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Geochemical Characteristics of Different Salinized Lacustrine Shales and the Evaluation of Shale Oil Potential: A Case from Bohai Bay Basin

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Abstract

Shale oil exploration is a hot topic of global oil and gas exploration. China has great potential for shale oil resources. At present, the discovered shale oil resources in China generally exist in lacustrine shale sediments with salt interlayer. The geochemical characteristics of shales formed in salt water environment (saline-shales) and shales formed in fresh water environment (freshwater-shales) is vital for the shale oil exploration in China, and is useful for the evaluation of hydrocarbon potential in saline sediments.

The s saline-shales have higher organic matters enrichments than the freshwater-shales. Meanwhile, the hydrocarbon potential in freshwater-shales is higher, while saline-shales have higher shale oil potential in the saline-shales. The high thermal conductivity of salt sediments facilitate the hydrocarbon generation. The organic matters in freshwater-shales are mainly I/II_1 types and dominated by sapropelic substance, dominantly origin from the aquatic organism. While, the organic matters in saline-sahles are dominated sapropelinite and liptinite with II_1/II_2 types, which derive from the mix source of aquatic algae and terrestrial higher plants. The biomarkers shows that the organic matters in saline-shales deposited under strong reducing environment, while freshwater-shales were under generally reductive to weak oxidation environment. The depositional environment of shale sediments was affected by the climate. The Nanpu depression had higher the mean annual temperature (MAT) and mean annual precipitation (MAP) than Dongpu depression during middle Eocene. The warm and humid climate in Nanpu depression facilitated the weathering of parent intermediate igneous rocks, and led to the runoff and enrichment of elements during middle Eocene. The cooler and drier condition Dongpu depression led more weathering of felsic igneous provenance. The difference of provenance between Nanpu and Dongpu depression mainly were affected by the tectonic background. The Nanpu depression had active continental margin tectonic setting, and Dongpu depression was occanic island margin tectonic setting during middle Eocene.

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Introduction

In recent years, international crude oil consumption is increasing. Especially in China, the dependence on foreign crude oil has exceeded 70% in recent years. Therefore, it is very important to increase domestic crude oil exploration. With the in-depth exploration in recent years, China's shale oil resources show great resource potential. With the development of drilling and completion technologies, such as horizontal drilling and hydraulic fracturing, China's shale oil exploration continues to achieve breakthroughs. In China, shale oil has also been discovered in terrestrial lake basins, including Eocene Qianjiang shales in Qianjiang Depression, Eocene Shahejie shales in Zhanhua Depression, and Eocene Hetaoyuan shales, among other locations [1,2]. The terrestrial shale reservoir for shale oil production layers in China share a notable characteristic that the terrestrial sediments is accompanied by interbedded salt rocks, as observed particularly in Eocene Shahejie shales in Dongpu Depression of the Bohai Bay Basin, east China [3]. Meanwhile, shale formed in freshwater environment also contains huge shale oil resources, but no major breakthrough has been made. At present, there is a lack of systematic comparative study on the organic geochemical characteristics of shale formed in saline sedimentary environment and freshwater environment, as well as the formation paleoenvironment of these shale sediments. Such comparison is helpful to a deeper understanding of the impact of saline sediments on the hydrocarbon generation potential of organic matter in shale. At the same time, it is also very helpful for the deep understanding of the formation mechanism of shale and the enrichment mechanism of organic matter in shale.

Compared with shales deposited in freshwater basins, saline lacustrine shales are more favorable for hydrocarbon generation, accumulation and preservation, and earlier hydrocarbon generation-expulsion [4-8]. Previous studies show that, salt formation is closely associated with the paleoenvironment in various aspects, such as paleosalinity, paleoredox conditions, occlusive-open system, and hydrothermal [9,10,6,7]. Shale and mudstone reservoirs with interbedded salt deposited under low energy environmental settings, often underwent complex paleoenvironmental changes, which are

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more sensitive to high-frequency climate changes down to seasonal scales [11-13]. Not only had the influence on lithological facies and mineral composition, the variations of paleoenvironment also notably the abundance and types of organic matter, and the expulsion efficiency of hydrocarbon from the derivation and preservation conditions. The abundance of organic matter is mainly attributed to paleoproductivity, redox conditions, and sedimentation rate, among others. Climate controls the freshwater inflow that influences the accommodation space of paleolakes and land plant-derived organic matter input [14,15]. Organic matter is oxygenated and dissipated in oxic water, whereas it is conserved and enriched under anoxic conditions. Thus, an anoxic environment is beneficial to the accumulation of organic matter and results in high productivity. On the other hand, organic matter primarily originates from lower hydrobiont organisms and terrigenous organic matter; the former prefers to generate crude oil, and the latter tends to generate gas. The types of palaeobios varing in fresh, brackish, and saline water, also affected differences in types of organic matter [16-22].

This study try to analyze the difference of organic geochemical characteristics of shales formed in salt water environment (saline-shales) and shales formed in fresh water environment (freshwater-shales), and try to better understanding the mechanism of enrichment of organic matter. The shale sediments of third member of Shahejie Formation (Es_3 shales) in the Bohai Bay Basin will be analyzed in this study. Es_3 shales are stably distributed in the whole Bohai Bay basin, and are important hydrocarbon source rocks. The different sub-basins of Bohai Bay Basin have different saline depositional environments during Es_3 shales deposition. The south Dongpu depression is typical saline environment, and formed thick salt interlayer in Es_3 shales (Dongpu Es_3 shales; [23]). While, the north Nanpu depression is freshwater depositional environment with little salt sediments (Nanpu Es_3 shales, [24]). This study compares the organic geochemical characteristics and shale oil potential of Nanpu and Dongpu Es_3 shales, and tries to better understand the effect of salt sediments on the process of organic matter transferring to hydrocarbon. In addition, this study will also contrast the formation environment of different saline shale sediments, which is benefit for the deeper understanding of mechanism of enrichment of organic matter in different saline environments.

Geological Setting

The Bohai Bay Basin, located between the Tanlu and Cangdong faults, is one of the most important oil and gas basin in Eastern China (Figure 1a, [25,26]). The basin contains 15 major sags including Bozhong, Huanghekou, Qikou, Nanpu, Liaozhong, Liaoxi, and Laizhouwan sags, and 16 uplifts including the Bonan, Shijiutuo, Liaoxi, and Shaleitianuplifts [27].The Nanpu and Dongpu depressions are two important oil-bearing sub-tectonic belts in the north and south of Bohaibay Bay Basin, and are deeper studied in this study. The Bohai Bay Basin experienced a crystal basement formation stage from the Archean to the Paleoproterozoic, a platform cover deposition stage from the Mesoproterozoic to the Triassic, and a continental rift stage from the Mesozoic to the Cenozoic (Figure 1, [28-31]). The rifting stage includes four substages: early synrift substage, late synrift substage during, the first thermal subsidence substage and renewed rifting substage. The postrifting thermal subsidence stage includes two substages: (1) a second thermal subsidence substage during 24.6~5.1 Ma and (2) a neotectonic activity substage from 5.1 Ma to present.

