Distribution of Rare Earth Elements in Early Permian Reef-Island Ocean Sediments in Eastern Kunlun

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Abstract Based on the study of stratigraphy and fossils, the Early Permian ocean in eastern Kunlun is recognized as a kind of reef-island ocean, in which there exist many different kinds of sediment, including patch carbonate platform, reef facies, transitional facies and deep basin sediments. It has been found that the total contents of REEs increase gradually from carbonate platform facies to deep basin facies. Meanwhile, sediments of different facies have different REE distribution patterns and different Ce anomalies. Most of the sediments of patch carbonate platform facies or reef facies are characterized by extremely negative Ce anomalies or moderately negative Ce anomalies (Ce/Ce*=0.33 to 0.55), and medium or thin-bedded limestones of transitional facies by moderately negative Ce anomalies (Ce/Ce*=0.49 to 0.60). However, sediments of deep basin facies show weak or no negative Ce anomalies (Ce/Ce*=0.69 to 1.47), among which the value of Ce/Ce* in the radiolarian chert is 1.47.

Key words: rare earth elements, reef-island ocean, Early Permian, eastern Kunlun

1 Introduction

Rare earth elements (REEs) are widely used in the study of magmatite. Haskin et al. (1966) and Wideman et al. (1965) did a lot of work in the study of REEs in sedimentary rocks in the 1960s. Later, with the development of analysis methods and equipment, especially with the utilization of the neutron activation technique, mass spectrometry and ICP spectrum analyzer, the accuracy of REE data has been greatly improved. People began to show more interests in the REE geochemistry of sedimentary rocks, as well as in many other branches of REE geochemistry.

So far, most of the studies of REEs in sedimentary rocks are focused on chert and shale, especially on the genesis of different kinds of chert (Zhou, 1990; Jin, 1992; Zhang et al., 1992; Liu et al., 1993; Zhou et al., 1994; Xia et al., 1995; Yang et al., 1997; Xu, 1998). However, studies of REEs in carbonate sediments are scarcely reported except Zhao's research (1997) on the Silurian limestone in western Qinling. With the hope of trying to find something interesting, we systematically analyzed the REEs of different kinds of Early Permian sediments in eastern Kunlun. The samples were selected from massive limestone of shallow-water platform facies, medium or thin-bedded limestone of transitional facies, very thin-bedded limestone of deep basin facies, red mudstone and radiolarian chert of the abyssal facies. As a result, we found there exist different models of REE distribution in different sedimentary facies and the REE distribution patterns change regularly from the carbonate platform facies through transitional facies to deep basin facies. Because the above sedimentary rocks are deposited in the same age, our research could be regarded as a new trial and a systematic geochemical analysis of the syndeposits of different facies. The study, we think, will be helpful for people to know more about the nature and environment of the Early Permian ocean in eastern Kunlun.

2 Sedimentary Facies in the Early Permian Reef-Island Ocean

Based on three years of field research and synthetic analysis afterwards, we found there exist reef-islands, patch carbonate platforms and deep basins which are distributed between reef islands or carbonate plat-

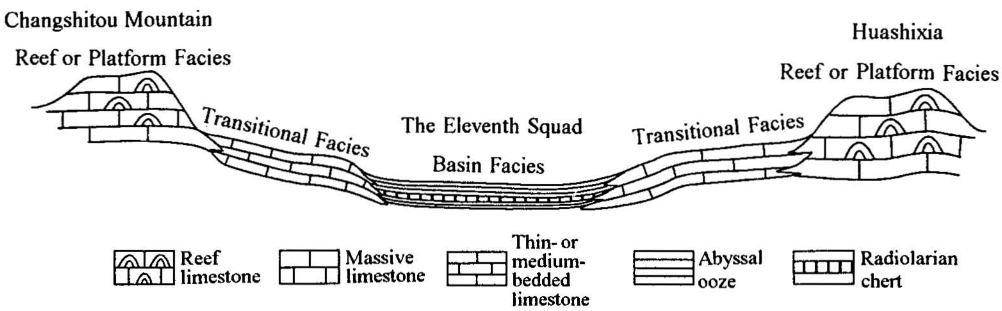

Fig. 1. Sketch map showing the relations between different facies in early Permian ocean in Eastern Kunlun.
1. Reef limestone; 2. massive limestone; 3. thin- or medium-bedded limestone; 4. abyssal ooze; 5. radiolarian chert.

