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## RARE EARTH ELEMENTS IN LATE PRECAMBRIAN PHOSPHORITES\*

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**Abstract:** Rare earth elements (REE) concentrations in nine phosphorite samples and three phosphatic fossils, including two phosphatic acritarchs and one phosphatic oncolite, from the Late Precambrian Doushantuo Formation in Guizhou Province were determined. The REE distribution patterns are similar to that of the sea-water and reflect the original REE signatures of the sea-water at that time. Cerium variations in phosphorites and fossil apatites are controlled by redox conditions. Weak to moderate negative Ce anomalies(0.543-0.805) and Ce/La ratio values(1.10-1.81) suggest that the original phosphogenic environment might be suboxic.

**Keywords:** Rare earth element, Phosphorite, Late Precambrian, Weng'an, Guizhou.

### INTRODUCTION

The rare earth elements (REE) include the fifteen elements of the lanthanides including the element lanthanum (La) and the fourteen elements that follow La and yttrium (Y) in the periodic table, which form a very coherent group because of the lanthanide contraction and have similar chemical properties, although two elements, cerium (Ce) and europium (Eu), may develop anomalies due to changes in their oxidation states (Henderson, 1984).

The most stable oxidation state of all lanthanides is the REE (III) form. The gradual filling of the inner 4f shell with increasing atomic number leads to gradual changes in chemical properties. Such gradual changes of properties in aqueous solution make the REE series a unique group of elements in marine chemistry (De Baar, *et al.*, 1985).

The Ce<sup>4+</sup> and Eu<sup>2+</sup> cations represent the only other kind of geochemically important oxidation states. These different valences lead to distribution anomalies compared to the strictly trivalent REE. Cerium may exhibit anomalies in sea-water due to oxidation to quadrivalent Ce<sup>4+</sup> which is virtually insoluble in aqueous solution, and thus Cerium depletion by comparison with neighbouring La and Pr has been found exclusively within the ocean basin (Elderfield, *et al.*, 1982; De Baar *et al.*, 1985), while ferromanganese nodules often show a cerium enrichment (Piper, 1974b; Fleet, 1984). Accordingly, cerium is particularly interesting and useful because its anomaly can be easily and quantitatively defined by comparison with the strictly trivalent neighbors in the REE series.

REE varies consistently in marine waters owing to various inputs and controls of REE behaviour. The major input of REE into the oceans is thought to be by rivers that derive their REE from the weathering of continental rocks. Eolian transport may be an additional source of REE into the oceans (Elderfield, *et al.*, 1982), and submarine volcanogenic input of REE into the oceans may be relatively minor and its distribution restricted (Piper, 1974). Removal of REE from the sea-water column to the

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sediments is dominated by scavenging on settling particles (De Baar, *et al.*, 1985; Murry, *et al.*, 1990). Minor portion of REE in sea-water may be removed by incorporation in the crystal matrix of skeletal material, and this phase, by and large, would record the sea-water pattern at the time of deposition (Palmer, 1983).

Researches on REE in phosphorite and fossil apatite have been reported by many authors (Goldberg *et al.*, 1963; Altschuler, *et al.*, 1967; Piper, 1988, 1991; Hein, *et al.*, 1993; McArthur, *et al.*, 1984; Wright, *et al.*, 1987; Grandjean, *et al.*, 1993). They have studied the distribution patterns and chemical properties of REE in phosphorites of different ages, from Paleozoic phosphorite to modern ocean phosphorite nodules. The results indicate that most of the phosphorites exhibit a pattern similar to that of the sea-water, with negative Ce anomalies and a slight heavy REE enrichment, except the Devonian phosphorite and phosphate conodonts, which exhibit a "Cap-like" REE pattern (middle REE enrichment). However, very few data on REE in phosphorite of Precambrian have been reported up to now.

This paper will present the REE data of phosphorites and phosphatic fossils from the Late Precambrian Doushantuo Formation at Weng'an Phosphorite Deposit in Guizhou Province, and discuss briefly the implications of REE geochemistry on Late Precambrian oceanic environments.