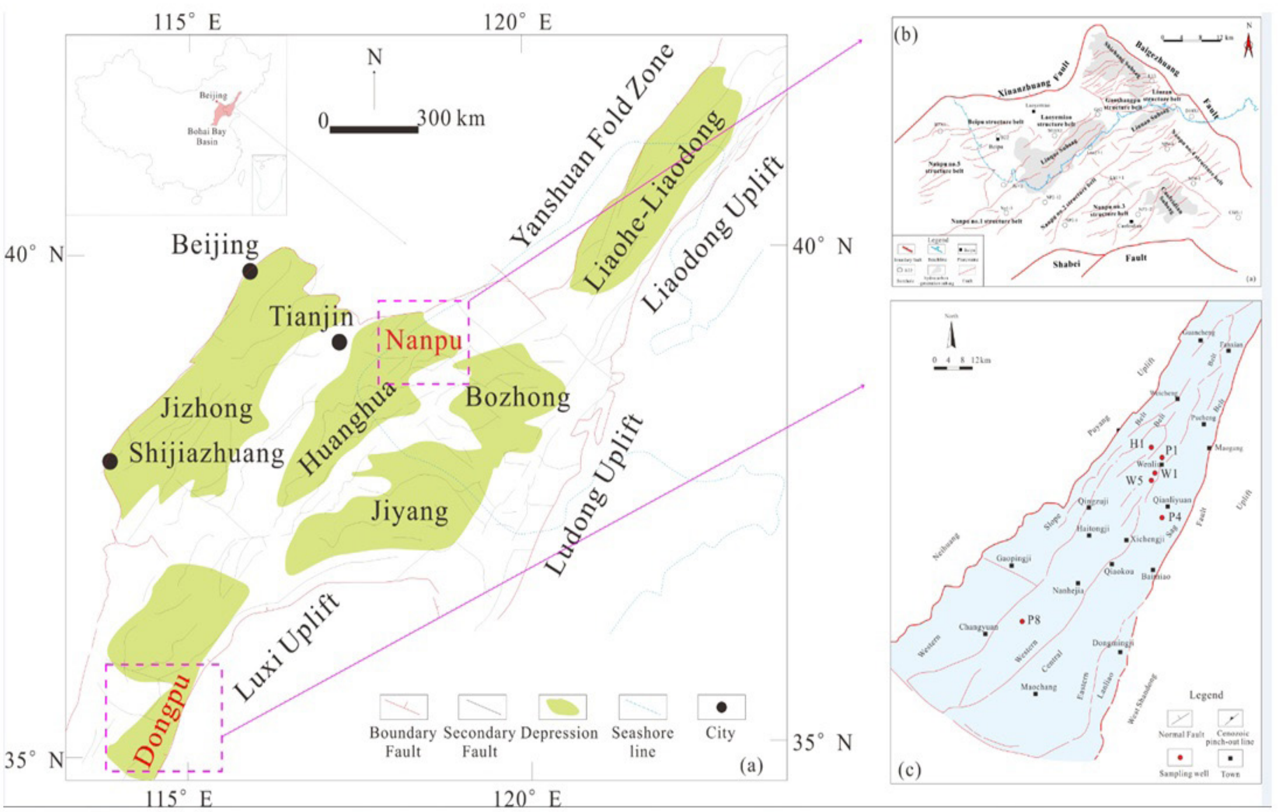

Figure 1: Regional location of the Nanpu (b) and Dongpu (c) depressions in the Bohai Bay Basin (a) (modified after [40,23]).

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The Cenozoic of Bohai Bay Basin deposited thick sediments, including Paleogene, Neogene, and Quaternary (Figure 2). The main formations contains Paleogene Kongdian (Ek), Shahejie (including Es_1, Es_2, Es_3, and Es_4) and Dongying (including Ed_1, Ed_2, and Ed_3) Formations, the Neogene Guantao (N_1g) and Minghuazhen (N_{1-2} m) Formations, and the Quaternary Pingyuan Formation (Qp, Figure 2) from the bottom to the top. Four sets of source rocks developed in the Bohai Sea area: (1) Es_3, (2) Es_{1-2}, (3) Ed_3, and (4) Ed_2 [32-34] (Figure 2). The Es_3 set is oldest and buried the deepest; the base of the unit in the Bozhong sag is at a depth of more than 8000 m, and the depth exceeds 3000 m in most of the study area. The source rocks of Es_3, which are very thick, represent lacustrine sedimentary facies.

The Shahejie Formation (Es) can be divided into four members with distinct lithologies [35,36] which are abbreviated as Es_1, Es_2, Es_3, and Es_4. The Es_3 set is oldest and buried the deepest; the base of the unit in the Bozhong sag is at a depth of more than 8000 m, and the depth exceeds 3000 m in most of the study area. Es_3 has been regarded as one of the most important resource rocks of Bohai Bay Basin [37,38], and have contributed plenty of oil and gas resources, where shale

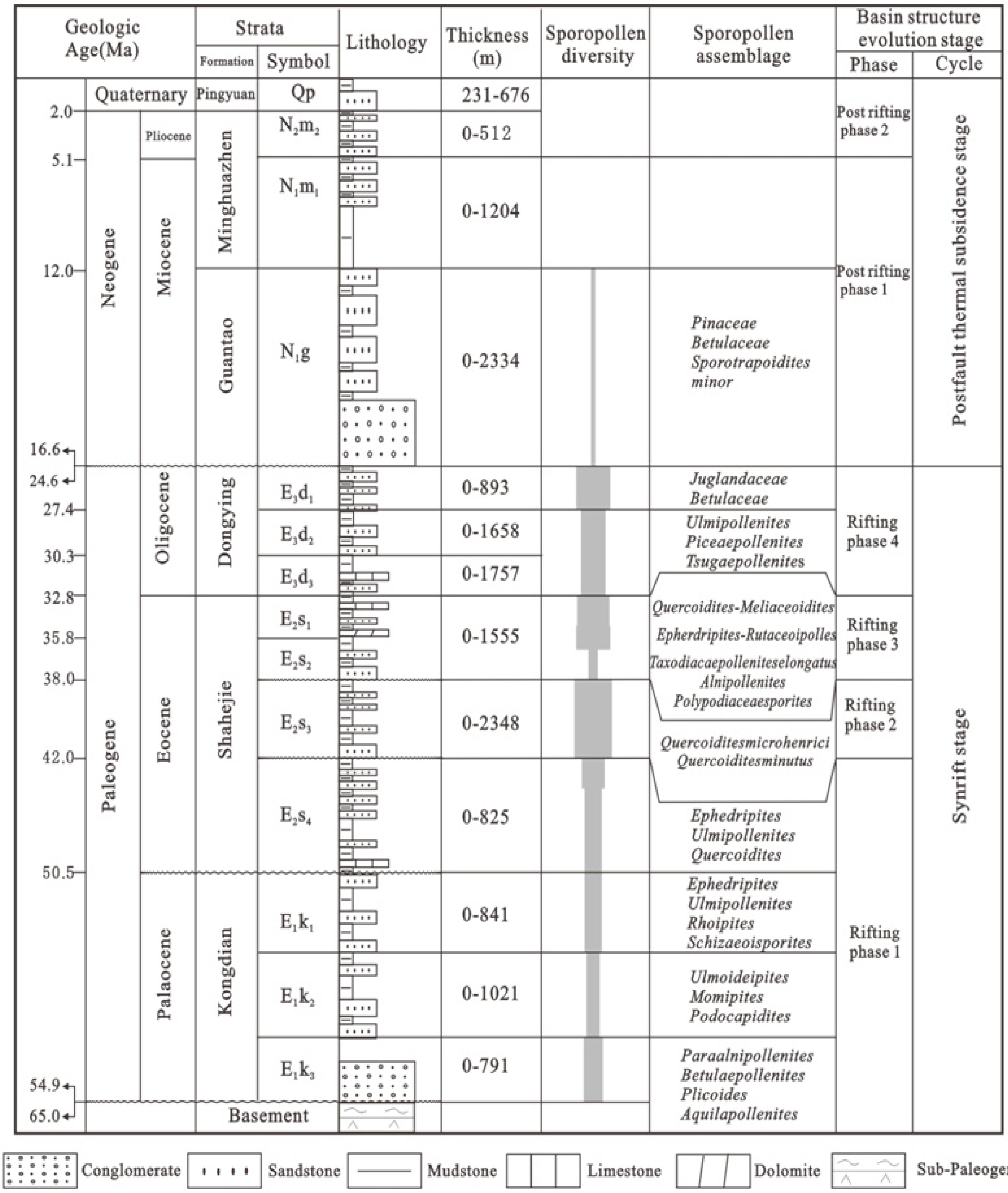

Figure 2: Stratigraphic column of the Bohai Bay Basin (modified form [27]).

oil have been discovered since 2010 in many sub-tectonic belts. The main lithologies of Es_3 are mudstone and dark gray mudstone [39]. While, there are extensive salt and and gypsum interbedding within the shale sediments in many depressions such as Dongpu and Dongying depressions. However, the other depressions are typical shale sediments without salt sediments, and the Nanpu depression is typical freshwater sediments in Es_3 Formation.

Sampling and Method

In this study, petrogeochemical method has been used to reconstruct the paleoenvironment. The TOC tests, rock pyrolysis and saturated hydrocarbon gas chromatin were used to obtain the research data. All experiments were carried out in China University of Petroleum (Beijing). To reconstruct the paleoenvironment, the samples were dried and ground to a powder for elemental analyses. The major elements were tested by X-ray fluorescence spectroscopy (XRF) using an Axios-mAX XRF Spectrometer. The results were presented as the weight percent of major elements. The chemical analysis results for the major elements have precisions better than 5% based on duplicate and standard analyses.

The TOC contents were measured using a CS-600 carbon analyzer. Before the experiment, one gram samples were ground and remove carbonate carbon. After that, dry samples were burned in a carbon analyzer to determine the TOC content. The results are presented in weight percent (wt. %).The powdered samples were further carried out with rock pyrolysis using a Rock-Eval 6 instrument. The pyrolysis results are reported with free hydrocarbon (S_1; mg HC/g rock), cracked hydrocarbons (S_2; mg HC/g rock) and the temperature at which the maximum rate of pyrolysis yield occurred (Tmax; °C).The bitumen "A" in twenty-eight samples was extracted with chloroform using a YS multifunction automatic extraction meter. The chloroform extraction results are expressed in weight percent (wt. %).

