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Article *in* Geochemistry International · July 2001

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Geochemistry International, Vol. 39, No. 7, 2001, pp. 692–701. Translated from Geokhimiya, No. 7, 2001, pp. 762–772.

Behavior of Rare Earth Elements during Leaching of the Oceanic Sediments

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Received May 20, 1999

Abstract—Oceanic sediments (volcanoterrigenous mud and hemipelagic and eupelagic clay) were leached by 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH at different solid/liquid ratios (from 1/800 to 1/20) to study the REE behavior in the leachates. At pH 2, no REE readsorption is observed. Kinetic experiments on leaching of the eupelagic clay (solid/liquid = 1/67) showed that equilibrium conditions for trivalent REEs are attained after four hours, while those for Ce are attained only after eight hours. This may indicate a tetravalent state of Ce in the oxidized pelagic sediments. Under equilibrium conditions, the introduction of trivalent REE during leaching leads to REE redistribution between 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH and the solid phase: added REEs disturb the equilibrium and cause the partial adsorption of these elements by the sediment. Under unequilibrium conditions (for Ce), no Ce redistribution was observed after Ce inroduction into the solution–sediment system. The experiments demonstrated that the amount of exchangeable REEs, which were determined in the leachate after four hours of treating the sediments with Chester’s reagent at a solid/liquid ratio of 1/400, approximates the REE concentrations equilibrated with the solid phase. The REE concentrations are similar in repeated experiments with solid/liquid ratios from 1/800 to 1/100 and can be used to characterize the exchangeable portion of the bottom sediments. The contents of the major elements (Fe, Al, and P) in the leachate significantly depend on the conditions of the sediment treatment.

INTRODUCTION

The geochemical study of polygenic oceanic and marine sediments shows that trace elements are associated with different phases of sedimentation. The element distribution data can be obtained by separating the individual sedimentary phases using lithological methods with subsequent geochemical investigations [1–4] or by less time-consuming leaching, i.e., the treatment of sediments with acids and/or salts of various concentrations under certain conditions. The chemical composition of the exchangeable constituents of the sediments depend on the acid (salt) concentration in the applied leachate, redox properties of the reagents, liquid/solid ratio, time of treatment, and grain size of the sedimentary material [5–14].

The leaching reagents differ in their capability to dissolve the major sedimentary mineral phases: iron and manganese oxyhydroxides, calcium carbonate, amorphous silica, and authigenic aluminosilicates. The stability of trace elements in the leachate must be studied to determine their association with certain phases of the bottom sediments. It is commonly believed that dissolution of a phase leads to the release of associated elements, which then are stable in solution. It is very important to test this assumption, because some elements are readily hydrolyzed in solutions (REEs, Th, Zr, Hf) or form poorly soluble compounds in acid environments (Si, W, Mo).

The REE stability in the leachates is presumably limited by a pH value of 6–8, at which REE hydroxides begin to precipitate [15]. At higher pH, REEs either are not dissolved or are readsorbed during dissolution of the corresponding phase. Moreover, the study of redistribution of radioactive ^{152}Eu between solution and sediment showed that the portion of the readsorbed isotope is up to 26–57% even in the acid leachates (pH 2) [9].

The aim of this work is to study REE behavior during leaching of the oceanic sediments by a 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH (pH 2) mixture, which was proposed by Chester and Hughes [5].

MATERIALS AND METHODS

For the experiments, we selected three bottom sediment samples representing different types of oceanic sedimentation: a SDO-2 (volcanoterrigenous mud) reference sample, hemipelagic clay from site 6171 (0–2 cm) (water depth, 5993 m, 33°48.3′ N, 151°19.1′ E), and zeolite-bearing eupelagic clay from site 645 (0–2 cm) (water depth, 5480 m, 18°11.1′ N, 141°08.8′ W). All these samples mainly consist of the abiogenic material with less than 1% $CaCO_3$. The hemipelagic and eupelagic clays contain 2–8% amorphous silica.

The sediments dried in air (SDO-2 was dried to a constant weight at $T = 105°C$) were ground in a jasper mortar to a grain size of less than 5 μm. Then they were

Table 1. The results of leaching of hemipelagic sediments from site 6171 with 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH reagent

Element		Solid/liquid ratio												Total content
		1/800		1/400		1/267		1/200		1/100		1/67		
		x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	
La	ppm	5.10	0.08	4.95	0.12	4.93	0.06	5.11	0.11	4.99	0.09	4.85	0.07	21.1
Ce	ppm	17.8	0.3	17.9	0.3	18.0	0.04	17.9	0.2	17.7	0.1	17.3	0.2	51.9
Pr	ppm	1.52	0.03	1.52	0.02	1.52	0.01	1.53	0.01	1.48	0.02	1.44	0.01	5.17
Nd	ppm	6.24	0.12	6.39	0.06	6.44	0.02	6.37	0.03	6.24	0.05	6.04	0.04	20.4
Sm	ppm	1.62	0.10	1.58	0.09	1.59	0.05	1.55	0.01	1.53	0.04	1.49	0.06	4.29
Eu	ppm	0.35	0.02	0.37	0.01	0.36	0.01	0.38	0.01	0.36	0.01	0.35	0.01	0.83
Gd	ppm	1.57	0.04	1.58	0.05	1.60	0.05	1.57	0.04	1.53	0.02	1.55	0.03	3.54
Tb	ppm	0.23	0.005	0.24	0.01	0.25	0.02	0.23	0.01	0.22	0.01	0.22	0.01	0.55
Dy	ppm	1.36	0.01	1.36	0.04	1.40	0.03	1.36	0.01	1.34	0.01	1.31	0.04	3.03
Ho	ppm	0.25	0.004	0.25	0.01	0.26	0.01	0.25	0.01	0.24	0.01	0.24	0.01	0.64
Er	ppm	0.70	0.03	0.70	0.02	0.73	0.02	0.71	0.01	0.68	0.01	0.70	0.03	1.85
Tm	ppm	0.10	0.01	0.10	0.004	0.10	0.003	0.10	0.003	0.09	0.004	0.09	0.003	0.27
Yb	ppm	0.61	0.03	0.62	0.02	0.63	0.02	0.60	0.01	0.57	0.01	0.56	0.02	1.92
Lu	ppm	0.09	0.01	0.10	0.002	0.09	0.003	0.09	0.004	0.09	0.003	0.08	0.003	0.28
Al	%	0.50		0.49		0.49		0.47		0.46		0.43		7.45
Fe	%	0.66		0.64		0.60		0.59		0.55		0.54		4.21
Mn	%	0.36		0.37		0.36		0.35		0.38		0.38		0.45
P	%	0.037		0.038		0.036		0.038		0.035		0.037		0.063

