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Geochemical characteristics of REE in the Late Neo-proterozoic limestone from northern Anhui Province, China

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Abstract Ten representative limestone samples [six from Wangshan Formation (WL) and the other four from Gouhou Formation (GL)] were collected from outcrops of the northern Anhui Province, and REE concentrations in limestone were measured by ICP-MS. The depositional environment and source of the REE were analyzed, and the results implys that the total REE of samples are low compared with the recent marine sediments, which range from 9.61 to 54.18 mg/kg and an average of 22.93 mg/kg. The PAAS-normalized REE+Y patterns of limestone are characterized by (1) light REE depletion in WL and enrichment in GL with the values of $(Nd/Yb)_{SN}$ ranging form 0.65 to 0.91 and 1.12 to 1.46, respectively; (2) light negative Ce anomaly (0.85–1.02) and positive La anomaly (0.92–1.27); and (3) both Eu (0.91–1.23) and Y (1.42–2.38) expressing light positive anomaly. The character indicated that the depositional environment was oxygenated, with infection by the hydrothermal activity and contamination of detritus.

Key words rare-earth elements; geochemistry; Late Neo-proterozoic; limestone; Anhui Province

1 Introduction

Rare-earth elements (REE) concentrations were highly interested by many geologists for their unique characteristics (Henderson, 1984). A series of previous studies have shown that chemically sedimentary rocks (e.g. carbonate or banded iron formation) are useful proxies for the recording of REE patterns in the water where they were precipitated (Bolhar, 2007; Northdurft, 2004). Though the REE concentrations in carbonate rocks are low (Goldberg, 1963; Tlig and M'Rabet, 1985), they are useful to identify the marine versus non-marine sources of REE (Frimmel, 2009; Zhao, 2009). REE is considered as an indicator to identify the depositional environmental system (such as widespread marine anoxia, oceanic redox conditions, proximity to source area, lithology and diagenesis, and paleogeography and depositional models), for the distribution of REE is sensitive to water depth, salinity, oxygen level, and input sources (Northdurft, 2004).

The previous study showed that marine chemical sediments (e.g. carbonates) are characterized by a uniform light REE depletion, a negative Ce anomaly, a slight positive La anomaly and remarked positive Y anomaly in PASS-normalized diagrams, which are conform to the Seawater REE patterns (Northdurft, 2004), however, the acidic hydrothermal fluids show very different REE+Y patterns (e.g. positive Eu anomaly and MREE enriched) (Bau, 1999).

Northern Anhui Province is located on the southeastern margin of the North China Craton (NCC), with huge Neoproterozoic sedimentary which constituted mainly by carbonates (Fig. 1A). Since 1960's, many related researches on stratigraphy, paleontology, petrology, sedimentology and geochemical have been conducted (Qiao and Gao, 2000; Sun, 2011). However, no systematic study has yet been carried out on REE geochemistry of the Late Neoproterozoic limestone in northern Anhui Province. In the paper, we report new

REE data and its variations in limestone. Our aims are to trace the depositional environment, and to interpret the source of REE and anomalies (e.g. Ce, Eu, and Y).

2 Geological background

The study area which belongs to Xuzhou-Suxian stratigraphic minor region, Huaibei superregion, is located in the Lingbi uplift of the Huaibei depression on the southeastern margin of NCC (Fig. 1A), about 120 km west to the Tancheng-Lujiang Fault. The tectonic framework is mainly NE-SW trending, which was controlled by northwestward compression from the convergence of the Yangtze Craton and NCC during the Mesozoic-Cenozoic (Wang, 1999). The study area is located at Langan villages, north part of Lingbi County, northern Anhui Province. The Neoproterozoic strata in the area from the bottom to top are mainly constituted by carbonate rocks, which were formed on a carbonate platform, a shallow epi-continental environment, with the frequently raising and declining of sea level (Fig. 2).

3 Sample collection and analysis

Samples were collected from the outcrops of the Wangshan Formation (WL) and Gouhou Formation (GL) (Fig. 1B and Fig. 2). The samples were washed thoroughly with distilled water to remove the contamination. Ten representative samples were selected to analyses, including six WL and four GL. The selected samples were washed with distilled water, air dried and grinded with an agate mortar and sieved through a 200 mesh for chemical analysis. Trace elements (rare-earth elements) of rocks were analyzed by PE Elan 6000 ICP-MS at the Key Laboratory of Isotope Geochronology and Geochemistry, CAS, the relative derivations were lower than 5% (determined by the analysis of USGS international standard samples), and detail analytical procedures are after Liu (1996). Each sample was analyzed three times, and the final results were presented as average (n=3).