The saturated hydrocarbon fraction was determined by gas chromatography (GC) and GC-mass spectrometry (GC-MS) in this study. GC-MS was performed with an Agilent 7890-5975 coupled gas chromatograph-mass spectrometer, with a fused silica column (60 m×0.25 mm×0.25 μm) with injector and detector temperatures of 300°C. The biomarker compounds were identified through comparison of retention time in their mass spectra and previous works [41]. The ratios of biomarkers in the appropriate molecular ion chromatograms were calculated by comparing peak areas.

Results and Discussion

Geochemical characteristics and hydrocarbon potential

The hydrocarbon potential evaluation is significant for the exploration of shale oil resources. Geochemical method is one of the important technologies to evaluate the potential of shale oil. The free hydrocarbon (S_1) and chloroform asphalt "A" are two important indexes that can directly reflect the residual hydrocarbon content in source rocks [42-44]. Total organic carbon (TOC) does not directly reflect the hydrocarbon potential, but it is useful to describe the quality of source rocks [45,46]. TOC contents of the Nanpu Es_3 shales ranges from 0.8 wt. % to 8.8 wt. %, averaging 2.7 wt. %, and the TOC contents of the Dongpu Es_3 shales varies 0.1-5.7 wt. % (avg. 1.3 wt. %) (Figure 3a). According to the evaluation and classification of organic matter abundance, the quality of source rock can be subdivided into "poor" (TOC <0.5 wt. %), "fair" (TOC of 0.5-1.0 wt. %), "good" (TOC of 1.0-2.0 wt. %), "very good" (TOC of 2.0-4.0 wt. %) and "excellent" (TOC >4.0 wt. %) [45,46]. As shown in Figure 3a, the Nanpu Es_3 shales are "good" and "very good", and the Dongpu Es_3 shales locate at "fair" and "good" categories. These results indicate that the Nanpu Es_3 shales have higher degree of organic matter enrichment than Dongpu Es_3 shales.

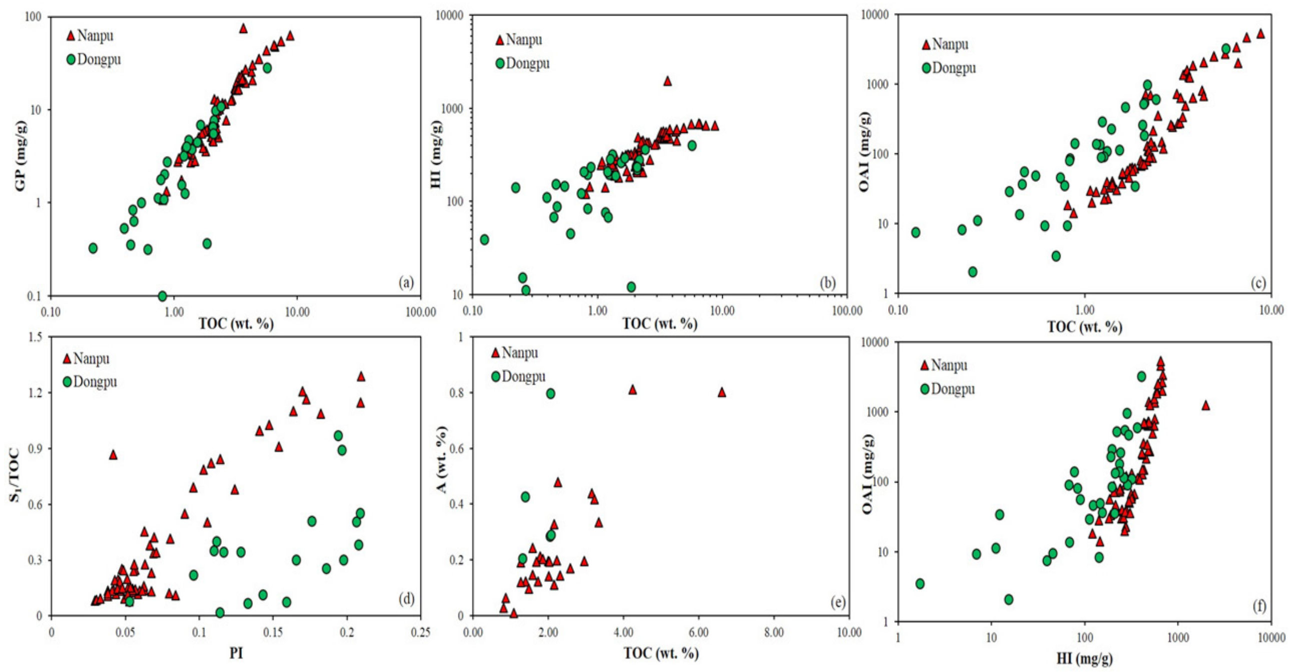

Figure 3: The comparison of the hydrocarbon potential of Es_3 shales in the Nanpu and Dongpu depressions. (a), (b), (c), and (e) show the relationships of GP, HI, the shale oil accumulation index (OAI; [44]) and chloroform bitumen "A" content with TOC, respectively. PI=S_1/(S_1+S_2). (d) shows the correlation between S_1/TOC and PI. (f) shows the Relationships of OAI and HI index.

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The S_1 content of Dongpu Es_3 shales varies from 0.01 to 5.3 mg/g, with a mean of 0.8 mg/g, and the pyrolysis hydrocarbon (S_2) value varies greatly from 0.01 to 22.9 mg/g, averaging 2.8 mg/g. The S_1+S_2 (GP) values of the Dongpu Es_3 shales range from 0.03 to 28.5 mg HC/g rock, averaging 3.6 mg HC/g rock. These values are lower than those of Nanpu Es_3 shales. The Nanpu Es_3 shales have the relatively high S_1 content of 0.1-6.2 mg/g (avg. 1.4 mg/g) and S_2 values of 0.9-72.5 mg/g (avg. 13.3 mg/g). The GP values of Nanpu Es_3 shales are high ranging 1.1-75.7 HC/g rock (avg. 16.7 HC/g rock). The GP has obvious positive relations with TOC (Figure 3a), suggesting higher hydrocarbon generation capacity of Nanpu Es_3 shales than that of Dongpu Es_3 shales. This finding is in agreement with the results of the hydrogen index (HI) vs. TOC diagrams (Figure 4a and 4b, [47]). The HI value of the Nanpu Es_3 shales ranges from 120.9 to 1986.8 mg/g (avg. 405.1 mg/g) and is higher than that of Dongpu Es_3 shales (1.1-403.6 mg/g, avg. 164.3 mg/g), indicating that the Nanpu Es_3 shales have a higher hydrocarbon generation potential than the Dongpu Es_3 shales. The evaluation of shale oil could also be analyzed by the diagram of the shale oil accumulation index (OAI), S_1/TOC, and chloroform bitumen "A" content [44]. The OAI, S_1/TOC and chloroform bitumen "A" content of Nanpu and Dongpu Es_3 shales are shown at Figure 3c, Figure 3d and Figure 3e.

According to the previous studies, S_1/TOC > 1 mg HC/g rock seems likely be regarded as a window for the show of considerable free oil in the sample for the conventional and unconventional hydrocarbon exploration [48,49]. For Dongpu Es_3 shales, the value of S_1/TOC ranges from 0.01 to 1.7 mg HC/g rock (avg. 0.5 mg HC/g rock), which is higher than that in Nanpu Es_3 shales (0.1-1.3; avg. 0.4). The chloroform bitumen "A" content of Dongpu Es_3 shales ranges 0.2 wt. % to 0.8 wt. % (avg. 0.4 wt. %) which is also higher than that in Nanpu Es_3 shales (0.01-0.8 wt. %, avg. 0.2). At the same values of HI and TOC, the OAI values of Dongpu Es_3 shales are higher than that of Nanpu Es_3 shales. According to the above analysis, it can be seen that the Nanpu Es_3 shales have higher hydrocarbon potential than Dongpu Es_3 shales, while the occurrence of shale oil in Dongpu Es_3 shales is better than than in Nanpu Es_3 shales. These may be caused by the organic matter type and geothermal gradient. In addition, the existence of salt will have an important impact on the evolution of organic matter.