Note: The average REE contents (x) and standard deviations (S_{n-1}) are listed for four independent determinations.

treated by 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH with continuous shaking for four hours. The 25- to 1000-mg samples were mixed with constant amounts (20 ml) of this reagent having pH 2.0 ± 0.1. The leachate was passed through filter paper with 1- to 2-μm pores. Upon heating, concentrated nitric acid was added to the filtrate to destroy the hydroxylamine. Then it was evaporated and the filtrate was dissolved in 5% HNO_3. In some experiments, the sample residues were examined. For this purpose, they were decomposed by a mixture of concentrated HF and $HClO_4$.

In order to determine the time of attaining equilibrium in the solution–sediment system, a series of kinetic experiments was performed to leach the pelagic sediment from site 645. The 300-mg sample was treated with 20 ml of Chester's reagent at room temperature ($T = 20°C$) for 0.5, 1, 4, 8, 12, and 24 h, being shaken intermittently. Only filtrate was used for further analysis.

The distribution of La, Ce, Nd, Eu, Tb, Tm, and Lu was studied in the solution–solid phase system. The 300-mg sediment sample from site 645 or hematite (Fe_2O_3) was treated by a mixture of 1M $NH_2OH \cdot HCl$ and 25% CH_3COOH and shaken. The analytical grade hematite was ground to a grain size of less than 5 μm. After one hour, the HNO_3 solutions of REEs were simultaneously added to three samples (or four for Tb, Tm, and Lu in experiments with eupelagic clay). The REE content was comparable to their initial contents in the solution for the site 645 sediment and subsequently increased from the first to last samples. After four hours, the pH (2.0 ± 0.1) was measured and solutions were passed through filter paper with 1- to 2-μm pores. The contents of 14 REEs were determined with ICP-MS on a PlasmaQuad PQII STE spectrometer following the procedure described in [16]. The accuracy of the measurements was controlled by AGV-1 and SDO-2 standards. The relative standard deviation for all REEs was less than 5%. The Fe, Mn, and Al contents during the experiment were measured with flame absorption, P was measured with spectrophotometry.

RESULTS

REE Leaching by Chester's Reagent at Different Solid/Liquid Ratios

The solid/liquid ratios during leaching ranged from 1/800 to 1/67 for the sediment from site 6171, from 1/800 to 1/40 for SDO-2, and from 1/400 to 1/20 for eupelagic clay. In all experiments, samples were treated with 20 ml of 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH mixture and the pH value was controlled. Experiments lasted four hours. Results are listed in Tables 1–3. With an increasing solid/liquid ratio, the release of Fe, Al, and P into the solution decreases. This presumably

Table 2. The results of the leaching of volcanoterrigenous mud (SDO-2 reference sample) with 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH reagent

Element		Solid/liquid ratio												Total content
		1/800		1/400		1/200		1/100		1/67		1/40		
		x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	
La	ppm	12.4	0.08	13.0	0.06	12.8	0.06	12.8	0.24	12.6	0.22	12.2	0.20	27.8
Ce	ppm	25.9	0.07	27.9	0.20	27.1	0.13	26.8	0.51	26.7	0.38	24.7	0.22	54.6
Pr	ppm	3.84	0.03	4.01	0.02	3.97	0.04	3.91	0.07	3.91	0.07	3.70	0.04	7.8
Nd	ppm	15.8	0.12	16.5	0.21	16.4	0.06	16.3	0.16	16.3	0.15	15.4	0.20	33.0
Sm	ppm	3.75	0.02	3.90	0.11	3.94	0.02	3.88	0.09	3.90	0.07	3.60	0.13	8.1
Eu	ppm	0.86	0.02	0.92	0.01	0.96	0.01	0.95	0.01	0.96	0.02	0.88	0.03	2.23
Gd	ppm	3.79	0.11	3.88	0.08	3.86	0.04	3.87	0.08	3.83	0.12	3.53	0.12	7.3
Tb	ppm	0.55	0.005	0.57	0.01	0.58	0.01	0.57	0.01	0.57	0.01	0.53	0.02	1.12
Dy	ppm	3.13	0.02	3.24	0.07	3.25	0.05	3.27	0.09	3.26	0.09	3.03	0.16	6.6
Ho	ppm	0.60	0.01	0.62	0.01	0.62	0.01	0.63	0.01	0.62	0.01	0.58	0.02	1.31
Er	ppm	1.62	0.03	1.63	0.03	1.67	0.003	1.66	0.03	1.67	0.04	1.54	0.06	3.3
Tm	ppm	0.22	0.01	0.23	0.01	0.24	0.01	0.23	0.01	0.23	0.01	0.21	0.003	0.43
Yb	ppm	1.33	0.05	1.40	0.02	1.41	0.05	1.41	0.07	1.38	0.03	1.29	0.04	2.99
Lu	ppm	0.20	0.003	0.19	0.004	0.21	0.01	0.20	0.01	0.20	0.01	0.19	0.01	0.43
Al	%	0.39		0.36		0.40		0.30		0.35		0.25		7.58
Fe	%	0.54		0.62		0.62		0.60		0.51		0.43		8.33
Mn	%	0.13		0.13		0.13		0.14		0.14		0.13		0.21
P	%	0.071		0.071		0.070		0.070		0.066		0.062		0.12

