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Geochemical characteristics and their significances of rare-earth elements in deep-water well core at the Lingnan Low Uplift Area of the Qiongdongnan Basin

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Abstract

A geochemical analysis of rare-earth elements (REEs) in 97 samples collected from the core of deep-water Well LS-A located at the Lingnan Low Uplift Area of the Qiongdongnan Basin is conducted, with the purpose of revealing the changes of sedimentary source and environment in the study region since Oligocene and evaluating the response of geochemical characteristics of REEs to the tectonic evolution. In the core samples, both ∑REE and ∑LREE (LREE is short for light-group REEs) fluctuate in a relatively wide range, while ∑HREE (HREE is short for heavy-group REEs) maintains a relatively stable level. With the stratigraphic chronology becoming newer, both ∑REE and ∑LREE show a gradually rising trend overall. The ∑REE of the core is relatively high from the bottom of Yacheng Formation (at a well depth of 4 207 m) to the top of Ledong Formation, and the REEs show partitioning characteristics of the enrichment of LREE, the stable content of HREE, and the negative anomaly of Eu to varying degrees. Overall the geochemical characteristics of REEs are relatively approximate to those of China's neritic sediments and loess, with significant "continental orientation". The ∑REE of the core is relatively low in the lower part of Yacheng Formation (at a well depth of 4 207–4 330 m), as shown by the REEs partitioning characteristics of the depletion of LREE, the relative enrichment of HREE, and the positive anomaly of Eu; the geochemical characteristics of REEs are approximate to those of oceanic crust and basalt overall, indicating that the provenance is primarily composed of volcanic eruption matters. As shown by the analyses based on sequence stratigraphy and mineralogy, the provenance in study region in the early Oligocene mainly resulted from the volcanic materials of the peripheral uplift areas; the continental margin materials from the north contributed only insignificantly; the provenance developed to a certain extent in the late Oligocene. Since the Miocene, the provenance has ceaselessly expanded from proximal to distal realm, embodying a characteristic of multi-source sedimentation. In the core strata with 31.5, 28.4, 25.5, 23, and 16 Ma from today, the geochemical parameters of REEs and Th/Sc ratio have significant saltation, embodying the tectonic movement events in the evolution of the Qiongdongnan Basin. In the tectonic evolution history of the South China Sea, the South China Sea Movement (34–25 Ma BP, early expansion of the South China Sea), Baiyun Movement (23 Ma BP), late expansion movement (23.5–16.5 Ma BP), expansion-settlement transition, and other important events are all clearly recorded by the geochemical characteristics of REEs in the core.

Key words: Qiongdongnan Basin, deep-water well core, rare-earth elements, sedimentary source and environment, response to tectonic movement

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1 Introduction

As a typical marginal sea of the West Pacific Ocean, the South China Sea, an essential part of the West Pacific trench-arc-basin system, is characterized by extremely dynamic tectonic activities and complex formation and evolution processes. The South China Sea holds an important position in paleoceanography and in the evolutionary studies of sedimentary basins. Most types of tectonic movement, magmatism, sedimentation, and mineralization show development and evolution to varying degrees in the South China Sea (Liu et al., 2002). In the northern South China Sea, the sedimentary environment has been changeable since the Oligocene, accompanied by regional tectonic activities and sea-level fluctuations, and went through evolution processes including terrigenous facies, transitional facies, littoral-neritic facies, and bathyal-abyssal facies, leading to the development of several hydrocarbon source rocks (Zhang et al., 2009; Huang, Li, Wang et al., 2012; Wang et al., 2014). The favorable petroleum conditions and vast resource potential have made the Qiongdongnan Basin a hot spot in the exploration and development of oil and gas resources in China (Zhu et

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al., 2008; Wang et al., 2011; Huang, Li, Huang et al., 2012).

The REEs in sediments and their characteristic parameters are closely related to both the sedimentary source and environment, which have been extensively applied to the source tracing and source-sink analyses of marine sediments (Zhu et al., 2007; Xu et al., 2011; Eker et al., 2012; Lim et al., 2014). Various REEs have similar chemical properties with low solubility and high stability; therefore, a significant fractionation is rarely observed among these elements in weathering, transportation, sedimentation, and diagenesis of cuttings, possessing a very strong inheritance from parent rocks. The composition of sediments are influenced by the complex physical and chemical effects during sedimentation, however, studies show that the geochemical characteristics of clastic rocks are mainly dependent on the type of the parent rocks in the provenance (Rollinson, 1993). Both Taylor and McLennan (1985) believe that, REEs and Th, Sc, Co, and Y have favorable chemical differentiation indexes and stable geochemical properties in processes of weathering, denudation, transportation, and sedimentation, as mainly determined by the properties of source rocks; thus, they act as important tracers to determine the evolution of sedimentary source.

Until now, the studies on the sedimentary source and environment in the deep-water area of the Qiongdongnan Basin mainly interpreted the geophysical data and concluded the evolution of the sedimentary source and environment based on the biostratigraphic division, comparison and tracing of seismic stratigraphy, composition of granularity and mineral from the well cores, however, there is still a lack of detailed geochemical studies. The core samples of Well LS-A located at the Lingnan Low Uplift Area of the Qiongdongnan Basin were selected as the study object to conduct a geochemical characterization of REEs, with the purpose of revealing the changes of sedimentary sources in the study region since Oligocene and evaluating the response of the geochemical characteristics of REEs to the tectonic evolution.

2 Regional geology and well core characteristics

The Qiongdongnan Basin is located in the northwest continental margin of the South China Sea and spans between the Hainan Uplift Area and the Yongle Uplift Area in the northeast (NE) direction, adjoining the Yinggehai Basin in the west and connecting to the Zhujiang River (Pearl River) Mouth Basin via the Shenhu Uplift Area with a total area of over 5.3 × 10^4 km^2 (Fig. 1). Since the Cenozoic, the Qiongdongnan Basin has gone through two evolutionary phases, i.e., (1) the faulted period controlled by the tensional fracture in the Paleogene and (2) the depression period controlled by the thermal settlement from the Neogene to Quaternary (Zhao et al., 2010; Lei et al., 2011; Hu et al., 2013). The basement of the Qiongdongnan Basin is composed of pre-Tertiary igneous, metamorphic, and sedimentary rocks, with sedimentary filling sequences mainly dominated by the Cenozoic stratum and successively including (from the bottom to the top) the Eocene , Oligocene Yacheng and Lingshui Formations, Miocene Sanya, Meishan and Huangliu Formations, Pliocene Yinggehai and Quaternary Ledong Formations. Well LS-A ended when it got close to the basement at a well depth of 4 350 m, indicating that the sedimentary stratum before the Eocene is missing in the Lingnan Low Uplift Area.

In recent years, the offshore oil exploration unit represented by the China National Offshore Oil Corporation (CNOOC) has conducted a series of regional geophysical explorations and studies in the deep-water area in the northern South China Sea (He et al., 2010; Wang, 2012; Zhu et al., 2012; Zhang et al., 2014). In 2011, Well LS-A was drilled in the central Lingnan Low Uplift Area of the Qiongdongnan Basin (Fig. 1), at a water depth of 1 463 m, a drilled depth of 4 350 m, and spanning from the Yacheng Formation to Ledong Formation.

The core lithology of Well LS-A is shown in Fig. 2 and described below:

The Yacheng Formation is divided into three segments: (1) the bottom Yacheng Formation Segment III, in which the lower part is composed of dark grayish-green to gray mudstone

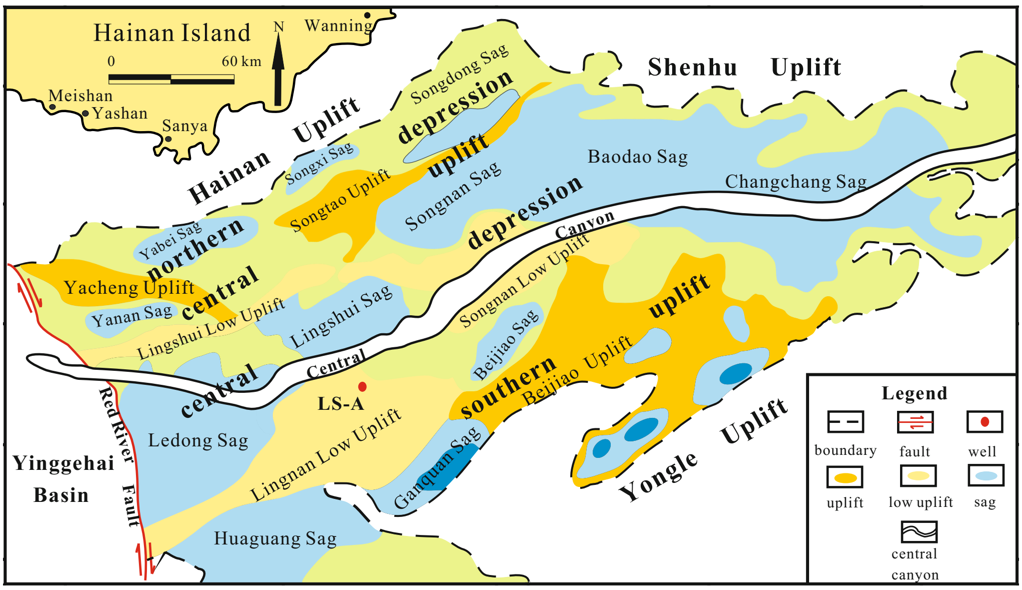

Fig.1. The regional tectonic map of the Qingdongnan Basin.

