Study on Geochemical Characteristics and Genesis of Dalianhe Oil Shale in Heilongjiang Province

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Abstract

This paper discusses the geochemical characteristics and genesis of the Dalianhe oil shale in both the coal and the oil shale members. The oil shale of the two members is quite similar in geochemistry in that both are of high percentage of SiO_2, Al_2O_3 and Fe_2O_3 (middle to difficult lava silicon ash), Mn/Ti ratios are less than 0.1, Sr/Ba ratios between 0.1 and 0.5 and Vi/Ni between 2.6 and 7.0. The organic types are mainly composed of sapropel humus. OEP values of n-alkanes are between 1.55 and 3.67, showing outstanding odd carbon number distribution, with nC_{23} and nC_{29} as the highest peaks. Average Pr/Ph ratio is up to 2.30, indicating pristine dominance. Pr/nC_{17} ratios are between 1.18 and 2.30. All these characteristics reflect that oil shale in the two members was deposited in fresh water, lake-swamp, alongshore and in lower oxygen and anoxic environment conditions. The parent material styles from the coal member are richer in hydrogenous component related to water-loving flora, which is the main reason for the quality difference of the oil shale in the two members.

Introduction

Oil shale generally refers to any sedimentary rock with ultrafine bedding containing relatively large amounts of organic matter that can be burned with associated high ash. Total world resources of oil shale are enormous. With the continuing decline of petroleum supplies, accompanied by increasing costs of petroleum-based products, oil shale presents opportunities for supplying energy needs of the world in the years ahead. Therefore, there has been great interest in the exploration and investigation of oil shale.

Oil shale was originally deposited in a wide variety of depositional environments including freshwater to saline lakes, epicontinental marine basins and related subtidal shelves. Oil shale was also deposited in shallow lakes and limnic and coastal swamps.

The Dalianhe oil shale, accompanied with lignite, mainly occur in the Dalianhe Formation located in the Yilan County of Heilongjiang province. Preliminary studies on Dalianhe oil shale include Deshi Guan et al., 1995. This paper discusses the geochemical characteristics and the genesis of Dalianhe oil shale based on a quantitative analysis data from a large number of oil shale samples.

Depositional assemblage characteristics of the oil shale-bearing strata

The Dalianhe formation mainly developed in the northern part of the Fangzheng Faulted depression, which is a secondary tectonic element of the Yi-Shu Graben. Hercynian granite and Cretaceous clastic rocks form the basement of the faulted depression. The overlying sedimentary unit is the Palaeogene Dalianhe Formation, composed of clastic sedimentary rock of continental facies, mainly fluvial, slough and lacustrine, containing coal and oil shale. The lithology includes glutenite, sandstone, oil shale, coal, sandy shale, etc. The coal and oil shale are distributed in the lower section of the Dalianhe Formation. Using the marker bed of thick oil shale, from bottom to top, the Dalianhe Formation can be subdivided into three members. The stratigraphic succession, lithology and thickness are illustrated in Figure 1.

