

Article

Application of Elemental Geochemistry in High-Frequency Sequence—Stratigraphic Analysis of Lacustrine Shale

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Abstract: The successful development of shale gas and oil in North America has created considerable interest in shale. The analysis of genetic types, the sedimentary environment, and the mudstone development mechanism within sequences is critical for evaluating shale gas and oil exploration prospects, exploration favorable zones, and resource potential. This study focused on the shale of Shahejie Formation in Dongying Depression of Bohai Bay Basin. Shale lithofacies division, geochemical analysis, and well-log analysis were performed for a sedimentary environment and its related elemental response characteristics' identification. Based on the results, we concluded that the sedimentary environment of the lake basin evolved from the saltwater lake to the ambiguous lake and then the open lake to the delta. In response, we observed gradually decreasing Sr/Ba and Ca/Mg ratios and increasing Rb/Ca and Fe/Mn ratios during the whole process during the reduction of the salinity and the decrease in PH value and sediments' transport distance. The relationship between ratio elements and high-frequency sequences was initially established within the shale strata. Our results show that ratios of Sr/Ba and Ca/Mg ratios near the sequence boundary are relatively low, and ratios of Fe/Mn and Rb/Ca are relatively high, while ratios of Sr/Ba and Ca/Mg near the flooding surface are relatively high, and ratios of Fe/Mn and Rb/Ca are relatively low. Those features can be used as a marker for high-frequency sequence division of shale strata. Our results provided a new theoretical basis and technical method for shale gas and oil exploration and development.

Keywords: lacustrine shale; high-frequency sequence; geochemical characteristics; elemental geochemistry; combination of elements



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1. Introduction

The analysis of genetic types, the sedimentary environment, and the mudstone development mechanism within sequences is critical for evaluating shale gas and oil exploration prospects, exploration favorable zones, and resource potential. In the past, shale was only studied as a source rock for hydrocarbon exploration. Most sedimentologists believed that the changes within mudstone formation are negligible. Mudstone in outcrop or core observation in geologic study was simply defined as “massive mudstone” and “rich organic mudstone” or “oil shale” [1]. Due to the successful development of shale gas and oil in recent years, shale has attracted great interest as a reservoir formation for researchers [2].

Studies have been performed on the sedimentary environment, sediment origins, rock type, and characteristics of shale [1,3–10]. In recent years, the sequence stratigraphy of

shale has also been analyzed in various countries. Those studies concluded that even in an environment favorable to organic matter accumulation, the properties and distribution of source rocks underwent systemic changes both vertically and laterally. This change can be laminae to the super-sequence and range from a few centimeters to thousands of meters [11–19]. The change is controlled by the sedimentary environment and stratigraphic stacking patterns and exists in both sequence and para-sequence scales. Para-sequence is the basic unit of describing organic matter enrichment, and the internal rock properties (or litho-faces/facies) of the para-sequence also underwent systematic changes [20].

Previous studies have shown that shale formation division has a unique correlation with its sequence hierarchy [4,10]. The most promising exploration of shale sections developed in the transgression stage of the second-order sequence. For basins with a high amount of allochthonous sediment supply, good reservoirs with storage particles are mainly formed in the high or low stand in system tracts within the third-order sequence. For basins with significant internal biogenic substances deposited, the best reservoirs are usually developed in the condensed sections of the third-order sequence [21].

In previous research, the high-frequency sequence division of the lake-facies sediments was mainly in the deposition of coarse debris sediments. Coarse-grained sediment has obvious lithologic changes, which made it easy for progradation and retrogradation identification and high-frequency sequence division. However, the division of shale sequence stratigraphy (especially high-frequency sequence) is difficult to carry out and a difficult point in the study of high-frequency sequence.

The index of elemental geochemistry has now been a successful indicator for marine and lake environments. The difference in elemental geochemical parameters is a reflection of shale lithofacies and the sedimentary environment [22–24]. Guo et al. (2015) found that lake-water depth changes from deep to shallow in a high-frequency sequence unit, and ratios of elements in shales show regular change accordingly, especially in the high-frequency cycle interface. Consequently, the periodical vertical variation of organic geochemical parameters provides a basis for sequence stratigraphic unit classification and correlation in the lacustrine basin. Jin, Han, Wang, Guo, and Gao (2008) [25] found good correlations between the vertical change of geochemical elements and para-sequence cycle changes in lake-facies shales, and the cyclic change of the geochemical element can also be used for the classification of high-frequency sequences' stratigraphy division in shales. Their study specified the significance of using geochemical elements in high-frequency shale sequence stratigraphy division study and has great significance for shale gas and oil exploration and development.

