GEOCHEMISTRY AND THEIR GENESIS OF RARE EARTH ELEMENTS OF FERROMANGANESE NODULES AND CRUSTS FROM THE SOUTH CHINA SEA

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ABSTRACT

Based on the X-ray fluorescence spectrum analysis of 15 rare earth elements in 6 ferromanganese nodules and 5 ferromanganese crusts from the South China Sea, their abundances, distribution patterns, sources and relationships with associated elements are discussed in detail in this paper. The results show that: 1) The average abundance of rare earth elements in ferromanganese nodules and crusts is 1.625 g / kg and 2.167 g / kg respectively, which is 1-2 times, 5-6 times and 15-20 times higher than that in the Pacific, in the sediments of the North Pacific and the South China Sea, respectively; 2) The distribution patterns of rare earth elements standardized by the globular aerolite in ferromanganese nodules and crusts are basically similar, that is, Ce is positively abnormal and Eu is in deficit slightly; 3) The relationships between rare earth elements and associated elements, sediments and rocks show that the source of rare earth elements in ferromanganese nodules and crusts have mainly come from slow deposition caused by weathering and leaching of medium acidic rock of the South China Sea.

INTRODUCTION

It is well known that the rare earth element of sediment, rock or ferromanganese nodule in oceanic floor can provide a lot of geological information. So such researches on source of sediment and formative mechanism of ferromanganese nodule are made by Wang *et al.* (1982, 1984), Gu *et al.* (1989), Zhao *et al.* (1990), Courtois and Claver (1980), Goldberg *et al.* (1963) and Piper (1974).

In order to study the geochemistry, formative mechanism and environment of ferromanganese nodules and crusts of the South China Sea, 15 rare earth elements out of the samples from 11 stations are identified by X-ray fluorescence spectral analysis. Meanwhile a comparison between the ferromanganese nodules, sediments of the South China Sea and the North Pacific has been made, and a formative mechanism of ferromanganese nodules and crusts has been raised. The samples were collected by Dreget Dregehammer and Piper Drege during 1987 cruise. Sampling stations and some parameters of ferromanganese nodules and crusts are provided by SIO, SOA (1989).

CHARACTERISTICS OF CONCENTRATION AND DISTRIBUTION

It can be seen from Table 1 that ΣREE (rare earth elements) in ferromanganese nodules is higher than that in crusts in the South China Sea, and its ΣREE in ferromanganese nodules of the North Pacific, over 5 times higher than that in sediments of the North Pacific and over 10 times higher than that in sediments of the South China Sea, respectively. So rare earth elements of ferromanganese nodules and crusts from the South China Sea may be one of the potential resources of rare earth elements. As for the comparison between ferromanganese nodules and crusts, obviously, their common characteristic is that ΣCe Light REE is higher than that Σ Heavy REE. This is in agreement with that of rare earth elements of ferromanganese nodules, sediments of the North Pacific and sediments and rock of the South China Sea. It is typical rare earth element of continental crust. However, the difference between nodules and crusts is that concentrating degree of LREE in nodules is higher than that in crusts and its Σ Ce / ΣY is close to that of granite and far from that of sediments in the South China Sea. The result hints that there may be a relationship between rare earth elements in ferromanganese nodules (crusts) and medium acidic rock in the South China Sea.

Table 2 shows that: 1) ΣCe is obviously richer than ΣY in both KD17 ferromanganese crust and KD35 ferromanganese nodule of every layer; 2) In KD17 ferromanganese crust, ΣREE is higher on surface than in deep layer, while the situation in KD35 ferromanganese nodule is on the contrary, and so are ΣCe, ΣY, and ΣCe / ΣY as well. ΣCe is approximately 4 times of ΣY which is close to the ratio of rare earth elements in sediments of China continental shelf (Zhou *et al.*, 1990); 3) The relative difference between the highest and lowest concentration of ΣREE is over one third in both ferromanganese nodules and crusts, that is, the concentration range in nodules is from 1880.2 to 2526.3 mg / kg, and in crusts from 1583.5 to 2566.5 mg / kg. In their forming and growing processes, ferromanganese crusts and nodules may be caused either by environ mental variation or by the concentration change of clastic rock contained in nodules and crusts.