The types and maturity of organic matter

The organic matter types could be preliminarily identified by HI versus Tmax diagram (Figure 4a). The organic matters in Nanpu Es_3 shales are dominated by type I/II_1, and those in Dongpu Es_3 shales mainly are II_2/III types. The results of rock pyrolysis analysis are affected by the thermal evolution; therefore, other indicators, such as maceral and biomarkers, are needed to comprehensively determine the type and organic matter source [50]. The composition of organic macerals has been widely used to describe the types of kerogen and evaluate the potential of hydrocarbon generation in source rocks based on the origin of the organic macerals [51-54]. The assemblage of maceral groups in the Es_3 shales can be shown in a ternary diagram (Figure 4b) with sapropelinite, liptinite, and huminite (vitrinite and inertinite) as the three vertices. The organic matters in Nanpu Es_3 shales main contain sapropelinite and little vitrinite and inertinite, without liptinite. While, the organic macerals in Dongpu Es_3 shales are dominated by sapropelinite and liptinite, but the vitrinite and inertinite are low (0-25%). These results show that the source of organic matter in Nanpu and Dongpu Es_3 shales are different. The organic matters in Nanpu Es_3 shales are mainly sapropel input, while those in Dongpu Es_3 shales are the mix of sapropel and humic debris input.

Vitrinite reflectance (Ro) is another parameter that helps determine the temperature history of the sedimentary basins and is also used to verify the Tmax [55,56]. Ro values can also be calculated by Tmax (EVRo) as follows: %EVRo= 0.0180×Tmax-7.16 [57]. The %EVRo volues of Dongpu Es_3 shales range from 0.9 to 3.0% with mean value of 0.9%, which are higher than those of Nanpu Es_3 shales (0.6-0.9%, avg. 0.8%). The higher thermal maturity of Es_3 shales in Dongpu

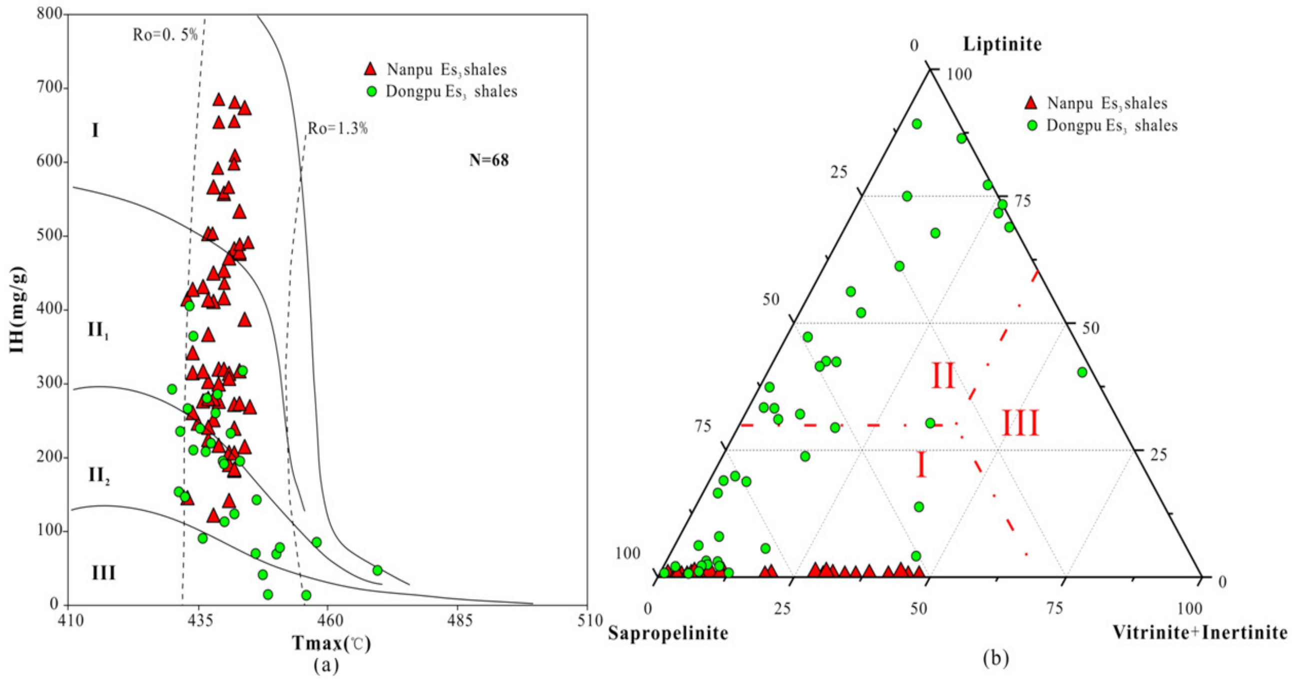

Figure 4: Plots of hydrogen index (HI) versus Tmax (a) and kerogen macerals ternary diagram (b) for Es_3 shales in the Nanpu and Dongpu depressions.

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depression may be caused by the salt sediments. The salt sediments have higher thermal conductivity than shale sediments, which lead the organic matters preference to transfer to hydrocarbon at same conditions and get higher thermal maturity.

The source and preservation of organic matter

Pyrolytic parameters and organic macerals show that the enrichment and types of organic matters in Dongpu and Nanpu depressions are obviously different. The source and preservation of organic matters in Es_3 shales need be further analyzed. One important method to analyze the source and preservation conditions of organic matters is the biomarker analysis.

Many sterane compounds could be tested in Es_3 shales of Bohai Bay Basin, which could be discerned in m/z 217 GC-MS chromatogram. The sterane compounds of saturated hydrocarbon extracts are characterized by a predominance of C_{27}-C_{30} steranes. Sterane homologues (C_{27}-C_{28}-C_{29}) could reflect the marine eukaryotic and terrestrial organic input into sedimentary OM [58]. Regular steranes are derived from sterols such as the constituents of the cell membranes in all eukaryote [59]. C_{27} sterols are regarded as being derived from algae, while land plants are proposed as the producers of C_{29} sterols [60]. C_{28} steranes are more associated with various sources [61,62]. In this study, all the shale samples contain low C_{28} sterols. The content of C_{27} sterols (23.3%~51.3%, avg. 34.8%) is lower than that of C_{29} sterols (33.5%~64.1%, avg. 47.1%) in Nanpu Es_3 shales. C_{27} sterols (17.1-64.8%) in Dongpu Es_3 shales higher than C_{29} sterols (14.8-51.7%). These results imply more aquatic organisms source Dongpu depression than Nanpu depression which have more plant origin (Figure 5).

Index C_{27}/C_{29} can reflect the relative contribution of aquatic algae and terrestrial higher plants in the source of organic matter more obvious [58], and the values of Es_3 shales are shown in Figure 6. Most values of C_{27} / C_{29} in the Dongpu Es3 shalesare greater than 1, implying the large contribution of aquatic algae and low contribution of terrestrial higher plants. The C_{27} / C_{29} values in Nanpu Es_3 shalesare lower than 1, indicating that the more source of organic matter from terrestrial higher plants.

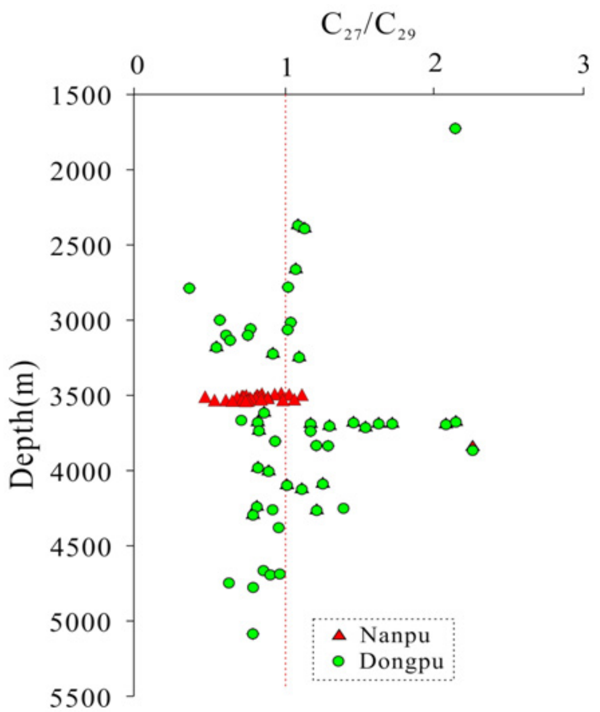

Figure 6: The distribution of C_{27}/C_{29} of Es_3 shales in the Nanpu and Dongpu depressions.

