Basin is somehow different from that in Kuche, Qigu and Dushanzi and quite different from that in Minhe Basin and Jiuxi Basin. This difference evidently mirrors the distinction of the parent material which forms crude oil and the synthetic influence of different evolution levels, and it can be regarded as an index to distinguish different oil sources. Although the oil-bearing strata in the northwestern margin of Zhungeer Basin belong to different ages (from Carboniferous till Jurassic), the concentration of the free radical of crude oil varies within a narrow range, mainly around $5\times10^{18}$/g crude oil. Therefore, the crude oil in these

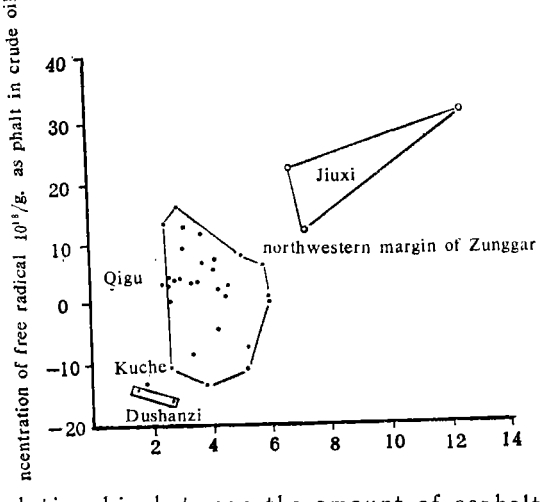


Fig. 3 Relationship between the amount of asphalt in crude oil and free radical of asphalt(%) in Zungeer Basin

ages should be homologous. The previous studies* made by us have shown that the crude oil in the northwestern margin of the basin, in the main,

comes from the Permian oil-bearing strata. The homology of the oil sources in the northwestern margin of Zhungeer Basin has been evidenced by studying the free radical of crude oil as well.

2 The Free Radical of the Asphalt in Crude Oil

The concentration of the free radical is, in general, distributed most highly in asphalt than in other components in crude oil. The concentration of the free redical and the content of asphalt of crude oil in different ages in Zhungeer Basin are illustrated in Fig. 3, from which one can see that in different basins and areas there is a tendency of direct proportion between the concentration of the free radical and the content of asphalt in crude oil. Although as to each individual area, this tendency may not be apparent, the concentration of the free radical of asphalt in crude oil can serve for classifying different oil-source areas.

3 The Free Radical of Kerogen

In studying the free radical of kerogen, the EPR signals of paramagnetic minerals may bring about the superposed affection for lack of the neccessary purification of kerogen. The purity processing, especially the heating processing may, however, change the free radical of kerogen. Hence the purity processing of kerogen should avoid destroying the free radical as far as possible.

The free radical of kerogen comes, in the main, from the light paraffin, water and carbon dioxide of low molecular weight compounds produced by biopolymer in the pyrolyzation of organic matters. After they are fragmentized from organic parent matters, there is a break chemical bond and an unpaired electron occurs. Meanwhile, a new pair of electrons is consequently formed and the reassociation of the chemical bond causes hydrogen atoms to replace some alkyl-group chains broken from organic parent matters or some functional groups upon aromatic rings. Some free radicals, however, are retained in kerogen and they are a bit more stable. High temperature and long degradation will lead to increasing the concentration of the free radical in kerogen as well as strengthening the aromaticity of these free radicals. The free radical can be rebound after its concentration reaches to the highest point and when the speed of its rebinding is faster than that of its production, its concentration begins decreasing.

The change of the concentration of the free radical of crude oil in Zhungeer Basin usually ranges from $0.07\times10^{15}$/g to $18\times10^{15}$/g organic

* Fan Pu and Wang Youxiao, 1983, A Preliminary Evaluation of the Oil-Forming Depressions in Zhungeer Basin.

matter. Fig.4 shows that in the eastern area the concentration of the free radical of the Carboniferous and Permian kerogen is higher, and the kerogen is at the mature stage. However, in the northwestern area the Carboniferous and Lower Permian kerogens concentrate much less free radicals and are at the over-mature stage with the exception of the Upper Permian kerogen which remains at the mature stage, and moreover the Tertiary kerogen in the southwest of the basin is at the lower or medium-mature stage. Owing to the difference of geological history, kerogens in various areas of the basin have underdone different thermal-degradation and have different maturities, which, therefore, can calculate their respective potential of oil forming. The oil-bearing strata in the northwestern margin of the basin are mainly Permian and the Carboniferous kerogen has degenerated. But the Carboniferous and Permian strata in the east of the basin are all at the stage of oil forming.