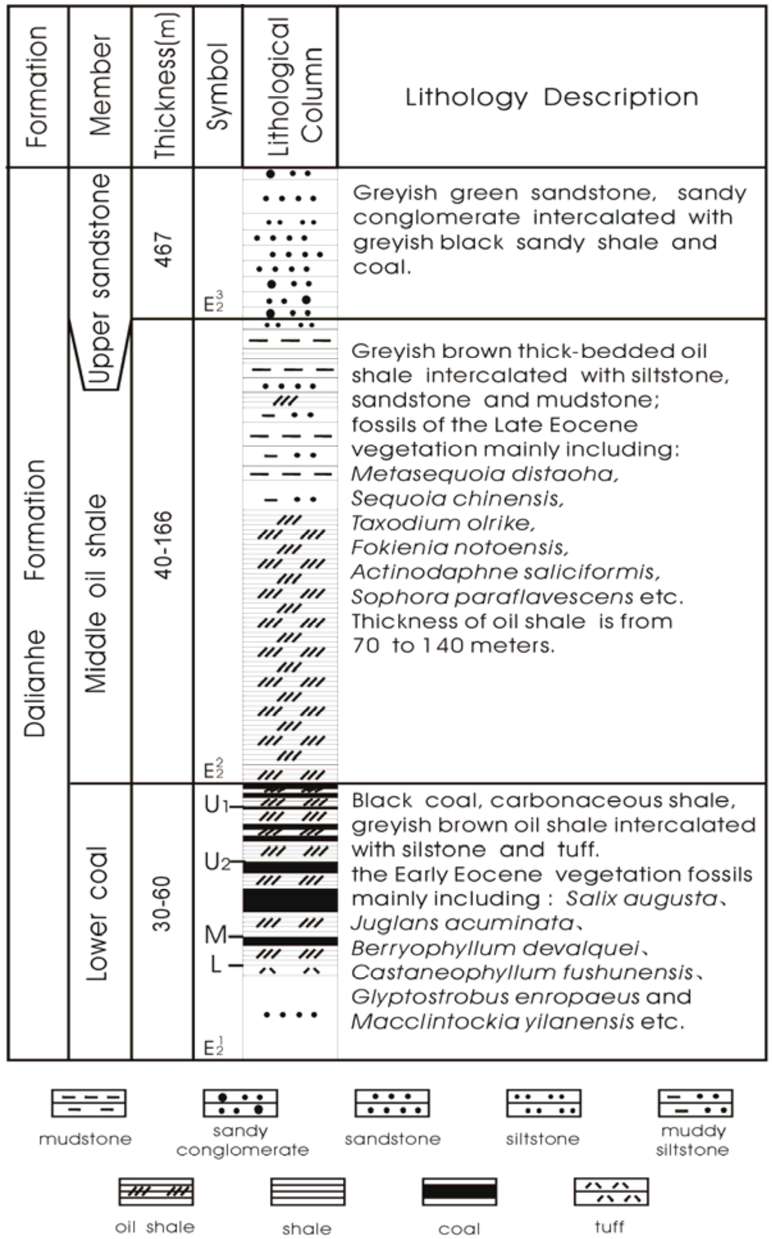

Figure 1: Diagram showing comprehensive columnar section of the Dalianhe Formation

Lower coal member (E_2^1): The lower coal member is composed of coal, black carbonaceous shale, oil shale, etc. The thickness is generally from 30m to 60m and the thickest is 63m. The lower part is granite, feldspar sandstone, mudstone and oil shale of diluvium and alluvium and the upper part is made up of coal and charcoal shale of slough facies and oil shale and sandstone of lacustrine facies. This member contains fossils of the Early Eocene, mainly vegetation of evergreen broad-leaved forests and deciduous broad-leaved forests, such as *Salix augusta, Juglans acuminate, Berryophyllum devalque, Castaneophyllum fushunensis, Glyptostrobus enropaeus, Macclintockia yilanensis* etc.

Middle oil shale member (E_2^2)
The middle oil shale member is composed of oil shale, thin bedded siltstone and fine sandstone in stagnant lacustrine facies and is developed across the whole region. The lithology is uniform and stable. The thickness generally ranges from 70m to 140m and the thickest is 166m. It can be divided into three sections. The lower section is about 30m to 40m thick, mainly brown massive oil shale, which is dense and rigid, with interbedded siltstone, fine sandstone and nodules of siderite in the bottom 0.05m to 0.7m. The middle section is about 40m to 60m thick, made up of black fine oil shale; bedding planes are horizontal or sometimes crinkled where diagonal bedding can be observed. The upper section is about 10m to 30m thick, comprised of light brown oil shale with interbedded siltstone, fine sandstone and grit. The sandstone component is mainly quartz and highly kaolinitic feldspar, the siltstone contains abundant mica, and the shale contains grains of gravel. This section contains many fossils of the Late Eocene, mainly vegetation of deciduous broad-leaved forest of warm temperate zone, such as *Metasequoia distaoha, Sequoia chinensis, Taxodium olrike, Fokienia notoensis, Actinodaphne saliciformis,*

Sophora paraflavescens etc. In addition, entomolites including *Pseudotettiginia yilanensis* and *Prophalangopsis* sp. are also found in this member.