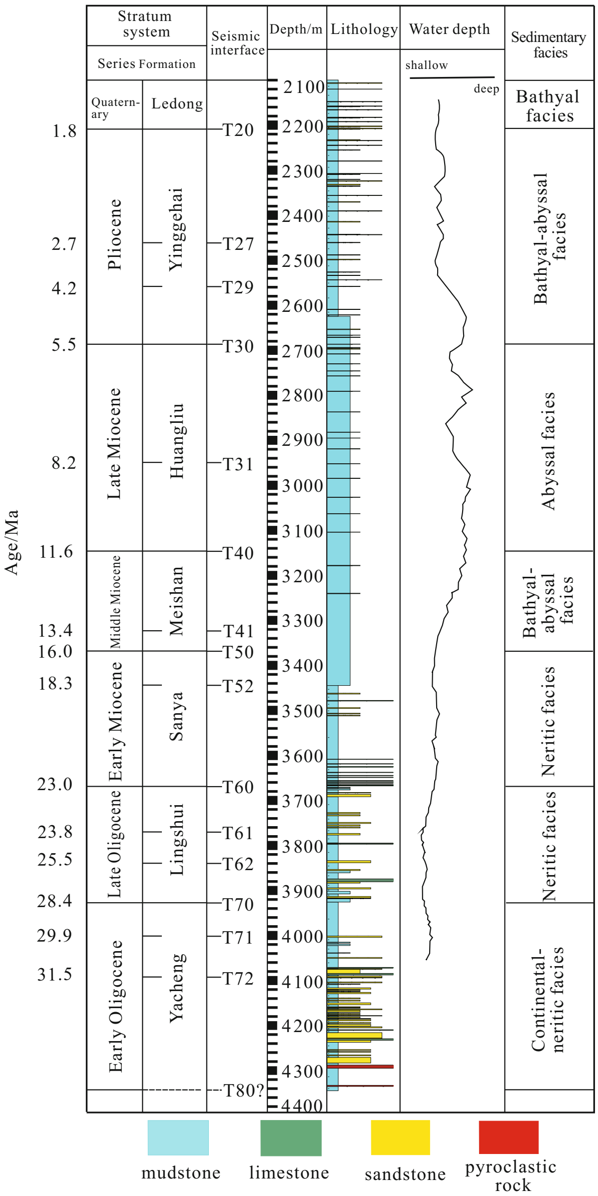

Fig.2. Core profile of Well LS-A (modified from the foundation drawing provided by Zhanjiang Branch of CNOOC)

blended with pyroclastic rock, while the middle and upper parts are mainly interbedded with an unequal thickness of brownish-gray mudstone and light-gray siltstone; (2) the middle Yacheng Formation Segment II, which is mainly composed of brownish-gray mudstone blended with light gray siltstone, fine sandstone (unequal thickness), and limestone (low content); and (3) the top Yacheng Formation Segment I, which is composed of brownish-gray and dark green-gray calcareous mudstone.

The Lingshui Formation is also divided into three segments from the bottom to the top: (1) The Lingshui Formation Segment III is mainly composed of dark gray mudstone blended with thin-bedded sandstone, with local light-gray limestone; (2) the Lingshui Formation Segment II is mainly composed of dark gray mudstone, with light thin-bedded siltstone in the upper part; and (3) the Lingshui Formation Segment I is mainly composed of the interbed with unequal thickness of dark gray mudstone, light thin-bedded sandstone, and fine sandstone.

The Sanya Formation is divided into two segments. The middle and lower strata are mainly composed of massive mudstone blended with gray thin-bedded argillaceous siltstone, with argillaceous limestone at the bottom, while the upper stratum is mainly composed of dark green-gray calcareous mudstone. The Meishan Formation is divided into two segments and mainly composed of dark gray mudstone, with thin-bedded gray siltstone blended in the upper part. The Huangliu Formation is divided into two segments and mainly composed of a large set of dark gray lime mudstone blended with thin-bedded dark gray siltstone.

The Yinggehai Formation is mainly composed of a large set of dark gray massive mudstone blended with thin-bedded gray siltstone and argillaceous sandstone, and also with thin-bedded massive fine sandstone in the middle. The Quaternary Ledong Formation is mainly composed of light gray and green-gray mudstone, blended with nondiagenetic thin-bedded silt and fine sand.

3 Materials and methods

Considering the actual coring of Well LS-A and stratigraphic variations, a total of 97 core samples were collected from the Yacheng Formation to the Ledong Formation (from the bottom to the top) to conduct the geochemical analysis of REEs, including 38 samples collected from the Yacheng Formation, 18 samples collected from the Lingshui Formation, 20 samples collected from the Sanya Formation, four samples collected from the Meishan Formation, nine samples collected from the Huangliu Formation, six samples collected from the Yinggehai Formation, and two samples collected from the Ledong Formation. The lithology of core samples is mainly composed of mudstone and siltstone with several argillaceous limestone samples and one pyroclastic rock sample (Table 1). The processing and analysis of these core samples were conducted in the Key Laboratory of Submarine Geosciences and Technology of Ministry of Education, Ocean University of China. After washing oil (specifically reported in another paper), the samples were ground to a size below 200 meshes using an agate mortar, wrapped in a parchment paper, and then placed in a constant temperature oven for drying at 110°C. Forty milligrams of the sample was accurately weighed and placed in a Teflon digestion tank, in which 2 mL of a mixture of HF and HNO_3 mixed at a volume ratio of 3:1 was added. The digestion tank was sealed, and the samples were dissolved using a hot plate at 150°C for 12 h. Then, the digestion tank was opened, and 0.25 mL $HClO_4$ was added. The digestion tank was placed on the hot plate to evaporate acid until nearly dry; then, 2 mL HNO_3 solution (50%) was added. The digestion tank was sealed for redissolution at 120°C for 12 h. Finally, HNO_3 solution (2%) was added to reach a weight of 40 g, and the samples were analyzed by the ICP-MS (Agilent 7500C). During the analytical process, every ten samples were added with a parallel sample, and every batch was added with a blank sample and four standard samples (GBW07315, GBW07316, BCR-2, and BHVO-2). The results of the tests were corrected with reference to the standard samples, and the precision was controlled with reference to the blank and parallel samples, with the relative de-