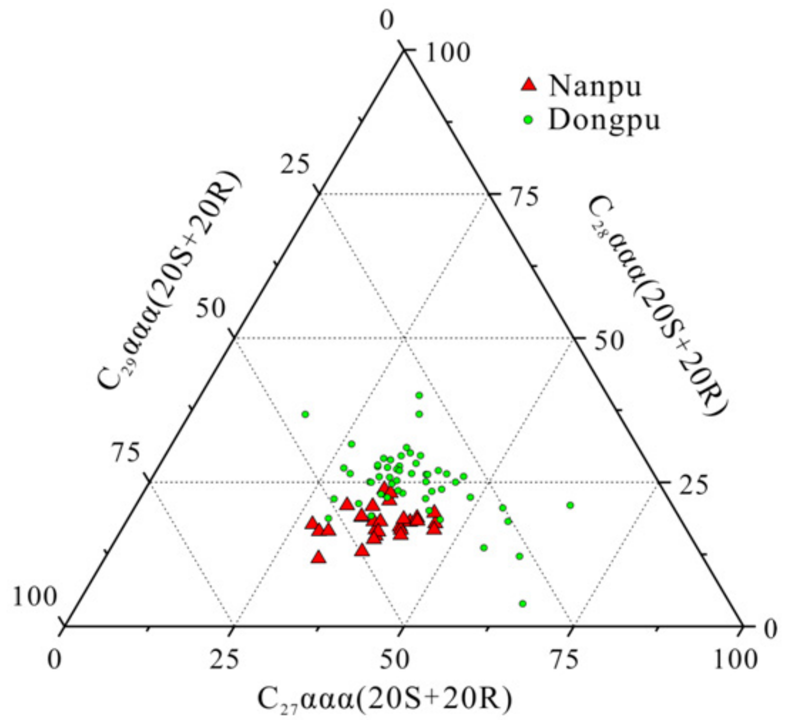

Figure 5: Ternary diagram of C_{27}-C_{28}-C_{29} of Es_3 shales in the Nanpu and Dongpu depressions.

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These phenomena indicate that the Es_3 shales are typical of sediments deposited in lacustrine environment with mixed OM input of terrestrial higher plants material and aquatic algae (phytoplankton, zooplankton) [63]. While, the saline distribution effects the source of organic matter. The high C_{27} content in Dongpu Es_3 shales implies the aquatic algae origin in the saline environment. While, most organic of orgmic matters in Es_3 shales is mix of higher plants and aquatic organisms. Meanwhile, the interpretation of C_{29}-sterols is controversial and has great effect on the origin judge. Some studies suggest that the C_{29}-sterols have also been presented in microalgae such as diatoms and freshwater eustigmatophytes, and originate from nonmarine algae and bacteria, as well as the marine pelagic sediments deposited far away from terrestrial input [64,58,65,66]. Therefore, the origin of organic matters need further study.

Preservation condition is one of the important factors affecting the enrichment of organic matter, which also could be determined by biomarker compound. Abundant isoprenoid alkanes could be tested in Es_3 shale samples. The pristine (Pr) and phytane (Ph) are short-chain acyclic isoprenoids, and are nearly ubiquitous in crude oil and sediment extracts [41]. The ratio of Pr/Ph is commonly used to interpret the redox conditions and the source of OM at the sediment-water interface for OM preservation [67]. A comparable low Pr/Ph <0.5 typically occurs in strong reductive high salt sedimentary environment. The value of 0.5-1.0 implies reductive environment, and 1.0-2.0 for Weak reduction weak oxidation environment. The Pr/Ph >2.0 demonstrates oxidizing environment, and >2.5 hints a coal strata [68,67]. Nevertheless, the ratio may be affected by thermal maturity and differences in the precursors for acyclic isoprenoids to some extent [69,70], therefore it should be used with care.

The Pr / Ph values in Dongpu Es_3 shales are small as a whole, mostly less than 1.0, which has the advantage of phytane. The relationship between Pr/nC_{17} and Ph/nC_{18} indicates that the sedimentary environment during the formation of Dongpu Es_3 shales was a strong reducing environment (Figure 7). The Pr/Ph ratio of Dongpu Es_3 shales increases obviously, with obvious change of the distribution of Pr/ nC_{17} and Ph/nC_{18}. It implies that the reducibility of sedimentary water body is weakened, which proves that the sedimentary water body becomes shallower in Es3 shales deposting period. The Nanpu Es_3 shales low Pr/Ph value (0.2-1.7, avg. 0.9), and Pr/nC_{17} and Ph/ nC_{18} reflect that the sedimentary environment of the source rock is generally reductive to weak oxidation environment. The whole is a weak reduction / oxidation freshwater environment, which may lead to low enrichment of organic matter.

Major elements and mineral composition

The elemental concentrations of the Es_3 shales in the Nanpu and Dongpu depressions are shown in Figure 8a. The Nanpu Es_3 shales contain higher SiO_2 and CaO than Dongpu Es_3 shales. The other oxides of major elements in the two depressions are close. To compare these results with the average values of the upper continental crust (UCC) and post-Archean Australian shales (PAAS), the major element compositions of the Es_3 shale samples were standardized to the UCC and PAAS compositions [71]. The gain or loss of elemental mass relative to the UCC and PAAS could be observed in Figure 8b. Values >1 indicate an increase in the relative abundance of the element in the sample compared to the UCC and PAAS, and values <1 indicate a decrease in the relative abundance of the element mainly due to the paleo weathering processes [72]. In this study, the values of K, Al and Na in Es_3 shales are less than 1 comparing with UCC and PAAS, implying that the formation of the Es_3 shales involved moderate weathering of continental crustal material in both Nanpu and Dongpu depressions. K, Al and Naare typical incompatible elements and are important components of chemically stable minerals, such as quartz and feldspar, which are commonly concentrated in geochemically mature sediments [73,74,72]. This result suggests that the Bohai Bay Basin most likely experienced active tectonic conditions during the middle Eocene. The strong depletion in Na implies intense dissolution

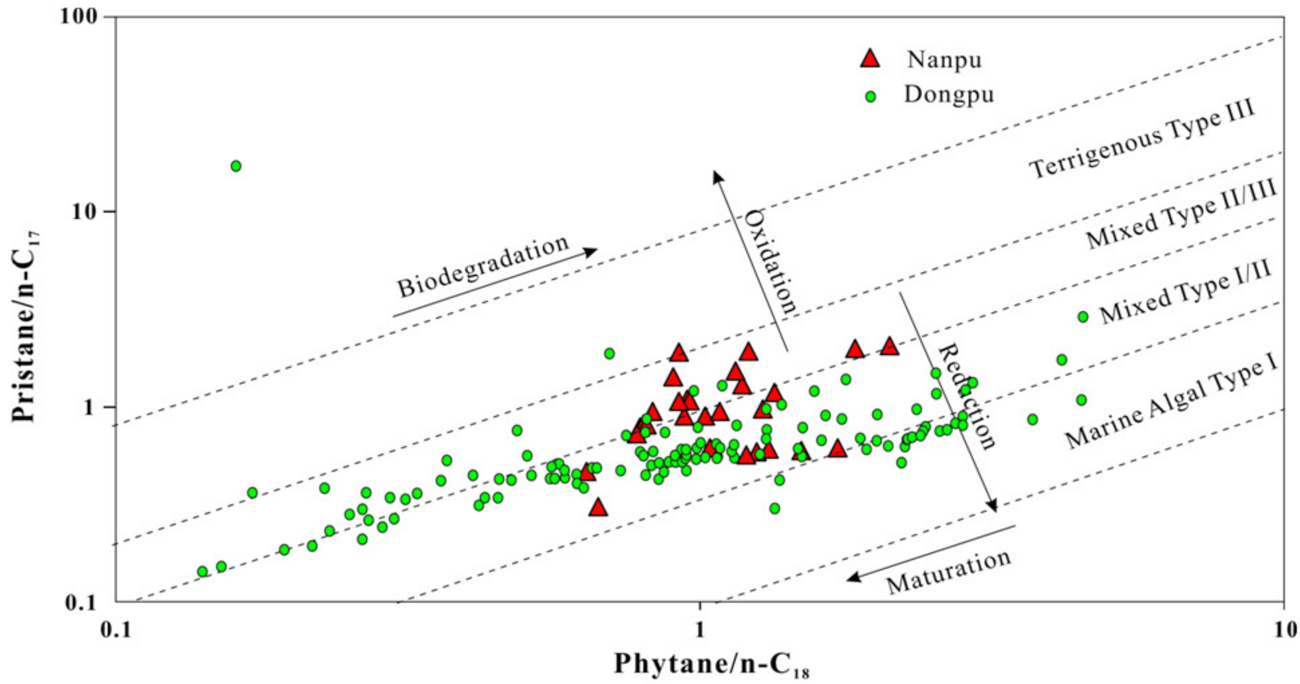

Figure 7: The relation of Ph/C_{18} and Pr/C_{17} of Es_3 shales in the Nanpu and Dongpu depressions.

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of albite, which is the main host mineral of the Na^+ mobile cation. The Ca in both Nanpu and Dongpu Es_3 shales have obvious enrichment comparing with UCC and PAAS. The Nanpu Es_3 shales enrich in P and Mn comparing with UCC and PAAS, while the P and Mn concentrations in Dongpu Es_3 shales are close to UCC and PAAS. However, the Mg is aggregating in Dongpu Es_3 shales comparing with UCC and PAAS.