Note: The average REE contents (x) and standard deviations (S_{n-1}) are listed for four independent determinations.

Table 3. The results of leaching of eupelagic clay from site 645 with 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH reagent

Element		Solid/liquid ratio																Total content
		1/400				1/200		1/100				1/67		1/40		1/20		
		leachate		residue		leachate		leachate		residue		leachate		leachate		leachate		
		x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	
La	ppm	23.5	0.2	22.8	0.2	23.10	0.03	22.9	0.4	22.5	0.07	22.2	0.2	21.5	0.1	20.9	0.1	46.0
Ce	ppm	62.3	0.2	45.5	0.3	61.8	0.1	61.3	0.9	45.1	0.2	58.1	0.5	54.7	0.4	46.0	0.3	108
Pr	ppm	7.71	0.01	5.10	0.04	7.71	0.03	7.60	0.09	5.07	0.06	7.37	0.03	7.23	0.06	7.03	0.02	12.9
Nd	ppm	33.6	0.2	18.9	0.07	33.01	0.08	32.9	0.3	18.9	0.1	32.1	0.1	31.4	0.05	30.9	0.4	52.5
Sm	ppm	8.27	0.03	3.51	0.02	8.29	0.06	8.29	0.05	3.62	0.03	8.12	0.03	7.92	0.02	7.8	0.1	12.0
Eu	ppm	2.09	0.03	0.70	0.01	2.07	0.02	2.06	0.01	0.69	0.004	2.03	0.02	1.98	0.02	1.97	0.03	2.82
Gd	ppm	9.1	0.1	2.61	0.02	8.78	0.05	8.8	0.1	2.70	0.02	8.66	0.10	8.51	0.06	8.6	0.2	11.7
Tb	ppm	1.34	0.02	0.38	0.01	1.29	0.01	1.30	0.01	0.38	0.004	1.29	0.02	1.28	0.01	1.27	0.04	1.71
Dy	ppm	8.11	0.06	2.13	0.03	7.75	0.07	7.8	0.1	2.18	0.02	7.72	0.06	7.55	0.07	7.6	0.2	10.2
Ho	ppm	1.58	0.03	0.43	0.01	1.52	0.02	1.51	0.01	0.44	0.02	1.53	0.005	1.48	0.01	1.49	0.03	2.01
Er	ppm	4.42	0.04	1.26	0.03	4.23	0.04	4.24	0.10	1.32	0.03	4.18	0.06	4.10	0.01	4.20	0.07	5.61
Tm	ppm	0.60	0.003	0.19	0.01	0.57	0.001	0.57	0.02	0.19	0.00	0.56	0.01	0.56	0.003	0.56	0.01	0.79
Yb	ppm	3.83	0.03	1.20	0.02	3.69	0.04	3.68	0.07	1.32	0.004	3.61	0.05	3.57	0.01	3.55	0.03	5.03
Lu	ppm	0.60	0.01	0.19	0.01	0.56	0.002	0.56	0.01	0.20	0.01	0.57	0.002	0.55	0.01	0.54	0.003	0.78
Al	%	0.53		8.10		0.63		0.37		8.69		0.29		0.26		0.23		8.85
Fe	%	0.62		4.76		0.58		0.57		4.80		0.53		0.50		0.46		5.37
Mn	%	0.73		0.03		0.75		0.74		0.02		0.73		0.74		0.73		0.76
P	%	0.123		0.023		0.120		0.117		0.026		0.121		0.118		0.104		0.145

Note: The average REE contents (x) and standard deviations (S_{n-1}) are listed for three independent determinations.