4 Results and discussion

The REE concentrations and related ratios are listed in Table 1. REE abundance was normalized to a standard shale average (PAAS of Talyor and McLennan) (Taylor and McLennan, 1985). The total REE contents of measured samples range from 9.61 to 54.18 mg/kg, with an average of 22.93 mg/kg, which are very low compared with recent marine sediments and PAAS. PAAS-normalized REE+Y patterns of WL and GL are given in Fig 3 (A, B).

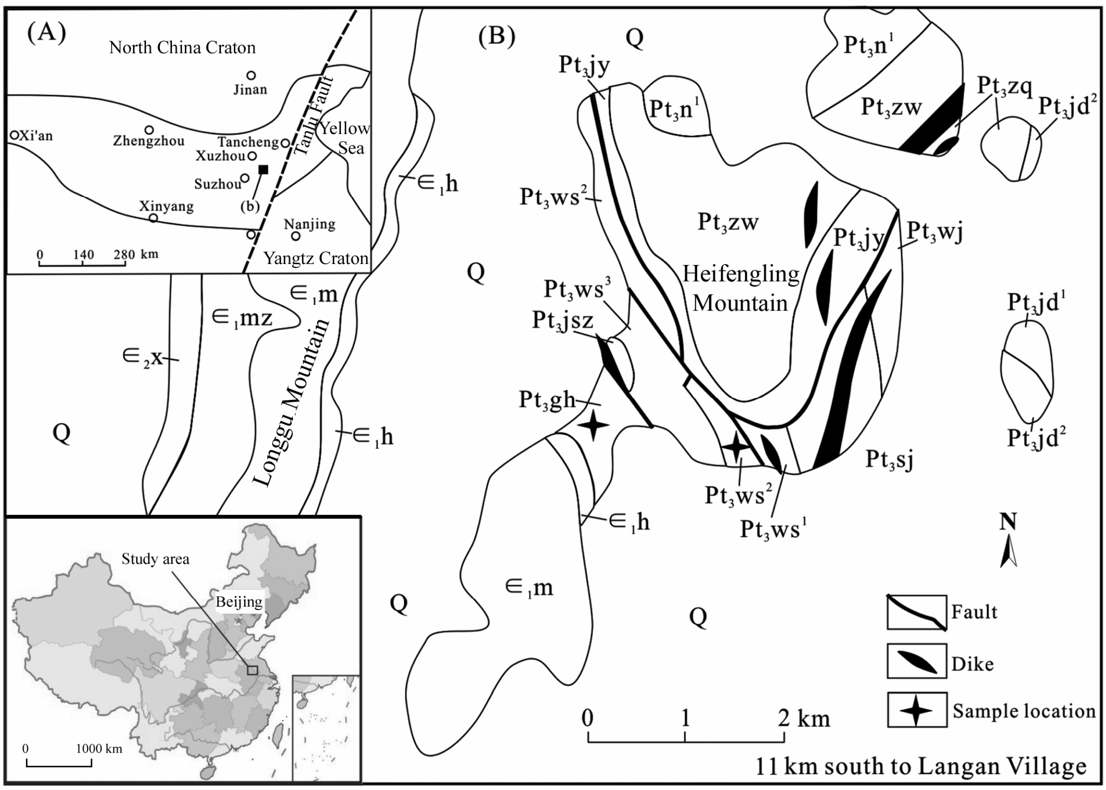

Fig. 1 Location (A) and simplified geological (B) map of the study area.

As shown in Fig 3(A), the REE of WL were characterized by uniform LREE depletion, positive La anomaly, a negative Ce anomaly, and remarked positive Y anomaly. The LREE depletion was expressed by their Nd_{SN}/Yb_{SN} ratios (0.65–0.91) (SN means PAAS normalized). The REE+Y patterns of GL display differently by with the WL, including the HREE depletion [expressed by their Nd_{SN}/Yb_{SN} ratios (1.12–1.46)] and the lightly positive Y anomaly. La_{SN} and Ce_{SN} anomalies were calculated using the relationship shown in Fig. 3(C), following the technique of Bau and Dulski (1996) (modified by Webb and Kamber, 2000; Bau, 1996; Webb and Kamber, 2000), most of the samples show positive La and negative Ce anomalies (Ce/Ce^*=0.85–1.02; Pr/Pr^*=0.99–1.11). All of the samples have positive Gd anomalies, with the ratio of Gd/Gd^* ranging from 1.03 to 1.17. In conclusion, the PAAS-normalized REE+Y patterns of limestone (Fig. 3A, B, Table 1) are characterized by the unique positive La anomaly (La/La^*=0.92–1.27), negative Ce anomaly (Ce/Ce^*=0.85–1.02), a light Eu positive anomaly (Eu/Eu^*=0.91–1.23) and Y positive (Y anomaly1.42–2.38).

