

Rare Earth Elements in Phosphate–Ferromanganese Crusts on Pacific Seamounts

G. N. Baturin and I. G. Yushina

Shirshov Institute of Oceanology, Russian Academy of Sciences, Nakhimovskii pr. 36, Moscow, 117997 Russia

e-mail: gbatur@ocean.ru

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Abstract—Based on publications devoted to the composition of P-rich ferromanganese crusts on Pacific seamounts, relationships between the REE distribution in the crusts and the contents of phosphates and Fe–Mn hydroxides therein are considered. It is shown that REEs in the crusts are related to all three mineral phases and their contents are variable. In general, the REEs show weak correlations with P, Mn, and Fe in different varieties of ore crust. Average REE contents are comparable in samples with the maximal and minimal phosphorus contents, suggesting irregularity of REE distribution in the phosphates and ferromanganese phases. This fact is consistent with data on the presence of natural REE minerals in the phosphates.

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The REE distribution in rocks and ores is widely used for the reconstruction of their primary settings in various environments, including the ocean. Marine geologists and geochemists are particularly interested in the REE distribution in ferromanganese crusts and nodules with high concentrations of nonferrous metals, as well as in phosphorites that are among the major useful minerals on the ocean floor. At the same time, ferromanganese crusts (also called “ore crusts”) of seamounts often overlie phosphorites and contain phosphate interlayers and inclusions. Therefore, the ore crusts are enriched in phosphorus.

The REE distribution in ore crusts and phosphorites of seamounts is discussed in numerous publications (Anikeeva and Kazakova, 2000; Aplin, 1984; Baturin, 1986, 1993, 2004; Baturin and Yushina, 1991a, 1991b, 1996, 1998; Baturin et al., 1972; Bogdanov et al., 1990, 1995, 1998; Burnett et al., 1983; De Carlo, 1991; De Carlo and McMurtry, 1992; De Carlo et al., 1991; Dubinin, 2004; *Gaioty zapadnoi...*, 1995; Hein et al., 1990, 1993; Toth, 1980). Authors of these publications have noted a significant difference in the REE distribution in the crusts (positive Ce anomaly) and phosphorites (negative Ce anomaly). For example, the layer-by-layer analysis of ore crust from seamount near Kiribati Island (central Pacific) revealed that the La/Ce ratio varies from 0.1–0.4 in the upper ferruginous portion of the crust to 2.3–8.4 in the lower phosphate portion (De Carlo et al., 2000). Based on results of the analogous investigation of REE distribution in ore crusts recovered by the DSDP holes from Pacific guyots, Bogdanov et al. (1995, 1998) proposed a model of the REE composition variation depending on relationships between the ferromanganese and phosphate phases. In

so doing, they used conditional pure standards for each mineral phase.

However, the available data suggest that the REE content and composition are variable even in relatively pure ferromanganese and phosphate samples. Moreover, the bulk REE composition in some samples with a subordinate content of the associated (secondary in abundance) phase is strongly governed by the latter phase. In other words, the REE distribution is characterized by the phosphate trend in some ore crusts with a minor phosphate admixture. In contrast, some phosphorites with a minor admixture of oxides demonstrate the ferromanganese trend.

Therefore, the present communication attempts to scrutinize specific features of the REE distribution based on the study of several samples of ore crusts with different phosphorus contents.

MATERIALS AND METHODS

Our choice of representative material was dictated by the following principles: confinement to a single region; single analytical method; and compositional diversity in terms of both general chemistry and REE distribution. In this respect, the northwestern Pacific near the Marshall Islands (Fig. 1) is a perfect region, where ore crusts were sampled from 17 seamounts and guyots during the joint South Korean-American (KORDI-USGS) R/V *Farnell* cruise F10-89-CP in 1989 (Hein et al., 1990). During the subsequent international DSDP program (Leg 144), some guyots were explored by drilling deep holes that recovered compositionally analogous ferromanganese crusts (Bogdanov et al., 1995, 1998). These researchers investigated the REE distribution in ore crusts from the Wodejebato and