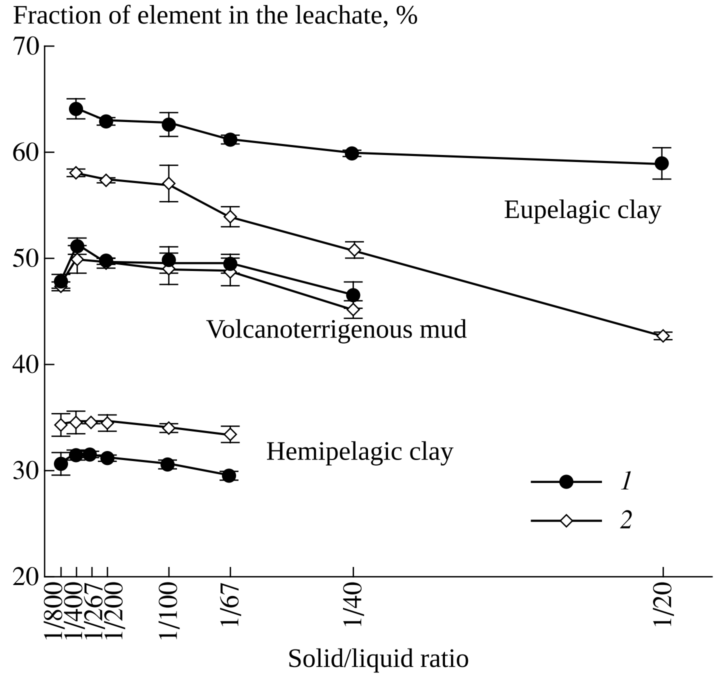

Fig. 1. The fraction of elements in the exchangeable mode of occurrence (in % of total content in sediment) for Nd (*1*) and Ce (*2*) versus solid/liquid ratio. The confidence interval corresponds to two standard deviations.

results from the low rate of dissolution of the Fe-bearing (oxyhydroxides and silicates) and Al-bearing phases (aluminosilicates and less abundant iron oxyhydroxides). This assumption is confirmed by kinetic experiments. In the experiments with a variable solid/liquid ratio, Al shows the lowest solubility (<7 rel. %). Phosphorus in sediments may occur in adsorbed forms, bone detritus, organic compounds, and lithoclastic components. The Chester's reagent may extract phosphorus of the first two forms, completely dissolving silt-size bone detritus in four hours at a solid/liquid ratio of 1/400 [11]. Thus, a decrease in P release may be related to a decrease of Fe extraction from oxyhydroxides containing adsorbed phosphates. The released manganese accounted for 66–99% of the total manganese content. The total manganese content and its release into the leachate increases in the sequence of volcanoterrigenous mud ⇒ hemipelagic clay ⇒ eupelagic clay owing to an increase of Mn(IV) in the oxide form.

The REE contents in the leachate practically do not depend on the solid/liquid ratio (the standard deviation for all REEs is less than 5 rel. %) (Fig. 1). The extraction degree depends on the REE atomic number and is highest for MREEs. Only the Ce content in leachates of the pelagic clay shows significant variations at a solid/liquid ratio >1/100 (standard deviation reaches 11 rel. %). With an increase of the solid/liquid ratio, the Ce content in the solution decreases and a negative anomaly appears in the NASC-normalized distribution pattern (Ce/Ce* < 1) (Fig. 2). The leached residues of the sediments from site 645 demonstrate a LREE-enriched normalized pattern.

Kinetics of REE Leaching

To explain the anomalous Ce behavior in the leachate of the site 645 sediment, the sediment was leached at the same solid/liquid ratio (300 mg/20 ml)

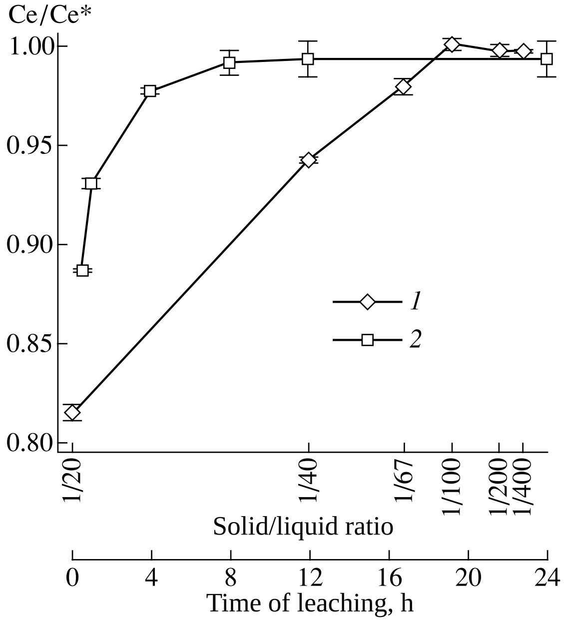

Fig. 2. Cerium anomaly (Ce/Ce* = $2\mathrm{Ce}/\mathrm{Ce}^{\mathrm{NASC}}/(\mathrm{La}/\mathrm{La}^{\mathrm{NASC}} + \mathrm{Pr}/\mathrm{Pr}^{\mathrm{NASC}})$, where NASC is the North American Shale Composite [17]) in the eupelagic clay leachate versus solid/liquid ratio (*1*) and time of leaching (solid/liquid ratio = 1/67) (*2*). The confidence interval corresponds to one standard deviation.