## SAMPLES

Eleven representative samples, including eight phosphorite samples and three phosphatic fossil samples, were collected from the upper member of the Late Precambrian phosphorite-rich Doushantuo Formation at Weng'an Phosphorite Deposit, Guizhou Province (for locality and stratigraphy, see Yin *et al.*, 1993). The phosphorite samples are mainly dolomitic phosphorites. Thin sections of samples show that intraclastic phosphorites, hardground phosphorites and algal phosphorites are the main rock types of the phosphorite-bearing sequences. All the phosphorites have few terrigenous components. Algal phosphorites and hardground phosphorites have more dolomitic matrix or interbedded phosphatic dolostone, so their  $P_2O_5$  content and  $\Sigma REE$  are lower than those of intraclastic phosphorites which are made up of phosphatic intraclasts and less matrix of dolomite and/or phosphate or even silicate, therefore, their  $P_2O_5$  content increase reasonably with the reduction of dolomite contents.

Three phosphatic fossil samples, including two acritarch samples (W049b, W143b) and one oncolite sample (W156), were recovered from the dolomitic phosphorites by the acid maceration method. They were separated from the dolomite matrix by dissolution in about 15% acetic acid, and fossils in the insoluble residue were collected by hand-pick. The results of Electron Probing Analysis of fossil apatites show that the fossils are composed of nearly pure apatite.

## METHODS

The REE in these samples has been measured on a Inductively Coupled Plasma Spectrometer (ICP) at the Modern Analytical Centre of Beijing University.

REE data are normalised to the North American Shale Composite Standard (Gromet, *et al.*, 1984) to remove the odd-even effect of elemental abundances, The NASC normalised REE abundances are plotted on a logarithmic scale vs. atomic number on a liner scale. The main variation discussed here is the enrichment or depletion of Cerium relative to measured neighbouring elements. The Ce

variation can be stated mathematically by:  $Ce_{anom.} = 2Ce_N / (La_N + Pr_N)$ , where "N" signifies shale-normalised concentrations (De Baar, *et al.*, 1983).

## RESULTS

Fig.1 presents the REE data on phosphorites and fossil apatites determined in this study. All the analyzed samples show a strikingly uniform shale normalised REE distribution patterns, with a slight heavy REE enrichment relative to light REE, and a moderate negative Cerium anomaly. Fig.1 also shows that fossil apatite samples closely resemble the NASC normalised REE distribution patterns of their mother rocks, and the only difference is a remarkable increase in the concentration of each REE (Tab. 1).

Table 1 REE data of phosphorites and fossil apatites

	W4	W037	W049a	W049b	W059	W072	W136	W143a	W143b	W156	Y064
La	13.22	35.69	6.58	12.00	8.04	7.30	18.66	12.84	23.56	68.50	33.88
Ce	18.82	49.20	11.91	18.53	13.14	11.81	24.03	20.32	32.84	75.35	39.85
Pr	4.84	10.20	2.42	4.14	1.89	2.32	4.53	4.66	7.13	16.00	9.25
Nd	21.46	40.10	9.84	22.17	7.50	10.73	19.62	20.49	31.24	70.40	41.70
Sm	4.27	8.42	2.74	6.28	1.66	2.64	5.27	4.88	7.81	14.10	9.76
Eu	0.97	1.96	0.51	1.24	0.47	0.59	1.27	1.04	2.01	2.63	2.22
Gd	5.20	10.80	3.01	6.90	1.92	2.91	6.23	5.28	8.96	12.10	10.70
Tb	0.78	1.39	0.44	1.07	0.32	0.41	0.95	0.77	1.36	1.67	1.60
Dy	4.48	6.91	2.46	5.97	1.76	2.48	5.35	4.31	7.93	9.15	9.07
Ho	1.00	1.60	0.62	1.25	0.42	0.61	1.20	1.02	1.72	1.98	1.89
Er	2.64	4.24	1.81	3.19	1.35	1.85	3.28	2.45	4.46	5.37	4.60
Tm	0.42	0.57	0.26	0.45	0.20	0.28	0.43	0.33	0.58	0.71	0.67
Yb	1.88	2.32	1.42	2.05	1.00	1.36	2.07	1.70	2.71	3.36	3.51
Lu	0.24	0.33	0.21	0.30	0.16	0.21	0.29	0.26	0.37	0.55	0.51
Y	34.24	55.55	15.91	44.77	11.22	19.79	44.80	37.96	68.46	82.30	67.63
ΣREE	114.46	229.30	60.14	130.31	51.08	65.29	137.98	118.31	201.16	364.14	236.83
δCe	0.54	0.61	0.69	0.61	0.79	0.67	0.61	0.61	0.59	0.53	0.53
Ce/La	1.42	1.38	1.81	1.54	1.63	1.62	1.29	1.58	1.39	1.10	1.18