Table 1. REE content (μg/g) analysis results of Well LS-A

Stratum system	Well segment/m	Lithology	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ledong Formation	2180–2185	mudstone	37.50	75.10	8.67	32.20	6.18	1.39	6.82	0.79	4.08	0.84	2.33	0.36	2.23	0.34
	2205–2210	mudstone	38.80	75.60	8.77	32.70	6.33	1.41	7.64	0.86	4.45	0.93	2.53	0.40	2.40	0.37
Yinggehai Formation	2260–2265	mudstone	38.90	76.00	8.76	32.60	6.27	1.76	7.47	0.82	4.43	0.93	2.57	0.39	2.52	0.37
	2310–2315	siltstone	35.80	68.80	7.91	29.70	5.91	1.64	8.10	0.77	4.23	0.91	2.51	0.39	2.35	0.36
	2390–2395	mudstone	38.50	74.30	8.74	32.40	6.26	1.58	7.56	0.84	4.45	0.93	2.54	0.39	2.44	0.36
	2445–2450	siltstone	37.90	72.50	8.46	31.70	6.10	1.63	8.23	0.79	4.27	0.90	2.48	0.39	2.33	0.37
	2520–2525	mudstone	34.30	65.60	7.60	28.60	5.69	1.88	7.98	0.72	3.90	0.84	2.31	0.36	2.19	0.33
	2630–2635	mudstone	34.00	65.50	7.47	28.00	5.31	1.38	7.03	0.70	3.89	0.83	2.33	0.37	2.20	0.33
Huangliu Formation	2695–2700	mudstone	36.80	72.60	8.26	30.30	5.98	1.88	8.28	0.79	4.20	0.90	2.42	0.39	2.35	0.37
	2725–2730	mudstone	38.40	74.80	8.40	31.00	6.00	1.48	7.04	0.80	4.27	0.91	2.51	0.39	2.43	0.37
	2770–2775	mudstone	38.20	75.50	8.59	32.30	6.03	1.26	7.05	0.81	4.31	0.90	2.49	0.39	2.43	0.37
	2865–2870	mudstone	38.40	75.70	8.52	31.60	6.09	1.42	6.66	0.79	4.29	0.90	2.45	0.39	2.40	0.36
	2900–2905	mudstone	37.50	72.70	8.13	30.30	5.93	1.41	6.95	0.79	4.07	0.87	2.40	0.38	2.35	0.36
	2960–2965	mudstone	37.20	74.30	8.33	30.90	5.88	1.24	6.66	0.81	4.24	0.88	2.43	0.39	2.34	0.35
	3010–3015	mudstone	36.30	71.70	7.96	29.30	5.59	1.43	7.12	0.74	3.97	0.84	2.30	0.36	2.25	0.34
	3080–3085	mudstone	37.90	73.30	8.30	31.10	6.03	1.67	6.71	0.77	4.27	0.91	2.44	0.38	2.33	0.35
	3115–3120	mudstone	38.30	73.70	8.45	31.40	5.98	1.58	6.96	0.76	4.21	0.89	2.41	0.37	2.33	0.36
Meishan Formation	3155–3160	mudstone	34.10	63.70	7.15	26.70	5.41	2.00	9.09	0.69	3.63	0.78	2.17	0.34	2.04	0.31
	3250–3255	mudstone	33.20	63.50	7.23	26.90	5.27	1.59	9.18	0.72	3.70	0.79	2.17	0.34	2.08	0.31
	3300–3305	mudstone	34.90	65.90	7.53	28.10	5.59	1.95	8.08	0.72	3.82	0.81	2.23	0.35	2.15	0.33
	3335–3340	mudstone	35.90	68.10	7.78	29.20	5.78	1.41	8.25	0.79	4.16	0.89	2.41	0.38	2.34	0.35
Sanya Formation	3405–3410	mudstone	29.70	56.00	6.47	24.80	4.94	1.86	6.79	0.69	3.69	0.79	2.12	0.33	2.07	0.31
	3448–3451	mudstone	32.90	62.00	6.93	26.50	5.31	1.30	7.65	0.73	3.80	0.82	2.15	0.35	2.10	0.32
	3466–3469	siltstone	36.50	69.60	7.98	29.80	5.96	1.39	7.44	0.81	4.19	0.90	2.40	0.38	2.31	0.35
	3487–3490	mudstone	35.40	67.80	7.71	28.70	5.79	2.54	9.54	0.78	3.94	0.84	2.23	0.36	2.18	0.33
	3496–3499	mudstone	34.30	65.00	7.28	27.40	5.68	1.74	9.05	0.73	3.80	0.82	2.22	0.34	2.11	0.32
	3511–3514	siltstone	35.50	67.20	7.56	28.40	5.71	1.71	9.58	0.75	3.99	0.84	2.30	0.36	2.20	0.33
	3520–3523	mudstone	37.80	73.40	8.22	30.80	6.09	1.72	8.16	0.82	4.25	0.91	2.37	0.38	2.28	0.34
	3526–3529	mudstone	39.10	75.20	8.36	31.60	6.29	2.39	10.10	0.84	4.34	0.91	2.45	0.39	2.34	0.36
	3538–3541	mudstone	37.50	73.50	8.25	30.40	6.04	1.43	8.23	0.79	4.13	0.88	2.41	0.38	2.32	0.34
	3556–3559	mudstone	37.50	73.90	8.29	30.00	5.94	1.41	8.51	0.77	4.04	0.87	2.37	0.37	2.25	0.34
	3565–3568	mudstone	36.10	70.30	7.82	28.50	5.51	1.76	7.73	0.70	3.80	0.83	2.30	0.36	2.18	0.33
	3571–3574	mudstone	37.50	73.60	8.18	30.30	5.94	1.27	7.57	0.74	4.01	0.87	2.37	0.37	2.25	0.34
	3580–3583	mudstone	38.90	75.90	8.48	30.70	6.00	1.47	7.57	0.77	4.10	0.87	2.38	0.38	2.29	0.34
	3595–3598	mudstone	37.00	71.50	8.12	29.90	5.83	1.40	8.40	0.74	3.93	0.84	2.32	0.37	2.25	0.33
	3607–3610	mudstone	37.80	73.30	8.33	29.90	5.92	1.54	7.91	0.79	4.18	0.89	2.47	0.38	2.40	0.36
	3616–3619	mudstone	36.70	70.80	8.12	29.70	5.84	1.09	8.00	0.75	3.95	0.84	2.32	0.37	2.27	0.34
	3625–3628	mudstone	36.90	71.10	7.98	29.30	5.75	1.33	6.86	0.77	4.03	0.85	2.34	0.37	2.26	0.34
	3652–3655	argillaceous limestone	28.10	54.50	6.16	22.60	4.57	1.51	6.88	0.60	3.22	0.70	1.90	0.29	1.81	0.27
	3661–3664	argillaceous limestone	24.10	45.60	5.25	19.40	4.17	1.95	7.40	0.51	2.77	0.61	1.67	0.27	1.57	0.25
	3670–3673	argillaceous limestone	26.30	50.90	5.79	22.00	4.45	0.94	5.77	0.59	3.02	0.65	1.72	0.27	1.70	0.26
Lingshui Formation	3691–3694	mudstone	27.30	50.80	5.91	22.40	4.52	1.00	6.87	0.62	3.20	0.68	1.84	0.28	1.76	0.26
	3706–3709	mudstone	29.40	57.20	6.49	24.40	4.85	1.06	6.41	0.62	3.31	0.71	1.93	0.30	1.84	0.28
	3715–3718	mudstone	30.00	58.40	6.51	24.50	5.02	1.52	7.75	0.63	3.37	0.73	1.94	0.30	1.83	0.28
	3727–3730	mudstone	30.20	60.00	6.54	24.30	5.03	1.64	6.95	0.65	3.44	0.71	1.96	0.31	1.86	0.28
	3736–3739	siltstone	30.60	59.30	6.55	24.30	4.96	1.69	7.92	0.64	3.37	0.73	1.98	0.31	1.93	0.29
	3748–3751	mudstone	32.90	65.10	7.27	27.00	5.44	1.72	7.14	0.69	3.69	0.79	2.14	0.33	2.08	0.31

to be continued

Continued from Table 1

Stratum system	Well segment/m	Lithology	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	3 763–3 766	siltstone	30.80	61.10	6.75	25.30	5.23	1.37	7.98	0.69	3.60	0.75	2.02	0.31	1.97	0.30
	3 787–3 790	mudstone	34.30	70.10	7.50	27.90	5.58	1.51	8.14	0.71	3.82	0.80	2.21	0.35	2.17	0.32
	3 802–3 805	mudstone	31.00	64.20	6.82	24.90	5.00	1.62	7.75	0.65	3.47	0.74	2.03	0.32	1.98	0.30
	3 814–3 817	mudstone	35.30	72.00	7.79	28.80	5.91	1.55	9.19	0.75	4.00	0.84	2.26	0.36	2.15	0.33
	3 835–3 838	mudstone	27.00	53.40	5.79	21.50	4.40	1.41	6.87	0.57	3.03	0.64	1.77	0.28	1.75	0.27
	3 844–3 847	mudstone	28.20	55.70	6.12	23.10	4.77	1.19	7.58	0.66	3.31	0.71	1.90	0.30	1.88	0.30
	3 856–3 859	mudstone	30.70	59.70	6.64	24.50	5.06	1.49	8.58	0.62	3.40	0.73	1.99	0.32	2.04	0.31
	3 868–3 871	mudstone	32.60	64.30	7.15	26.40	5.24	0.89	7.37	0.69	3.71	0.79	2.16	0.35	2.11	0.32
	3 886–3 889	mudstone	32.00	62.20	6.95	25.70	5.11	1.39	8.11	0.67	3.55	0.75	2.04	0.32	2.00	0.32
	3 904–3 907	mudstone	30.50	60.70	6.78	25.40	5.14	1.54	8.13	0.69	3.72	0.78	2.08	0.34	2.12	0.32
	3 922–3 925	mudstone	27.20	52.50	5.88	22.00	4.46	0.80	7.87	0.58	3.07	0.66	1.73	0.27	1.74	0.27
	3 928–3 931	mudstone	28.80	56.00	6.29	23.70	4.69	1.52	7.43	0.63	3.23	0.69	1.85	0.29	1.85	0.29
Yacheng Formation	3 940–3 943	mudstone	28.30	55.80	6.27	23.50	4.79	1.48	7.34	0.64	3.34	0.70	1.87	0.30	1.85	0.28
	3 952–3 955	mudstone	29.80	58.40	6.56	23.90	5.02	1.73	7.98	0.62	3.34	0.71	1.90	0.30	1.87	0.29
	3 967–3 970	mudstone	30.40	60.40	6.55	23.80	4.79	0.76	7.28	0.64	3.26	0.69	1.86	0.29	1.84	0.28
	3 976–3 979	mudstone	30.90	61.20	6.62	24.40	5.00	1.58	9.15	0.62	3.23	0.69	1.86	0.30	1.82	0.28
	3 988–3 991	mudstone	34.10	67.60	7.36	26.60	5.21	1.26	7.27	0.67	3.50	0.73	2.01	0.32	1.95	0.29
	4 000–4 003	mudstone	35.40	71.90	7.75	28.50	5.85	1.29	9.78	0.73	3.80	0.79	2.16	0.34	2.03	0.32
	4 012–4 015	mudstone	34.40	70.10	7.66	28.60	5.87	2.19	10.30	0.75	4.00	0.84	2.26	0.37	2.27	0.35
	4 021–4 024	mudstone	36.50	72.70	8.05	30.50	6.14	1.55	9.11	0.79	4.33	0.92	2.51	0.40	2.45	0.39
	4 030–4 033	mudstone	36.80	73.50	8.17	30.50	6.02	1.48	7.56	0.78	4.16	0.87	2.35	0.37	2.27	0.36
	4 045–4 048	mudstone	32.90	65.90	7.32	27.10	5.53	1.70	9.63	0.73	3.79	0.78	2.09	0.34	2.12	0.33
	4 054–4 057	mudstone	33.90	67.20	7.51	28.20	5.73	1.55	9.34	0.71	3.85	0.81	2.15	0.34	2.14	0.33
	4 069–4 072	mudstone	41.30	79.20	8.85	32.90	6.41	1.43	7.37	0.84	4.38	0.92	2.49	0.39	2.48	0.38
	4 075–4 078	mudstone	36.10	70.80	8.09	30.50	6.40	1.78	8.99	0.83	4.41	0.93	2.51	0.39	2.40	0.37
	4 090–4 093	limestone	19.80	38.80	4.48	17.30	4.15	2.13	9.35	0.62	3.56	0.79	2.15	0.35	2.11	0.34
	4 099–4 102	mudstone	38.20	73.70	7.97	29.30	5.60	1.21	7.48	0.69	3.71	0.79	2.18	0.36	2.24	0.35
	4 108–4 111	mudstone	41.70	81.30	8.98	33.30	6.54	2.88	7.78	0.81	4.17	0.88	2.37	0.37	2.26	0.35
	4 117–4 120	mudstone	42.70	82.70	9.65	36.00	7.01	2.22	6.84	0.74	3.89	0.78	2.16	0.33	2.00	0.32
	4 126–4 129	mudstone	44.70	83.80	9.86	36.80	7.09	1.81	8.68	0.76	3.69	0.73	1.95	0.28	1.74	0.26
	4 138–4 141	mudstone	36.70	68.40	8.08	30.60	5.77	1.97	6.81	0.57	2.70	0.53	1.40	0.20	1.19	0.18
	4 147–4 150	mudstone	43.00	81.20	9.62	36.10	6.90	2.09	8.20	0.73	3.58	0.72	1.85	0.27	1.61	0.24
	4 159–4 162	mudstone	37.00	68.30	7.99	29.70	5.68	1.63	5.76	0.62	2.97	0.58	1.59	0.23	1.39	0.21
	4 165–4 168	siltstone	35.00	63.90	7.38	27.40	5.54	2.11	7.99	0.61	2.96	0.58	1.47	0.21	1.28	0.19
	4 177–4 180	mudstone	41.30	79.80	9.09	34.00	6.58	1.72	6.19	0.88	5.11	1.07	2.78	0.42	2.44	0.36
	4 186–4 189	siltstone	38.20	70.90	8.16	30.40	5.67	1.99	5.62	0.56	2.55	0.49	1.29	0.19	1.11	0.17
	4 198–4 201	siltstone	35.40	65.40	7.53	28.00	5.34	1.65	5.61	0.57	2.72	0.55	1.45	0.21	1.26	0.19
	4 207–4 210	siltstone	14.85	30.00	3.75	15.67	3.88	1.55	4.90	0.77	4.60	1.07	2.88	0.46	2.85	0.45
	4 216–4 219	mudstone	7.01	14.87	1.96	9.08	2.76	1.78	5.69	0.57	3.45	0.81	2.24	0.37	2.35	0.38
	4 228–4 231	siltstone	7.48	15.56	2.03	9.03	2.68	1.72	8.09	0.54	3.37	0.79	2.18	0.37	2.26	0.36
	4 240–4 243	mudstone	6.51	14.10	1.92	8.81	2.78	2.39	8.28	0.62	3.77	0.88	2.40	0.40	2.44	0.40
	4 249–4 252	mudstone	7.26	16.03	2.07	9.47	2.84	1.55	7.61	0.66	4.07	0.96	2.64	0.43	2.63	0.42
	4 261–4 264	mudstone	6.96	14.26	1.86	8.67	2.91	1.50	7.58	0.59	3.57	0.83	2.31	0.37	2.26	0.36
	4 273–4 276	mudstone	5.98	12.76	1.72	7.92	2.54	1.09	6.56	0.59	3.72	0.88	2.45	0.41	2.51	0.40
	4 282–4 285	mudstone	5.90	12.83	1.74	8.21	2.65	1.43	6.47	0.60	3.73	0.88	2.46	0.40	2.50	0.38
	4 297–4 300	pyroclastic rocks	6.76	13.34	1.75	8.19	2.87	2.62	10.72	0.59	3.57	0.84	2.32	0.38	2.32	0.37
	4 303–4 306	mudstone	7.23	15.11	1.95	8.80	2.69	2.27	7.20	0.50	3.13	0.76	2.20	0.39	2.38	0.39
	4 312–4 315	mudstone	5.86	11.83	1.54	7.14	2.40	1.05	6.22	0.50	3.16	0.77	2.22	0.37	2.30	0.37
	4 318–4 321	mudstone	6.66	13.45	1.76	8.01	2.61	2.09	8.87	0.54	3.51	0.87	2.49	0.42	2.64	0.42
	4 327–4 330	mudstone	5.78	11.46	1.45	6.60	2.17	1.42	4.40	0.40	2.55	0.65	1.81	0.31	1.95	0.32