forms in the Early Permian ocean in eastern Kunlun (Fig. 1). Reef framestone and grey-white massive bioclastic limestone are the main kinds of rock in reef facies or carbonate platform facies, in which many Early Permian fusulinid fossils such as *Neoschwagerina* sp. can be found. Reef framestone is dominated by calcisponges, bryozoans, hydrozoans and different kinds of algae. These reef-building organisms are almost the same as those in the Early Permian reefs in South China. In the reef facies or patch carbonate platform facies, we can see that bioclastic limestone and reef framestone usually appear alternately or penetrate each other, indicating that the reef facies and carbonate platform facies were formed in similar environments on the whole. In deep basin facies, there are much more kinds of sediments. So far, three types of deep basin facies have been identified and they are the abyssal red mudstone or ooze, radiolarian chert and very thin-bedded limestone. In chert, abundant radiolarian fossils have been found, among which *Pseudoalbaillella elogans* Ishiga and Imoto, *P. scalprata postscalprata* Ishiga and *P. scalprata scalprata* Ishiga can be recognized as indicators of the Early Permian (Zhang et al., 1999). According to the study of radiolarian palaeoecology by Feng (1992), the above radiolarian fauna reflects a deep basin sedimentary environment. The red mudstone, which is widely distributed in the study area, should also belong to the deep basin sediment because this kind of mudstone or ooze is interbedded with radiolarian chert in A'nyêmaqên. On the southern slope of the eastern Kunlun, red mudstone is accompanied by blue-green mudstone and very thin-bedded limestone, which shows that they were all formed in a deep basin. What is more, there usually exists medium or thin-bedded limestone of the transitional facies between the carbonate platform (or reef island) and deep basin facies. The Early Permian fusulinid fossils *Neoschwagerina* sp. and *Verbeekina* sp. and other kinds of foraminifers have been also found in the transitional facies, indicating that the carbonate platform facies, reef facies, deep basin facies and transitional facies all belong to syndeposits in the Early Permian ocean.

3 Total Contents of REEs in Different Facies

Differences can be clearly seen among the patch carbonate platform facies (including the reef facies), transitional facies and deep basin facies not only in their lithofacies but also in their lithogeochemistry. The total contents of REEs ($\sum$REE) in different sedimentary facies are illustrated in Fig. 2 and Table 1.

In the reef facies or patch carbonate platform facies, grey or grey-white massive bioclastic limestone or framestone is the main kind of rock. Based on the analysis of geochemistry, it is found that the $\sum$REE in patch carbonate platform facies is relatively low, which varies from about 6 μg/g to 18 μg/g. Only in one of the reef rock samples the $\sum$REE is 26.69 μg/g, much higher than that in the patch carbonate platform facies.

The transitional facies is characterized by medium or thin-bedded limestone, and much thinner in layer and darker in colour compared with the carbonate platform facies or reef facies. The $\sum$REE values in different samples of carbonate platform or reef facies are not identical. Contrarily, those in samples of the

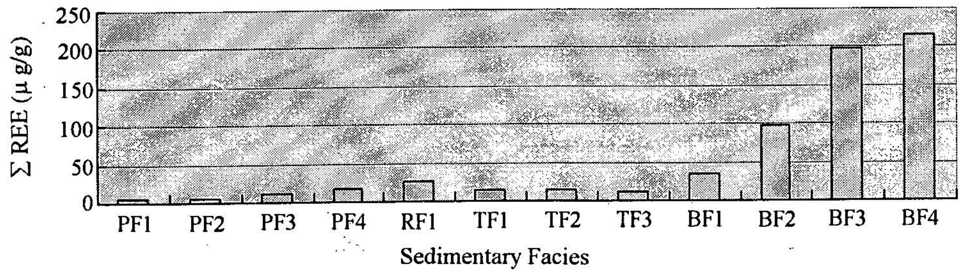

Fig. 2. Variation of total contents of REE in different sediments.
PF–Carbonate platform facies; RF–reef facies; TF–transitional facies; BF–basin facies.

