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Geochemical characteristics of rare earth elements in Wuhan section of the Yangtze River*

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Abstract—The contents and speciation characteristics of rare earth elements (REE) in Wuhan section of the Yangtze River were analysed by neutron activation analysis (NAA). The contents of solvable fraction of REE in the river are very limited, with the same results as other rivers. On the other hand, the content of suspended fraction of REE in the river varies in a wide range. It varies with the variation of suspended matter in the water. The distribution patterns showed significant light REE enrichment and relative Eu - depletion. The speciation characteristics of REE in the sediments or suspended matter are quite similar, with the main amount in residual form. The amount of five forms obey the following order: residual>>bound to organic matter, bound to Fe - Mn oxides>bound to carbonates>>exchangeable. Compared with light and heavy REE, the mediate REE (Eu, Sm, Tb) have relatively low percentages in the residual form and high in the forms of bound to organic matter and Fe - Mn oxides. The water bodies in Wuhan section of the Yangtze River have not been polluted by REE.

Keywords: geochemical characteristics; rare earth elements; Yangtze River

1 Introduction

There are very abundant resources of rare earth elements (REE) in China. Mining, industrial and agricultural usages of REE are increasing rapidly. Since 1970s, quantity of REE has been the first for industrial usages, and the fourth for agricultural usages. Since 1990, REE fertilizer has been widely used in more than 20 provinces of China, and it has caused some problems to the terrestrial and aquatic environments. But there are very few studies focused on the environmental behavior and biological effect of REE. In the recent years, studies on the background values of REE in water and sediments in the Yangtze River system have been carried out (Xie, 1991; Zhang, 1983). It is seldom to study the REE characteristics for treating water, suspended matter, and sediments in a whole circulatory system, and the study of REE speciation in water body is even less.

Samples of water (raw and filtered), suspended matter, and sediments were taken from Wuhan section of the Yangtze River simultaneously and at the same sites. Speciation study has

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been carried out for suspended matter and sediments. Contents were detected by neutron activation analysis(NAA Laboratory, 1992). The distribution patterns and speciation characteristics of REE in the water body have been studied as well as the geochemical relationships of REE among water, suspended matter and sediments. Some reliable foundation for the environmental impact assessment and reasonable usages of water resources of this section should be proposed

2 Method

2.1 Sampling locations

Two sampling sites were located at the upper and lower reaches of Wuhan (Zhuangkou and Yangluo). The sites were far away from industrial pollution area and municipal wastewater outlets.

2.2 Sampling and sample preservation

Samples of water, suspended matter and sediments were taken simultaneously. Raw water were preserved for the total amount of REE. Filtered water through 0.45 μm filtration membrane were preserved for detecting the dissolved fraction of REE. Both raw water and filtered water were preserved under pH 2 by HNO_3. Suspended matter were taken from the membranes directly. The fractions of suspended matter and sediments were passed through a 20 mesh sieve for speciation analysis. For detecting the total content of REE, the fractions of suspended matter and sediments were also ground until all the samples passed through a 100 mesh sieve.

2.3 Method for speciation

According to the chemical characters of REE and characteristics of NAA, the improved Tessier method(1979) were used for speciation analysis of suspended matter and sediments. Five forms were extracted: exchangeable; bound to carbonates; bound to Fe - Mn oxides; bound to organic matter; and residual(Table 1).

Table 1 Sequential extraction method of REE in suspended matter and sediments

No.	Form	Extraction reagent	Extraction method
1	Exchangeable	1 mol/L $MgCl_2$, pH 7	Vibration 1 hour(25℃)
			Centrifugation 20 min.
2	Bound to carbonates	1 mol/L NH_4Ac	Vibration 5 hours(25℃)
		pH 5 adjusted by HAc	Centrifugation 20 min.
3	Bound to Fe—Mn	0.04mol/l $NH_2OH \cdot HCl$	95℃ heating in water bath
	oxides	with 25% HAc	vibration 5 hours; centrifugation 20 min.
4	Bound to organic matter	6ml 0.02mol/L HNO_3 and 10ml 30% H_2O_2, then 8ml 30% H_2O_2	86℃ heating in water bath for 2 hours Vibration and heating for 5 hours
		10ml 3.2mol/L NH_4Ac	Vibration 0.5 hour
			Centrifugation 20 min.
5	Residual	NAA direct measure	Oven dry