The ΣREE of phosphorites and fossil apatites vary from  $51.08 \times 10^{-6}$  to  $364.14 \times 10^{-6}$ , with a mean of  $156.36 \times 10^{-6}$ . Obviously, the ΣREE is corresponded with the  $P_2O_5$  content. The lowest total is for dolomitic phosphorite (W059), and the highest total is for phosphate oncolite (W156) (Table 1).

The Ce/La ratios, ranging from 1.10 to 1.81 (Tab. 1), are in agreement with the Ce/La ratios of phosphorite from Pleistocene to now, such as apatite pellets from of the Peru shelf, with a Ce/La ratio of 1.18 (Piper, *et al.*, 1988), but smaller than the mean ratio of 4.63 of the Devonian nodular concretions from New York State (McArthur, *et al.*, 1984), and also smaller than those of Devonian phosphate conodonts (Grandjean, *et al.*, 1993). The Ce anomaly values of our samples range from 0.543 to 0.805, with a mean of 0.643, exhibit a weak to moderate negative Ce anomaly.

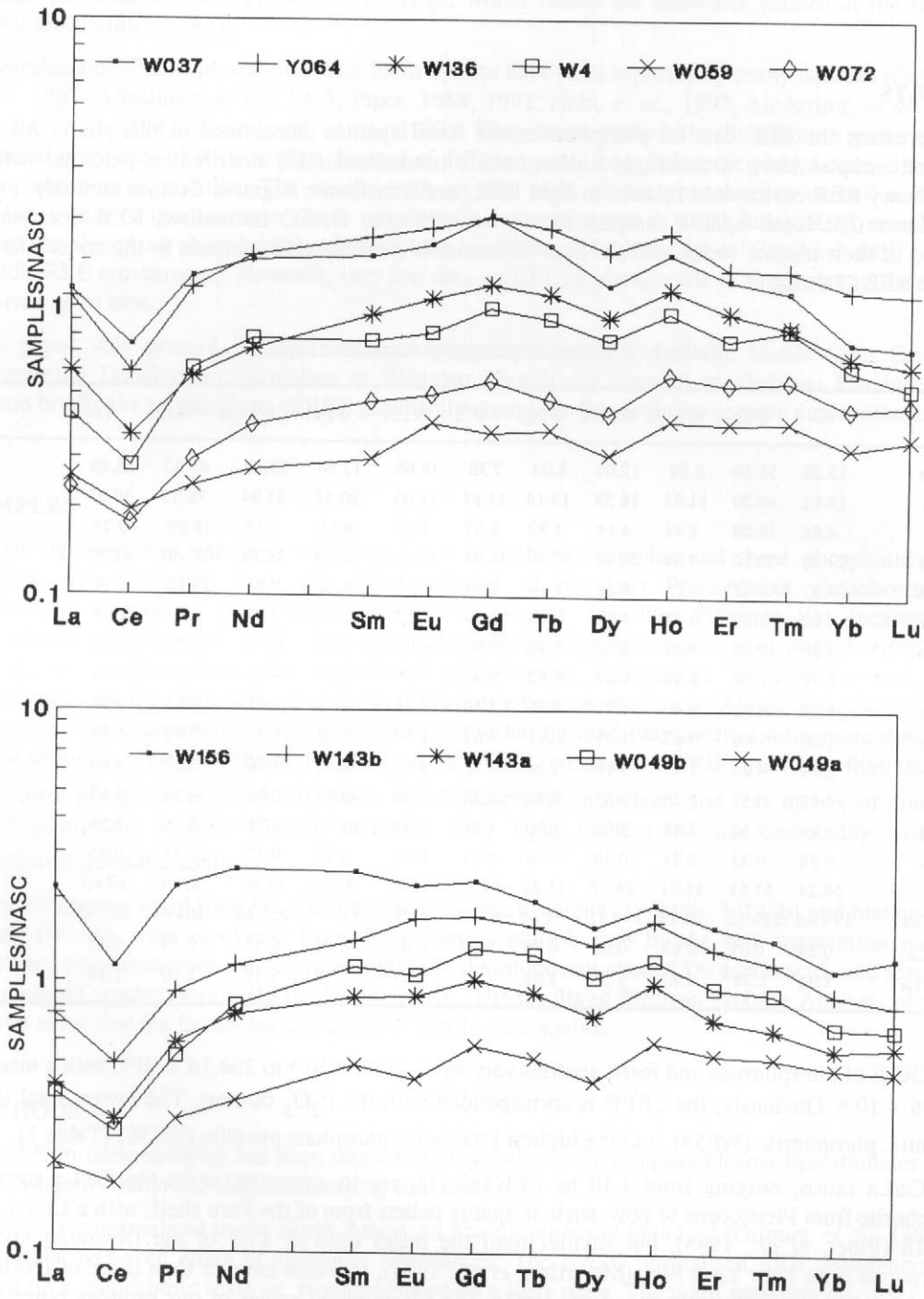


Fig. 1 NASC-normalised REE patterns of phosphorites and fossil apatites

## DISCUSSION

### REE characteristics of phosphorite

To summarize, regardless of  $\Sigma$ REE, the NASC normalised REE patterns of phosphorites and fossil apatites are nearly identical to those reported for the present sea-water. This suggests that these patterns might be the result of incorporations of the REE directly from sea-water, or from pore-water after early burial diagenetic remobilization of REEs from a REE carrier which has itself incorporated REEs directly from sea-water (McArthur, *et al.*, 1984). Because of the similarities of REE characteristics of all samples, it seems that the REE in Precambrian phosphorite might reflect the original features of the ocean water at that time.

