Origin and hydrocarbon source of the Ordovician high wax content oil in Southern Slope Zone of Dongying Depression

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Abstract. Exploration has inevitably extended into deep layers with ever-increasing exploration for oil and gas. Oils from Ordovician burial hill are recently discovered from Ordovician burial hill in the south slope of Dongying Depression, Bohai Bay basin, and the oils are characterized by high content of waxy alkanes with a low concentration of biomarker and sulphur content. Several types of oils also existed in the south slope of Dongying depression, such as biodegraded oil, normal oils in Shahejie Formation and high wax oils in Kongdian Formation. Forty-three oil samples and twenty-three source rock samples are finely analysed by inclusion analysis, monomer hydrocarbon isotope analysis and absolute content of biomarkers. On the basis of isotope compositions, biomarkers and integrating the physical properties of the hydrocarbons including densities and PVT relationships, it can be speculated that the oils from Ordovician buried hill and Kongdian Formation have the same source, obviously different from the overlying oils from Shahejie Formation. Combined with maturity parameters, biomarkers, and inclusions analysis, it is speculated that the oils are a secondary hydrocarbon accumulation from the mixing of earlier formed oil and a late formed gas, and the oils of Ordovician and Kongdian bear a typical features of deep Es4 source rocks. Aquatic organism, higher plants and bacteria are the source of the waxy oil, and the gas invasion in geological history should be responsible for the formation of the high waxy oils. This study is helpful for unravelling hydrocarbons accumulation mechanisms and deep petroleum resources evaluation in this area. Besides, the research process in this paper can also be applied to other basins to explore for high wax oil reservoirs.

1. Introduction
With ever-increasing exploration for oil and gas, exploration has inevitably extended into deep layers. Considerable quantity of high wax oils are discovered from an Ordovician buried hills in the WG1 well in the southern slope of Dongying Depression. Both the physical properties and chemical compositions of the oils differ significantly from the previously discovered oils of the Paleogene Shahejie and overlying formations, which are sourced from the Es3 and Es4 members of the Shahejie Formation, the most important source rocks in the Dongying Depression [1]. In this paper, the source of the Ordovician buried hill oils and the origin of the high wax oils are finely discussed.

2. Geology
The Dongying Depression, developed during the Cenozoic rifting, lies in the southeast of the Bohai Bay Basin and has an area of 5850 km², and it is one of the most oil rich rift areas in the east of China. The Dongying Depression is an asymmetric “dustpan-shaped” lacustrine basin. From north to south, it
can be divided into five secondary tectonic units, i.e., steep slope zone, northern sag zone, central anticline zone, south sag zone and gentle slope zone. The basin evolution can be divided into pre-rift stage, rift stage and depression stage by tectonic history and sedimentary sequences. By several normal faults and the Central Anticlinal Belt, the Dongying Depression is subdivided into the Minfeng Sag, the Lijin Sag, the Niuzhuang Sag and the Boxing Sag. During the pre-rift stage, Lower Paleozoic marine platform sediments and Upper Paleozoic paralic facies of coal measures are developed on the Precambrian crystalline basement; and for the second rift stage, abundant Mesozoic and Paleogene fluvi-lacustrine sediments are deposited, finally, during the depression stage, Neogene fluvi-terrestrial sediments are developed[2].

3. Methodology
The samples used in this investigation include one Ordovician oil, one Ordovician carbonate fluid inclusion one oil from the WG-1 well, 12 rock samples and 35 oils samples from the Paleogene Shahejie Formation and Kongdian Formation. The powdered samples are extracted using Soxhlet with chloroform to obtain bitumen. The extracted bitumen and oils are filtered out of asphalt using hexane, and then the samples are fractionated on a silica-alumina column using hexane, hexane/chloroform and alcohol/chloroform as eluants to yield saturated, aromatic and resin fractions, respectively. The saturated and aromatic fractions are analyzed by GC-FID and GC-MS. The δ13C values of saturated, aromatic, resin and bitumen fractions are determined using an isotope ratio mass spectrometer. Saturated fractions isotope analyzed are dominated by n-alkanes with a carbon distribution ranging from n-C11 to n-C36 with a low level background. The fluid inclusion oils are extracted following an approach similar to that used for the clastic reservoir rock.

Diamondoid hydrocarbons and drimanes in crude oils can be analyzed directly using GC-GC-TOFMS without any pre-treatment. The GC-GC analytical conditions are set as follow: a DB-petro column (50 m, 0.2 mm i.d. and 0.5μm film thickness) is selected for the 1D phase, and RESTEK-Rix column (2 m, 0.15 mm i.d. and 0.15μm) is used for the 2D column. The programmed temperature for the first column increased to 300°C at a rate of 4 °C/min and is isothermal for 50 min; meanwhile, the second column is programmed initially at 4 °C /min to 310 °C and is isothermal for 50 min. A low amount of oil samples are injected into a heated (300°C) split injector, with a split ratio of 100:1. The injection temperature is set at 300 °C. Helium is used as carrier gas with a constant flow rate at 1.5 ml/min, the modulation cycle is 10 s including 2.5 s for heating blow. Temperatures of the ion source and transfer line are set as 250°C and 280°C, respectively. Ionization voltage is 70 eV and the MS detector Voltage is 1500 V. The rate of data acquisition is 100 spectra/s and data is collected over a mass range of 40–600 μm.