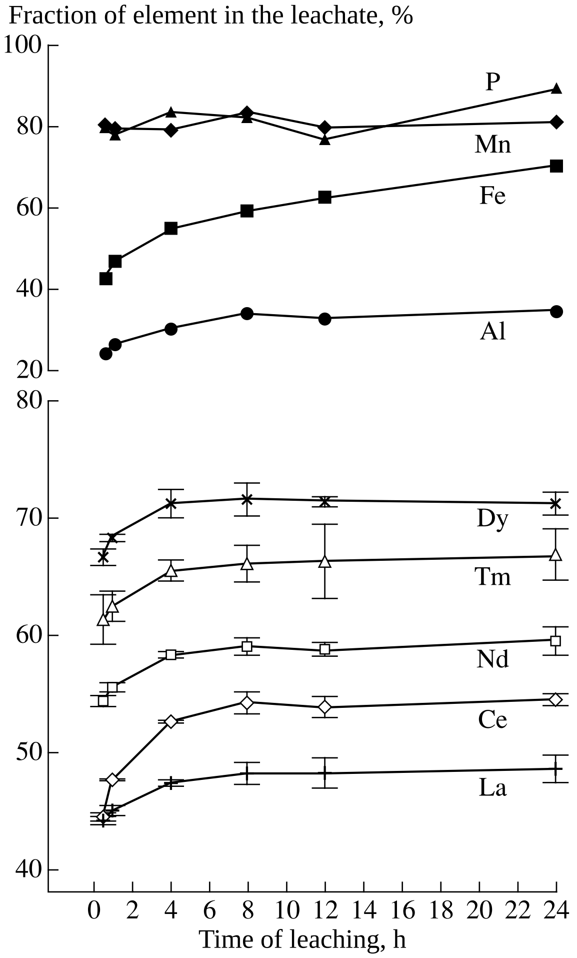

Fig. 3. The fraction of elements in the exchangeable mode of occurrence (in % of total contents in sediment) for Al, Fe, Mn, P, and REE versus time of leaching of the eupelagic clay (solid/liquid = 1/67).

during different times. The results are presented in Table 4. The contents of liberated P and Mn practically do not depend on leaching time, whereas the Al content continues to increase after eight hours of leaching and the Fe content increases even after a 24-h leaching (Fig. 3).

The REE contents, except for Ce, become stable after four hours (Fig. 3). Both the Ce content and the Ce anomaly (Fig. 2) become stable in the leachate only after eight hours. Such a difference between the behavior of Ce and trivalent REE may indicate the tetravalent state of Ce in the pelagic sediments.

REE Distribution in the Solid–Liquid System

In order to examine the exchange reactions for REEs between solution and solids (eupelagic clay), seven REEs were added to the leachate at a solid/liquid ratio = 1/67 after one hour. After four hours, the solution was filtered and analyzed. Table 5 lists the amounts of added REEs and their quasiequilibrium final contents. It can be seen that 10% of the added REEs are readsorbed by the solid phase. The solutions more readily keep LREEs than HREEs, except for Ce, which remains stable and, hence, is not adsorbed by solid phase.

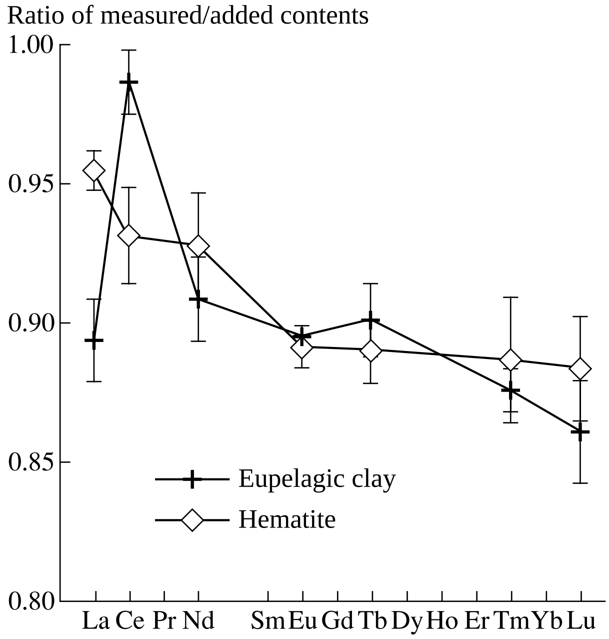

Fig. 4. Average "measured/added" ratios for REE contents in the solution during leaching of eupelagic clay and hematite. The confidence interval corresponds to one standard deviation.

Since REE fractionation during leaching of the Site 645 sediment was performed in the already REE-bearing solution and sediment, the anomalous Ce behavior could be related with the lower rate of sediment–solution exchange. In order to exclude the natural REE background contents, to simplify the solid phase composition, and consider the REE behavior in the leachate, hematite leaching was performed (Table 6). The weight loss of hematite was determined from the Fe content in the leachate and accounted for 0.08% for all experiments. It is seen in Table 6 that LREEs are more compatible with the solution than HREEs. The cerium shows no anomalous behavior. The ratios of the measured final REE contents in the solution to the added REE amounts in the experiments with eupelagic clay and hematite (Fig. 4) were significantly different only for La and Ce. A "measured/added" ratio in the case of La was 0.89 ± 0.01 (average value ± standard deviation) for the pelagic sediment and 0.95 ± 0.01 for hematite. For Ce, these values were 0.99 ± 0.01 and 0.93 ± 0.02 (Tables 5 and 6), respectively.

Table 4. REE contents in the leachate from the eupelagic clay versus time of leaching