4.1 Sources of REE

The average REE concentrations of limestone are more or less comparable with typical marine carbonate value (~28 mg/kg) (Bellanca, 1997). The PAAS-normalized REE+Y patterns of limestone were expected the retention of seawater characteristics including: (1) uniform light REE depletion, (2) a negative Ce anomaly, and (3) a slight positive La anomaly (Bau, 1999). Additionally, seawater Y/Ho ratios are distinctively high, for their different complexation behavior in surface. However, a few of the REE+Y patterns obtained in this study do not conform to typical seawater patterns. Thus the possibility of sources from contamination needs to be assessed carefully before deducing chemical peculiarities for the precipitating waters and thus depositional environments. The major possible sources of contamination include: (1) terrestrial particulate matter, which is a major source for marine REE, without the seawater-like patterns (e.g. shale); (2) Fe and Mn oxides; (3) phosphates, which have a high affinity for REE in diagenetic fluid (Northdurft, 2004).

Table 1 Trace element (REE) concentrations (mg/kg) of the Late Neoproterozoic limestone from northern Anhui Province, China

Formation	Wangshan Formation						Gouhou Formation			
Sample No.	H-2	H-3	H-5	H-6	H-9	H-10	GH-1	GH-2	GH-3	GH-4
La	3.98	2.98	1.36	1.70	9.15	1.81	3.82	2.44	7.29	5.61
Ce	7.93	5.47	2.46	2.96	16.50	3.45	7.51	4.50	11.70	11.20
Pr	0.96	0.66	0.30	0.33	1.98	0.40	0.89	0.51	1.54	1.22
Nd	3.77	2.61	1.20	1.32	7.71	1.46	3.26	1.82	5.71	4.61
Sm	0.83	0.53	0.26	0.28	1.68	0.30	0.62	0.36	1.09	0.92
Eu	0.17	0.12	0.07	0.07	0.36	0.06	0.11	0.07	0.23	0.18
Gd	0.90	0.57	0.27	0.31	1.61	0.30	0.50	0.32	1.03	0.89
Tb	0.14	0.09	0.05	0.05	0.25	0.05	0.08	0.05	0.16	0.13
Dy	0.79	0.53	0.28	0.28	1.39	0.25	0.37	0.24	0.81	0.67
Y	5.72	4.68	2.93	2.67	11.40	1.97	2.18	1.61	5.30	4.47
Ho	0.17	0.13	0.06	0.07	0.32	0.06	0.08	0.05	0.17	0.16
Er	0.52	0.34	0.19	0.21	0.85	0.17	0.21	0.15	0.46	0.41
Tm	0.07	0.04	0.02	0.03	0.12	0.02	0.03	0.02	0.06	0.06
Yb	0.43	0.30	0.15	0.17	0.75	0.13	0.19	0.11	0.38	0.34
Lu	0.07	0.04	0.02	0.02	0.11	0.02	0.03	0.02	0.05	0.05
REE	17.65	19.10	9.61	10.46	54.18	10.45	19.86	12.27	35.98	30.93
Ce/Ce*	0.91	0.91	0.89	0.98	0.92	0.98	0.95	1.00	0.85	1.02
Eu/Eu*	0.94	1.01	1.23	1.09	1.04	0.99	0.94	0.91	1.04	0.96
Pr/Pr*	1.03	1.02	1.03	0.99	1.03	1.04	1.05	1.05	1.11	1.00
Y anomaly	1.69	1.98	2.38	2.11	1.87	1.78	1.42	1.57	1.57	1.51
La/La*	1.00	1.13	1.12	1.27	1.10	0.97	0.92	0.97	1.02	1.03
Nd_{SN}/Yb_{SN}	0.74	0.74	0.68	0.65	0.86	0.91	1.46	1.34	1.26	1.12
Y/Dy	7.25	8.81	10.39	9.43	8.20	7.94	5.97	6.65	6.52	6.63
Y/Ho	32.87	36.85	45.29	39.38	35.40	33.11	28.02	31.14	31.74	28.47
Zr	18.50	8.32	3.16	5.03	15.50	6.51	10.20	6.27	20.50	23.10
Th	0.99	0.46	1.31	1.48	1.69	0.77	0.24	0.36	1.33	0.49
Er/Nd	0.14	0.13	0.16	0.16	0.11	0.12	0.06	0.08	0.08	0.09