viations of test elements all below 5%. During the test, 20 ng/L Rh was added as the internal standard solution to ensure the stability of the ICP-MS.

4 Geochemical characteristics of REEs

The mean value of the element content in different lithologies of a stratigraphic unit can represent the abundance of elements in this stratigraphic unit (Zhao et al., 1990). Considering the relatively long length of the core and large number of samples analyzed, this study selected the mean value of samples from the same stratigraphic unit to represent the abundance of elements in this stratigraphic unit.

4.1 *Distribution of REEs in strata*

The analysis results of the 97 core samples are shown in Table 1. As shown in Table 1 and Fig. 3, the ∑REE (total REE content) of the core changes in a relatively large range of 41.27–202.15 μg/g, with a mean value of 148.53 μg/g; its ∑LREE (total LREE content) changes in the range of 28.88–184.06 μg/g, with a mean value of 130.61 μg/g; and its ∑HREE (total HREE content) changes in the range of 11.97–21.73 μg/g, with a mean value of 17.93 μg/g. With stratigraphic chronology becoming newer, both ∑REE and ∑LREE show a gradually rising trend overall, while ∑HREE shows no significant change. Considering the gradually rising trend of ∑REE and ∑LREE overall, the change can be divided into five phases: (1) From the Yacheng Formation to the Sanya Formation through the Lingshui Formation, ∑REE and ∑LREE rapidly increase, indicating the intense changes in the sedimentary environment and the gradual increase in the water depth; (2) from the Sanya Formation to the Meishan Formation, ∑REE and ∑LREE remain basically unchanged, indicating the relative stability of the sedimentary environment; (3) from the Meishan Formation to the Huangliu Formation, ∑REE and ∑LREE increase rapidly again with intense changes and further increase in the water depth; and (4) and (5) in the rest two phases, from the Huangliu Formation to the Yinggehai Formation and then to the Ledong Formation, ∑REE and ∑LREE first decrease and then increase; however, the changes are not intense, indicating that the sedimentary environment fluctuates, but does not change dramatically.

In the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m), the mean values of ∑REE and ∑LREE are only 55.27 and 37.63 μg/g, respectively, and both show the minimum values in the entire core. At a well depth of above 4 207 m, both ∑REE and ∑LREE abruptly increase, indicating the intense changes in the sedimentary source and environment (Fig. 3a). The mean values of ∑REE and ∑LREE of Yacheng Formation at a well depth of 4 207 m abruptly increase to 167.10 and 149.55 μg/g, respectively, but ∑HREE shows no significant change, remaining at a mean level of 17.55 μg/g. However, at a well depth of 4 100 m, both ∑REE and ∑LREE go through a large-scale saltation and form a wave trough, with the maximum saltation degree from the Yacheng Formation (at a well depth of above 4 207 m) to the Ledong Formation. This represents a large-scale tectonic event, which has also been recorded in other well cores in the northern South China Sea (Wang et al., 2003; Pang, Chen, Peng, 2007; Shao et al., 2009). On the interface between the Yacheng and Lingshui Formations (at a well depth of 3 931 m), both ∑REE and ∑LREE decrease again, but at a relatively small degree. The mean values of ∑REE and ∑LREE of the Lingshui Formation are 145.55 and 128.48 μg/g, respectively, while the mean value of ∑HREE is 17.06 μg/g. Thus, overall, there are two "high–low" wave-mode fluctuations, embodying the instability of the sedimentary environment. In particular, in the late Oligocene, the ∑REE, ∑LREE, and ∑HREE all decrease sharply at a well depth of 3 672 m (23 Ma BP), with a saltation degree less than that of the Yacheng Formation at a well depth of 4 207 m, indicating another significant tectonic activity, which has been referred to as the "Baiyun Movement" by some scholars (Pang, Chen, Shao et al., 2007; Shao et al., 2007; Liu et al., 2011). After the abrupt decrease in the late Oligocene, both ∑REE and ∑LREE of the Sanya Formation increase again, with the mean values of 163.06 and 144.61 μg/g, respectively, while that of ∑HREE is 18.45 μg/g. The change in the REE content reflects the increase in the sedimentary water-depth. However, wave troughs are observed on the interface between Sanya and Meishan Formations, indicating the persistent occurrence of tectonic activities in the northern South China Sea.

The sea-floor spreading of the South China Sea terminated after the middle Miocene, meaning that the basin gradually stabilized. The REE content of the Meishan Formation is relatively approximate to that of the Sanya Formation and has a relatively small degree of fluctuation, with the mean values of ∑REE, ∑LREE and ∑HREE being 161.32, 142.22, and 19.10 μg/g, respectively. The REE contents of the Huangliu, Yinggehai, and Ledong Formations are obviously higher than those of the underlying formations, and only a relatively small degree of fluctuation is observed in the individual segments, indicating relatively weak tectonic activities and fluctuation events of sedimentary environment. The mean values of ∑REE, ∑LREE and ∑HREE of the Huangliu Formation are 176.60, 158.15, and 18.45 μg/g, respectively; those of the Yinghaige Formation are 172.36, 153.24, and 19.12 μg/g, respectively; and those of the Ledong Formation are 181.00, 162.33, and 18.68 μg/g, respectively. In terms of the mean values of their ∑REE, ∑LREE and ∑HREE, the insignificant differences among the three formations indicate that the sedimentary source and environment in the study region have been relatively stable since the sedimentary period of the Huangliu Formation (ca. 11.6 Ma BP).