High Ca enrichment in the Es3 shales compared to the UCC and PAAS (Figure 8). P_2O_5 show scattered positive relation with CaO in Nanpu Es_3 shales, and emerges negative relation in Dongpu Es_3 shales (Figure 9a). These hinting additional CaO possibly residing in carbonate in Nanpu Es_3 shales and phosphate in Dongpu Es_3 shales. In addition, CaO is obviously negative related to both Al_2O_3 and SiO_2 (Figure 9b and 9c), suggesting a possible source of CaO from silicate and secondary origin from carbonate minerals. In addition, the Dongpu Es_3 shales may contain a certain amount of phosphate for the saline environment. The depletion in Na and positive correlation between Na and Si (Figure 9d) implies intense dissolution of albite, which is the main host of the mobile cation Na^+. Al^{3+} and Ti^{4+} precipitate as hydroxides or oxides or are incorporated into the structure of clay minerals [75]. Two good positive linear correlations exist between TiO_2 and Al_2O_3 for Nanpu and Dongpu Es_3 shales (Figure 9f), and these fairly constant Al/Ti ratios indicate that Ti is mainly associated with clay minerals [76].

Weathering characteristics and paleoclimate conditions

Chemical weathering strongly affects the geochemical and mineralogical variability of sedimentary rocks [77]. Paleoweathering processes can be quantifiably evaluated by the chemical index of alteration (CIA), which was proposed by Nesbitt and Young [78] as: CIA = $[Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$.CaO* is the amount of CaO present in the silicate fraction of the rock. In this study, phosphate and carbonate may exist in the Nanpu and Dongpu Es_3 shales. Therefore, the CaO in phosphate was corrected [79]. In addition, reasonable CaO/Na_2O ratio was proposed to indirectly estimate the CaO in silicate fraction by distinguishing it from carbonate CaO directly [79,80]. When $CaO/Na_2O > 1$, silicate CaO is the Na_2O content; when $CaO/Na_2O \le 1$, silicate CaO is the

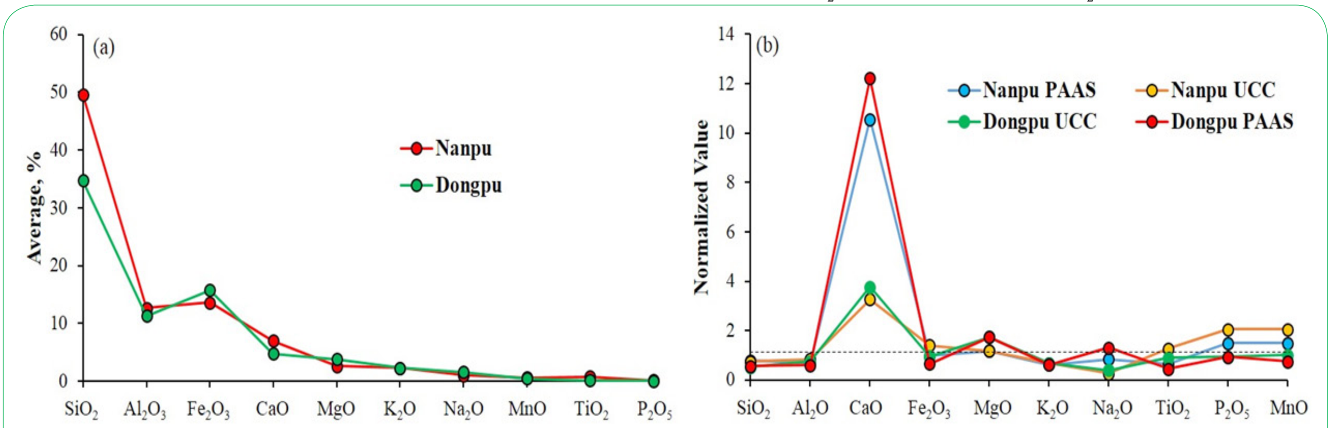

Figure 8: Major elements content (a) and mass-balance calculation compared to the UCC and PAAS (b) for the Es_3 shales in the Nanpu and Dongpu depressions.

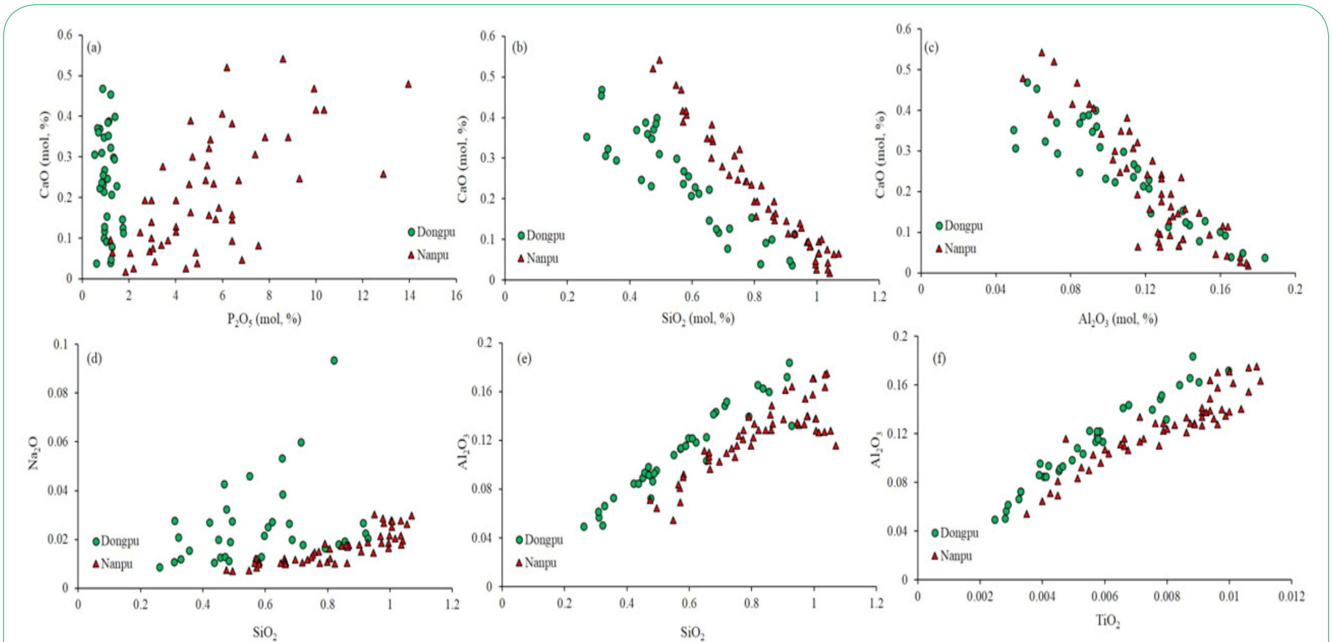

Figure 9: Correlations among the major element oxides (in molar proportions) in the Es_3 shales of the Nanpu and Dongpu depressions.

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measured CaO. The CIA is a dimensionless parameter ranging from 0 to 100. CIA values of 45-55 indicate no weathering, while a CIA value of 100 indicates intense weathering. CIA values between 50.0 and 60.0 indicate a low degree of chemical weathering, and 60.0-80.0 for moderate weathering, and >80.0 for extreme chemical weathering [78,81,82].

In this study, the CIA values of the Nanpu Es_3 shales range from 57.3 to 75.5 with an average of 68.9, which are higher than those in Dongpu Es_3 shales (46.9-71.7, avg. 60.9). These results indicate that the Es_3 shales went through moderate weathering, and the Dongpu Es_3 shales suffered lower degree of chemical weathering comparing to Nanpu Es_3 shales. The CIA values of Es_3 shale sediments are significantly higher than that of the UCC (47.7), but CIA values of Nanpu Es_3 shales are similar to that of post-Archean Australian shales (PAAS) (70.3, [71], Figure 10a).

In addition, based on the proportion of secondary aluminous minerals relative to primary mineral phases, the Al_2O_3-(CaO*+Na_2O)-K_2O (A-CN-K, Figure 10a) ternary plot has been widely used to analyze the weathering rates of primary minerals and weathering-induced diagenetic alteration [83,84,75]. Almost all of Es_3 shale samples were plotted on the straight line subparallel to A-CN (Figure 10a). It reflects the typical sediments that have been subjected to different degrees of chemical weathering, leading to the predominant removal of silicatic Ca and Na due to the destruction of plagioclase feldspars [78,83,85]. This plots along the predicted weathering trend, shows that the leaching of Ca^{2+} and Na^{+} via moderate weathering processes. Furthermore, it resulted in the formation of some minerals compositionally between illite and kaolinite (Figure 10a). There is no obvious tendency towards to the K_2O vertex for Es_3 shale samples, suggesting little K-metasomatism and metamorphism participated in the chemical weathering process [81].