Our study focused on sequence stratigraphy of shale in the third member of Shahejie Formation in the Dongying Depression of the Bohai Bay Basin. We analyzed high-frequency sequence stratigraphy of lacustrine shale using elemental geochemistry. The Shahejie Formation in the Dongying Depression is enriched in organic matter and has good potential for shale gas and oil reservoirs [26]. The lithofacies classification, sedimentary environment, and elemental characteristics of shale were carried out based on observation and description of cores and analysis of laboratory data. Combining geochemical elements analysis results, the relationship between ratios of elements and high-frequency sequence stratigraphy is initially vertical in the whole formation. Our study provided a good example and basis for the high-frequency sequence division in shale and could be a guidance for the exploration and development of shale gas and oil.

2. Data and Methods

Our research included macroscopic core description, sedimentary environment analysis technology, high-frequency sequence stratigraphic analysis technology, element phase analysis, and element ratio analysis technology.

Our study analyzed 600 m long cores of Well Niu 38 in the Dongying depression of the Bohai Bay Basin. There are 2390 samples in our study for elemental analysis; 73 samples were used for total organic carbon (TOC) analysis, and 42 samples were used for vitrinite

reflectance (Ro) values from five studied wells. Geochemical elements' contents and ratios were analyzed using atomic absorption spectrometry. TOC contents were detected by a carbon–sulfur analyzer (Leco444). Ro values were tested using a microscope photometer (UMSP-50). All the analyses were performed in the Geological Research Institution Center at Shengli Oil field.

3. Results and Discussions

Overall, sediments are dominated by fine-grained sedimentary rocks in the middle and lower parts of the third member of Shahejie formation in the study area. Dark grey mudstones and calcareous mudstones constitute multiple couples. Thin (<10 cm) grey fine-grained sandstones are deposited in the lower part of the third member of the Shahejie formation. In the middle part of the third member of the Shahejie formation, sediments are dominated by dark grey mudstone and silty mudstone couples. The middle strata contain much more sand than the lower strata do. Thin (<10 cm) gray muddy sandstones, thin (<10 cm) gray muddy siltstones, thin (<10 cm) gray fine-grained sandstones, and calcareous mudstones are shown. Elemental ratios can be used to divide the sequence of fine-grained sedimentary rocks.

3.1. Elemental Ratios

Elemental Ratios as Indicators for Facies

In this study, the ratios of Sr/Ba, Ca/Mg, Fe/Mn, and Rb/Ca were selected as indicators for facies changes. Those ratios could be used to indicate physical and chemical conditions such as water salinity and sediment transport distance [27–29]. The ratios have different features (Figure 1, Table S1).

Sr/Ba: Sr and Ba can both form soluble bicarbonates and sulfates dissolved into aqueous solutions. The solubility of Ba-containing compounds and salts is relatively low, which made the migration capacity of Ba significantly lower than that of Sr [10,27]. Deng and Qian (1993) [10] provided a classification regarding the ability of element migration, which decreased in the order: Type I, Type II, and Type III. In our studied area, Sr is the most easily migrated element and classified as Type I. Ba is classified as Type III, which is difficult to migrate. The high content of Sr is related to the salinity of the lake. Salinity increased as the sediment changed from shore to deep water, so Sr/Ba ratio can be a good sign of the salinity of the water medium.

Ca/Mg: The content of Ca in lacustrine shale in our studied layer is higher than that of Mg, and the content of Ca in lacustrine shale is significantly higher than that of fluvial facies shale. The solubility of calcium salt and magnesium salt varies in the lake. According to the principle of sedimentation differentiation, magnesium salt is more difficult to deposit compared to calcium salt, and the precipitation of Ca is more significantly affected by the acidity and alkalinity of the water medium. Therefore, the Ca/Mg ratio in lacustrine shale is significantly higher than in the fluvial facies shale. In lacustrine shale, the ratio of Ca/Mg can be used as a sign to indicate acidity and alkalinity in the water medium.

Fe/Mn: The difference between the geochemical properties of Fe and Mn determines their differentiation in the sediment transportation process. Fe-containing compounds are easier to gather in coastal areas, while Mn has the highest content in brackish–salt intermittent occlusion–occlusion of the lake. Therefore, Fe/Mn ratio can be used as a sign of offshore distance (or depth). Some research results have shown that the Fe/Mn ratio is related to salinity and decreases with salinity [10].

Rb/Ca: Rb can be adsorbed by clay minerals and is enriched in sand and mudstone but poor in carbonate rocks, which makes the ratio of Rb and Ca in sediment have a clear negative correlation. Therefore, the ratio of Rb/Ca can clearly indicate the lake regression and aggression process due to the delta's progradation and retrogradation. Due to the increase in the composition of terrestrial sand and mud because of regression, the ratio of Rb/Ca is high during the retrogression of the lake. During the transgression of the lake, the Rb/Ca ratio is low, because the carbonate content increased due to the alkalinity of

the medium. Therefore, the Rb/Ca ratio can be used as an indirect symbol of the distance to offshore.

In our study, five different wells were selected, each of them located in places with different sedimentary environments. There are also large differences in the types of shale generated from different sedimentary environments, which also proved that the difference in the geochemical properties of the elements reflects the genesis and sedimentary environment of the shale (Figure 2).