4.2 *Chondrite-normalized REE partitioning patterns*

Studies have shown that the REEs derived from the upper crust show the partitioning characteristics of the enrichment of LREE, the stable content of HREE, and the negative anomaly of Eu to varying degrees; the positive anomaly of Eu in the lower crust is because its enrichment caused by an elemental differentiation (McLennan et al., 1993). The chondrite-normalized (Haskin et al.,1966) REE partitioning patterns in the core samples of Well LS-A are shown in Fig. 4; the REE partitioning patterns are basically the same from the bottom of Yacheng Formation (at a well depth of above 4 207 m) to the top of Ledong Formation and exhibit the right-leaning characteristics of the relatively enrichment of LREE, the uniform content of HREE, the clear fractionations of LREE and HREE, and the negative anomaly of Eu to varying degrees, indicating that the sediments mainly result from the weathering products of the upper crust. The REE partitioning pattern in the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m) is clearly different from that of the overlying formations and shows a relatively gradual right-leaning pattern characterized by the nonobvious enrichment of LREE (except in one sample), the relative enrichment of HREE, the insignificant fractionations of LREE and

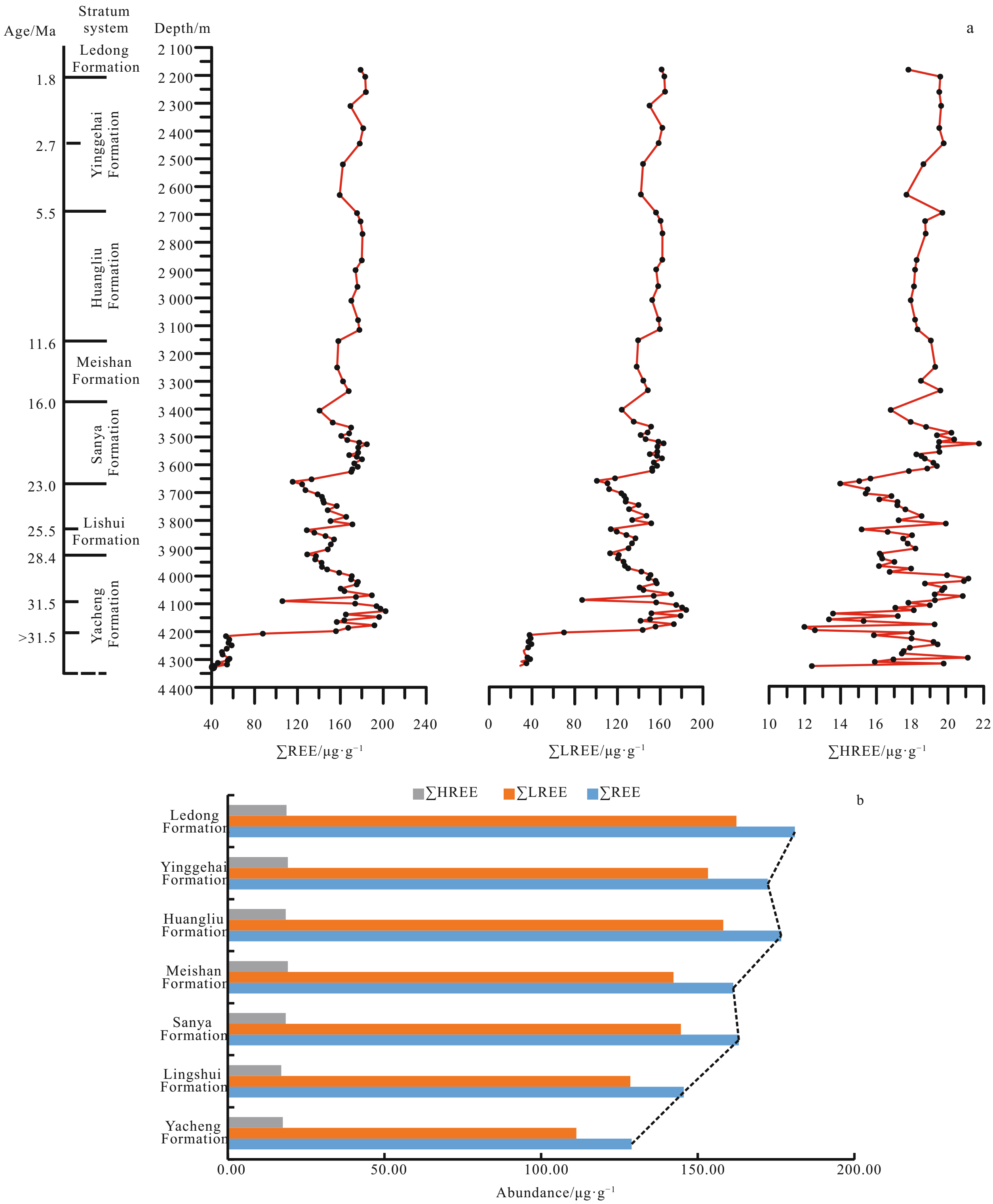

Fig.3. REE abundance in the core of Well LS-A.

HREE, and the positive anomaly of Eu, indicating the important role of basic materials in the provenance. Notably, compared with the strata from Lingshui Formation to Ledong Formation, the Yacheng Formation (3 931–4 207 m) shows differences in the anomaly degree of Eu, and some well segments even show the positive or no anomaly of Eu, which may be explained by the mixture of basic components in the provenance, whose proportion gradually decreases.

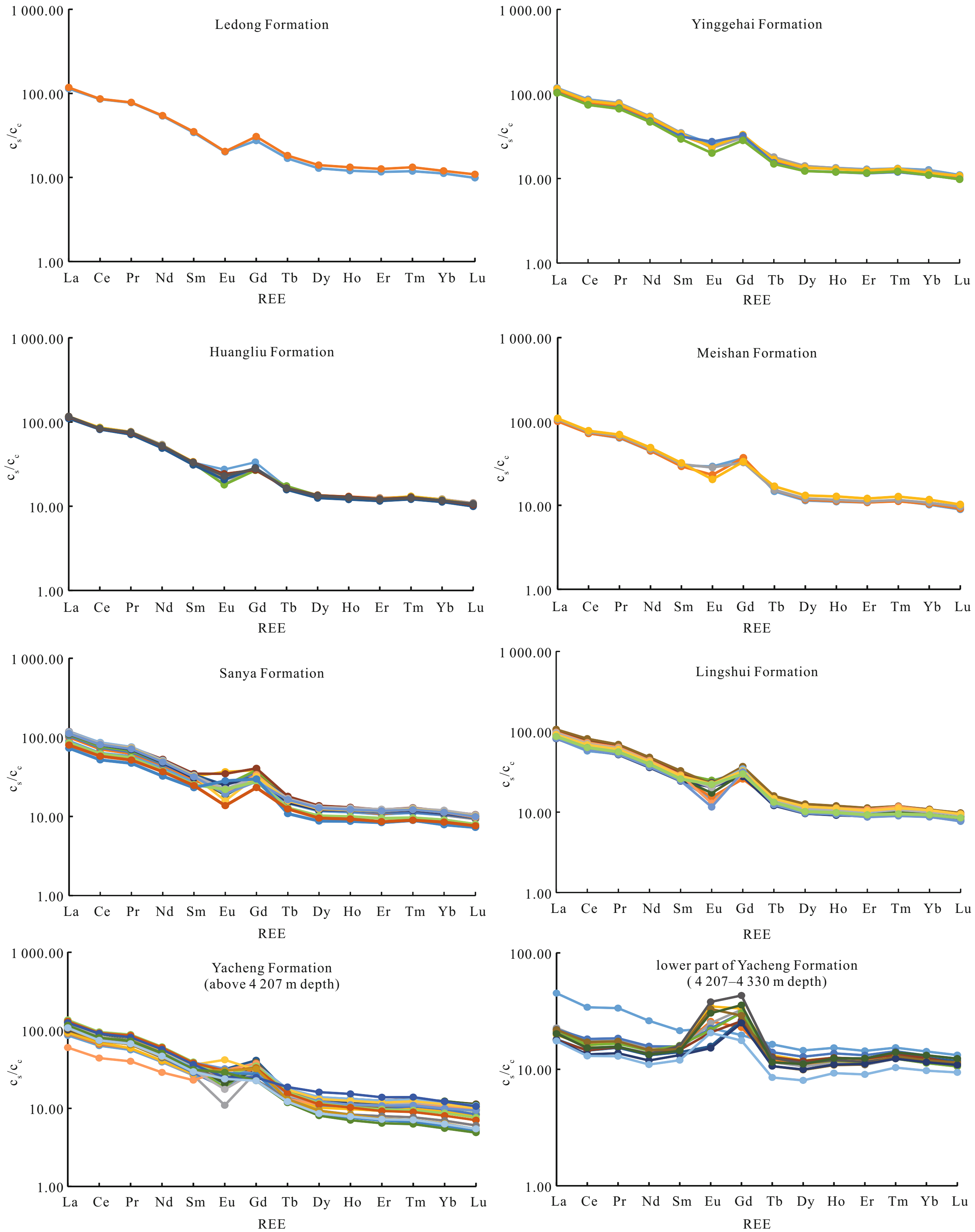

Fig.4. Chondrite-normalized (Haskin et al., 1966) REE partitioning patterns in the core samples of Well LS-A. c_s represents the REE content of the sample and c_c represents the REE content of chondrite.

5 Discussion

5.1 *Effects of diagenesis and granularity on REEs*

Shields and Stille (2001) pointed out that diagenesis could change the anomaly of Ce, exhibiting good correlations with other geochemical parameters of REEs. When influenced greatly by diagenesis, δCe has good correlation with δEu, negative correlation with $(Dy/Sm)_N$, and positive correlation with ∑REE. However, the δEu-δCe and ∑REE-δCe correlations of Well LS-A are relatively poor, with coefficients (R^2) of 0.1847 and 0.081, respectively, indicating that diagenesis only insignificantly influences the REE differentiation of the core samples.