The relationship between the infrared spectrum $\frac{2920cm^{-1}}{1610cm^{-1}}$ of kerogen and its free radical has shown that the concentration of the free radical

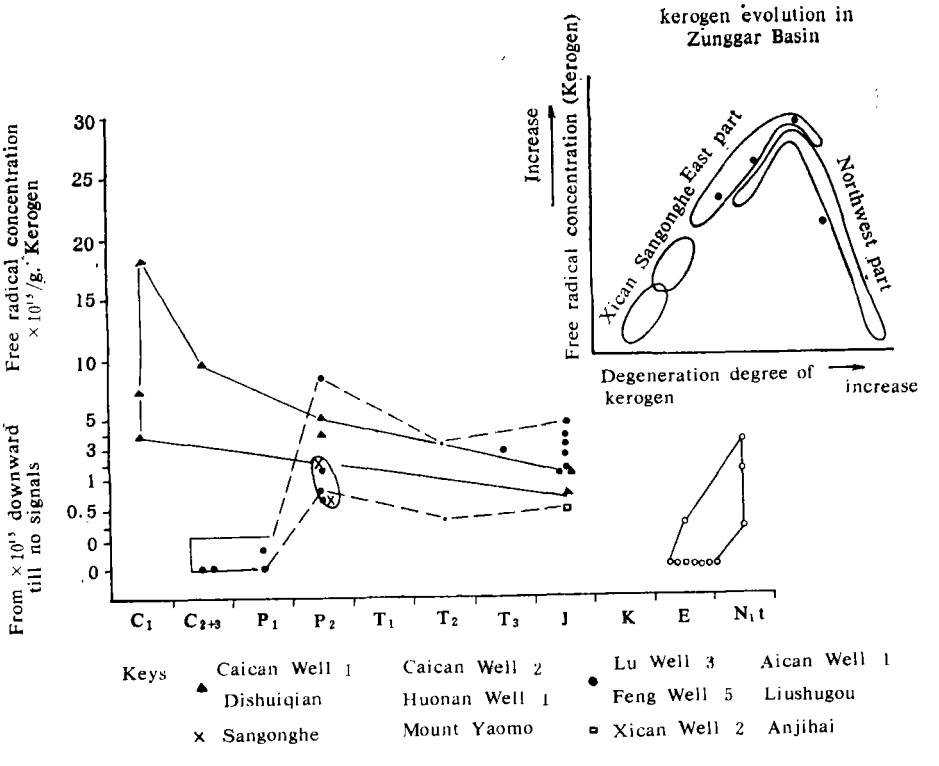


Fig. 4 Concentration distribution of free radical in kerogen in different areas of Zungeer Basin

falls down with the increase of the $\frac{2920cm^{-1}}{1610cm^{-1}}$ value (i. e. the increase of $CH_3CH_2$ in kerogen); while the $\frac{2920cm^{-1}}{1610cm^{-1}}$ value decreases and the aromaticity of kerogen strengthens, the concentration goes up.

4 The Free Radical of Asphalt in Chloroform Extractives of Sedimentary Rocks

The mean value of the concentration of the free radical of asphalt in crude oil in different ages and areas is similar to that of the free radical of crude oil (Fig.5). The concentration of the free radical of asphalt in the Carboniferous and Permian source rocks in the east of the basin as well as in the Permian source rocks in the northwestern margin is high and both source rocks are at the mature stage. However, the souce rocks of Xican Well 2 in the southwest are at the lower-mature stage. As far as the relationship between the concentration of the free radical of asphalt and saturated and aromatic hydrocarbons in source rocks is concerned, the concentration of the free radical in asphalt reaches to the highest value when the percentage content of the components of saturated and aromatic hydrocarbons increases to 45—60%,and it,however,tends to gradually fall down with the continuous increase of the percentage content of the components of saturated and aromatic hydrocarbons,possibly because of the synthetic affection of

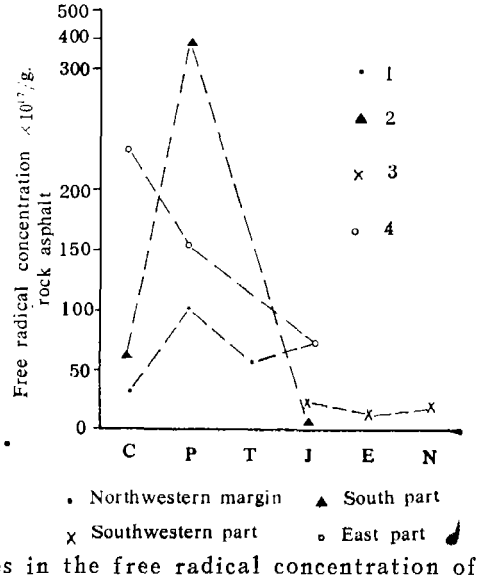


Fig. 5 Changes in the free radical concentration of rock asphalt in different ages and areas of Zungeer Basin

degeneration level and hydrocarbon migration.