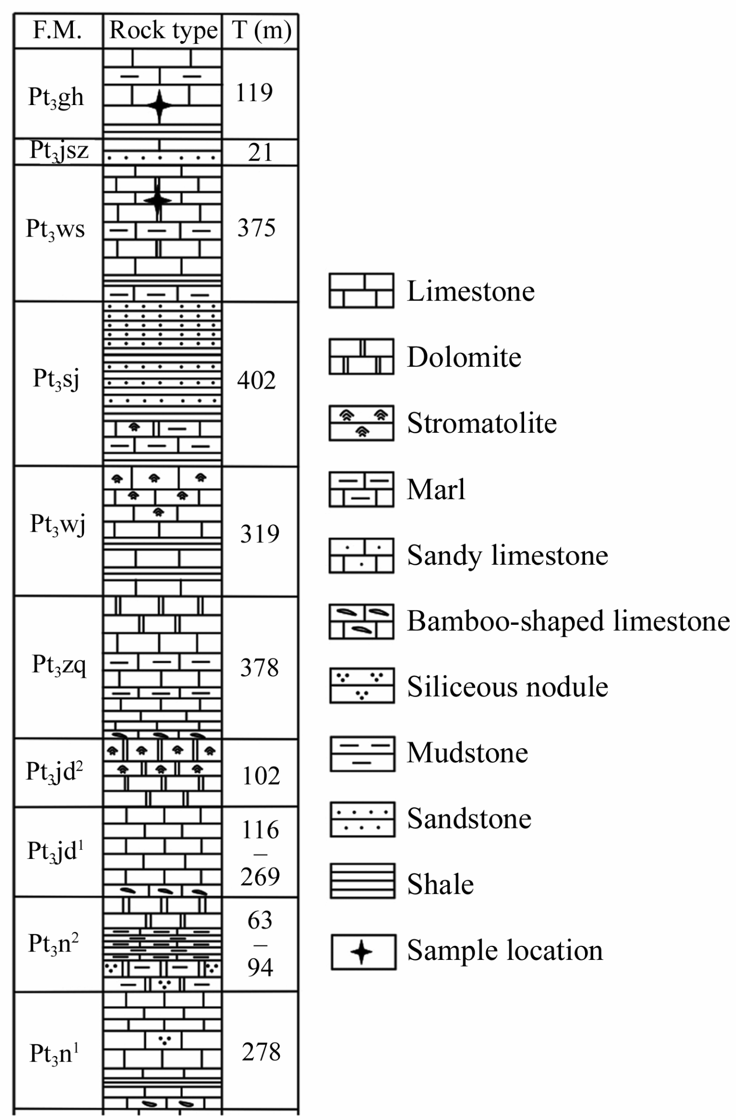

Fig. 2. Stratigraphic column of the study area and the distribution of samples.

Previous research showed that as little as 2% shale contaminations could change REE patterns (Northdurft, 2004). Trace elements (such as Zr and Th) could infer terrigenous material, what are concentrated in different detrital minerals. Good positive correlations between REE and Zr, and between REE and Th of samples were expected for terrestrial clastic contaminating. Fig. 3 (E, F) shows that a good positive correlation exits between Zr and Th (R^2=0.89), and a positive correlation also exits between Zr and REE. Thus, the view that REE in limestones having been variously affected by detrial materials could be reliable.

The value of Er/Nd ratio is about 0.27 in normal seawater (De, 1988). The high Er/Nd ratio of limestone effectively reveals the seawater signature retained by the marine carbonate. The detrital material or diagenesis can reduce the Er/Nd value to lower than 0.1, for the preferential concentration of Nd relative to Er (Bellanca, 1997). The Er/Nd ratios of the limestone are ranging from 0.11–0.16 in WL and 0.06–0.09 in GL (Table 1), with a good positive correlation between Nd and Er (R^2=0.87) (Fig. 3D), indicating that the influence of detrial materials in limestone are reliable, especially in GL.