Table 1 REE Contents in different facies（μg/g）

Sample number	Sedimentary facies	Lithologic character	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
5821-3	PF1	Bioclastic limestone	1.95	1.33	0.37	0.99	0.17	0.03	0.15	0.03
HQP4-22-1	PF2	Bioclastic limestone	1.7	1.12	0.24	0.89	0.21	0.04	0.19	0.03
HQP4-24	PF3	Bioclastic limestone	3.17	4.92	0.7	2.1	0.42	0.08	0.39	0.06
HQP4-19-1	PF4	Bioclastic limestone	5.34	5.32	0.85	2.4	0.48	0.09	0.39	0.06
HQP4-7-2	RF1	Sponge reef framestone	5.48	6.38	1.18	3.93	0.76	0.15	0.78	0.13
HQP6-12-1	TF1	Medium or thin-bedded limestone	3.84	4.17	0.69	2.35	0.38	0.06	0.3	0.04
HQP6-14-1	TF2	Medium or thin-bedded limestone	4.05	4.84	0.73	2.35	0.36	0.06	0.27	0.04
HQP6-1	TF3	Medium or thin-bedded limestone	4.38	4.3	0.82	2.34	0.41	0.06	0.29	0.05
0764-2	BF1	Very thin-bedded limestone	7.76	11.39	1.63	6.07	1.03	0.19	0.78	0.12
HUZ-A	BF2	Radiolarian chert	10.28	37.54	3.13	11.77	2.69	0.52	3	0.53
0764-1	BF3	Red abyssal ooze	35.74	79.6	8.59	31.41	5.8	0.96	4.47	0.67
0764-3	BF4	Blue-green abyssal ooze	35.65	80.65	9.5	36.17	6.61	1.22	5.16	0.81

Sample number	Sedimentary facies	Lithologic character	Dy	Ho	Er	Tm	Yb	Lu	Y	ΣREE
5821-3	PF1	Bioclastic limestone	0.12	0.03	0.07	0.01	0.04	0.01	1.36	6.66
HQP4-22-1	PF2	Bioclastic limestone	0.17	0.04	0.1	0.01	0.07	0.01	1.9	6.72
HQP4-24	PF3	Bioclastic limestone	0.34	0.07	0.19	0.03	0.12	0.02	3.21	11.84
HQP4-19-1	PF4	Bioclastic limestone	0.33	0.07	0.19	0.03	0.13	0.02	2.9	18.6
HQP4-7-2	RF1	Sponge reef framestone	0.75	0.15	0.37	0.05	0.26	0.04	6.28	26.69
HQP6-12-1	TF1	Medium or thin-bedded limestone	0.22	0.04	0.11	0.01	0.08	0.01	1.4	13.7
HQP6-14-1	TF2	Medium or thin-bedded limestone	0.22	0.04	0.09	0.13	0.07	0.01	1.17	14.43
HQP6-1	TF3	Medium or thin-bedded limestone	0.22	0.05	0.11	0.02	0.08	0.01	1.44	12.65
0764-2	BF1	Very thin-bedded limestone	0.63	0.11	0.27	0.04	0.22	0.03	3.51	33.78
HUZ-A	BF2	Radiolarian chert	3.46	0.69	2.21	0.43	2.95	0.5	18.52	98.22
0764-1	BF3	Red abyssal ooze	3.87	0.8	2.28	0.37	2.3	0.34	21.82	199.02
0764-3	BF4	Blue-green abyssal ooze	4.94	0.89	2.47	0.44	2.65	0.44	26.51	214.11

Note: Samples analyzed by the Wuhan Centre of Rock and Mineral Analysis of the former Ministry of Geology and Mineral Resources.

transitional facies are very close, mostly from about 12 μg/g to 15 μg/g. On the whole, there is the trend that the ΣREE in transitional facies goes higher than that in carbonate platform facies, but much lower than that in basin facies.