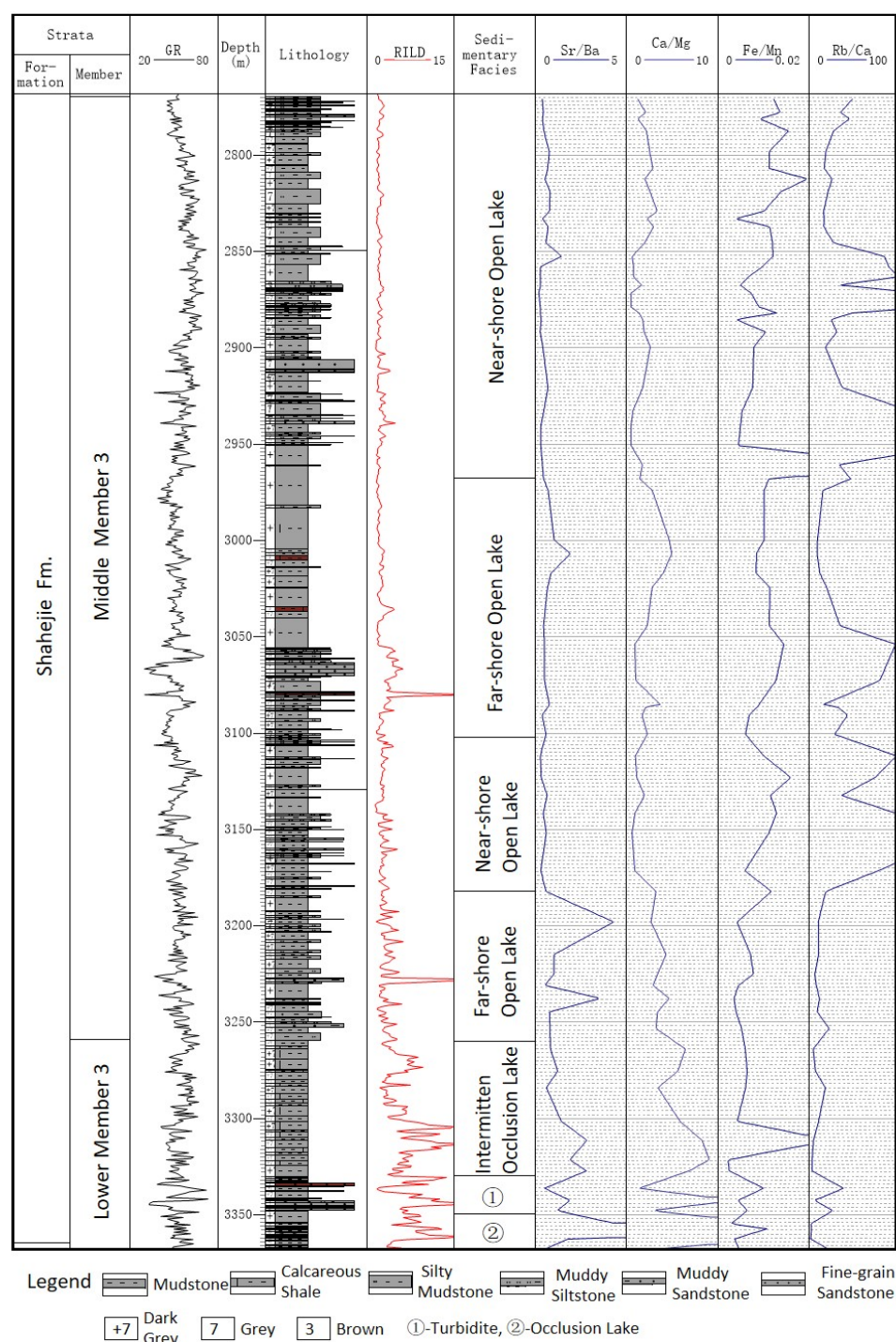


Figure 1. Longitudinal variation of element ratio in Well Niu 38, Dongying Depression.