DISTRIBUTION PATTERNS OF RARE EARTH ELEMENTS OF FERROMANGANESE NODULES AND CRUSTS

The distribution patterns of rare earth elements of ferromanganese nodules and crusts (Fig.1) are most similar, both of which are of negative slopes that is light REE is relatively concentrated.

Ce is in positive abnormality, and Eu in more or less deficit. The distribution pattern is obviously gentle and different from ferromanganese nodules of the North Pacific (Fig.1c) and sediments of the South China Sea and the North Pacific (Fig.1d).

As is well known, rare earth elements possess very similar chemical nature, but with the increase of atomicity, they can be separated from each other by variation of physical and chemical environments, of which the most obvious separation is that of LREE from HREE and of variable elements Ce (Ce^{3+}, Ce^{4+}) from Eu (Eu^{2+}, Eu^{3+}). Thus, the affection of sea water on ferromanganese nodules and crusts of the South China Sea is larger than that in the North Pacific and sediments of the South China Sea. On the contrary, the affection of early diagenesis of sediments on ferromanganese nodules of the North Pacific is larger than that of the South China Sea (Elderfield *et al.*, 1981). It also indicates that source of rare earth elements of ferromanganese nodules and crusts of the South China Sea may be different from the ferromanganese nodules of the North Pacific and sediments of the South China Sea.

Table 1 Concentration of rare earth elements in ferromanganese nodule (crust), sediment and rock of the South China Sea (mg / kg)

Samples	No.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	ΣREE	ΣCe	ΣY	$\frac{\Sigma Ce}{\Sigma Y}$	Source
Ferromanganese crusts of the South China Sea	5	165.80	917.00	41.00	132.60	44.00	12.76	48.00	9.74	53.00	7.30	22.12	5.44	19.60	4.98	141.80	1625.14	1313.16	311.98	4.21	this paper
Ferromanganese nodules of the South China Sea	6	233.00	1315.50	52.83	170.50	52.83	13.95	55.83	7.65	59.00	5.82	22.00	4.95	19.00	4.87	149.17	2166.90	1838.61	328.29	5.60	this paper
Ferromanganese nodules of the North Pacific	5	120.54	383.66	38.39	124.45	31.75	7.72	30.21	5.24	29.33	5.35	15.26	2.40	14.81	2.24	112.77	924.46	706.51	217.95	3.24	Piper (1974)
Sediments of the North Pacific	1	87.06	134.57	23.65	99.37	31.22	6.03	25.90	4.27	25.23	5.11	14.26	2.27	13.18	2.13	158.02	632.27	381.90	250.37	1.53	Piper (1974)
Sediments of the South China Sea	53	28.63	55.80	6.31	22.65	4.71	1.09	4.27	0.68	4.00	0.82	2.43	0.34	2.18	0.43	21.81	156.15	119.19	36.96	3.22	Bao (1990)
Granite of the South China Sea	1	18.01	84.36	3.35	11.10	1.69	0.92	0.66	0.06	1.13	0.03	0.44	0	0.24	8.12	13.00	143.11	119.43	23.68	5.04	this paper
Gabbro of the South China Sea	1	27.00	101.26	7.97	38.03	10.90	9.29	10.56	2.74	13.87	6.94	7.91	1.82	6.67	2.31	47.95	295.22	194.45	100.77	1.93	this paper

Table 2 Concentration of rare earth elements in different layer of ferromanganese nodules and crusts from the South China Sea (mg / kg)