Upper sandstone member (E_2^3): The upper sandstone member is composed of glutinite, sandstone and bedded sandy shale of alluvial flat and swamp facies. The clastic debris is rather coarse, the grading is not good and the cement is relatively loose. The thickness is about 500m. It can be divided into three sections. The lower section is composed of sage green grit and gravel grit, sometimes with interbedded granite wash. The middle section consists of interlaminated of grey black and sage green sandy shale, argillaceous shale and sage green siltstone, with interbedded thin layer danks. The upper section is made up of yellow brown glutinite which can be changed into sandstone. It is the top member of the formation. The gravel component is predominantly granite and vein quartz. Gravel diameter is from 4mm to 40mm, with good sphericity and loose cement made up of fine sand and silt.

Inorganic geochemical characteristics and depositional environmental indications

Characteristics of inorganic elements: Residual ash from oil shale combustion is mainly inorganic compounds including SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and so on. The percentage of ash is generally more than 40%. It is very important for developing and utilizing oil shale to study the ash composition.

The ash of Dalianhe oil shale is composed of SiO_2 (63.56 wt %), Al_2O_3 (18.28 wt %), Fe_2O_3 (6.08 wt %) and others, as is shown in Figure 2. According to the classification criteria established by Deshi Guan et al. (1995) it is classified as middle to difficult lava silicon ash.

Knowledge of trace elements in ash of oil shale facilitates the multipurpose utilization of useful trace elements, the recovery of poisonous or harmful trace elements for environmental protection. Trace elements in the ash of Dalianhe oil shale were analyzed, but they do not reach to production grade, only the Ba content reaches to 279.2μg/g and the others are lower than 100μg/g (Figure 3).

Depositional environmental indications of inorganic elements: Oxides and sulphides of Mn can migrate a long distance in basins, but chemical compounds of Ti usually are deposited near shore. The change in Mn and Ti content can be used to reflect the relative migration distance in a basin and the depth of water. The Mn/Ti ratio can be seen as a sign of the distance from land, increasing with the distance to land (Deng and Qian, 1993). The Mn/Ti ratios in Dalianhe oil shales are very low (less than 0.1), which reflects the near shore depositional environment.

The microelement Sr/Ba ratio can distinguish between fresh water and salt water. In salt water sediment, Sr/Ba is >1 but in fresh water sediment, Sr/Ba is <1. The Sr/Ba ratios in Dalianhe oil shales are relatively low, between 0.1 and 0.5, which indicates fresh water when the oil shale was depos-

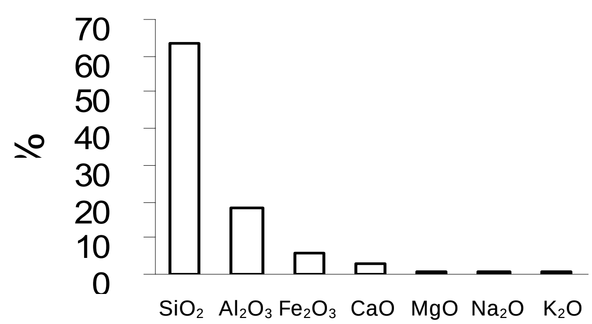

Figure 2: Histogram showing the major elements in the Dalianhe oil shale

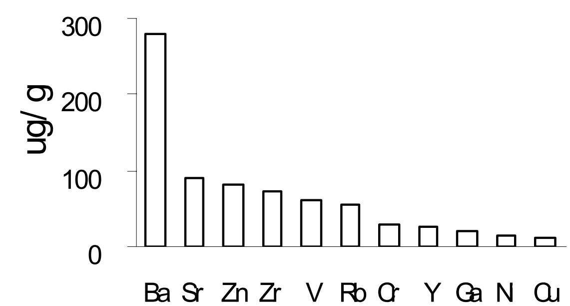

Figure 3: Histogram showing the trace elements in the Dalianhe oil shales

ited.

The V/Ni ratio is related to the redox potential of the water body and the organic content. The V/Ni ratios in Dalianhe oil shale are between 2.6 and 7.0, indicating a weak redox depositional environment.

In sum, inorganic geochemical characteristics indicate the Dalianhe oil shales were deposited in fresh water, near shore and in a weak redox sedimentary environment.

Organic geochemical characteristics and depositional environment

Kerogen type: Kerogen is derived from organic matter in sedimentary rocks that have undergone a series of biological and chemical actions. Kerogen type is related to development degree of the aquatic organisms and terrestrial plants. Organic matter of Type I kerogen (sapropel type) is derived from aquatic plankton and algae, formed in deep-sea (or deep lake) facies environments. Organic matter of Type III kerogen (humic type) is derived from the higher plants and algae of seashore swamp and lacustrine bog depositional environments. Type II kerogen (mixed type) between Type I and Type III is subdivided into Type II_A (humic sapropel) and Type II_B (sapropel humus) indicating they were formed in the nearshore-shallow water depositional environment (Wang and Chi, 2001).