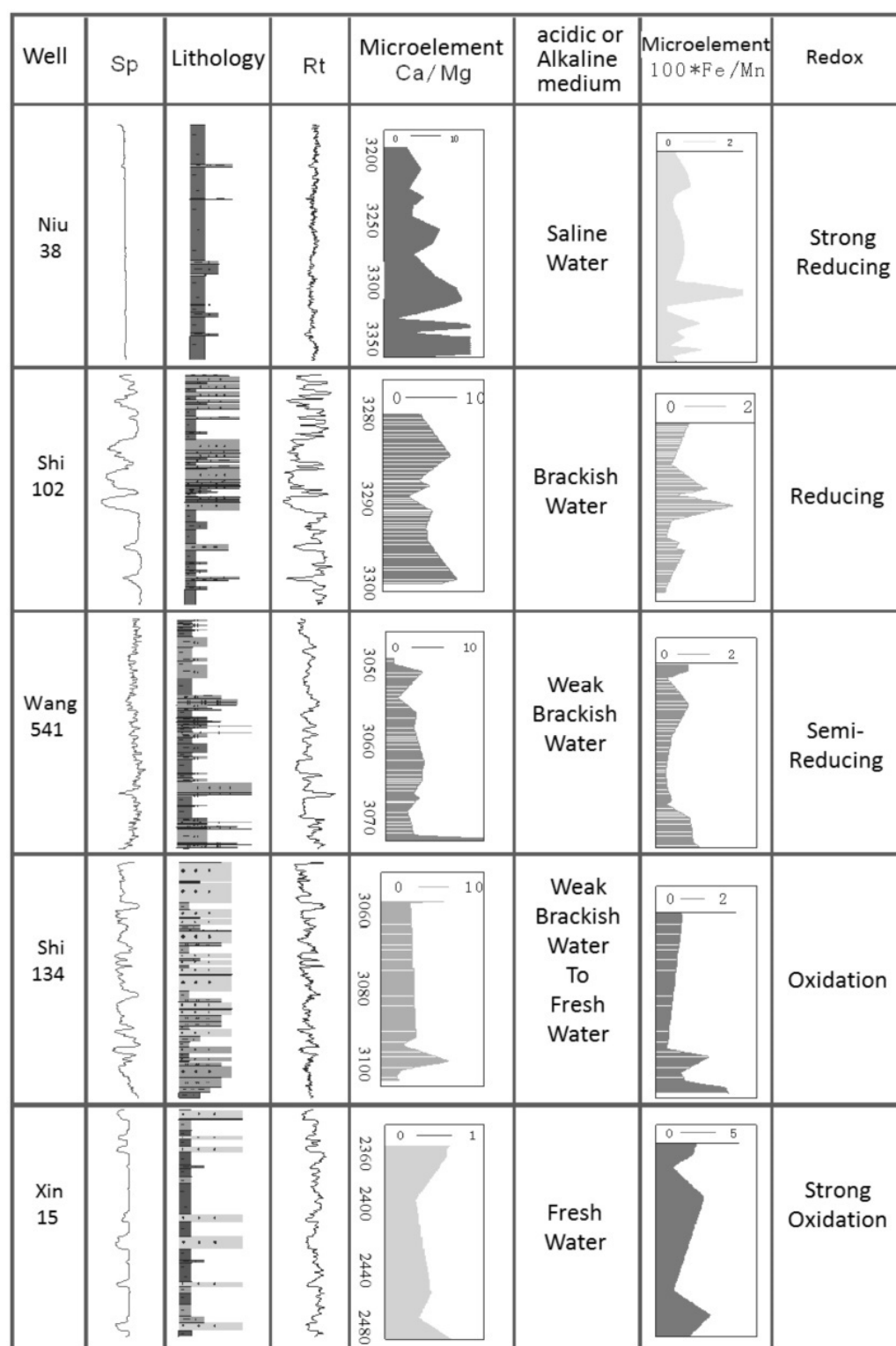


Figure 2. Variation of element ratios in different sedimentary environments of shale in Dongying Depression.

3.2. TOC Changes in Different Lake Shale Sediments

The organic matter abundance of different sedimentary facies can be very different (Table 1) [10]. In the third Middle Member of Shahejie Formation, the organic matter content of shales deposited in the blocked lake was 2.55% on average. However, in the third Lower Member of Shahejie Formation, the organic matter content of shales in the open

lake is 2.93% on average. The occluded lacustrine facies are more organic-matter-enriched than the open lake facies. The content of organic matter in saltwater lake facies is no less than that of freshwater and brackish water lake facies. In the same saltwater lake, the shale deposit during the relative desalination period in deep water was higher in organic matter content than the gray mudstone deposit during the relative salination period in shallow water. Similarly, in freshwater facies, the mudstone in the open lake far from the shore is higher in organic matter content than the mudstone in the open lake facies on shore (Figure 3; Tables 2 and 3).

Table 1. TOC contents of lacustrine mudstones in different sedimentary facies (modified after Deng and Qian, 1993 [10]).

Scheme	Un-Occlusive Lake	Occlusive Lake	Intermittent Occlusive Lake	Open Lake		Turbidity Mudstone
				Far Shore	Near Shore	
Lithofacies	Gray Mudstone	Black Shale	Calcareous Laminas Shale	Even Massive Mudstone Horizontally Bedded Mudstone	Gray Mudstone	Uneven Massive Mudstone
TOC (%)	2.3 0.59–3.86	3.5 2.11–5.7	2.8 2.73–3.00	1.6 1.01–1.97	0.9 0.46–1.37	0.5 0.46–0.51

