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Baseline

Geochemical characteristics of rare earth elements in the surface sediments from the Spratly Islands of China

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ABSTRACT

The geochemistry of rare earth elements (REE) in surface sediment from Cuarteron reef (N1), Johnson reef (N2), Hugh reef (N3), Gaven reef (N4), Fiery cross reef (N5), and Subi reef (N6) were firstly studied. The total REE abundance ($\sum$REE) varied from 2.244 $\mu g \cdot g^{-1}$ to 21.661 $\mu g \cdot g^{-1}$, with an average of 4.667 $\mu g \cdot g^{-1}$. The LREE/HREE was from 2.747 to 9.869, with an average of 3.687, which indicated that the light REE was evidently enriched. Fractionation was observed between LREE and HREE. Gd with a negative anomaly was also detected in all of the stations. The negative anomalies of δEu from 0.11 to 0.25, with an average of 0.22, and the positive anomalies of δCe from 1.38 to 3.86, with an average of 1.63. The REE individual correlation values with Ca, Mn, Mg, Sr were $r_{Ca} = -0.05$, $r_{Mn} = 0.26$, $r_{Mg} = -0.14$, and $r_{Sr} = 0.08$.

Rare earth elements (REE) normally migrate collectively through chemical reactions occurring on Earth; however, REE slightly differ in nature (Caccia and Millero, 2007; Kim et al., 2012 and Budakoglu et al., 2015). REE in sediments have been widely used as powerful indicators of fundamental geochemical processes associated with the chemical evolution of the continental crust, tectonic setting, chemical weathering in drainage basins, and sediment sources in different environmental systems because of their unique chemical properties (Olías et al., 2005; Sholkovitz and Szymczak, 2000; Bai et al., 2014 and Cullers, 2000). Thus, the abundance and distribution pattern of REE in submarine sediments are significant to examine the formation conditions and provenance characteristics of submarine sediments (Mondal et al., 2012; Chen et al., 2000; Pérez-López et al., 2010; Singh, 2009 and McLennan, 1989). Fractionation may occur among different REE because of the changes in external conditions (Von Eynatten et al., 2012 and Niels et al., 2003). Over the past two decades, distinct anthropogenic REE compositions, which are caused by unnatural liquid or solid inputs derived from human activities, have been observed in aquatic environments (Mao et al., 2010; Xu and Han, 2009; Zhang and Wang, 2001 and Mao et al., 2014), such as rivers, lakes, and estuarine and ocean sediments, as a result of domestic pollution and industrial activities (Dadson et al., 2003 and Liu et al., 2015).

The distribution characteristics of REE in the submarine sediments of the coasts and estuaries in China were comprehensively studied (Wang et al., 1995; Wang and Liu, 2000; Zhuang et al., 2005 and Lan and Shen, 2002). Most studies on REE in marine environments have focused on estuaries and greater coastal areas. However, research on the REE in the Spratly Islands of China remains relatively insufficient. So in the study, Cuarteron reef (N1), Johnson reef (N2), Hugh reef (N3), Gaven reef (N4), Fiery cross reef (N5), and Subi reef (N6) had yet to be explored.

The Spratly Islands are among the major archipelagos in the South China Sea that comprises >30,000 islands and reefs; this archipelago complicates governance and economic issues in its borderlines in Southeast Asia because it is strategically located in shipping lanes of various countries (Hutchison and Vijayan, 2010; Ding and Li, 2011 and Sun et al., 2013). The Spratly Islands consists of reefs, banks, and shoals composed of biogenic carbonate. Biogenic carbonate accumulates on the higher crests of major submarine ridges that are uplifted fault blocks known to geologists as horsts (Owen and Schofield, 2012 and Dorman et al., 2015). Thus far, studies have focused on marine organisms and natural features of the Spratly Islands. The geochemistry of REE has been rarely analyzed.

Table 1
The working parameters of microwave digestion.

Stage	Power/W Max	%	Temperature T/°C	Ramp t/min	Hold t/min
1	1500	100	100	3:00	3:00
2	1500	100	150	7:00	3:00
3	1500	100	170	5:00	3:00

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Table 2
The concentrations of REE in standard sediment samples ($\mu g \cdot g^{-1}$).

Elements	Reference value ($\mu g \cdot g^{-1}$)	Mean ($\mu g \cdot g^{-1}$)	Relative error (RE)%	Relative standard deviation (RSD)%
^{139}La	40.8	40.5	0.74	1.23
^{141}Pr	8.32	7.98	4.09	2.05
^{146}Nd	33.1	32.4	2.11	3.43
^{147}Sm	6.28	5.95	5.25	1.28
^{153}Eu	1.26	1.29	2.38	2.38
^{157}Gd	5.44	5.25	3.49	4.10
^{159}Tb	0.76	0.79	3.95	3.13
^{163}Dy	4.59	4.64	1.09	1.29
^{165}Ho	0.96	0.99	3.13	3.20
^{166}Er	2.57	2.6	1.17	1.19
^{169}Tm	0.38	0.40	5.26	3.89
^{172}Yb	2.46	2.41	2.03	2.93
^{175}Lu	0.37	0.38	2.70	3.70

In this study, sediment samples were collected from six reefs (56 stations) in the archipelago on August 2015. The samples were immediately frozen under −20 °C and transported to the laboratory. In the laboratory, The sediments were dried to a constant weight at 60 °C for 24 h and ground to fine powder using a pestle in an agate mortar before further chemical analysis. Then 0.20 g powdered samples were digested with a mixture of 6 mL HNO_3, 2 mL H_2O_2 and 1 mL HF in teflon digestion vessels and digested by microwave system (CEM, digestion procedures in Table 1). Subsequently, the solution was weighed with 25 g ultrapure water for measurement after digestion. The REE contents (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.) were determined using ICP–MS (Agilent ICP-MS 7500a). Meanwhile, the Re element was considered as the internal standard element.