Diagenesis would change the values of Ce and Eu anomaly, along with good correlations between Ce/Ce^* and REE, and between Ce/Ce^* and Eu/Eu^*(Liu, 2006). As shown in Fig. 3 (G, H), there are no significant correlations or weak correlations between the Ce/Ce^* and REE, and between Ce/Ce^* and Eu/Eu*, suggesting that the affection of diagenesis process on the REE concentrations is limited.

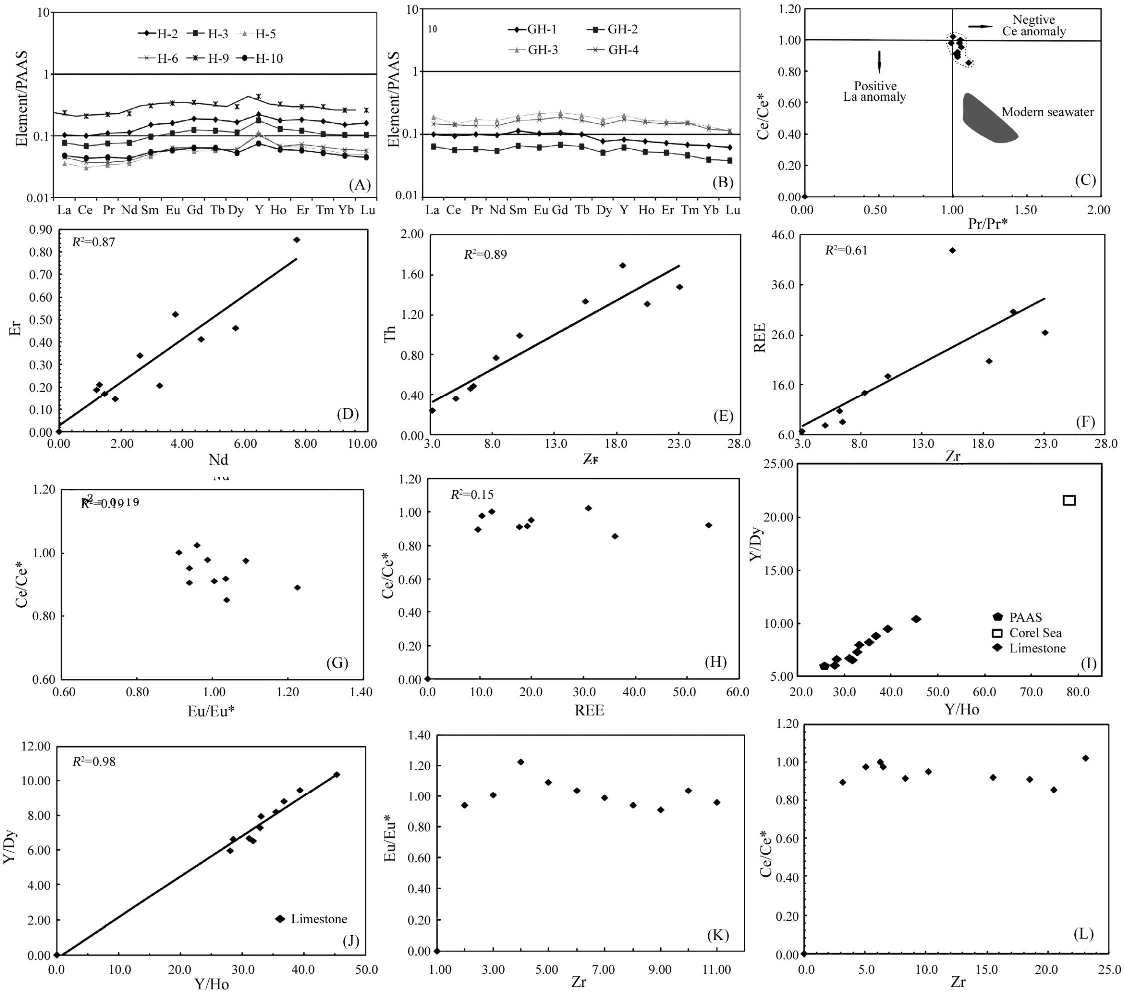

Fig. 3. Diagrams of REE and related values of the Late Neoproterozoic limestone from northern Anhui Province, China.