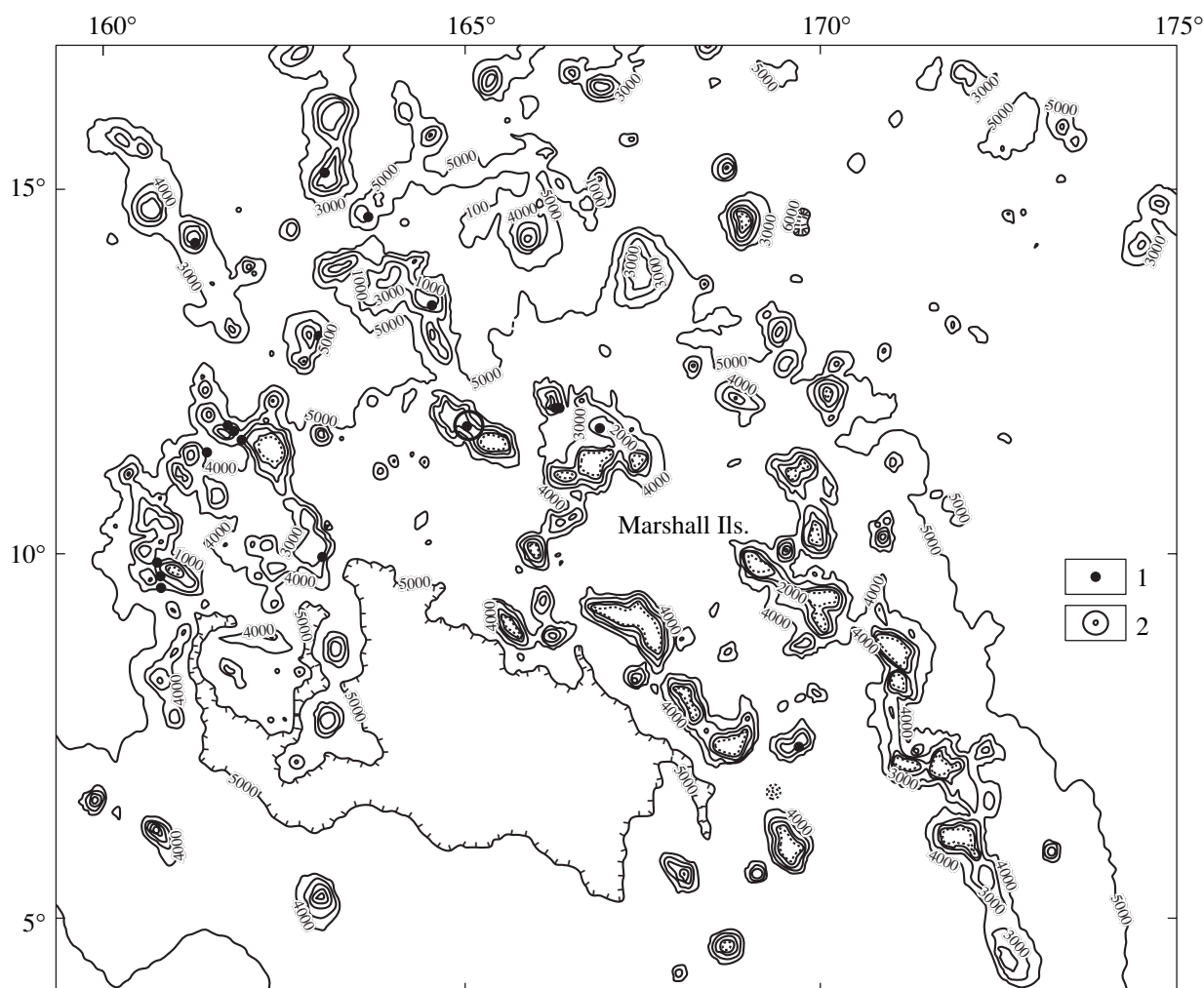


Fig. 1. (1) Scheme of the location of sampling points of ore crusts; (2) location of DSDP Hole 144 on the Wodejebato Guyot, Pacific (Bogdanov et al., 1995).

MIT guyots. In total, 107 high-precision analyses of REE contents and general chemical analyses were carried out in materials collected in the course of cruises mentioned above. However, Lu is absent in the first data array (Hein et al., 1990), while Ca is missing in the second data array.

According to data presented in the works mentioned above, the Sr isotopic age of volcanic rocks from the seamounts ranges from 75 to 85 Ma. The ore crust overlies breccias, basalts, hyaloclastites, partially phosphatized limestones, volcanoclastites, and phosphorites. The predominant breccias are composed of basalt clasts with compositionally variable cement or matrix of fine-grained volcanoclastic material and carbonate sediment. The cement consists of the following components (in the decreasing order): phosphate, phillipsite, calcite, Fe–Mn oxyhydroxides, and iron hydroxides. Based on one isotope dating, the breccias are Campanian rocks. Layered hyaloclastite–sandstone sequences from

another seamount contain Eocene or Oligocene nannofossil.

The ore crusts vary from <1 to 18 cm in thickness and reveal a layered structure (from two to seven layers). Vernadite, the major component, makes up intergrowths with the amorphous goethite. Carbonate-fluorapatite (francolite) occurs as inclusions and interlayers in several samples (up to 27 wt %). Average contents of other components in the crusts are as follows (%): Fe 12.2, Mn, 18.8, and total REE 0.16 (variation from 0.09 to 0.28). The maximal REE content is recorded in the lower layer of sample RD59-2L (horizon 53–63 mm) characterized by high Mn/Fe ratio, phosphorus concentration (3.9%), and low content of clastic material.

Based on the study of cores, Bogdanov et al. (1995, 1998) revealed that the ferromanganese ore material continued to accumulate on seamounts until the late Paleocene–early Eocene. The seamounts with summits primarily represented by islands formed in the Cretaceous in the southwestern sector of the Pacific. During

the subsequent 90 Ma, the lithospheric plate with the seamounts underwent northwestward migration toward their present-day location.