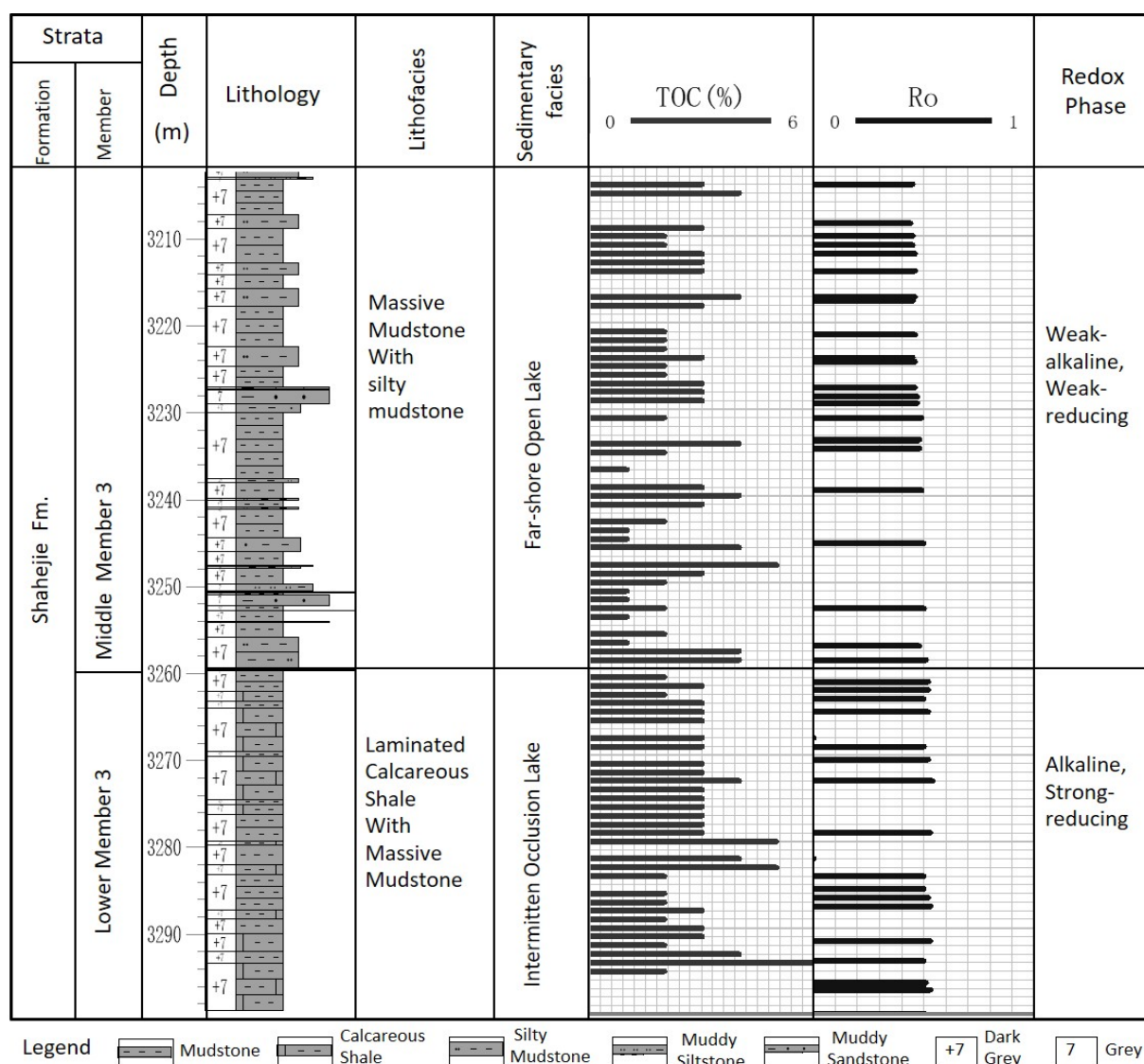


Figure 3. TOC content changes in different lithofacies and sedimentary environments in Well Niu 38, Dongying.

Table 2. TOC contents of shale samples from well Niu 38.