Based on organic element analysis data of Dalianhe oil shale samples from two different members, the following conclusions can be drawn:

- The oil shale in the oil shale member has H/C ratios ranging from 0.79 to 0.94 and O/C ratios ranging from 0.17 to 0.30. On an H/C versus O/C diagram, the oil shale plot within the Type II_B kerogen band.
- The oil shale in the coal member has H/C ratios ranging from 0.91 to 1.28 and O/C ratios ranging from 0.14 to 0.28. On an H/C versus O/C diagram, the majority of oil shale samples plot within the Type II_B kerogen band and the minority within the Type II_A kerogen band (Figure 4). The organic parent matter has a relatively high H component content, showing derivation from aquatic plankton and algae.
- The dominant kerogen in the Dalianhe oil shale is Type II_B and the oil shale was deposited in shallow-water environments.

Normal alkanes: The n-alkanes from the organic matter in sedimentary rocks originated from lipids in bodies of plants and animals. Inhomogeneous n-alkanes have a great variety in their composition and structure. Gas chromatographic analysis of saturated hydrocarbon from Fushun and Maoming oil shale were performed by Huang et al. (1984). Results show that the n-alkanes are characterized by a bimodal cluster distribution in which the former is low and the latter is high, with nC_{17} and nC_{27} as the prominent peak and with outstanding odd carbon number predominance about high carbon number peak cluster. Results indicate that the organic parent matter of Fushun and Maoming oil shale was derived from low aquatic organisms and terrigenous higher plants.

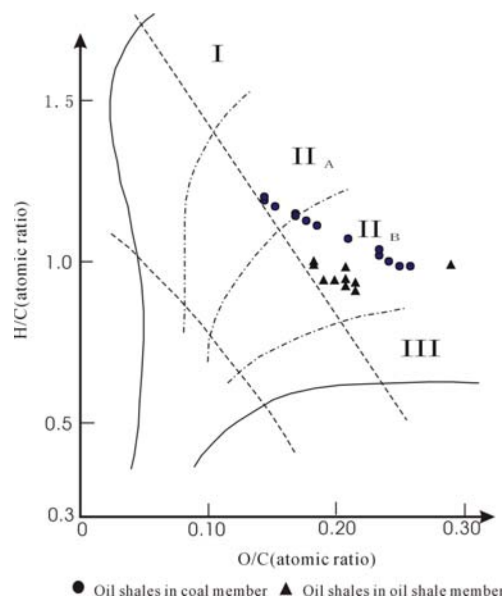

Figure 4: Kerogen classification of the Dalianhe oil shales

Comparison of the saturated hydrocarbon gas chromatographic diagram of Dalianhe oil shale with that of Fushun and Maoming oil shale shows that the two member oil shales of Dalianhe have analogous character in n-alkanes which are characterized by unimodal distribution with nC_{23} and nC_{29} as the prominent peaks and with outstanding odd carbon number predominance. The light and heavy hydrocarbon ratios ($\sum n_{21-}/\sum n_{22+}$) range from 0.24 to 0.45 and OEP values range from 1.55 to 3.67 (Table 1). These distributional features indicate that the organic parent matter of Dalianhe oil shale is mainly derived from terrigenous high plants, which generally corresponds to inland lake delta plain paludal facies and limnetic facies.

Isoprenoid alkanes: The phytal in side chain of plant chlorophyll transform into phytol with microbial action. In strong anoxic environments, the phytol reacts with hydrogen to produce dihydrophytol which turns into phytane with dehydration and hydrogenation. By contrast, in a weak oxygenic environment, the phytol reacts with oxygen to produce phytanic acid, which turns into pristane with decarbonylation and hydrogenation (Huang et al., 1984; Shen et al., 1999). So the ratio of pristane to phytane is generally used to indicate the oxidizing condition of the original depositional environment.