In addition, the geochemical weathering conditions can also be predicted by the M-F-W ternary diagram, which was developed from a statistical analysis of element behavior during the course of igneous rock weathering [86]. M and F represent mafic and felsic igneous source rocks respectively, and W represents the degree of weathering [87]. In this study, the W value of the Nanpu Es_3 shales ranges from 31.0 to 69.0 with an average of 54.6, which is higher than that in Dongpu Es_3 shales (15.3-65.7, 37.9), implying higher weathering in Nanpu depression than that in Dongpu depression during Es_3 shales deposion. These results are consistent with the evidences from CIA (Figure 10), suggesting a good reliability for identifying weathering conditions. The Es_3 shales plots show a trend toward the W vertex (Figure 10b), indicating a moderate weathering condition.

Paleotemperature and paleoprecipitation

The chemical weathering process is primarily controlled by the prevailing climate, including the surface temperature and precipitation regime [88-91], and leads to geochemical and mineralogical variability in sedimentary rocks. Sheldon et al. [89] proposed the mean annual temperature (MAT) and mean annual precipitation (MAP) as two climofuctions to reconstruct the paleoclimate under which paleosols formed, and the results are comparable to other independent proxies. This method has been used by Passchier et al. [90,91] to reconstruct Antarctic continental paleotemperature and precipitation during the Eocene and Miocene. The mean annual temperature is calculated as MAT = -18.516(S)+17.298, where S is defined as the molar ratio of Na_2O and K_2O to Al_2O_3. For MAP (mm/yr). Passchier et al. [90] modified the climofunction based on Sheldon et al. [89] to emphasize the silicate mineral-bound components: MAP = 147.75×exp(0.0232×CIA-K), where CIA-K is the CIA without potassium (potassium is excluded to remove the effects of potassium metasomatism on paleosols; [92]).

The MAT and MAP in Nanpu and Dongpu depressions are compared in this study. The MAT values in Nanpu Es_3 shales range from 8.3°C to 12.9 °C with an average of 11.3 °C, which are higher than those in Dongpu Es_3 shales (8.1-12.0°C; avg. 9.0°C). The MAT shows good positive relation with MAP for Es_3 shales (Figure 11). The MAP values in Nanpu depression are in the range of 137.9-1099.8 mm/yr

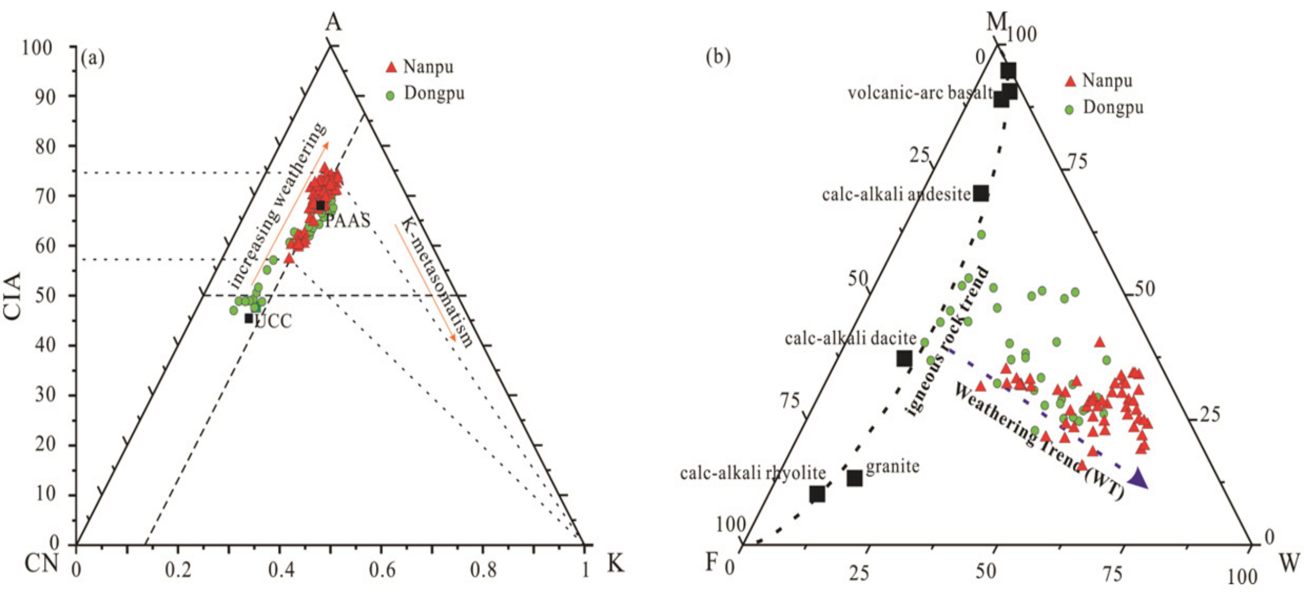

Figure 10: The comparison of geochemical weathering trends of the Es3 shales in the Nanpu and Dongpu depressions. (a) A-CN-K (Al_2O_3-CaO* + Na_2O-K_2O, all in molar proportions) ternary diagram. UCC, upper continental crust; PAAS, post-Arche an Australian shales [71]. (b) Weathering trends of the Es_3 shales depicted on the M-F-W diagram [86]. The black dashed line represents a compositional linear trend for igneous rocks.

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(avg. 896.3 mm/yr), which are higher than those in Dongpu depression varying from 133.1 mm/yr to 1032.1 mm/yr with average value of 766.1 mm/yr. These results suggest that the Es_3 shales suffered seasonally dry and cool conditions (600-1200 mm/yr; [89] during the middle Eocene. Furthermore, the climatic conditions in Dongpu depression are drier and cooler than those in Nanpu depression. While, Nanpu depression locates at the higher latitudes than Dongpu derpresssion, which should have cooler conditions. These abnormal conditions may be caused by two reasons: 1) the uplift between Nanpu and Dongpu depression in Bohai Bay Basin may have obvious effect on the climate in Bohai Bay Basin; 2) the material source in the two depressions are different which leading to the non-determinacy of geochemical characteristics.

Provenance of shale sediments

Provenance and tectonics are important factors affecting weathering products [93-95]. The A-CN-K plots show moderate paleoweathering for the Es_3 shales relative to the UCC and PAAS, and the provenances are close to mafic and felsic igneous rocks (Figure 10a). Furthermore, the M-F-W diagram suggests that the provenances of the Es_3 shales are intermediate in composition (Figure 10b). To identify the provenance of the Es_3 shales more exactly, a discrimination diagram based on seven major element compositions proposed by Roser and Korsch [96] is further used in this study. As shown in Figure 12a, the Es_3 shale samples are mainly located in the P_2 and P_3 field, and part Nanpu Es_3 shale samples at P_3 fields. This pattern implies a mainly intermediate provenance and less mafic and felsic sources. This result also is supported by Al_2O_3/TiO_2 ratio. The Al_2O_3/TiO_2 value of Nanpu Es_3 shale samples are 16.9-31.1 (avg. 20.3), and those of Dongpu Es_3 shale samples range from 21.1 to 31.0 (avg. 25.8). These results locate at the range of 21-70, indicative of a provenance from intermediate igneous rocks for Nanpu Es_3 shales and felsic igneous provenance for Dongpu Es_3 shales [97]. The log (SiO_2/Al_2O_3) - $\log(Fe_2O_3/K_2O)$ diagram shows that the Dongpu Es_3 shales are typical shale sediments, while the Nanpu Es_3 shales are iron enrichment. The K_2O/Na_2O vs. SiO_2 diagram further reveals that the Nanpu depression suffered an active continental margin and Dongpu depression went thorough occanic island margin (Figure 12c; [96,98]). This result is supported by Al_2O_3/SiO_2 vs. Fe_2O_3 and MgO diagram (Figure 12b; [99]). The Nanpu depression had many volcanic activities and active structures during the middle Eocene [24], which led the warm and moist condition and facilitated the wreathing of parent rock.

Conclusions

Based on comparative analysis of geochemical characteristics of shales formed at different depositional environments in the Bohai Bay basin, this study reveals the difference of shale oil potential between saline-shales and freshwater-shales. The shales deposited at saline environment have higher organic matters enrichments with higher TOC contents than than the shales deposited at freshwater environment. Meanwhile, the hydrocarbon potential in freshwater-shales is higher with high HI value than that in saline-shales. While, the free hydrocarbon in the saline-shales is higher than that in freshwater-shales, meaning higher shale oil potential in the saline-shales. This is caused by the salt sediments, which have high thermal conductivity and facilitate the hydrocarbon generation at the same condition. The organic matters in freshwater-shales are mainly I/II_1 types and dominated by sapropelic substance, which is dominantly origin from the aquatic organism. While, the organic matters in saline-sahles are dominated sapropelinite and liptinite with II_1/II_2 types, which derive from the mix source of aquatic algae and terrestrial higher plants. The salt sediments contribute to the higher thermal maturity in the saline-shales at the same conditions. The biomarkers shows that the organic matters in saline-shales deposited under strong reducing environment, while freshwater-shales were under generally reductive to weak oxidation environment.