During test procedure, firstly, 0.0 $\mu g \cdot L^{-1}$ ~ 20.0 $\mu g \cdot L^{-1}$ of rare earth multi-element standard solutions were measured through ICP-MS using 5.0 $\mu g \cdot L^{-1}$ Re internal standard elements for correcting. The re-

Table 3-1
The REE concentrations in surface sediments from N1 Island ($\mu g \cdot g^{-1}$).

Elements	Sampling no. N1-01	N1-02	N1-03	N1-04	N1-05	N1-06	N1-07	N1-08	N1-09
La	1.116	0.723	0.705	0.719	0.566	0.586	0.599	0.595	0.971
Ce	1.311	0.582	0.487	0.657	0.524	0.392	0.403	0.400	0.847
Pr	0.196	0.136	0.130	0.134	0.110	0.112	0.115	0.115	0.193
Nd	0.763	0.606	0.610	0.599	0.484	0.491	0.524	0.514	0.852
Sm	0.147	0.142	0.144	0.143	0.118	0.120	0.132	0.122	0.210
Eu	0.033	0.036	0.038	0.035	0.032	0.028	0.031	0.031	0.051
Gd	0.170	0.171	0.183	0.171	0.151	0.147	0.157	0.159	0.253
Tb	0.023	0.027	0.028	0.026	0.022	0.021	0.025	0.022	0.038
Dy	0.161	0.165	0.170	0.163	0.151	0.137	0.148	0.147	0.246
Ho	0.034	0.036	0.037	0.035	0.031	0.031	0.034	0.032	0.051
Er	0.096	0.099	0.106	0.099	0.092	0.088	0.093	0.093	0.145
Tm	0.013	0.014	0.014	0.014	0.013	0.012	0.013	0.013	0.020
Yb	0.078	0.080	0.083	0.080	0.077	0.069	0.082	0.074	0.120
Lu	0.011	0.012	0.013	0.012	0.011	0.010	0.012	0.011	0.017
ΣREE	4.150	2.828	2.748	2.888	2.383	2.244	2.369	2.327	4.015
ΣLREE	3.565	2.225	2.114	2.288	1.834	1.729	1.805	1.776	3.125
ΣHREE	0.586	0.603	0.634	0.601	0.549	0.515	0.564	0.551	0.890
L/H	6.088	3.689	3.334	3.809	3.341	3.355	3.198	3.224	3.510
δEu	0.21	0.23	0.23	0.23	0.24	0.21	0.22	0.22	0.22
δCe	2.81	1.86	1.61	2.12	2.10	1.53	1.53	1.53	1.96

Table 3-2
The REE concentrations in surface sediments from N2 Island ($\mu g \cdot g^{-1}$).

Elements	Sampling no. N2-01	N2-02	N2-03	N2-04	N2-05	N2-06	N2-07	N2-08	N2-09
La	0.875	0.710	0.693	1.071	1.307	1.227	1.259	1.246	4.608
Ce	0.534	0.439	0.441	0.655	0.837	0.771	0.799	0.813	8.774
Pr	0.153	0.127	0.125	0.191	0.248	0.225	0.236	0.231	1.119
Nd	0.702	0.586	0.547	0.858	1.117	1.007	1.069	1.038	4.263
Sm	0.182	0.140	0.141	0.214	0.266	0.248	0.262	0.251	0.819
Eu	0.044	0.038	0.035	0.055	0.067	0.064	0.064	0.061	0.085
Gd	0.221	0.174	0.172	0.270	0.332	0.310	0.308	0.303	0.699
Tb	0.033	0.026	0.026	0.040	0.047	0.045	0.043	0.043	0.089
Dy	0.208	0.175	0.162	0.256	0.300	0.280	0.269	0.275	0.524
Ho	0.046	0.038	0.036	0.054	0.063	0.061	0.057	0.058	0.102
Er	0.128	0.109	0.098	0.155	0.170	0.162	0.152	0.158	0.282
Tm	0.018	0.014	0.014	0.021	0.023	0.022	0.021	0.021	0.038
Yb	0.099	0.085	0.078	0.116	0.129	0.120	0.115	0.120	0.225
Lu	0.015	0.013	0.011	0.018	0.019	0.017	0.016	0.017	0.033
ΣREE	3.256	2.675	2.578	3.973	4.926	4.558	4.670	4.636	21.661
ΣLREE	2.489	2.040	1.982	3.043	3.843	3.541	3.689	3.639	19.668
ΣHREE	0.767	0.634	0.596	0.930	1.084	1.017	0.981	0.996	1.993
L/H	3.246	3.216	3.325	3.274	3.547	3.483	3.760	3.652	9.869
δEu	0.22	0.24	0.22	0.23	0.23	0.23	0.23	0.22	0.11
δCe	1.46	1.46	1.50	1.45	1.47	1.47	1.47	1.51	3.86

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