Stations and layers	ΣREE	ΣCe	ΣY	ΣCe / ΣY	Stations and layers	ΣREE	ΣCe	ΣY	ΣCe / ΣY
KD17–1	2444.30	1986.00	458.30	4.33	KD35–1	1583.50	1257.50	326.00	3.86
KD17–2	1986.90	1553.60	433.30	3.59	KD35–2	1681.90	1385.00	296.90	4.66
KD17–3	2055.10	1625.50	428.60	3.79	KD35–3	2187.80	1789.00	378.80	4.64
KD17–4	1987.30	1536.00	451.30	3.40	KD35–4	2119.10	1672.00	447.10	3.74
KD17–5	2026.20	1562.00	464.20	3.36	KD35–5	2130.90	1711.00	419.90	4.07
KD17–6	1880.20	1520.50	359.70	4.23	KD35–6	2566.50	2225.90	341.50	6.52
KD17–7	2316.20	1890.00	426.20	4.43	KD35–7	2440.60	2096.00	344.60	6.08
KD17–8	2298.70	1847.00	451.70	4.09	KD35–8	2199.70	1716.00	483.70	3.55
KD17–9	2526.30	2040.00	486.30	4.19	KD35–9	1780.00	1411.40	368.60	3.83
KD17–10	2480.10	2013.00	467.10	4.31	KD35–10	2369.70	2036.80	331.70	6.14

Note: KD17, crust; KD35, nodule.

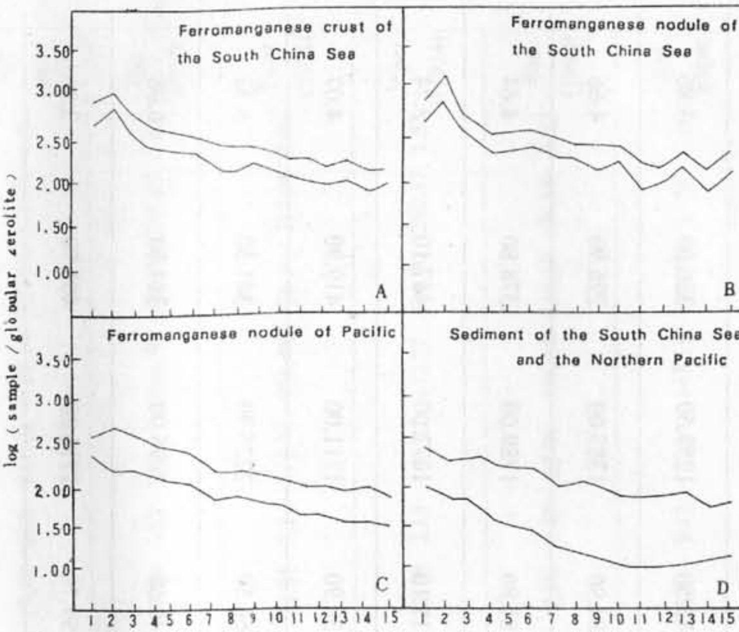

Fig.1 Distribution patterns of rare earth elements of ferromanganese nodules and crusts. 1—La; 2—Ce; 3—Pr; 4—Nd; 6—Sm; 7—Eu; 8—Gd; 9—Tb; 10—Dy; 11—Ho; 12—Er; 13—Tm; 14—Yb; 15—Lu.

The distribution patterns of rare earth elements standardized by globular aerolite in different layers of KD17 ferromanganese crust and KD35 nodule (SIO, SOA, 1989) show that the distribution patterns of rare earth elements of ferromanganese crust of different layer are basically the same. Ce is obviously in positive abnormality and Eu in more or less deficit. This shows that source of rare earth elements may be basically the same during the forming and growing processes of ferromanganese crusts, though ΣREE of every layer is different. The distribution patterns of rare earth elements from 1−5 layer of ferromanganese nodules are similar to those of crusts. Yet, they are obviously different in 6−10 layers. It is necessary further to study whether they are caused by clastic rock, nuclear or the variation of environment of the South China Sea and material source. A lot of investigation information has confirmed that the distribution pattern of rare earth elements can differ with the different material in the nuclear and on the surface of ferromanganese nodules and crusts. Yet, chemical analysis information had shown that the concentration of rare earth elements in clastic rock is less than 2000 mg / kg (Tables 1 and 2) (Goldberg *et al*, 1963, Wildman and Haskin, 1965). Perhaps, the variation of material source of rare earth elements is caused by the variation of sedimentary environment.