Element		Time of leaching, h											
		0.5		1		4		8		12		24	
		x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}	x	S_{n-1}
La	ppm	20.3	0.06	20.7	0.1	21.8	0.06	22.1	0.2	22.2	0.3	22.3	0.3
Ce	ppm	47.9	0.2	51.3	0.05	56.7	0.08	58.4	0.5	57.9	0.5	58.6	0.2
Pr	ppm	6.68	0.03	6.82	0.02	7.18	0.02	7.28	0.04	7.15	0.06	7.27	0.08
Nd	ppm	28.5	0.1	29.2	0.09	30.6	0.09	31.0	0.2	30.9	0.1	31.2	0.3
Sm	ppm	7.11	0.06	7.22	0.05	7.66	0.04	7.76	0.05	7.72	0.07	7.79	0.08
Eu	ppm	1.74	0.03	1.80	0.01	1.88	0.01	1.92	0.02	1.89	0.01	1.90	0.01
Gd	ppm	7.53	0.09	7.74	0.07	8.12	0.03	8.2	0.1	8.2	0.2	8.26	0.08
Tb	ppm	1.13	0.01	1.15	0.01	1.21	0.01	1.21	0.01	1.22	0.01	1.21	0.01
Dy	ppm	6.77	0.04	6.94	0.02	7.24	0.06	7.27	0.07	7.26	0.02	7.23	0.05
Ho	ppm	1.32	0.01	1.35	0.01	1.41	0.01	1.41	0.01	1.40	0.01	1.41	0.01
Er	ppm	3.62	0.03	3.69	0.06	3.88	0.04	3.91	0.06	3.93	0.05	4.00	0.06
Tm	ppm	0.48	0.01	0.49	0.01	0.52	0.003	0.52	0.01	0.52	0.01	0.53	0.01
Yb	ppm	3.15	0.03	3.18	0.04	3.29	0.06	3.39	0.03	3.32	0.04	3.37	0.08
Lu	ppm	0.47	0.005	0.48	0.003	0.51	0.01	0.52	0.01	0.50	0.004	0.52	0.003
Al	%	0.24		0.26		0.30		0.34		0.32		0.35	
Fe	%	0.42		0.47		0.55		0.59		0.62		0.70	
Mn	%	0.80		0.80		0.79		0.83		0.80		0.81	
P	%	0.116		0.113		0.121		0.119		0.111		0.129	

Note: The average REE contents (x) and standard deviations (S_{n-1}) are listed for three independent determinations (six determinations for the experiment lasted eight hours) for one sample.

Table 5. REE sorption from the 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH solution by site 645 eupelagic clay (solid/liquid ratio = 1/67)

Element	Added REE content (ppb)	Final REE content in the solution (ppb)	Measured/added ratio in the solution	Average measured/added ratio in the solution
La	86.7	76.3	0.88	0.89
	130	116	0.89	
	173	158	0.91	
Ce	200	197	0.99	0.99
	299	299	1.00	
	399	390	0.98	
Nd	86.1	77.8	0.90	0.91
	129	120	0.93	
	172	154	0.90	
Eu	23.5	21.1	0.90	0.90
	35.3	31.6	0.90	
	47.1	41.9	0.89	
Tb	4.87	4.47	0.92	0.90
	9.73	8.69	0.89	
	14.6	13.2	0.90	
	19.5	17.3	0.89	
Tm	4.98	4.35	0.87	0.88
	9.96	8.63	0.87	
	14.9	13.2	0.88	
	19.9	17.5	0.88	
Lu	5.02	4.30	0.86	0.86
	10.0	8.39	0.84	
	15.1	13.3	0.88	
	20.1	17.5	0.87	

Table 6. REE sorption from the 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH solution by hematite (solid/liquid ratio = 1/67)

Element	Added REE content (ppb)	Final REE content in the solution (ppb)	Measured/added ratio in the solution	Average measured/added ratio in the solution
La	86.7	82.8	0.96	0.95
	130	125	0.96	
	173	164	0.95	
Ce	200	184	0.92	0.93
	299	285	0.95	
	399	368	0.92	
Nd	86.1	79.1	0.92	0.93
	129	123	0.95	
	172	158	0.91	
Eu	23.5	20.9	0.89	0.89
	35.3	31.8	0.90	
	47.1	41.7	0.89	
Tb	9.73	8.57	0.88	0.89
	14.6	13.2	0.90	
	19.5	17.2	0.89	
Tm	9.96	8.70	0.87	0.89
	14.9	13.6	0.91	
	19.9	17.4	0.87	
Lu	10.0	8.67	0.86	0.88
	15.1	13.6	0.90	
	20.1	17.8	0.89	

DISCUSSION

The leaching reagents must show a selective dissolving ability. This problem has been repeatedly discussed in the literature [5, 6, 12]. The stability of trace elements in the leachates has been studied less. The 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH [5] dissolves manganese oxides, poorly crystallized iron oxyhydroxides, trace elements sorbed in sediments, and Fe–Mn nodules. The various modifications of this reagent have been widely used [6–8, 11–14, 18–20].

The REE stability in different leachates was studied by Sholkovitz [9]. It was shown that different reagents (25% CH_3COOH, 0.1M $NH_2OH \cdot HCl$, 0.02M $NH_2OH \cdot HCl$ + 25% CH_3COOH, 0.04M $NH_2OH \cdot HCl$ + 25% CH_3COOH) release 25 to 57% ^{152}Eu. Based on these data, the readsorption of REE even in the acid leachates was inferred. We believe that ^{152}Eu redistribution is related either to a disturbance of the sorption equilibrium caused by Eu addition or to rapid isotope exchange in the solution–sediment system. Based on later experiments on suspension treatment with 25% CH_3COOH at room temperature for four hours, Sholkovits argued that readsorption of REE will be insignificant at a ratio of (20 ml of solution)/(3 mg of suspended material) [19].

In our experiments, the increase of the solid phase content at a constant solution volume (the solid/liquid ratio ranges from 1/20 to 1/800) results in a very insignificant decrease in REE (III) content, thus indicating the absence of significant REE adsorption from acid solutions (pH 2) by various sediments (Tables 1–3).