Sample	Depth (m)	TOC (%)	Sample	Depth (m)	TOC (%)	Sample	Depth (m)	TOC (%)
1	3203.0	4.0	29	3239.7	3.2	57	3273.2	4.0
2	3204.1	2.1	30	3240.1	1.9	58	3274.1	3.2
3	3204.6	2.9	31	3241.0	3.1	59	3275.6	3.1
4	3205.1	3.9	32	3243.2	2.0	60	3276.3	3.0
5	3209.0	3.0	33	3244.3	1.2	61	3277.2	2.2
6	3210.2	2.1	34	3245.8	1.3	62	3277.8	3.1
7	3211.1	2.0	35	3246.5	4.2	63	3278.5	2.9
8	3212.3	3.1	36	3248.0	5.0	64	3279.4	2.0
9	3213.2	2.9	37	3249.1	3.3	65	3279.9	3.1
10	3214.6	2.9	38	3250.2	2.1	66	3280.2	2.0
11	3217.1	3.0	39	3251.5	1.1	67	3280.7	4.9
12	3217.5	4.0	40	3252.4	1.3	68	3282.1	1.1
13	3218.9	3.1	41	3253.3	2.0	69	3282.7	4.0
14	3221.2	2.2	42	3254.0	1.3	70	3283.2	2.2
15	3222.3	2.1	43	3256.5	2.2	71	3283.8	5.0
16	3223.5	2.2	44	3257.3	1.1	72	3284.3	1.3
17	3224.4	3.0	45	3258.1	4.0	73	3284.9	2.0
18	3225.6	2.1	46	3259.1	3.9	74	3286.2	2.2
19	3226.6	2.3	47	3261.0	2.2	75	3287.3	2.4
20	3227.2	2.9	48	3262.1	3.1	76	3288.5	3.0
21	3228.3	1.2	49	3263.3	2.2	77	3289.2	2.1
22	3228.7	2.9	50	3264.2	3.0	78	3290.4	2.3
23	3229.2	2.2	51	3265.1	3.1	79	3290.9	3.1
24	3229.8	3.0	52	3266.4	3.2	80	3291.6	2.9
25	3231.2	2.1	53	3268.7	3.3	81	3292.3	2.2
26	3234.3	3.9	54	3269.3	3.0	82	3293.2	3.0
27	3235.6	1.9	55	3271.2	3.2	83	3293.8	4.2
28	3237.8	1.1	56	3272.5	3.3	84	3294.6	6.0

It can be concluded that the lake water stratification is beneficial for the accumulation and preservation of organic matter, and therefore the organic matter abundance of mudstone is high. The reason is that the salt layer of the lake prevents the water circulation between the surface and the bottom of the lake; therefore, a strong anoxic reduction environment is formed at the bottom. In the large-body saltwater lakes at deeper desalination periods, due to the presence of salt transitions, the bottom water is in a strong reduction environment. The change in salinity resulting in biological cyclic death and reproduction can provide abundant raw material of organic matter, resulting in high organic matter content. When the water depth of the lake decreases, the increased hydrodynamic energy and weak reduction conditions can damage the storage of organic matter, which will reduce the abundance of organic matter content.

Table 3. Ro values of shale samples from well Niu 38. M. = Middle, L. = Lower.

Sample	Depth (m)	For	Ro (%)	Sample	Depth (m)	For.	Ro (%)
1	2771.00	Es3	0.67	71	3197.74	Es3	0.44
2	2777.65	Es3	0.42	72	3204.00	M. Es3	0.45
3	2784.70	Es3	0.50	73	3208.50	M. Es3	0.44
4	2798.17	Es3	0.48	74	3209.92	Es3	0.45
5	2804.40	Es3	0.43	75	3211.00	M. Es3	0.45
6	2815.23	Es3	0.60	76	3212.00	M. Es3	0.46
7	2828.70	Es3	0.52	77	3214.00	M. Es3	0.46
8	2836.54	Es3	0.52	78	3217.00	M. Es3	0.46
9	2843.60	Es3	0.64	79	3217.50	M. Es3	0.45
10	2857.27	Es3	0.75	80	3221.38	Es3	0.46
11	2874.88	Es3	0.81	81	3224.00	M. Es3	0.45
12	2898.72	Es3	0.77	82	3224.50	M. Es3	0.46
13	2901.02	Es3	0.56	83	3227.50	M. Es3	0.46
14	2918.50	Es3	0.69	84	3228.50	M. Es3	0.47
15	2926.00	Es3	0.48	85	3229.30	M. Es3	0.47
16	2943.00	Es3	0.70	86	3231.00	M. Es3	0.49
17	2944.81	Es3	0.39	87	3233.50	M. Es3	0.48
18	2951.40	Es3	0.62	88	3233.71	Es3	0.47
19	2952.80	Es3	0.49	89	3234.50	M. Es3	0.48
20	2953.40	Es3	0.51	90	3239.42	Es3	0.49
21	2954.20	Es3	0.58	91	3245.50	M. Es3	0.50
22	2955.60	Es3	0.45	92	3253.04	Es3	0.50
23	2958.65	Es3	0.43	93	3257.40	M. Es3	0.48
24	2960.15	Es3	0.44	94	3259.00	M. Es3	0.51
25	2960.50	Es3	0.48	95	3261.50	M. Es3	0.50
26	2962.15	Es3	0.51	96	3261.54	Es3	0.52
27	2964.15	Es3	0.54	97	3262.50	M. Es3	0.52
28	2966.15	Es3	0.51	98	3263.50	M. Es3	0.50
29	2967.55	Es3	0.47	99	3265.00	M. Es3	0.52
30	2969.05	Es3	0.59	100	3269.00	M. Es3	0.50
31	2969.40	Es3	0.46	101	3270.50	M. Es3	0.52
32	2971.05	Es3	0.62	102	3273.00	M. Es3	0.54
33	2973.85	Es3	0.47	103	3279.00	M. Es3	0.53
34	2974.60	Es3	0.62	104	3284.00	L. Es3	0.50
35	2977.75	Es3	0.42	105	3285.50	L. Es3	0.50
36	2991.77	Es3	0.61	106	3286.50	L. Es3	0.52
37	2994.47	Es3	0.53	107	3287.50	L. Es3	0.53
38	3001.30	Es3	0.35	108	3291.50	L. Es3	0.53
39	3001.43	Es3	0.56	109	3293.80	L. Es3	0.50
40	3004.40	Es3	0.57	110	3296.30	L. Es3	0.51
41	3010.73	Es3	0.52	111	3296.93	Es3	0.50

Table 3. Cont.