The matter appears to be more complicated in the basin facies. The ΣREE in very thin-bedded limestone (basin facies 1) is 33.78 μg/g, which is apparently higher than that in sediments of the patch carbonate platform, reef and transitional facies, but much lower compared with that in abyssal ooze. Abyssal ooze has the highest ∑REE among all the samples, which is about 200 μg/g on the average. Although there are two types of abyssal ooze, the red mudstone (basin facies 3) and the blue-green mudstone (basin facies 4), they have almost the same value of ∑REE. Radiolarian chert is a particular kind of rock. The ∑REE in radiolarian chert is 98.22 μg/g, which lies between that of very thin-bedded limestone and that of abyssal ooze.

The difference in lithologic characters is probably the main cause that leads to the variation of ∑REE in sedimentary rocks, although many other factors may also play a role. Generally, mudstone has higher values of ∑REE and carbonate sediments have relatively lower values of ∑REE. On the other hand, their lithological characters are often related to the depositional environments as known from the study in this area. For example, in the study area, the grey-white bioclastic limestone and reef framestone are formed in shallow water, while the mudstone and radiolarian chert are deposited in a deep basin environment. Therefore, the variation of ∑REE in different sediments can to some extent be used as indicators of different facies or environments.

4 REE Distribution Patterns in Different Facies

REE distribution patterns in the patch carbonate platform facies (including reef facies), transitional facies and deep basin facies are built upon the REE geochemical data which have been normalized. In this study, the REE data in patch carbonate platform facies and transitional facies are normalized by the North American Shale (Figs. 3 and 4), while the REE data in abyssal ooze, radiolarian chert and the quoted North American Shale (NAS) are chondrite-normalized (Fig. 5).

All the curves of the relative REE distribution patterns in patch carbonate platform facies (including reef facies) are in equilibrium or slightly tilts to the right. Among the four samples of the patch carbonate platform and reef facies, two samples exhibit great negative Ce anomalies (the Ce/Ce* values are 0.338

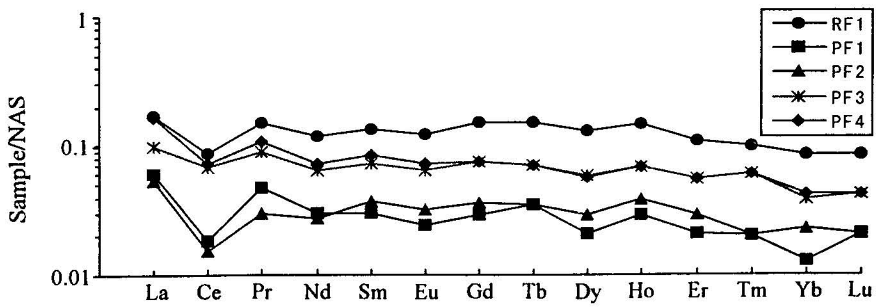

Fig. 3. REE distribution patterns in patch carbonate facies and reef facies RF-Reef facies, PF-Carbonate platform facies.

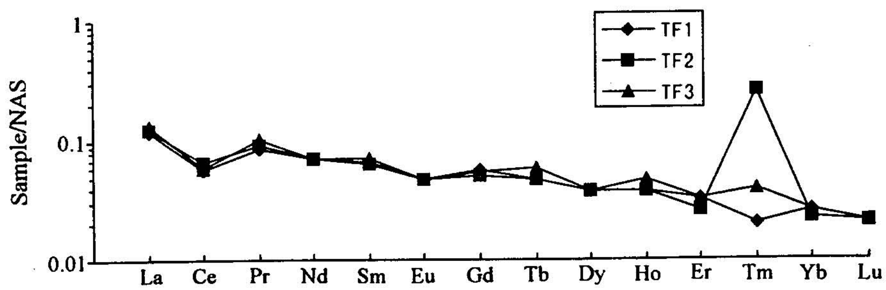

Fig. 4. REE distribution patterns in transitional facies TF-Transitional facies.