In general, the correlation of  $\Sigma$ REE with sample age is that the REE of the Late Precambrian phosphorites is lower than those of the Early Cambrian, Devonian, Permian and late Cretaceous to Pleistocene, and higher than those from post-Pleistocene to modern ocean phosphate nodules (Ge Dingyi, *et al.*, 1989; McArthur, *et al.*, 1984).

The REE data of phosphorites of different ages from Devonian to Recent provided by McArthur, *et al.* (1984) apparently indicate that the REE abundances generally increase with the age of samples. This may be interpreted as that older samples could have more time to incorporate REE after deposition than the younger ones. Studies on Quaternary phosphorites (McArthur *et al.*, 1984; Piper *et al.*, 1988) suggest that phosphorites are usually formed with low REE abundance. During the formation, the REE may be incorporated from sea-water, or from organic matter or clastic debris via remobilization into porewater (Elderfield, 1987). During burial and late diagenesis, phosphorites continue to incorporate REE from these sources. The REE of phosphorites is not simply an instantaneous recorder but instead it reflects an accumulative procedure through time. However, the REE of our samples is lower than the known Paleozoic and Mesozoic results. It seems possible that the REE of depositional environment could be the principal factor on the REE concentration of phosphorites, while post-depositional enrichment or reduction of each REE might also influence the REE pattern but probably of less significance.

The Ce/La ratios of phosphorites in the present study resemble the sea-water values just over the oxygen minimum zone previously reported from the VERTEX2 site of the Pacific Ocean (18°N, 108°W) and a site of the North Atlantic Ocean (De Baar, *et al.*, 1985; Elderfield, *et al.*, 1982). These similarities indicate that the REE could have been derived from the sea-water, probably over the oxygen minimum zone.