Sample	Depth (m)	For	Ro (%)	Sample	Depth (m)	For.	Ro (%)
42	3020.60	Es3	0.44	112	3297.20	L. Es3	0.53
43	3023.50	Es3	0.66	113	3300.00	L. Es3	0.51
44	3026.50	Es3	0.43	114	3302.10	L. Es3	0.54
45	3032.50	Es3	0.49	115	3304.40	L. Es3	0.53
46	3038.81	Es3	0.36	116	3307.80	L. Es3	0.53
47	3039.80	Es3	0.40	117	3309.66	Es3	0.49
48	3040.81	Es3	0.52	118	3311.50	L. Es3	0.51
49	3045.88	Es3	0.54	119	3313.50	L. Es3	0.50
50	3047.88	Es3	0.51	120	3317.00	L. Es3	0.53
51	3049.88	Es3	0.52	121	3319.07	Es3	0.53
52	3051.00	Es3	0.45	122	3320.30	L. Es3	0.54
53	3053.68	Es3	0.46	123	3321.60	L. Es3	0.51
54	3054.68	Es3	0.45	124	3324.20	L. Es3	0.51
55	3055.58	Es3	0.58	125	3328.00	L. Es3	0.51
56	3072.50	Es3	0.57	126	3329.53	Es3	0.53
57	3076.60	Es3	0.56	127	3330.70	L. Es3	0.51
58	3088.40	Es3	0.61	128	3332.20	L. Es3	0.00
59	3090.50	Es3	0.57	129	3337.00	L. Es3	0.50
60	3091.73	Es3	0.64	130	3339.70	L. Es3	0.45
61	3096.02	Es3	0.65	131	3340.90	Es3	0.47
62	3098.80	Es3	0.62	132	3341.30	Es3	0.53
63	3109.22	Es3	0.71	133	3342.10	L. Es3	0.51
64	3111.70	Es3	0.80	134	3353.00	L. Es3	0.53
65	3125.60	Es3	0.60	135	3356.20	L. Es3	0.57
66	3134.50	Es3	0.51	136	3357.60	L. Es3	0.54
67	3141.20	Es3	0.46	137	3364.50	L. Es3	0.75
68	3158.20	Es3	0.59	138	3365.80	L. Es3	0.59
69	3171.00	Es3	0.63	139	3366.93	Es3	0.39
70	3183.72	Es3	0.45	140	3367.50	L. Es3	0.74

3.3. Relationship Between the Change of Element Ratios and High-Frequency Sequence Stratigraphy Division in Shale

Previous studies on the high-frequency sequence division of the lake strata mainly applied to the coarse debris depositional system. Because of its obvious lithologic changes, it is easy to recognize the progradational and retrogradational changes in the sediment deposition process. However, for shale in a deep water deposition system, due to the lack of obvious cyclicity changes in lithology, the division of its sequence (especially high-frequency sequence) is difficult. This study attempts to divide the high-frequency sequence of fine-grained sediments in deep water (shale) by the element ratios and the changes of the sedimentary environment associated with the element ratios.

The different elements and element ratios in sediments reflect different sedimentary environments of mudstone, such as the distance from the shore, the depth of the lake, and the conditions of the water medium. The sedimentary environment of shale is closely related to the change in high-frequency sequence. For example, generally, the deepening of

lake water responds to the base level rising, which is identified as a transgression sequence. The sudden transgression and retrogression of the lake may leave traces in the strata, that is, the change of the elements. Therefore, the element phase can indicate the change of the sequence. According to the changes of the sedimentary environment indicated by the ratio of elements, the sequence division of the shale profile can be carried out.

As mentioned above, during the process of lake basin evolution, depositional facies change from salt lake to blocked lake, open lake, and then delta; as the sediment transport distance decreases, the water salinity of the ancient water body becomes lighter, the PH value decreases, the Eh value increases, the performance is gradually reduced by Sr/Ba and Ca/Mg ratios, and the Rb/Ca and Fe/Mn ratios increase. According to changes of elements, combined with data available in this study, we concluded that ratios Sr/Ba and Ca/Mg near the sequence boundary are low, and ratios of Fe/Mn and Rb/Ca ratios are high. In addition, the Sr/Ba and Ca/Mg ratios near the flooding surface are high, and ratios of Fe/Mn and Rb/Ca ratios are low (Figure 4). This conclusion provided an important theoretical basis for the division of high-frequency sequences in lacustrine shale and also provides new research ideas for the division of high-frequency sequences' stratigraphy in marine shale. The conclusion is of great importance for the evaluation and development of oil and gas resources in shales.