The Pr/C_{17} ratios can determine the water body properties during initial deposition of the source rock. If the Pr/C_{17} ratios are less than 0.5, the water body is an open system. Between 0.5 and 1.0, is an intermediate phase, and more than 1.0, indicates a swamp environment.

The isoprenoid alkanes from the two members of oil shale in Dalianhe have similar characters, both have outstanding pristane predominance. The Pr/Ph ratios range from 1.48 to 3.49 (average value up to 2.30), indicating a lower oxygen to anoxic condition and limnetic facies depositional characteristics. Pr/nC_{17} ratios are between 1.18 and 3.20, which shows that the Dalianhe oil shale was deposited in a lake-swamp environment condition.

Discussion of genesis of oil shale

The quality of oil shale in both the coal member and the oil shale member is evidently different. Average oil yield values of the oil shale from the coal member and the oil shale member are 9.58 wt%(the highest value up to 17.05 wt%) and 4.48 wt%, respectively.

The studies on paleobotany show that the Earth was in a warm and mild climate in Eocene (He and Tao, 1997). Asia Minor peninsula was in a subtropical climate, with vegetation mainly non-deciduous plants.

Table 1: Geochemical parameters of Dalianhe oil shale

Oil shale layer	**n-alkanes**			**Isoprenoid alkanes**		
	prominent peak carbon	OEP	$\sum nC_{21-}/\sum nC_{22+}$	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}
Coal member	nC_{23}	1.9	0.45	2.25	2.06	0.92
	nC_{23}	1.62	0.39	2.51	1.18	0.34
	nC_{23}	1.92	0.35	1.48	3.2	2.29
	nC_{29}	3.67	0.3	2.51	3.03	0.94
	nC_{29}	3.57	0.3	2.08	2.51	1.2
	nC_{29}	2.38	0.24	2.08	1.32	0.41
Oil shale member	nC_{27}	1.55	0.25	3.49	2.37	0.62
	nC_{29}	3.15	0.28	2.03	2.6	0.99

From Eocene to Oligocene, the climate began to get colder, leading to change of vegetation in middle and high latitudes.

The flora of the coal member of Dalianhe formation is mainly subtropical evergreen broad-leaved and deciduous broad-leaved Lauraceae and Magholiaceae, richer in water-loving vegetation such as metasequoia and yew. This reflects the warm, humid, rainy, plant-exuberant northern subtropical climate at the time. In late part of the Eocene, the flora of the oil shale member are mainly deciduous broad-leaved plants of the warm temperate zone, including hydrophyte and hygrophyte such as metasequoia and yew. But the abundance of hydrophyte and hygrophyte decreases distinctly.

The temperature decrease from the coal member deposition to the oil shale member deposition resulted in a diverse association of plants and aquatic organism (Feng et al., 2000, 2002). The two members of oil shale were deposited in fresh water, near shore and in a weak redox sedimentary environment. However, the organic parent matter of the oil shale in the coal member has a relatively high H component content, related to the aquatic organisms that flourished during its deposition, which is the main reason that the oil shale quality in the coal member is better than that in oil shale member.

Conclusions

Based on the above, we draw the following conclusions:

1. Dalianhe oil shale ash belongs to middle to difficult lava silicon ash. Mn/Ti ratios are very low (less than 0.1), and Sr/Ba ratios relatively low (between 0.1 and 0.5), V/Ni ratios are between 2.6 and 7.0, which indicate that the Dalianhe oil shales were deposited in fresh water, near shore and in a weak redox sedimentary environment.
2. The dominant kerogen in the Dalianhe oil shale is Type II_B (sapropel humus) and a minority of oil shale samples plot within the Type II_A kerogen band, which indicates the oil shale was deposited in shallow-water environment.
3. The two members of Dalianhe oil shale show an analogous character in n-alkanes characterized by the prominent peak of nC_{23} and nC_{29} and outstanding odd carbon number predominance. This indicates the organic parent matter of Dalianhe oil shale is mainly derived from terrigenous high plants. The isoprenoid alkanes have outstanding pristane predominance, the Pr/Ph ratios have the average value of 2.30., which shows a lower oxygen/anoxic condition and limnetic facies depositional characteristics.
4. The organic parent matter of the oil shale in the coal member has a relatively high H component content, related to the flourishing aquatic organisms during deposition. This is the main reason that the shale quality in the coal member is better than that in the oil shale member.

Acknowledgements

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