Note: Forms 1, 2, 3, 4 were unstable forms; forms 2, 3, 4 could be transformed into biological available form under some conditions; form 5 was stable. The speed of centrifugation was 3500 r/min

2.4 Analysis method

The REE samples of water, suspended matter and sediments in five forms were detected by

NAA. Samples were irradiated by a nuclear interaction heap, and analysed by Ge(Li) detector-multichannel analysor—personal computer system. The quality ensurement methods were used throughout sampling, sample treatment, extraction and detection(Wang, 1992).

3 Results and discussion

3.1 Contents of REE in the aquatic body

3.1.1 Contents of REE in river water

Contents of REE in Wuhan section of the Yangtze River have the following characteristics: (1) Concentrations of dissolved fraction of REE are very limited, with the range of $n\times10^{-3}$— $n\times10^{-1}\mu g/L$. The levels are similar with the Yangtze River system(Table 2). This is probably correlated with the high pH value(>8) of Yangtze River. In the alkaline condition, compounds of REE are very difficult to be dissolved , whereas very easy to be adsorbed by suspended matter. The REE dissolved in the Wuhan section of the Yangtze River follow the order: Ce>La>Nd>Sm>Eu, Yb, Tb, Lu. This shows that light REE is more solvable than heavy REE. (2) REE exist mainly in the suspended fraction. Concentrations of REE in raw water vary between $n\times10^{-2}$—$n\times10^{-1}\mu g/L$. These are much higher than those in the dissolved fraction. The concentrations were also much higher than background values of the Yangtze River system and most rivers in the world. Contents of REE in the suspended fraction contain more than 80% of total amount. This shows in the muddy water of Wuhan section of the Yangtze River, REE exist mainly in the suspended fraction, and varied with the contents of suspended matter in river water. Nevertheless, the order of REE concentrations in the Wuhan section of the Yangtze River are consistent with those in the Yangtze River system and most rivers in the world, that is Ce>La, Nd>Sm>Yb>Eu>Tb, Lu. The order is consistent with the abundances of REE in the crust (Table 3), showing contents of REE in suspended fraction are controlled by their abundance of in the crust. The distribution pattern is similar with that of the crust, showing enrichment in the light REE. (3) Concentrations of REE in the upper and lower reaches of Wuhan are quite similar, for both dissolved and suspended fractions, only with the exception of dissolved Lu. This shows that industrial wastes and municipal sewages influence on the REE in Yangtze River water insignificantly.

Table 2 Contents of REE in water phase in Wuhan section of the Yangtze River

Unit: μg/L

Element	Uper reaches(Zhuangkou)				Lower reaches(Yangluo)				Average			
	D	T	T/D, %	S/T, %	D	T	T/D, %	S/T, %	D	T	T/D, %	S/T, %
La	0.040	2.4	1.7	98.3	0.04	1.6	2.4	97.6	0.40	2.0	2.0	98.0
Ce	0.18	5.0	96.4	96.4	0.19	3.2	5.9	94.1	0.19	4.1	5.6	94.4
Nd	0.2	2.0	10.1	9.9	0.2	1.6	12.5	87.5	0.2	1.8	11.1	88.9
Sm	0.016	0.39	4.1	96.9	0.017	0.28	6.07	93.9	0.017	0.34	5.0	95.0
Eu	0.007	0.098	7.1	92.9	0.006	0.069	8.7	91.3	0.006	0.084	7.1	92.9
Tb	0.01	0.070	14.3	85.7	0.01	0.034	29.4	70.6	0.01	0.052	19.2	80.0
Yb	0.006	0.16	3.8	96.2	0.006	0.12	5.0	95.0	0.006	0.14	4.3	95.7
Lu	0.002	0.029	6.9	93.1	0.005	0.021	23.8	76.2	0.003	0.024	12.0	88.0