Because REEs do not form their own phases in sediments, their release into the leachate is caused by the dissolution of major minerals of a sediment, which include iron (oxyhydroxides and aluminosilicates), aluminium (aluminosilicates), manganese (oxyhydroxides), and phosphorus (bone detritus). None of the phases mentioned above prevail in the REE concentration in the hemipelagic sediment from site 6171. In the SDO-2 leachate, the Fe content shows a positive correlation with P and almost all REEs, except for Ce. In eupelagic clay (site 645), REEs show the highest correlation with iron. This indicates that the major REE source in the leachate is the iron oxyhydroxides (Fig. 5). The Fe also shows a correlation with P and Al. The LREEs (from La to Eu, excluding Ce) show a significant correlation with Al. This is consistent with data on REE content in the residues corresponding to LREE-enriched leachates (Table 3). In spite of a significant correlation between Fe and REEs in the sediments from site 645, the REEs show narrower variations than Fe and Al with an increase of the solid/liquid ratio (Fig. 5).

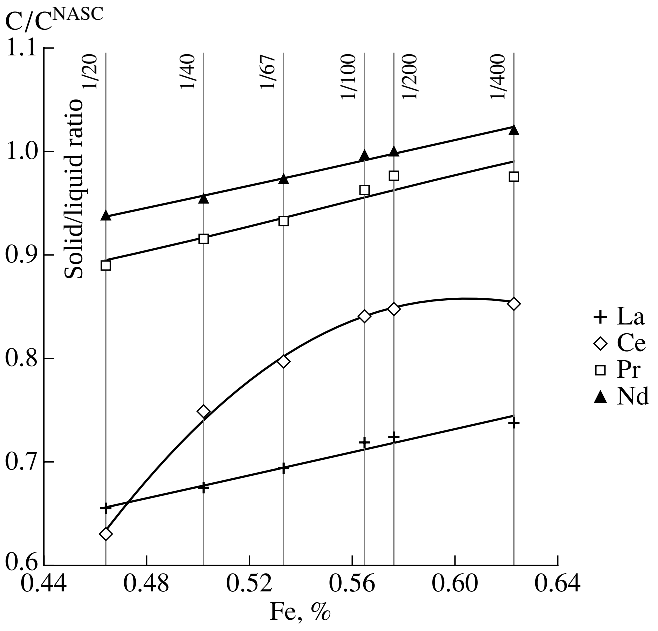

Fig. 5. NASC-normalized REE contents versus Fe content in the leachate of eupelagic clay at different solid/liquid ratio.

The REEs decrease by 5% (excluding Ce), whereas Al decreases two times, Fe decreases by 25%, and P decreases by 16% (Table 3). The high REE contents in the leachates as compared to major element contents in sediments and Fe–Mn nodules [4, 11, 13, 14] may be explained by REE adsorption on the mineral surface. This is also confirmed by kinetic experiments. The REE contents in the leachates become stable after four hours, whereas Fe and Al contents continue to increase (Table 4).

The leachate of the eupelagic clay shows a nonlinear decrease in Ce content as well as an Fe decrease upon an increasing solid/liquid ratio (Fig. 5). Such Ce behavior in the solution cannot be explained by simple dissolution of the sedimentary mineral phases. It may be explained only by Ce occurring in a tetravalent state in the sediment. In this case, the rate of REE (III) liberation into the solution is significantly higher than the rate of Ce^{4+} reduction and dissolution. This assumption is confirmed by kinetic experiments (Figs. 2, 3, Table 4). Unlike the trivalent REEs, the Ce content (and Ce anomaly) becomes stable only after eight hours.

In the kinetic experiments lasting four or more hours, the sediment–solution equilibrium was presumably attained for trivalent REEs and was not attained for Ce (Table 5). The reaction between acid leachate and REE adsorbed by sediments may be described as follows:

$$\equiv S\text{–}Ln + 3H^+ \rightleftharpoons \equiv S\text{–}3H + Ln^{3+}, \qquad (1)$$

with equilibrium constant

$$K = [\equiv S\text{–}3H][Ln^{3+}]/[\equiv S\text{–}Ln][H^+]^3, \qquad (2)$$

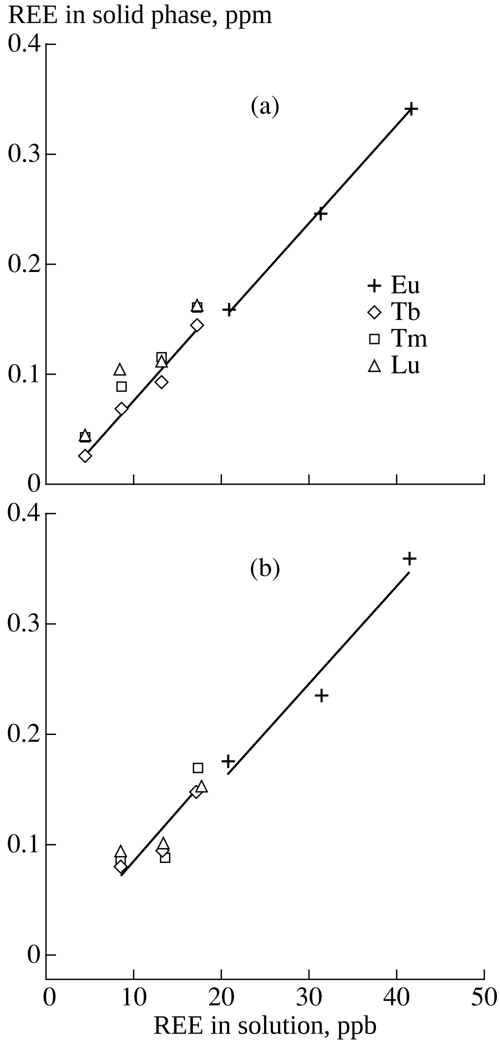

Fig. 6. Added REE contents in the eupelagic clay (a) and hematite (b) versus REE contents in the 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH solution after four-hour leaching.

where $[H^+]$ and $[Ln^{3+}]$ are, respectively, the equilibrium concentrations of protons and a lanthanide in the solution, and $[\equiv S\text{–}3H]$ and $[\equiv S\text{–}Ln]$ are the equilibrium concentrations of protons and a lanthanide in the adsorbed state. Any amount of added REEs shifts the equilibrium to the left; i.e., the sediment will adsorb some amount of the added element (Table 5). In the unequilibrium system (for Ce), no redistribution is observed between the sediment and solution (Table 5).