The geochemical compositions of sediments are generally controlled by the granularity to a degree (Cullers, 1994; Yang et al., 2002). Overall, ∑REE of mudstone is higher than that of siltstone, and ∑REE of argillaceous limestone is lower than the former two in the core samples of Well LS-A. The ∑REE in sedimentary rocks with different size fractions varies, however, characteristic ratios and chondrite-normalized REE partitioning patterns in the core samples are similar from the bottom of Yacheng Formation (at a well depth of above 4 207 m) to the top of Ledong formation, the same is true of the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m). Moreover, the lithology from the bottom of Yacheng Formation (at a well depth of above 4 207 m) to the top of Ledong Formation is similar to that of the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m), indicating that the geochemical characteristics of REEs in the core samples inherit the properties of source rocks.

5.2 *Types and changes of sedimentary source*

As mentioned above, there are saltations of REE content in Well LS-A at a well depth of 4 207 m. The Q-mode cluster analysis of the core samples on the basis of multiple geochemical indexes of REEs also indicates that the samples may be divided into two groups demarcated by the well depth of 4 207 m (Fig. 5), and that the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m) has a provenance with clearly different characteristics from those of the overlying formations. When comparing the REE characteristic parameters and partitioning characteristics of core formations with those of various end-members (Table 2 and Fig. 6), it can be found that the strata from the bottom Yacheng Formation (above 4 207 m) to the top of Ledong Formation show the enrichment of ∑LREE, the uniform content of ∑HREE, a LREE/HREE ratio of 7.45–8.69 with clear fractionation, and the negative anomaly of both δEu and δCe, which are approximate to the upper continental crust and to China's neritic sediments and loess. This shows a clear "continental orientation" characteristic, indicating that the core sediments mainly originate from the clastic products of the nearby continent. The ∑REE of the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m) is relatively low, and its characteristic parameters and partitioning patterns are relatively approximate to those of oceanic basalt and oceanic crust, and relatively significantly different from those of the upper continental crust, China's neritic sediments, China's loess, and abyssal sediments, indicating that the basic volcanic eruptions play an important role in determining the sources of the well core.

The trace elements and REEs have been extensively applied to the analyses of the sedimentary source and tectonic setting (Taylor and Mclennan, 1985; Gao et al., 2009; Villagómez et al.,

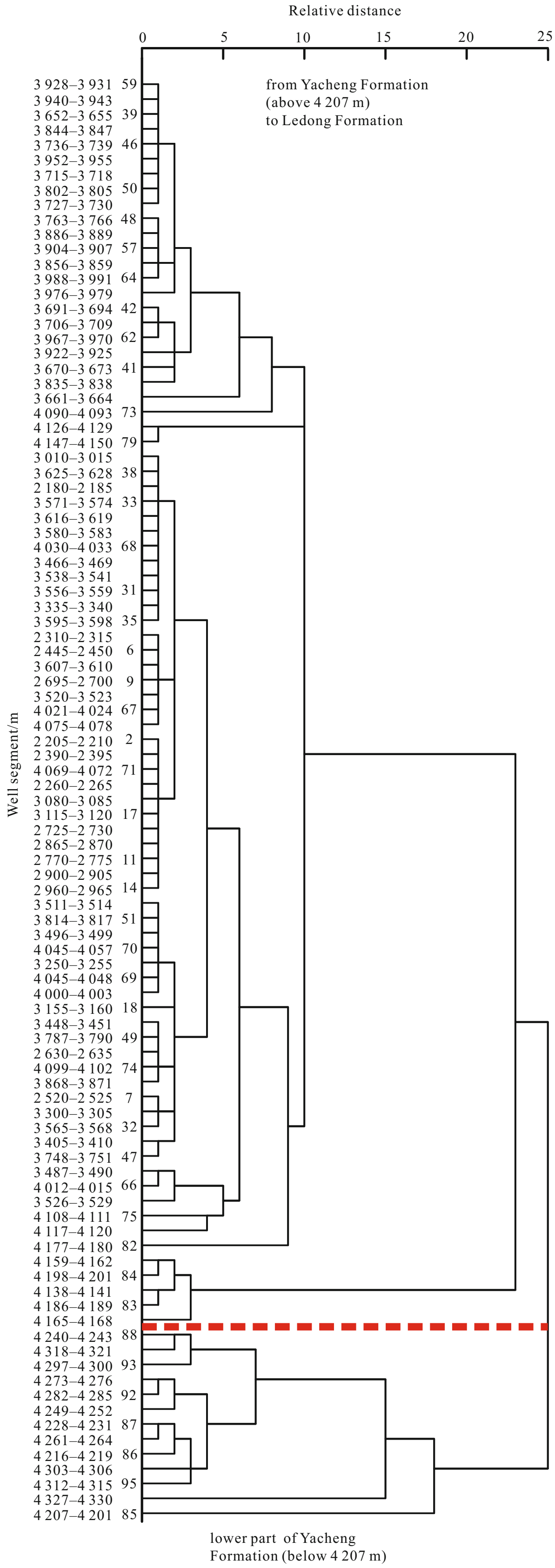

Fig.5. Q-mode cluster analysis for the core samples of Well LS-A.

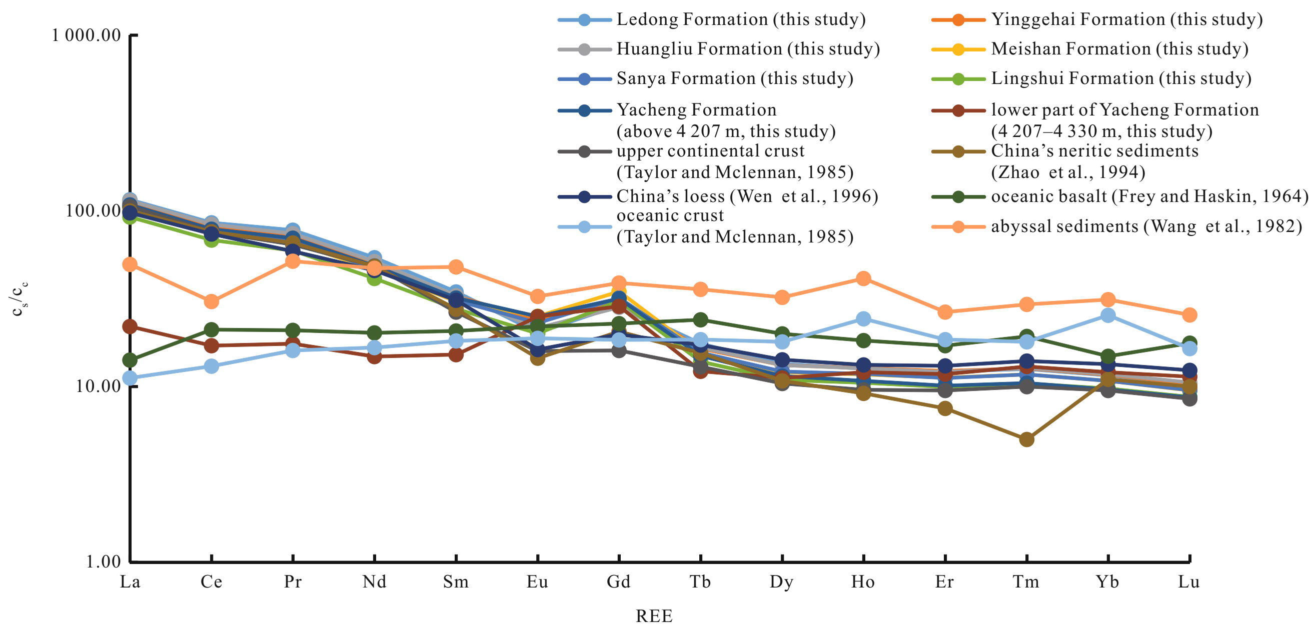

Fig.6. Chondrite-normalized (Haskin et al., 1966) REE partitioning patterns of core formations and various end-members.

Table 2. Comparison of REE characteristic parameters between core formations with various end-members

Sample		∑REE/ μg·g^{-1}	∑LREE/ μg·g^{-1}	∑HREE/ μg·g^{-1}	LREE/ HREE	δCe	δEu	Reference
Lower part of Yacheng Formation (4 207–4 330 m) (*n*=13)	minimum	41.27	28.88	12.39	1.18	0.84	0.80	this study
	maximum	87.68	69.7	21.11	3.88	0.90	1.50	
	mean	55.27	37.63	17.64	2.13	0.87	1.14	
Yacheng Formation (above 4 207 m) (*n*=25)	minimum	105.93	86.66	11.97	4.5	0.84	0.39	this study
	maximum	202.15	184.06	21.14	12.97	0.93	1.24	
	mean	167.10	149.55	17.55	8.52	0.89	0.79	
Lingshui Formation (*n*=18)	minimum	127.43	111.93	15.17	6.97	0.85	0.41	this study
	maximum	171.23	146.89	19.88	8.12	0.94	0.85	
	mean	145.55	128.48	17.06	7.53	0.90	0.68	
Sanya Formation(*n*=20)	minimum	115.51	100.47	13.97	6.68	0.86	0.49	this study
	maximum	184.67	162.94	21.73	8.63	0.90	1.07	
	mean	163.06	144.61	18.45	7.84	0.88	0.73	
Meishan Formation (*n*=4)	minimum	156.98	137.69	18.49	7.14	0.87	0.63	this study
	maximum	167.75	148.17	19.58	7.79	0.87	0.89	
	mean	161.32	142.22	19.10	7.45	0.87	0.77	
Huangliu Formation (*n*=9)	minimum	170.20	152.28	17.92	7.91	0.87	0.59	this study
	maximum	180.63	161.88	19.69	8.86	0.90	0.82	
	mean	176.60	158.15	18.45	8.57	0.89	0.70	
Yinggehai Formation (*n*=6)	minimum	159.34	141.66	17.68	7.63	0.87	0.69	this study
	maximum	183.81	164.29	19.76	8.42	0.88	0.86	
	mean	172.36	153.24	19.12	8.01	0.87	0.75	
Ledong Formation (*n*=2)	minimum	178.83	161.04	17.79	8.36	0.88	0.62	this study
	maximum	183.18	163.61	19.57	9.05	0.89	0.65	
	mean	181.00	162.33	18.68	8.69	0.89	0.64	
Upper continental crust		157.07	144.10	12.97	11.11	0.89	0.75	Taylor and McLennan (1985)
China's neritic sediments		156.46	142.37	14.09	10.10	0.92	0.60	Zhao and Yan (1993)
China's loess		155.31	138.01	17.30	7.98	0.87	0.66	Wen et al. (1996)
Oceanic basalt		58.64	42.96	15.68	2.74	1.20	1.01	Frey and Hasin (1964)
Oceanic crust		54.37	31.60	22.77	1.39	0.96	1.03	Taylor and McLennan (1985)
Abyssal sediments		125.93	88.16	37.77	2.33	0.60	0.75	Wang et al. (1982)