Notes: D—dissolved fraction; T—total; S—suspended fraction

Table 3 Contents of REE in water phase of various rivers

Unit: μg/L

Water type	River name	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Water	Wuhan section of the Yangtze River	2.0	4.1	1.8	0.34	0.084	0.053	0.14	0.025
	The Yangtze River system	0.24	0.49	0.26	0.055	0.011	0.008	0.017	0.004
	World fresh water average values	0.1	0.2	0.2	0.06	0.006	0.003	0.01	0.003
Filtered water	Wuhan section of the Yangtze River	0.035	0.19	0.02	0.017	0.007	0.01	0.006	0.003
	The Yangtze River system	0.05	0.22	0.07	0.023	0.004	0.004	0.008	0.002

Table 4 Comparison of REE contents between upper and lower reaches of Wuhan section of the Yangtze River

Item	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Lower/Upper dissfolved	1.0	1.06	1.0	1.06	0.86	1.0	1.0	2.50
Lower/Upper total	0.67	0.64	0.80	0.72	0.70	1.0	1.0	0.72

3.2 Geochemical characteristics of REE in the suspended matter and sediments

3.2.1 Contents

Contents of REE in suspended matter and sediments in Wuhan section of the Yangtze River are quite similar (Table 5), with the range of $n\times10^{-1}-n\times10^{2}$mg/kg. This result is consistent with those in the Yangtze River system (Zhang, 1983) and average values of sediments in the world (Table 6). But light REE such as La, Ce, Nd, Sm in sediments in Wuhan section of the Yangtze River are slightly low, while heavy REE such as Yb, Lu are a little bit high. The contents of REE follow the order: Ce>La>Nd>Sm>Yb>Eu, Tb>Lu.

3.2.2 Distribution pattern

Chondrite normalized REE distribution patterns have been commonly used (Wang, 1989; Haskin, 1968). The chondrite - normalized patterns of REE in suspended matter and sediments are shown in Fig. 1. It is obvious that the distribution patterns of REE in the upper reaches of Wuhan section of the Yangtze River are similar with those in the lower reaches, and also similar in suspended matter and sediments. All the curves have a minus slope. The section from La to Eu are rather gentle, and there are valleys caused by Eu - depletion. Both suspended matter and sediments have Eu - depletion phenomena. The non - detected REE were made up from linear interpolation in the normalized lines. The statistical results are listed in Table 7. The LREE/HREE values in sediments have a mean value of 9.69, and in suspended matter, 8.89. Eu/Eu * varies between 0.48—0.74. This shows that the distribution patterns of REE in suspended matter and sediments have the type of light REE enrichment and moderate Eu - depletion. The distribution pattern of REE in suspended matter and sediments are similar with that of average values of world shales (Fig. 1), with the total REE contents of 200—300mg/kg. This shows that suspended matter and sediments in Wuhan section of the Yangtze River have the typical REE features of sedimentary rock of shales. It is supposed that suspended matter and sediments are a mixture for all kinds of rocks in the drainage area through weathering and transportation processes. The weathering products in the drainage basin are carried into the river, and they are sedimented and resuspended over and over. The process of REE's transportation from suspended matter to sediments is mainly a physical process, rather than chemical and biological processes. Differences between suspended matter and sediments are thus quite little for REE.

Table 5 Contents of REE in suspended matter and sediments in Wuhan section of the Yangtze River

Element	Suppeded matter(SM)			Sediments			SM/Sediments			World shales
	Upper	Lower	Avg.	Upper	Lower	Avg.	Upper	Lower	Average	
La	45	45	45	47	49	48	0.96	0.94	0.95	41
Ce	89	87	88	91	97	94	0.98	0.90	0.94	83
Nd	41	45	43	45	40	43	0.91	1.13	1.00	38
Sm	6.1	6.2	6.2	6.3	6.7	6.5	0.97	0.93	0.95	7.5
Eu	1.42	1.40	1.41	1.07	0.97	1.02	1.33	1.44	1.38	1.61
Tb	1.00	1.10	1.05	1.20	0.96	1.08	0.83	1.15	0.97	1.23
Yb	2.4	2.5	2.5	2.4	2.3	2.4	1.00	1.09	1.04	3.5
Lu	0.40	0.40	0.40	0.37	0.38	0.38	1.08	1.05	10.5	0.6