The REE partition coefficient between liquid and solid phases can be expressed as

$$K_d = [Ln^{3+}]/[\equiv S\text{–}Ln]. \qquad (3)$$

Under equilibrium conditions and constant pH, the K_d value is constant according to Eqs. (2) and (3):

$$K_d = K[H^+]^3/[\equiv S\text{–}3H]\text{—const.} \qquad (4)$$

Figures 6a and 6b demonstrate the variations of Eu, Tb, Tm, and Lu contents in the solid phase of the eupelagic clay and hematite versus those in the liquid phase. The REE contents in solid phase were calculated. Taking into account the calculation accuracy of REE contents in the solid phase, the partition coefficient between solid and liquid phases remains constant. The constant K_d is indicative of equilibrium conditions.

The calculated partition coefficients (average value ± standard deviation) between the leachate and sediment from site 645 and between the leachate and hematite are similar for Nd (153 ± 30 and 204 ± 67, respectively), Eu (128 ± 5 and 124 ± 10), Tb (129 ± 11 and 123 ± 16), Tm (106 ± 8 and 121 ± 31), and Lu (94 ± 17 and 116 ± 20). The correlation between Fe and REEs in the leachates of the pelagic sediment at various solid/liquid ratios suggests that MREE and HREE partition is caused by exchange reactions between iron oxyhydroxides and 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH. The Ce^{3+} partition coefficient (215 ± 67) for hematite is between K_d of La (322 ± 51) and Nd (204 ± 67), unlike that for the sediment from site 645. The partition coefficients of LREE are higher than those of MREE and HREE, which is consistent with the higher LREE stability in the acid solutions. We believe that the differences revealed in the K_d values of Nd and, especially, La (K_d^{La} for sediment is 129 ± 21) for hematite and the sediment from the site 645 may result from the existence of clay constituents in the sediment.

Based on the results obtained, some comments can be made concerning the use of leaching for obtaining data on exchangeable REEs. These data are of great importance because of the unique features of REEs. The presence and quantity of different REEs are indicators of the sources of material and the physicochemical conditions of natural processes. The use of the leaching to determine the composition of the exchangeable REEs made it possible to justify that the exchangeable constituent of the pelagic sediments was a source of material for diagenetic Fe–Mn nodules and micronodules in oceanic areas with high bioproductivity [4, 11, 13, 14]. The treatment of the hydrogenic Fe–Mn crust with leaching reagents showed that Ce is partially incorporated into the lattice of manganese oxyhydroxides, which may be related to its oxidation together with manganese in surface oceanic water [20]. The wide application of leaching to determine the exchangeable REEs was hampered by the absence of systematic data on the behavior of trace elements in the leachates.

Our experiments were limited only by the composition of the reagent, which was often modified by investigators [5–9, 11–14, 18–20]. The data obtained indicated that four-hour treatment of sediments at a solid/liquid ratio less than 1/100 leads to equilibrium being attained between the solution and solid phase with respect to REEs. Under such conditions, equilibrium is also attained for Ce. This is confirmed by the reproducibility of the Ce anomaly value at a solid/liquid ratio from 1/400 to 1/100 (Fig. 2). However, the quantities of major elements (Fe, Al, and P) in the leachate significantly depend on the sediment treatment. The REE behavior depends not only on their quantities but on their valent state also. The lack of equilibrium for Ce in the sediment–solution system may cause the negative Ce anomaly in the solution and, as a consequence, an incorrect interpretation of the geochemical data.

CONCLUSIONS

Leaching of various oceanic sediments by 1M $NH_2OH \cdot HCl$ + 25% CH_3COOH (pH 2) at different solid/liquid ratios did not reveal REE readsorption by sediment. The release of major elements (Fe, Al, and P) into the solution depends more strongly on the solid/liquid ratio than REE release. This may be related to REE allocation at the surface of the mineral phases.

The kinetic study of leaching of the site 645 pelagic sediment demonstrated that trivalent REEs attained equilibrium after four hours, while Ce attained equilibrium only after eight hours at a solid/liquid ratio of 1/67. This suggests a predominant tetravalent state of Ce in the oxidized pelagic sediments. Under the unequilibrium conditions, Ce addition does not cause its redistribution between solution and sediment. At a solid/liquid ratio <1/100, the quantities of all REEs correspond to equilibrium between solution and sediment.

The data obtained show that the REE distribution can be readily reproduced in the acid leachates at a solid/liquid ratio <1/100. At higher solid/liquid ratios, the proportion of exchangeable Ce may be underestimated owing to its slower release from the oxidized pelagic sediments.

ACKNOWLEDGMENTS

We are grateful to N.M. Stepanov for help in the analytical investigations and to E. Sholkovitz (Woods Hole Oceanographic Institution) for critical comments.

This study was supported by the Russian Foundation for Basic Research (project no. 97-05-64346) and the Russian Foundation for Leading Scientific Schools (project no. 96-15-98440).

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