According to the relationship between the free radical and the H/C ratio

of asphalt in source rocks, it can be seen that tha concentration of the free radical of asphalt remains lower when the H/C ratio is below 0.7; then it reaches to the highest value as the H/C ratio is in the range of 0.9—1.0; and further it gradually decreases down with the continuous increase of the H/C ratio. All these changes mirror the relationship between the elemental composition of asphalt and its free radical, i. e. with the increase of degeneration level the components of asphalt lead for varying toward the light.

The varying tendency between the concentration of the free radical and the N/C ratio of asphalt shows that the concentration of the free radical reaches to the highest value when the N/C ratio is 0.02 and it drops down as the N/C ratio comes down.

## CARBON ISOTOPES COMPOSITION

The features of the carbon isotopes composition of the organic matters in crude oil and sedimentary rocks have something to do with the species of original organism as well as the isotopic differentiation of the chemical evolution in diagenesis process. Generally speaking, terrestrial plants enrich more $C^{12}$ isotopes than marine organisms, and in organic matters liquid

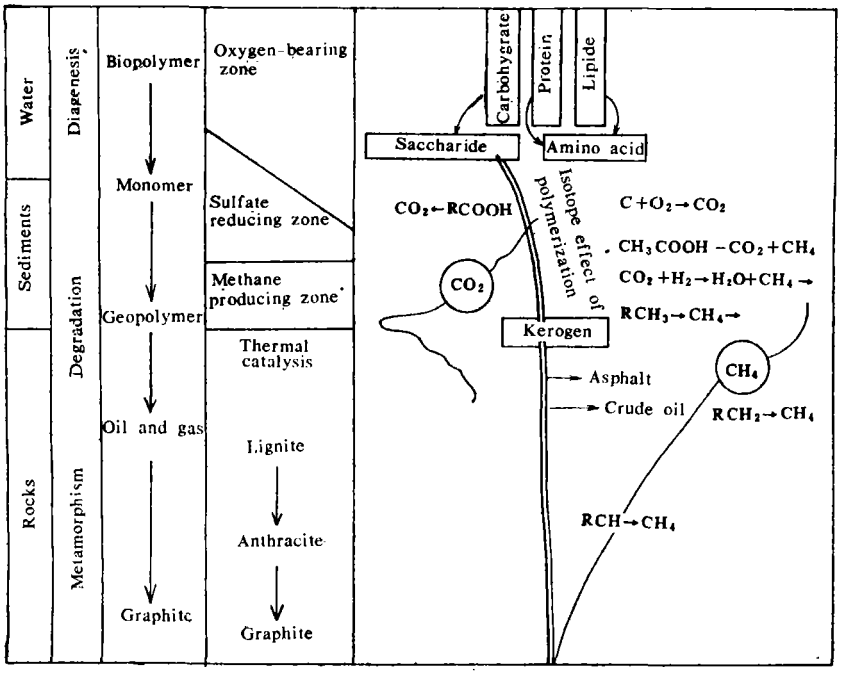


Fig. 6　synthesizes the common evolution pattern of organic matters

enriches more $C^{12}$ than amino acid and carbohydrate, whereas the carbon

atoms in hydroxyl group-ketone group as well as in aldehyde group and hydroxyl enrich $C^{13}$. During diagenesis process, dehydroxylation will cause in organic matters to enrich light carbon isotopes, meanwhile demethylation or demethoxylation will lead to the enrichment of heavier carbon isotopes[4][5]. Fig.6 synthesizes the common evolution pattern of organic matters during degeneration process[1][2][3].

The carbon isotopes composition of kerogen becomes comparatively stable after diagenesis and further degeneration has little effect on it. Therefore, studying the features of the carbon isotopes composition in crude oil and kerogen will provide an evidence for us to classify the oil sources in Zhungeer Basin.