Y.G. Liu and R.A. Schmitt (in Grandjean, 1993) have determined the REE patterns of several hundred samples of CaCO<sub>3</sub> oozes, chalks, and limestones deposited over the past 500 Ma in the oceans of the world. The data suggest that the REE patterns of the sea-water have not changed significantly over the past 500 Ma. Most of the phosphorites of the Cambrian, Permian, Late Cretaceous, Tertiary and Recent display a REE pattern similar to that of the present sea-water, with negative Ce anomalies and slight HREE enrichment (Ge Dingyi, *et al.*, 1989; McArthur, *et al.*, 1984; Piper, *et al.*, 1988). But REE distribution patterns of phosphorites and fossil apatites (e.g., phosphatic conodonts) of the Devonian are nearly uniform, with a middle REE enrichment unlike samples of other ages.

### Cerium anomaly and paleoredox

The cerium behaviour in the oceans is apparently controlled by oxidation/reduction conditions, since Ce has two possible oxidation states, Ce<sup>3+</sup> and Ce<sup>4+</sup>. The chemical and physical parameters that govern rare earth element behaviour have been discussed for the ocean system by Piper (1974a),

Elderfield *et al.* (1982) and De Baar *et al.* (1983, 1985a). In the oxygenated midocean waters, the oxidation of  $Ce^{3+}$  to relative insoluble  $Ce^{4+}$  allows the preferential removal of Ce from the sea-water, resulting in sea-water with a pronounced negative Ce anomaly. Accordingly, the negative Ce anomaly values indicate oxidizing conditions, and the positive ones, showing normal to enriched, unfractionated cerium concentrations, suggest anoxic conditions of the sea-water.

Cerium anomalies of the sea-water have been proved to be helpful to constraining the position of the boundary between oxic and anoxic conditions. De Baar *et al.* (1988) described the REE features of anoxic waters of the Caricaco Trench and found that all REE, notably Ce, exhibit a sharp increase just at or below the oxic/anoxic interface at the depth of 300 meters, with the overlying oxic water of a negative Ce anomaly and the underlying anoxic water of a weak positive Ce anomaly. In the East Pacific (at 18°N, 108°W), the negative Ce anomaly exist through the whole water column and increases downward, with very strong cerium depletion in the bottom water (De Baar, *et al.*, 1985a). A profile in the Sargasso Sea, Western Atlantic, exhibits negative Ce anomalies except for the sea-water of the upper 491 meters, which carries pronounced positive Ce anomalies (De Baar, *et al.*, 1983) owing to the input of cerium from reducing inshore sediments.

Cerium of fossil apatites appears to be a reasonable paleochemical indicator of variations in redox conditions of water column (Wright, *et al.*, 1987). The REE patterns of modern fish debris reflect redox conditions at the time of deposition because their REE contents remain unchanged during subsequent burial and diagenesis.

The negative cerium anomaly values of our samples imply that phosphorites formed originally in the slightly oxygenated depositional sea-water or pore-water environment, and phosphatic acritarchs and oncolites and other fossil apatites acquired REE content postmortally from suboxic sea-water. The above conclusion is supported by observation and study on stratigraphical sequence and sedimentary features, which indicate a shallow marine environment.

Cerium anomaly has often been proposed as a tracer for large scale marine anoxic in ancient oceans, this application certainly has potential, but understanding of exact reaction mechanism of Ce in marine environment is required (De Baar, *et al.*, 1988).

## CONCLUSIONS

1. NASC normalised REE distribution patterns of phosphorites and fossil apatites from the Late Precambrian Doushantuo Formation show slight heavy REE enrichment and weak to moderate negative Cerium anomalies, and nearly identical to that of the sea-water, indicating that REE in those samples reflect the REE features of the Late Precambrian ocean water.
2. Cerium variations in marine environment could be controlled by the redox potential. The negative values of Cerium anomalies (0.543-0.805) and Ce/La ratio values (1.10-1.81) in our samples imply that phosphorites originally formed in suboxic ocean environment just over the oxygen minimum zone and phosphatic acritarchs and oncolites acquired REE contents from suboxic sea-water, and REE signatures were unchanged during burial and diagenesis.

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