SOURCE OF RARE EARTH ELEMENTS OF FERROMANGANESE NODULES AND CRUSTS

Experiment of Absorption REE

KD17 ferromanganese crust and KD35 nodule were soaked by NaCl and $(NH_4)_2SO_4$, respectively. The result of chemical analysis indicates that REE in absorption state occupies

0.096% and is similar to absorption REE ore of South China granit (industrial grade is 0.1%). Because sample may change during preparing processes which may cause the decreasing of REE in ion absorption, the absorption REE in ferromanganese nodules and crusts of the South China Sea is over 0.096%. It shows that the rare earth elements in ferromanganese nodules and crusts have existed mainly in ion state instead of in crystal of clay as isomorphism, and are obviously different from the rare earth elements of sediments of the North Pacific, the South China Sea and the China Sea continental shelf (Gu *et al.*, 1989; Zhao *et al.*, 1990). The rare earth elements of ferromanganese and crusts of the South China Sea may mainly absorbed from sea water by the nucleus material.

Relationship between Rare Earth Elements and Associated Elements

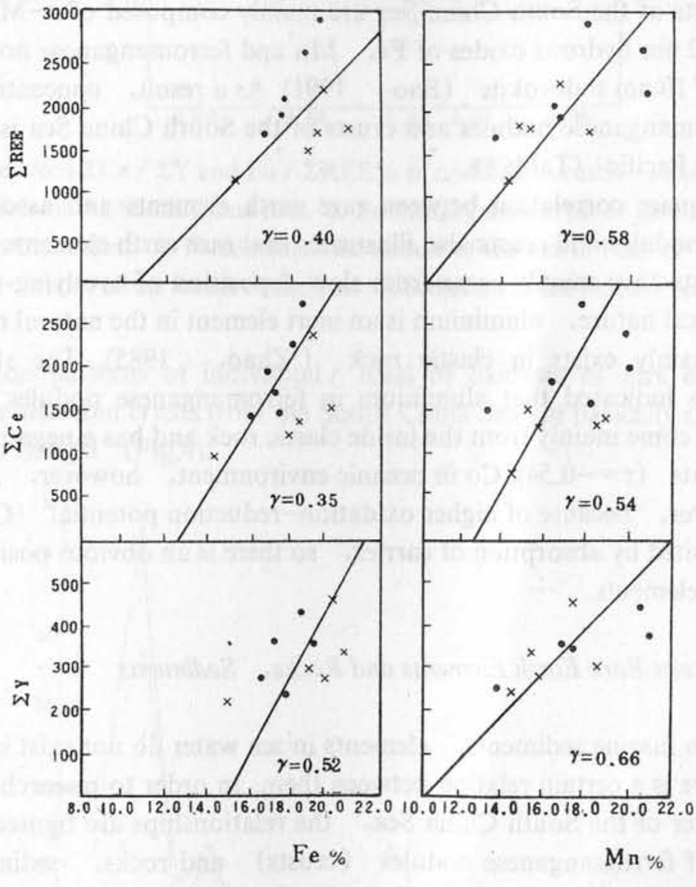

Fig.2 Relationship between REE and Fe, Mn in ferromanganese nodules (crusts).