Based on Fig.7, it is seen that the carbon isotopes of the Carboniferous ($C_1$,$C_{2+3}$) kerogen in the northwestern margin comparatively enrich $C^{12}$ and its original organic parent materials are, in the main, composed of marine organisms. The carbon isotopes composition of the Triassic and Jurassic kerogens shows that the organic parent materials composed mainly of terrestrial organic matters are not favorable to oil formation, and the mixed type of

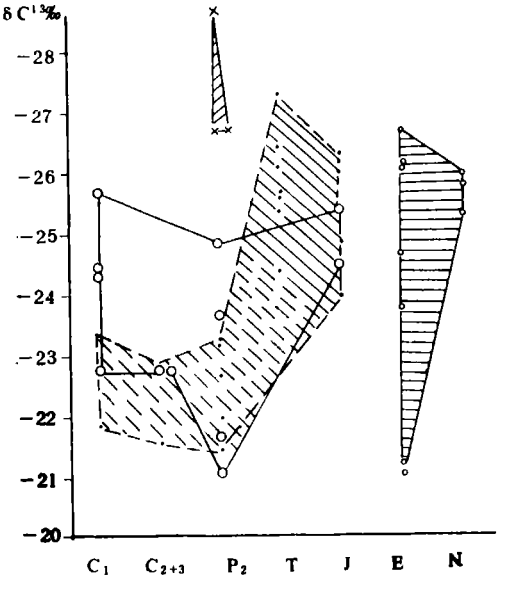


Fig. 7 Distribution of the carbon isotope of kerogen

the Permian kerogen gives priority to the sapropelic type. The types of kerogen in the east of the basin vary a lot and the Permian kerogen chiefly consists of the sapropelic-type composition. The Permian kerogen in the south of the basin is obviously different from the Lower Triassic kerogen in the southwest of the basin. In different areas of Zhungeer Basin the carbon isotopes compositions of kerogen in source rocks are of apparent difference, mirroring the difference of original organic parent materials.

As far as the carbon isotopes composition of crude oil in Zhungeer Basin is concerned, Fig. 8 shows that in the northwestern margin it varies within the generally coincident range, reflecting that the crude oils in this area are of homology, mainly originating from the Permian oil-bearing strata there is an apparent difference between the carbon isotopes composition of the Upper Triassic crude oil in Dushanzi and that of the Jurassic crude oil in Qigu of the southwest of the basin and this difference results from the different oil sources, coming from different oil-forming depressions of Middle Jurassic and Lower Triassic.

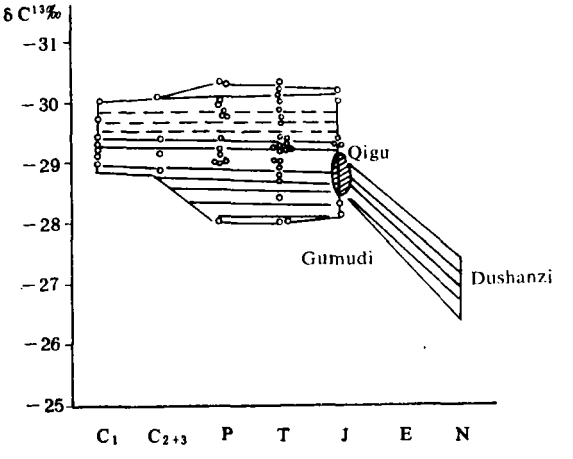


Fig. 8 Distribution of carbon isotopes in crude oil

## CONCLUSION

Having had a contrast between the features of the free radical and those of the carbon isotopes of crude oil as well as source rocks in Zhungeer Basin, we can draw a conclusion that in the basin oilforming depressions have developed in different ages. At present, the oil sources of the oilfields, so far discovered in the northwestern margin, chiefly come from the oil-forming depression in the east of the Ma Lake, and the origin of oil

and gas in the east is the Wucaiwan-Dajing oil-forming depression and the Wudong-Dalongkou oil-forming depression, whereas the oil in the southwest mainly originates from the Dushanzi oil-forming depression. The six oil-forming depressions dominate the distribution of oil and gas of Zhungeer Basin and supply the basin with rich oil-gas resources. We, therefore, suggest that the survey in Zhungeer Basin be extended to the six depressions mentioned above and their surrounding areas (including the bottom wall of Dushanzi Oilfield). It promises high hopes of success to pay attention to looking for nappetype oilfields and bedrock reservoirs, and what is more, the Wulonggu oil-foming depression has a prospective potential of oil formation.

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