2011; Xu et al., 2011). In the La–Th–Sc provenance discrimination diagram (Fig. 7a), the data of the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m) and those of the strata from the Yacheng Formation (above 4 207 m) to the Ledong Formation are projected onto completely different regions: the former is projected onto a region of typical magmatic arc-related sediments, exhibiting intensified tectonic activities in the Qiongdongnan Basin in the faulted period, while the latter is projected onto the overlapping or nearby regions of passive continental margin sediments and magmatic arc-related sediments, indicating that provenance changes occur with the transition from the early proximal magmatic provenance to distal and multi-source provenance. In the ∑REE-La/Yb ratio provenance determination diagram (Fig. 7a), the samples from the Yacheng formation (above 4 207 m) to the Ledong Formation are all projected onto or around the intersection region of the sedimentary rock and granite, indicating that the sediments of the study region originated from the sedimentary rock or granite in medium term of the early Oligocene. The results are consistent with basement composed of granite, sedimentary rock, and metamorphic rock, extensively distributed in the Qiongdongnan Basin and its nearby region (Mi et al., 2009; Xie et al., 2010; Zhang, 2010; Liu et al., 2012). Except for one sample, all samples of the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m) are projected onto the region between the sedimentary rock and basalt regions, indicating that its provenance is mixed, but mainly dominated by basic volcanic matters. The Eu in the lower part of the Yacheng Formation of Well YC13-1-2, located at the Yacheng Uplift Area, Qiongdongnan Basin, also shows a significantly positive anomaly (Shao et al., 2010), indicating the important role of basic volcanic matters in contributing to the sedimentary source in the early Oligocene. In the Qiongdongnan Basin, the Cenozoic volcanic rocks were rarely observed during the drilling, and the reflections similar to volcanic rocks were also rarely observed on seismic sections. Currently, there are no literature reports on

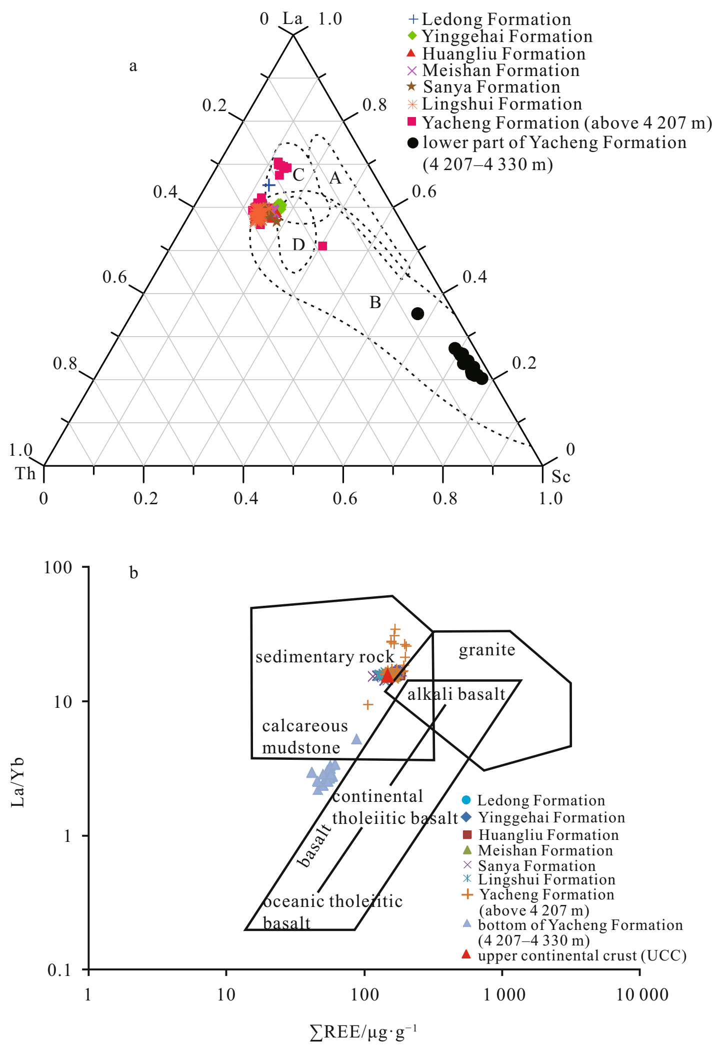

Fig.7. La–Th–Sc (a) and ∑REE-La/Yb (b) ratio provenance determination diagram. A is oceanic island alkaline basalt (OIAB), B is magmatic arc-related sediments (MAR), C is sediments from passive continental margin, and D is post Archean Australia shale (PAAS). Data of upper continental crust (UCC) come from Taylor and Mclennan (1985). Contents of Th and Sc come from Li et al. (2014).

the features or lithological characteristics of Cenozoic volcanic activities in Qiongdongnan Basin. Based on the volcanic rocks observed during the drilling in the Zhujiang River Mouth Basin, from the late Paleocene to the early Eocene, mainly neutral and acid volcanic rocks were found, and from the middle Eocene to the Oligocene, both the neutral and basic eruptive rocks were found, the latter of which are dominated by alkali basalt (Li et al., 1998). It can be concluded on such a basis that there may have been a similar lithological association of volcanic rocks in the Qiongdongnan Basin.

On the basis of the structural analysis of sequence stratigraphy, it can be concluded that during the sedimentary period of the Yacheng-Lingshui Formation in the Oligocene, the fault depression in the basin showed divisibility and the sedimentary source in the study region was mainly supplied by a proximal realm. The granularity analysis conducted on the core of Well LS-A indicates that in the early Oligocene, the granularity of sediments was relatively rough. Gravel and sand accounted for a certain proportion, and the provenance mainly resulted from the nearby uplift area. The terrigenous matter from the north contributed extremely insignificantly to the study region because of the obstruction and splitting of the multi-stage fracture terrace. With further extension and subsidence of the basin, the sedimentary water-depth further increased, and the provenance went through a transition from the dominant volcanic eruption matters to terrigenous clastic sediments. By the late Oligocene, the provenance had been expanded to a certain extent, but the spatial scale was still limited. Since the Miocene, the nearby low uplift areas and Yongle Uplift Area gradually submerged underwater, and the provenance expanded ceaselessly from the proximal realm to the distal realm, embodying a characteristic of multi-source sedimentation. The Hainan Island, South China Block and the Indo-China Peninsula supplied fairly well-sorted fine-grained materials to the study region; therefore, the percentage composition of silt and clay exceeds to 97% in the strata from the Sanyang Formation to the Ledong Formation.

5.3 *Geochemical responses to tectonic activities of basin*

On the basic pattern of the intense tectonic extrusion, subduction and collision, and large-scale block collage in the Mesozoic, the continental margin of the South China Sea transformed its property from an active to passive continental margins. The intense continental margin tension in the Cenozoic formed a series of rift basins. The intense tectonic movement and complex evolutionary process of the South China Sea change the sedimentary source and environment, which is inevitably reflected by the geochemical characteristics in the sedimentary core. Figure 8 shows that the South China Sea Movement (34–25 Ma BP) occurring in the Oligocene has been well reflected by the geochemical characteristics of the core of Well LS-A, and that both the characteristic parameters of REEs and Th/Sc ratio go through significant saltatory changes at a well depth of 4 207 m (>31. 5 Ma BP). The facts that the characteristic parameters of REEs and Th/Sc ratio both abruptly increase from the previous minimum values of the entire core, the fractionation between LREE and HREE (LREE/HREE) suddenly enhances, and Eu changes from positive to negative anomaly (Fig. 8), may all serve as the sedimentary record of the beginning of the sea-floor spreading of the South China Sea, marking the transition of provenance from the proximal volcanic matters to the distal and multi-source materials, and recording the transition of the sedimentary environment from continental to marine facies. The significant high–low alternating changes in the geochemical indexes of the Yacheng Formation indicate the intense changes in the sedimentary source and environment, corresponding to the early active period of the faulted activities in the Qiongdongnan Basin. Analyses of the paleontology and core minerals of Well LS-A indicate that from a well depth of 4207 m upward planktonic foraminifera, and glauconite gradually emerge; from the well depth of 4207 m downward, no marine-facies fossil or mineral is found in the core samples, indicating that the gradual transition of the sedimentary environment from continental to littoral-neritic facies. The changes in the sedimentary source and environment revealed by the above geochemical indexes are exactly the embodiment of the tectonic movement and evolution of the basin.