Fig.2 shows that there is an obvious positive correlation between REE and Fe, Mn, neither ΣY nor ΣCe. This indicates that sources of rare earth elements and Fe, Mn in ferromanganese nodules and crusts are basically similar. The study of element geochemistry of ferromanganese nodules and crusts has confirmed that Fe, Mn in ferromanganese nodules and crusts are mainly from deposition of overlying water, that is, they come from deposition of hydrous oxides of soluble Fe, Mn (Courtois and Claver, 1980; Bao, 1991; Carinneko, 1981). So rare earth elements of ferromanganese nodules and crusts of the South China Sea have mainly come from slow deposition of overlying water. Geochemical experiments have confirmed that Fe, Mn metal ion formed by weathering and leaching of volcanic material can be oxidated by reaction of its solution with fresh sea water before slowly depositing as the nucleus of ferromanganese nodule. Its solution is in the state of colloid and then makes the nodules into ringlike structure. While, deposition of Fe, Mn oxides has accelerated hydrolysis of rare earth elements, that is, Ce^{3+} can be transformed into Ce^{4+} by MnO_2 (Wang *et al.*, 1984). Since Ce^{4+} is easy to deposite, Ce is in obvious positive abnormality (Fig. 1a, b). Therefore, there is an obvious positive correlation between Fe, Mn and ΣREE, ΣCe, ΣY in ferromanganese nodules and crusts caused by hydrous oxides of Fe, Mn which acts both as a catalytic agent of hydrolysis of rare earth elements and as a carrier during the deposition processes of rare earth elements. And also ferromanganese nodules and crusts of the South China Sea are mainly composed of $\delta-MnO_2$ consisting of 2.45 nm and 1.42 nm hydrous oxides of Fe, Mn and ferromanganese nodules of the North Pacific mainly of 10 nm todorokite (Bao, 1991). As a result, concentration of rare earth elements of ferromanganese nodules and crusts of the South China Sea is much higher than that of the North Pacific (Table 1).

The least square correlation between rare earth elements and associated elements of ferromanganese nodules and crusts also illustrates that rare earth elements in ferromanganese nodules and crusts have mainly come from slow deposition of overlying water. For the elemental geochemical nature, aluminium is an inert element in the natural environment, and in general, mainly exists in clastic rock (Zhao, 1985). The study of elemental geochemistry has indicated that aluminium in ferromanganese nodules and crusts of the South China Sea come mainly from the inside clastic rock and has a negative correlation with rare earth elements ($r=-0.54$). Co in oceanic environment, however, is more stable than Mn^{2+} in sea water, because of higher oxidation–reduction potential ($Co^{3+}/Co^{2+}=1.84$) and can be deposited by absorption of carrier, so there is an obvious positive correlation between rare earth elements.

Relationship between Rare Earth Elements and Rocks, Sediments

Like those in marine sediments, elements in sea water do not exist in an isolated state. Moreover, there is a certain relation between them. In order to research into source of elements in sea water of the South China Sea, the relationships are figured out between rare earth elements of ferromanganese nodules (crusts) and rocks, sediments of the South China Sea and nodules of the North Pacific (Figs.3 and 4).

ΣCe / ΣY in ferromanganese nodules and crusts of the South China Sea is much than that of nodules of the North Pacific (Fig. 3), although ferromanganese nodules and crusts of the South China Sea and nodules of the North Pacific are all in the areas rich in Ce and poor in Eu (Eu / ΣREE% < 1.00). The former is larger than 4.50, which is in the same range as granite, and the latter is less than 3.00, and close to that of sediments of the South China Sea and the North Pacific. The result further indicates that source of rare earth elements differs from that of sediments in the South China Sea, and at the same time, they may be formed by weathering and leaching of medium acidic rocks.

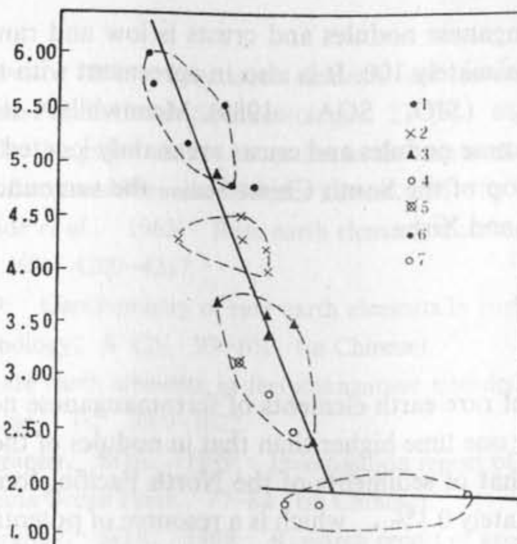

Fig.3 Correlation between $\Sigma Ce / \Sigma Y$ and $Eu / \Sigma REE\%$ in nodules, crusts, sediments and rocks. 1. Ferromanganese nodule of the South China Sea; 2. Ferromanganese crust of the South China Sea; 3. Granite of the South China Sea; 4. Ferromanganese nodule of the North Pacific; 5. Sediment of the South China Sea; 6. Gabbro of the South China Sea; 7. Sediment of the North Pacific.