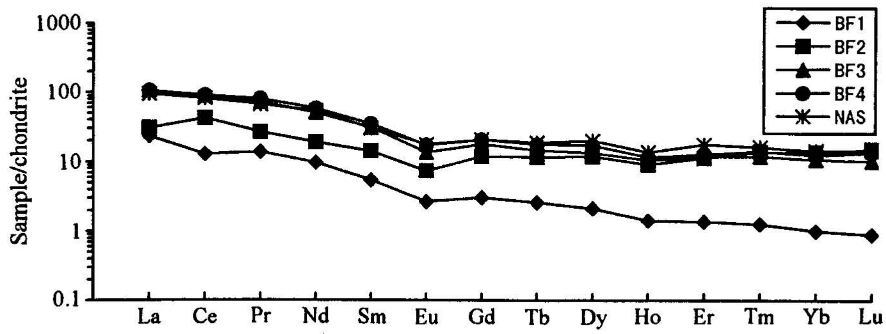

Fig. 5. REE distribution patterns in basin facies BF-Basin facies.

and 0.366 respectively), and the other two have moderately negative Ce anomalies with the Ce/Ce* values of 0.531 and 0.545 respectively. Different from the above four samples, one of the samples of the patch carbonate platform facies appears to have no negative Ce anomaly (Ce/Ce* = 0.947).

The curves of relative REE distribution patterns in transitional facies tilt much more apparently to the right than those in reef facies or patch carbonate platform facies. Cerium anomalies (Ce/Ce*) in three samples from transitional facies are calculated to be 0.49, 0.551 and 0.605 respectively, reflecting moderate Ce anomalies.

Just like the curves in transitional facies, those of relative REE distribution patterns in basin facies also tilt to the right. However, all the basin sediments except the very thin-bedded limestone show positive Ce anomalies, or no apparent negative Ce anomaly (Fig. 5). The very thin-bedded limestone (basin facies 1) has a slightly negative Ce anomaly (Ce/Ce*=0.69). Red abyssal ooze, blue-green abyssal ooze and radiolarian chert have Ce/Ce* values of 0.99, 0.97 and 1.47 respectively.

5 Analysis and Discussion of the Tectonic Setting of the Early Permian Ocean

Based on the above analysis, it is obvious that carbonate sediments often have negative Ce anomalies in the shallow-water facies, but no or slightly negative Ce anomalies in deep basin sediments. In some regions of modern oceans, there also exist negative Ce anomalies. According to the study of REEs in chert and shale along the western coast of California by Murray et al. (1990), three depositional regimes were identified: the spreading ridge proximal (within c. 400 km of the ocean ridge) with great negative Ce anomalies (Ce/Ce* about 0.29), ocean basin floor with less extreme Ce anomalies (Ce/Ce* about 0.55), and continental margin with no or slight anomalies (Ce/Ce* about 0.90 to 1.30). In our study, all the basin facies samples with only one exception have Ce/Ce* values more than 0.90, so that the depositional environments of these basin sedimentary rocks should be similar to the continental margin defined by Murray. In other words, according to Murray's model, the Early Permian basin in eastern Kunlun should belong to a continental-margin environment, not a widely open ocean basin. However, a paradox occurs when we consider the opposite conditions in the carbonate platform facies and transitional facies. Although the shallow water platform facies, transitional facies and basin facies in the study area are all located in the same tectonic environment, a negative Ce anomaly in the first two facies is a very common phenomenon. This particular phenomenon cannot be correlated with Murray's model, and we still cannot explain what is the main cause. However, we believe that Murray's model represents a whole trend of REE distribution in the marine environment, but the causes which can result in Ce anomalies may be in many ways. Local anomalies of geology or hydrochemistry in some areas will certainly influence the Ce anomalies and the REE distribution patterns even on the same continental margin. In a reef-island ocean environment like the eastern Kunlun, the sea floor topography and other geological conditions are very complicated, and a volcanic rock or volcaniclastic rock basement can often be seen under the reef facies or patch carbonate platforms. The volcanic basement provides a particular micro-environment which may lead to negative Ce anomalies because the terrestrial heat flow is often higher and the crustal movement is more active in such an area than the areas around. Of course, Murray et al. (1990) mainly studied chert and shale, not carbonate sediments, so this paper is not only a new attempt in the study of REEs in different kinds of sedimentary rocks but also a new discovery.

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