Table 6 Comparison of REE content in river sediments of Wuhan section with other rivers

River	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Wuhan section of the Yangtze River	48	94	43	6.5	1.02	1.08	2.4	0.38
Background values of the Yangtze River	47	87	43	7.1	1.3	1.0	2.9	0.42
World sediments average	41	83	32	3.4	1.2	1.0	3.6	0.70

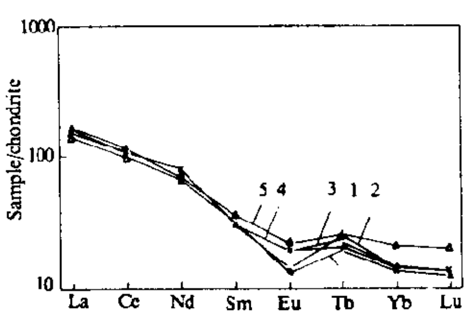

Fig. 1 REE patterns in suspended matter and sediments in Wuhan section of the Yangtze River

1. Sediments of upper reaches
2. Sediments of lower reaches
3. Suspended matter of upper reaches
4. Suspended matter of lower reaches
5. World shales

3.3 Speciation characteristics of REE in suspended matter and sediments

Five forms of REE in suspended matter and sediments were extracted by the method described in Table 1. From 1 to 4 are called "unstable forms", some of them are biologically available, while other can be transformed into biologically available forms. Form 5, existing in crystal lattices, is called "stable form". It is non-biologically available.

Percentages of five forms of REE in suspended matter and sediments of Wuhan section of the Yangtze River are diagramed in Fig. 2. The stacked-bar graph is presented in Fig. 3. The speciation characteristics of REE in suspended matter and sediments are shown in Table 7.

Table 7 REE parameters of suspended matter and sediments in Wuhan section of the Yangtze River

Sample type	Sample site	ΣREE	ΣLREE	ΣHREE	ΣLREE/ΣHREE	δEu*
Sediments	Zhuangkou	223.8	201.4	22.4	8.98	0.516
	Yangluo	223.8	204.4	19.4	10.53	0.483
	Average	223.8	202.9	20.9	9.69	0.500
Suspended matter	Zhuangkou	214.1	192.9	21.2	9.09	0.743
	Yangluo	218.9	196.4	22.6	8.71	0.702
	Average	216.5	194.7	21.9	8.89	0.723
North America shales		200	152.8	20.4	7.50	

Note: δEu is the ratio of measured content of Eu and content of Eu calculated from the normalization lines by linear interpolation supposing that there is no - Eu depletion

3.3.1 Similarities of distribution of five forms among REE

Contents of five forms of REE in both suspended matter and sediments follow the order: 5>4>3>2>1 (Fig. 2). Firstly, residual form has the highest content, ranging from 60% to 80%; secondly, contents of bound to organic matter and bound to Fe - Mn oxides forms are similar, ranging from 5% to 20%. In most cases, content of bound to organic matter form are slightly higher than that of bound to Fe - Mn oxides form. Contents of bound to carbonates are little, with the proportions of < 5% in most cases. Contents of exchangeable form are trace, and only a few elements could be detected by NAA. It is concluded that REE exist mostly in the stable form, keeping a part of unstable form. The relative consistence of speciation characteristics of all REE is determined by the similar electronic structures and chemical properties of REE. Lanthanum series shrinkage has made the crystal chemical properties of REE more similar. For these reasons, these elements have similar geochemical behavior during mineralization, rocking, and weathering processes. Speciation results of this study shows that +3 va-