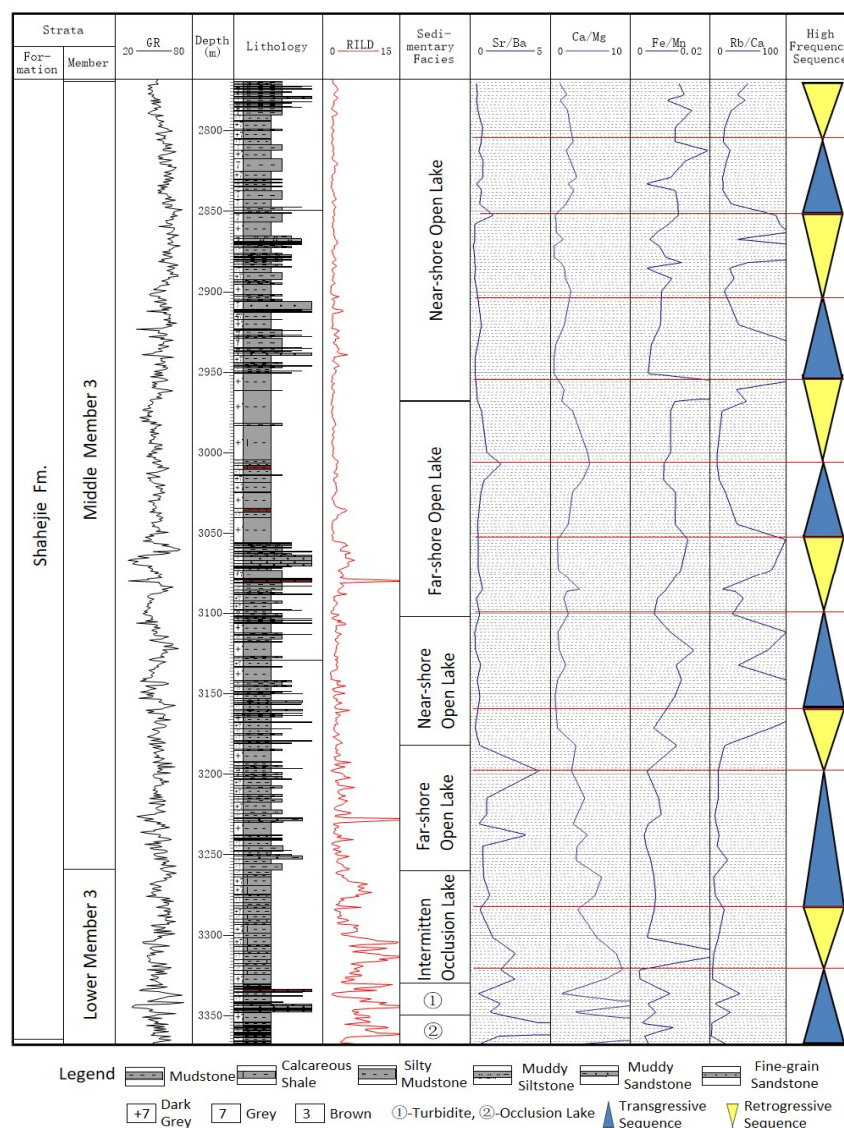


Figure 4. The element ratio of the shale and high-frequency sequence division in Well Niu 38 of Dongying Depression.

4. Conclusions

- (1) During the evolution of the lake basin, the depositional environment changes from salt lake to blocked lake, open lake, and finally delta. As the decrease of sediment transport, the salinity of the ancient water becomes lighter, and the element ratio also changes accordingly. Especially, during the above evolution, the Sr/Ba and Ca/Mg ratios increase, and the Rb/Ca and Fe/Mn ratios are increased.
- (2) The content of organic matter is high in occluded lake facies, intermittent lake facies, and open lake facies mudstone. Organic matter preservation can be damaged when the water depth becomes shallower, the hydrodynamic energy increases, and the reduction conditions become weaker. The stratification of lake water is beneficial for organic matter accumulation and preservation.
- (3) The element geochemical ratios can be used for high-frequency sequence stratigraphic division of lacustrine shale. The Sr/Ba and Ca/Mg ratios near the sequence boundary are low and the Fe/Mn and Rb/Ca ratios are high, while the Sr/Ba and Ca/Mg ratios near the flooding surface are high and the Fe/Mn and Rb/Ca ratios are low. The relationship between those element ratios and high-frequency sequences is initially established in the lake shale profile.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11060657/s1>, Table S1: Element contents and element ratios of shale in different wells, Dongying Depression.

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