In the early spreading stage of the South China Sea (34–25 Ma BP), the tectonic activities of the Qiongdongnan Basin were extremely dynamic. In the strata 31.5, 28.4, and 25.5 Ma from today, both the characteristic parameters of REEs and Th/Sc ratio go through significant saltations in varying degrees. Among them, the stratum 31.5 Ma BP shows the maximum degree of saltation from the Yacheng Formation (at a well depth of 4 207 m) to the Ledong Formation. The geochemical indexes in the well core of ODP Site 1148 and different sags of the Zhujiang River Mouth Basin show abrupt changes in the sedimentary stratum around 32 Ma BP (Pang, Chen, Peng, 2007; Shao et al., 2009). On the basis of the biostratigraphical analysis of ODP Site 1148, Wang et al. (2003) proposed that important tectonic events occurred around 32 Ma BP. Relative to the stratum around 32 Ma BP, the characteristic parameters of REEs and Th/Sc ratio in the interfaces of 28.4 Ma BP (a well depth of 3 931 m) and 25.5 Ma BP (a well depth of 2 844 m) show a relatively less degree of saltation, and the two time points correspond to the spreading termination of the Northwest Basin and the change in the spreading axis direction of the South China Sea, respectively. Thus, the tectonic activities during the early spreading stage of the South China Sea (34–25 Ma BP) have been well recorded by the geochemical characteristics of the deep-water well core in the Qiongdongnan Basin, and the saltatory interface of the core stratum with 32 Ma from today shows a better horizontal comparison and traceability in the northern South China Sea.

Some previous studies have already shown that in the late Oligocene (23 Ma BP), a relatively large-scale tectonic movement (Baiyuan Movement) occurred in the northern South China Sea, making the sedimentary source and environment of this region changes dramatically (Wu et al., 2003; Li et al., 2007; Pang, Chen, Shao, et al., 2007; Shao et al., 2007; Li et al., 2012). The characteristic parameters of REEs and Th/Sc ratio in the core of Well LS-A also show very clear fluctuations in the stratum interface, 23 Ma BP. The fluctuation is less than that of the stratum interface, 31.5 Ma BP. On the stratum interface, 23 Ma BP, the values of ∑REE, ∑LREE, ∑HREE, La/Sm ratio, and Th/Sc ratio are low. The LREE/HREE ratio remains basically stable, and δEu shows a significantly high value. The changes in the geochemical characteristics of the core sediments are exact reflections of the Qiongdongnan Basin to the Baiyun Movement as a tectonic event. After the Baiyun Movement, the South China Sea entered its late spreading period (23–16.5 Ma BP). The REE content clearly increases compared with that of the late Oligocene, and various geochemical parameters fluctuate

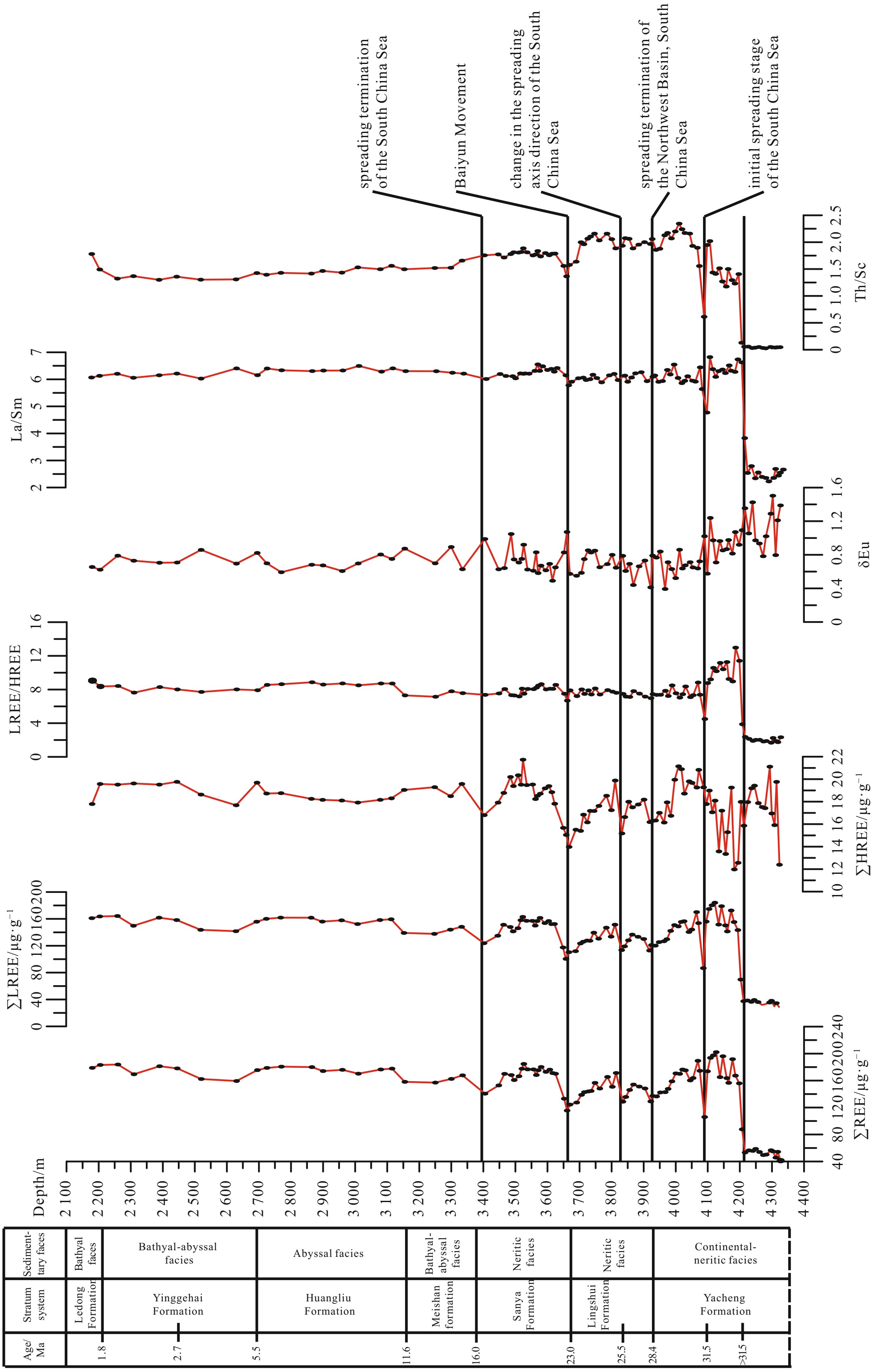

Fig.8. Variations of REE characteristic parameters and Th/Sc ratio with depth of Well LS-A. Data of Th/Sc ratio come from Li et al. (2014).

slightly, indicating that the tectonic activities of the South China Sea Basin gradually slow down. The basin is in a relatively stable slow subsidence period and marine environment. Because of the collision between the Liyue-Northeast Palawan Landmass and Kalimantan and West Philippines, the sea-floor spreading of the South China Sea ended around 16 Ma BP (Briais et al., 1993; Hall, 2002). Corresponding to this event, the geochemical characteristics change in the stratum interface, 16.5 Ma BP, similar to those in the stratum interface, 23 Ma BP (Fig. 8). In the core of ODP Site 1146, both mineral composition and sedimentary granularity record the tectonic event, only in a relatively less degree (Wan et al., 2007). After the spreading terminated, the South China Sea has entered a stable slow thermal subsidence period since the middle Miocene, characterized by the aggravated transgression and the transition to bathyal and abyssal sedimentary environment. The corresponding geochemical indexes of REEs are relatively stable, and both REE content and Th/Sc ratio increase slowly (Figs 3 and 8).

6 Conclusions

(1) Both ∑REE and ∑LREE in the core samples of Well LS-A fluctuate in a relatively wide range, while ∑HREE maintains a relatively stable level. With stratigraphic chronology becoming newer, both ∑REE and ∑LREE show a gradually rising trend overall. The ∑REE is relatively high from the bottom of Yacheng Formation (at a well depth of above 4 207 m) to the top of the Ledong Formation, and the REEs show the partitioning characteristics of the enrichment of LREE, the stable content of HREE, and the negative anomaly of Eu in varying degrees; the overall geochemical characteristics of REEs are relatively approximate to those of China's neritic sediments and China's loess, with significant "continental orientation". The ∑REE is relatively low in the lower part of the Yacheng Formation (at a well depth of 4 207–4 330 m), as shown by the REE partitioning pattern of the depletion of LREE, the relative enrichment of HREE, and the positive anomaly of Eu; the overall geochemical characteristics of REEs are approximate to those of oceanic crust and basalt, and the provenance is primarily composed of volcanic eruption matters.

(2) As shown by the analyses of sequence stratigraphy and mineralogy, in the early Oligocene the provenance of the study region mainly resulted from the volcanic matters from the peripheral uplift areas, while the continental margin matters from the north contributed only insignificantly. The provenance developed to a certain extent in the late Oligocene. Since the Miocene, the provenance has ceaselessly expanded from the proximal to the distal realm, embodying a characteristic of multi-source sedimentation.

(3) In the strata of the core, 31.5, 28.4, 25.5, 23, and 16 Ma from today, both the geochemical parameters of REEs and Th/Sc ratio go through significant saltations, embodying the tectonic movement events in the evolution of the Qiongdongnan Basin. In the tectonic evolution history of the South China Sea, the South China Sea Movement (34–25 Ma BP, early expansion of the South China Sea), Baiyun Movement (23 Ma BP), late expansion movement (23.5–16.5 Ma BP), expansion-settlement transition, and other important events are all clearly recorded in the geochemical characteristics of REEs in the core sediments.

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