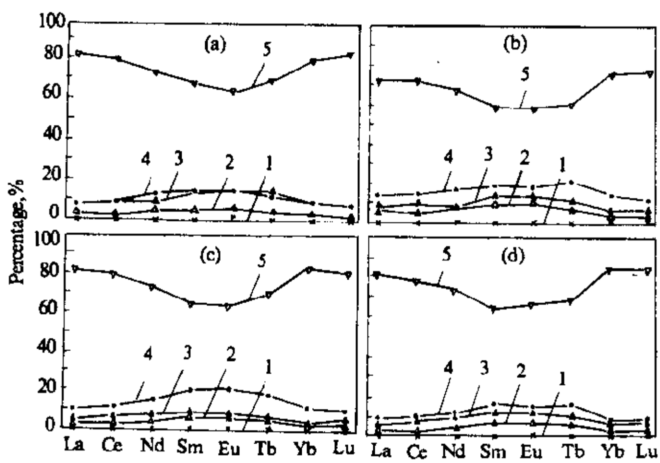

Fig. 2 Percentage of REE form in suspended matter and sediments in Wuhan section of the Yangtze River
a. sediments in upper reaches; b. sediments in lower reaches; c. suspended matter in upper reaches; d. suspended matter in low reaches 1. exchangeable; 2. bound to carbonates; 3. bound to Fe - Mn oxides; 4. bound to organic matter; 5. residual

lence cations of REE can be adsorbed onto the surfaces of clay minerals by hydroxyl groups in the form of hydrate ion, and can also produce complex compounds with the hydroxyl groups on the surface of Fe-Mn oxides by special adsorption (Ran, 1992), or form organic compounds with organic matter. These forms of REE can keep their geochemical properties during the transportation procedure with suspended matter and sediments.

3.3.2 Differences of proportions of five forms among REE

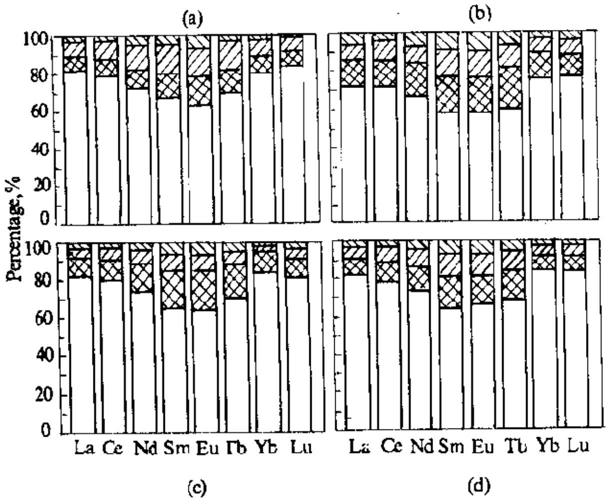

Fig. 3 Proportions of REE forms in suspended matter and sediments in Wuhan section of the Yangtze River (The legends are the same as in Fig. 2)

From Fig. 2 and Fig. 3, "V"-shape of percentage contents of residual forms of REE on the increase of atomic number in suspended matter and sediments can be seen. Mediate REE had less residual form contents than light and heavy REE. On the other hand, reverse "V"-shape of proportions of contents of bound to organic matter, Fe-Mn oxides and carbonates can be observed. Proportions of unstable forms of mediate REE (Sm, Eu, Tb) are higher than that of light and heavy REE. This indicated that the potential mobilities of mediate REE are great than light and heavy REE. The result remains to be explained. Perhaps it is connected with valence variation of mediate REE, especially for Eu.

4 Conclusion

Contents of REE in water, suspended matter and sediments in Wuhan section of the Yangtze River have the following characteristics:

Contents of dissolved fraction of REE in water are insignificant. It is coincident with other rivers; contents of suspended fraction of REE in water have a wide range, varying with contents of suspended matter in water; contents of REE in suspended matter and sediments are quite similar.

No significant differences of REE contents in water body between upper reaches and lower reaches of Wuhan are observed. This shows that the Wuhan section of the Yangtze River has not been polluted by REE.

The REE distribution patterns of suspended matter and sediments in Wuhan section of the Yangtze River have the type of light REE enrichment and moderate Eu-depletion, which is coincident with that of world shales.

Speciation characteristics of various REE in suspended matter and sediments in Wuhan section of the Yangtze River are similar, with the main proportions of residual form. Proportions of five forms of REE follow the order: residual>>bound to organic matter, bound to Fe - Mn oxides>bound to carbonates>>exchangeable. Compared with light and heavy REE, mediate REE have lower proportions of residual form, while higher proportions of bound to organic matter, bound to Fe - Mn oxides, and bound to carbonates forms.

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