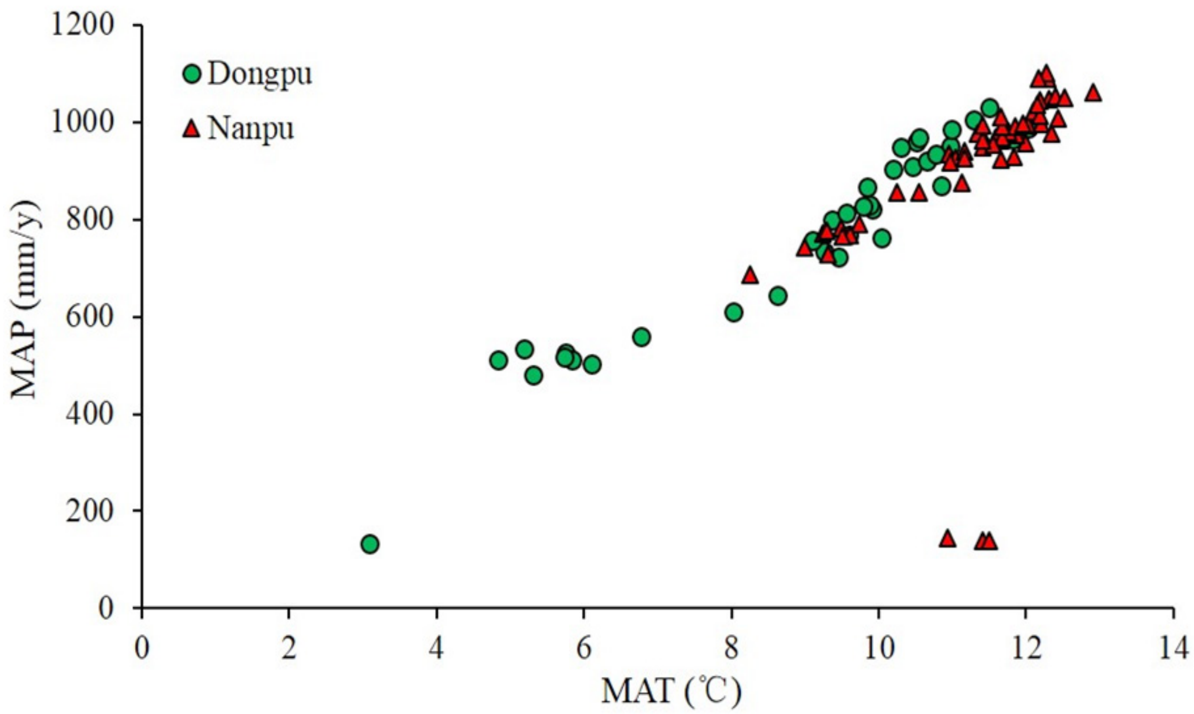

Figure 11: Correlations of MAP and MAT for Es_3 shales in the Nanpu and Dongpu depressions.

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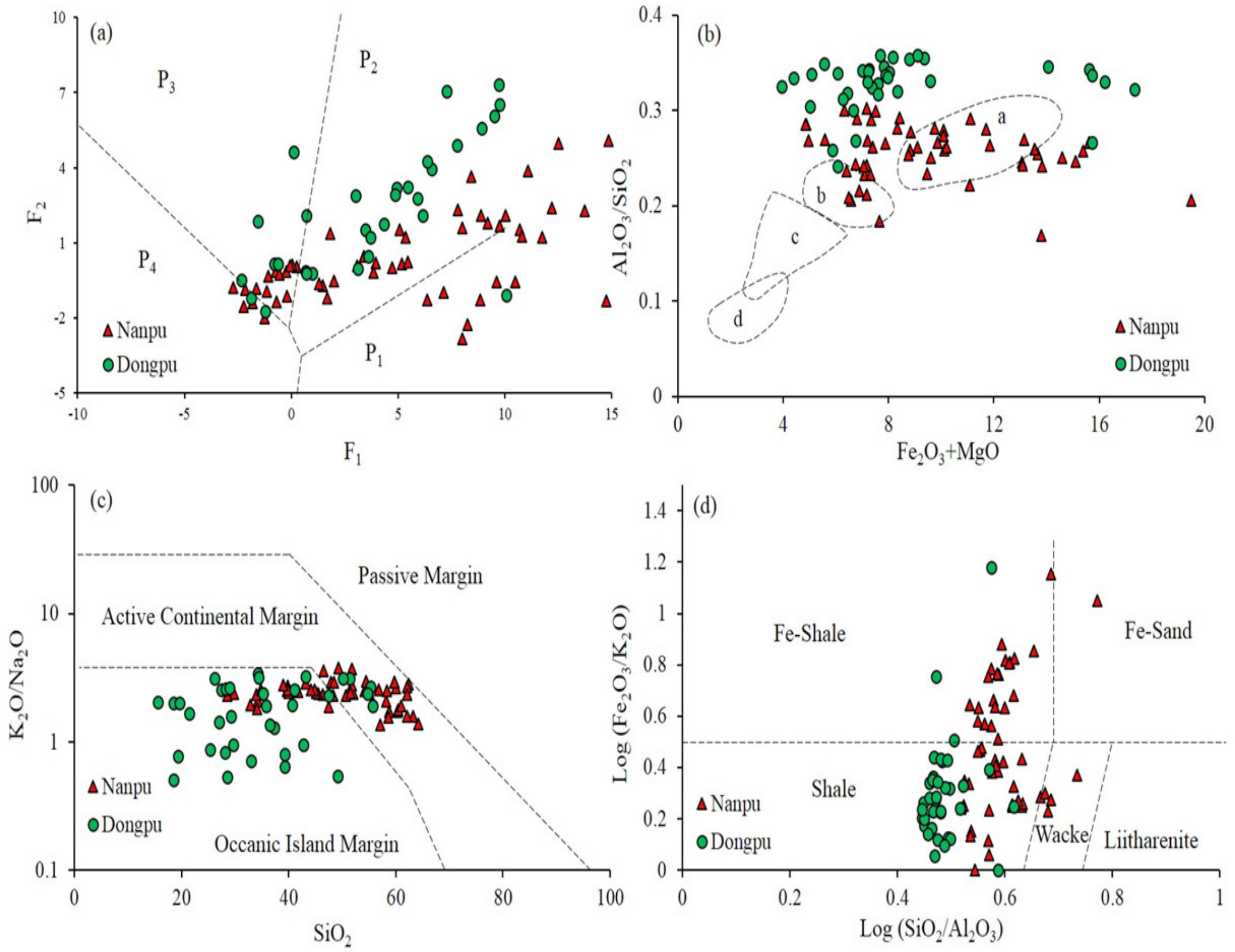

Figure 12: Provenance and tectonic discrimination plots for Es3 shales in the Nanpu and Dongpu depressions. (a) Provenance discrimination diagram proposed by Roser and Korsch [96]. P_1 indicates mafic provenance from ocean island arc. P_2 implies intermediate provenance from mature island arc. P_3 supports felsic provenance from active continental margin. P_4 indicates recycled provenance and grantitic-gneissic or sedimentary source. (b) is the Al_2O_3/SiO_2 vs. Fe_2O_3 and MgO diagram. a shows the occanic island arc, and b is the continental island arc. c is the active continental margin, and d implies the passive margin. (c) show the tectonic evaluation discriminations [99,100]. (d) shows the geochemical classification [101].

The saline-shales and freshwater-shales mainly have obvious Ca enrichments comparing to UCC and PAAS, with great difference in the elements enrichments. Those differences were caused by the chemical weathering. The Es_3 shales suffered a moderate weathering condition. The weathering condition in Nanpu depression is higher than that in Dongpu depression with higher CIA and W values. This is caused by the higher MAT and MAP in Nanpu depression than that in Dongpu depression during Es_3 deposition. The warm and humid climate in Nanpu depression facilitated the weathering of parent intermediate igneous rocks, and led to the runoff and enrichment of elements. The cooler and drier condition Dongpu depression led more weathering of felsic igneous provenance. The difference of provenance between Nanpu and Dongpu depression mainly were affected by the tectonic background. The Es_3 shales in Nanpu depression deposited under active continental margin tectonic setting, and those in Dongpu depression formed at the occanic island margin tectonic setting.

Competing Interests

The authors declare that they have no competing interests.

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