4. Results and discussion

4.1. Bulk geochemical characteristics of the Ordovician Oils
The Ordovician oils from the WG-1 well in the southern slope of the Dongying Depression are characterized by a high wax content (40.84%), high freezing point (49 °C), low density (0.827 g/cm3), low viscosity (4.79), and low sulfur content (0.07%). The oils from the Kongdian Formation also contain high wax content, ranging from 10.88% to 31.77%. The C30-octacosane 20R sterane concentrations of the Ordovician oils and Kongdian oils are quite low while variations of the C30-octacosane 20R sterane concentrations may reflect their differences in maturity. The C29-octacosane 20R sterane concentrations in source rock decrease dramatically with the depth increase, indicating the low C29-octacosane 20R sterane concentrations may reflect the high maturities. Thus, it can be...
speculated that the high wax oils contain a high maturity oils. Meanwhile, the distribution and composition of the alkylphenanthrene in the Ordovician oils indicate a relatively low thermal maturity, which is also supported by the drimanes parameters. The alkylphenanthrene is as lower as 0.2, and the drimanes parameter is 0.24, much lower than the shallow oils. Therefore, it can be concluded that the oils are a secondary hydrocarbon accumulation from the mixing of early formed oil and a late formed gas.

**Figure 1.** TIC of the saturate fractions of the oils from Kongdian Formation and Ordovician

**Figure 2.** Components Carbon isotope values of oils from Ordovician buried hill, Kongdian Formation, and Es₄ Formation.

**Figure 3.** Monomer hydrocarbon isotope values of oils from Ordovician buried hill, Kongdian Formation, and Es₄ Formation.

4.3. **Oil-source correlation**

Study of Galimov [3] demonstrated the isotope is the effective parameter in the oil-oil and oil-source correlation. Carbon isotope values of different components of high wax oils indicate that the oils from Kongdian Formation and Ordovician have the same source. Furthermore, n-alkanes are detected to be the dominant compounds in the saturated fractions, showing a symmetric distribution without odd to even carbon preference. The high wax oils from Kongdian Formation and Ordovician have a same n-alkanes distribution and a similar monomer hydrocarbon isotope value (Fig. 3), indicating the same hydrocarbon source. The absence of major biomarkers such as terpanes and steranes in Ordovician oils precludes an effective investigation of the oil source and oil depositional environment. As the Ordovician and Kongdian oils have the same source, the biomarkers in Kongdian oils can provide information of the Ordovician oil source and depositional environment. The abundance of
gammacerane is high in the oil with the average ratio of gammacerance/C$_{30}$ hopane being 0.51. Moreover, salinity of the brine inclusion can reach 16.5% in W100 (Fig.5), confirming the salt lake depositional environment. Combining depositional environment of the hydrocarbon sources in the southern slope of the Dongying depression, it is speculated that the oils of Kongdian and Ordovician bear a typical features of deep Es$_4$ source rocks.

![Figure 4](image1.png)

**Figure 4.** m/z 217, m/z 191 mass chromatograms for the oil of the Ek oil after removal of alkanes.

![Figure 5](image2.png)

**Figure 5.** Features of fluid inclusions in the south slope of Dongying Depression.

![Figure 6](image3.png)

**Figure 6.** Burial history and thermal evolution of deep source rock.

4.4. *Origin of the high wax oil*
The relative abundance of C_{27}, C_{28}, C_{29-αα} regular steranes in Kongdian Formation oils displays a “anti-L” shape, and the higher C_{29-αα} regular steranes may reflect the high plant contribution. The tricyclic terpane / pentacyclic terpanes ratio in high wax oils are much higher than that of the Shahejie oils, and suggesting the contribution of the bacteria in the high wax oils formation.

Recently, many researchers [4, 5] have found a late formed gas can exert a significant effect on hydrocarbon properties of a basin and can result in an increasing challenge in predicting the properties of the liquid hydrocarbons. Zhang et al conclude that the formation of the condensates and high wax oils can be attributed to the invasion of the gas as well as migration fractionation. In this area, to better understand the evolution of the petroleum system, thermal history and hydrocarbon generation modelling are conducted. The measured Ro T_{max} suggest that, at present, rocks deeper than about 4000 m are mature for condensate gas, the majority of Kongdian source rocks have generated gas after the Dongying sedimentary period. According to the Fig.4, quantities of gas inclusion can be observed, combined with the TIC of the saturate fractions of W46 well oil, which can be confirmed that the gas invasion has happened and the gas invasion can be considered as the main factor for the high wax oil generate.

5. Conclusion
The high waxy oil from the Ordovician buried hill in the Dongying Depression are finely characterized. The oils of Kongdian and Ordovician bear a typical features of deep Es_{4} source rocks and the higher plants and bacteria of the source rocks and gas invasion in geological history should be responsible for the formation of the high waxy oils. This study is helpful for unravelling hydrocarbons accumulation mechanisms and deep petroleum resources evaluation in this area. Besides, the research process in this paper can also be applied to other basins to explore for high wax oil reservoirs.

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