The distribution patterns of individual / total of oxidates of rare earth elements in ferromanganese nodules and crusts from the South China Sea are basically similar to those of volcanicrocks from Jiangxi (Fig.4).

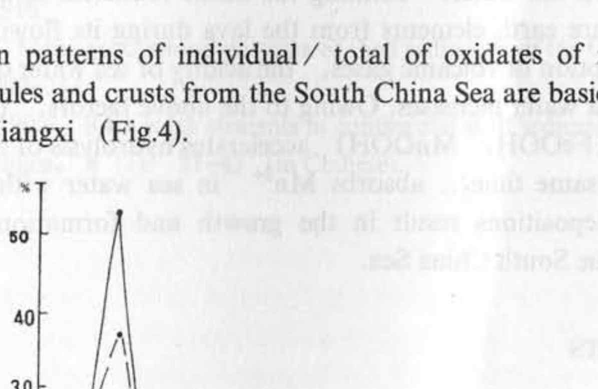

Fig. 4 Distribution patterns of rare earth elements of the South China Sea and volcanic rocks of Jiangxi. 1—La_2O_3; 2—CeO_2; 3—Pr_6O_4; 4—Nd_2O_3; 5—Sm_2O_3; 6—Eu_2O_3; 7—Gd_2O_3; 8—Tb_4O_7; 10—Ho_2O_3; 11—Er_2O_3; 12—Tm_2O_3; 13—Yb_2O_3; 14—Lu_2O_5; 15—Y_2O_3.

The result further indicates that rare earth elements of ferromanganese nodules and crusts in the South China Sea are mainly from weathering and leaching of volcanic material. It is in agreement with chemical analysis of the ferromanganese nodules and crusts, that is, K / Rb of the ferromanganese nodules and crusts is low and ranges from 10 to 223, and most of them are approximately 100. It is also in agreement with the negative correlation between Ni, V and SiO_2 (SIO, SOA, 1989). Meanwhile, it can be confirmed that the areas rich in ferromanganese nodules and crusts are mainly located in large fault zones such as the lower continental slop of the South China Sea, the surroundings of Zhongsha and the area between Zhongsha and Xisha.

CONCLUSIONS

1. Concentration of rare earth elements of ferromanganese nodules and crusts from the South China Sea is over one time higher than that in nodules of the North Pacific, and over five times higher than that of sediments of the North Pacific. Ion absorption rare earth elements occupy approximately 0.1%, which is a resource of potential rare earth ore.

2. Distribution patterns of rare earth elements of ferromanganese nodules and crusts from the South China Sea are basically similar. Ce is in obvious positive abnormality with a negative slope rich in LREE, and Eu deficis in more or less degree. It is typical of rare earth elements of continental crust.

3. The source of rare earth elements of ferromanganese nodules and crusts of the South China Sea may be supposed as the following. A large amount of gas formed during the volcanic eruption reacts on sea water, forming the acidic reducible solution, which carries some Fe, Mn and rare earth elements from the lava during its flowing back through the lava. Wiht the consumption of volcanic gases, the acidity of sea water drops and the concentration of oxygen in sea water increases. Owing to the above factors, the hydrous oxides of iron and manganese (FeOOH, MnOOH) accelerates hydrolysis of rare earth elements in sea water and at the same time, absorbs Mn^{2+} in sea water with such a cycle, the authigenic chemical depositions result in the growth and formation of ferromanganese nodules and crusts of the South China Sea.

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