4.2 Y/Ho

Yttrium is inserted between Ho and Dy in the REE pattern according to its identical charge and similar radius (Bau, 1996). The terrigenous materials and volcanic ash have constant chondritic Y/Ho ratio of ~28, and seawater generally displays high Y/Ho ratios (44–74). Y/Ho ratios express a significant variation among the open-ocean seawater and the ocean margin seawater (Nozaki, 1997). Although Y and Ho have similar ionic radius, identical charge and thus similar geochemical behaviour, Ho is removed from seawater twice as fast as Y, because of the differences in the surface complexation behavious (Nozaki, 1997). Thus, the Y/Ho ratios are different between marine and non-marine deposits (Bau, 1996; Northdurft, 2004).

As showed in Fig. 3(I, J), the Y/Ho ratios in the limestone are between those of the PAAS and Corel Sea, indicating that the limestone preserves the seawater information, though contaminated by the influence of terrigenous materials. The Y/Ho ratio and Y/Dy ratio are ranging from 28.02 to 45.29 and 5.97 to 10.39, respectively. The higher Y/Ho ratio, with a good positive correlation between Y/Ho and Y/Dy indicates that these limestones inherit the seawater characteristics.

4.3 Europium and cerium anomaly

Eu is the only REE showing a changing valency in the near surface environment, where Eu^{3+} was reduced to Eu^{2+} under extremely reducing conditions. Redox potential of Eu/Eu^* in aqueous solutions depends mainly on temperature and to a lesser extent on pressure, PH, and REE speciation (Bau, 1996), which explains that the positive Eu anomalies are typically found in acidic, reducing hydrothermal fluids.

In this study, the samples display a large variations in Eu/Eu^*, ranging from 0.94 to 1.23 in WL, and 0.91 to 1.04 in GL (normalized by PAAS values; Table 1). Positive Eu anomalies are uncommon in seawater, which is generally resulted by these actors: (1) an increased oceanic input of hydrothermally originated fluids at mid oceanic ridges (German, 1999); (2) a slight increase in the primary or detrital feldspar component (Madhavaraju, 2010); and (3) the diagenetic alteration in the limestone (Brand, 1980).

Elements like Zr and Th are useful for understanding the presence of detrital feldspar in the bulk sediments. As shown in Fig. 3 (K), the Eu/Eu* ratios do not show a good correlation with Zr, which suggests that the positive Eu anomaly in the limestone may not be due to the detrital inclusion. Weak or no correlations between Ce/Ce^* and Eu/Eu^*, and between Ce/Ce^* and REE (Fig. 3 G, H) also suggest that the affection of diagenetic process on REE concentrations is limited. Hence, we consider that the positive Eu anomalies are produced by the hydrothermal activity in the Neoproterozoic, and this view is supported by previous research (Sun, 2011).

Ce anomaly is mainly observed in the seawater (Elderfield, 1982), and the values of Ce anomalies in marine limestone provide important aspects of the geological record, i.e., terrigeous input and redox condition at the time and place of deposition (Madhavaraju, 2009, 2010). The light negative Ce anomalies could suggest that these limestones were deposited in oxygenated environment, for the terrigeous input is limited from the Fig. 3 (L).

5 Conclusions

The REE contents in the limestones of the Late Neoproterozoic are low compared with recent marine sediments, with an average value of 22.93 mg/kg. The PAAS-normalized REE+Y patterns of limestone are characterized by (1) light REE depletion in WL, and the opposite in GL; (2) a light negative Ce anomaly and positive La anomaly; and (3) positive Eu anomaly and Y anomaly.

There are few different characteristics of REE between GL and WL, including: (1) The positive Y anomaly in GL less than that in WL; (2) the Er/Nd ratios values in GL ranging from 0.06 to 0.09, while those in WL ranging from 0.11–0.16; and (3) the lowest and the highest Y/Ho ratios values in GL being 32.87 and 45.29, whereas those in WL being 28.02 and 31.74, respectively.

The REE+Y pattern of limestone mostly shows original characteristics, though some of them are modified by detrital input into the system, which is also the possible source of REE. The diagenetic process on the limestone REE concentrations is limited for the correlations between Ce/Ce^* and Eu/Eu^*, and between Ce/Ce^* and REE are weak. The light positive Eu and negative Ce anomalies could be produced by hydrothermal activity in the Neoproterozoic and oxygenated environment, respectively.

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