At the Wodejebato Guyot, the crust overlies late Paleocene and middle Eocene gravels related to the erosion of Late Cretaceous carbonate platform. The basal horizon was also repeatedly subjected to erosion, phosphatization, and ferromanganese mineralization. This is indicated by the alternation of ferromanganese oxide and phosphate layers in the ore crusts. At the MIT guyot, the crust was probably developed on the Albian carbonate platform at the Cenomanian–early Miocene interval (90–23 Ma ago).

The crust is mainly composed of Fe-vernadite at the Wodejebato Guyot and the asbolane–buserite association with a minor admixture of Fe-vernadite at the MIT Guyot. The chemical composition of the crust is dominated by Mn (5.10–24.70%) and Fe (3.92–15.08%). Among 30 samples studied, 20 samples are enriched in phosphate material (>5% P), and only five samples are depleted in P (<2%).

The studied data array also included P-rich ore crust from one of the seamounts of the Mid-Pacific system (Site 6369, northern equatorial Pacific) (Bezrukov, 1976).

All REE determinations were carried out with the ICP-MS method characterized by the highest sensitivity and accuracy (Dubinin, 2004).

Previous calculations of coefficients of correlation between elements in crust samples from the guyot surface (Hein et al., 1990) and DSDP cores (Bogdanov et al., 1995) did not reveal any distinct correlations between REE and other elements. However, according to (Dubinin, 2004), the crusts are generally characterized by correlation between the trivalent REE and Fe. For example, $\text{Nd (ppm)} = (15.5\text{Fe (\%)} - 36)$ at the correlation coefficient (r) equal to 0.657, while the r value for the Ce–Fe pair is low (0.289).

Therefore, we divided all compositional data on the ore crusts into different groups in terms of the Ce anomaly (groups 1 and 2) and the P content (groups 3 and 4). For each group, we calculated average contents of elements, coefficients of pair correlation between elements, and multiple correlations by the Q-factor method used previously for the elucidation of analogous problems (Baturin and Yushina, 1996, 1998). The main attention was devoted to samples with the P content of >2%, which corresponds to ~10% of the phosphate phase.

CRUSTS WITH DECREASED AND INCREASED VALUES OF THE CERIUM ANOMALY

The Ce anomaly (Ce^*) value in sedimentary rocks and ores is usually determined as the ratio of shale-normalized contents $2\text{Ce}_N/(\text{La}_N + \text{Nd}_N)$ (Balashov, 1976). Data presented in (Gromet et al., 1994) were accepted

as the average REE contents in shales. The Eu anomaly was similarly determined as $\text{Eu}^* = 2\text{Eu}_N/(\text{Sm}_N + \text{Gd}_N)$.

Group 1 included P-rich (>2% P) crusts with $\text{Ce}^* < 1.3$ (20 samples). Group 2 included P-poor (1.3–2%) crusts (23 samples).

Analysis of these data shows that the rocks are characterized by an insignificant discrepancy in terms of their major components (Tables 1, 2). Average contents of Mn, Ca, and P (14.43–15.48, 10.87–10.88, and 4.45–4.90%, respectively) in both groups are almost similar. However, samples of group 1 are slightly enriched in Fe than those of group 2 (9.38 and 7.60%, respectively) and more strongly enriched in Si (2.55 and 1.18%, respectively) and Al (0.87 and 0.21%, respectively). One can also see some discrepancies in the behavior of the major ore elements. For example, samples of group 1 are enriched in Cu, Ni, and Zn. At the same time, they are depleted in Co and Pb.

Discrepancy in the REE distribution is primarily related to the behavior of Ce. The Ce content varies from 100–730 ppm in group 1 to 532–2400 ppm in group 2. At the same time, the Ce^* value varies from 0.28 to 1.28 (average 0.91) in group 1 and from 1.45 to 3.9 (average 2.47) in group 2. In general, the Ce^* value varies nine times in the whole data array, and the average value in group 1 is 2.5 times lower than that in group 2. Discrepancy in the distribution of other REEs is insignificant: samples of group 1 are slightly enriched in MREE, HREE, and Y.

Values of pair correlation coefficient (r) for samples of group 1 (Table 3, upper side) show that Ti, V, and partly Pb correlate with Fe, while Co, Pb, Ce, and partly Zn correlate with Mn. The high Ca–P correlation ($r = 0.994$) suggests that both elements are almost totally incorporated in the apatite phase. As was shown in (Hein et al., 1990), the whole carbon dioxide of ore crusts is included in the apatite phase. Cu, Ni, and Zn are also partly related to this phase. In contrast to La, Ce is unrelated to the apatite phase, and the r value increases from LREE to MREE and, particularly, HREE. At the same time, all REEs, except Ce, correlate well with each other. Like the Ce^* value, Ce correlates with Mn, Co, Pb, and V.

In Ce-rich samples of group 2, Fe correlates with Ti. Correlation with V, Pb, and Zn is appreciably weaker (Table 3, lower side). Manganese has a stronger correlation with all these metals and Co. Its correlation is weaker with Ce^* ($r = 0.488$) and very weak with Ce ($r = 0.324$). As in the previous case, Ca is almost completely associated with P ($r = 0.986$). All REEs, except Ce, have a weak or moderate correlation with P and Ca (i.e., with calcium phosphate). In contrast to the previous case, Ce correlates with La and other REEs, but the correlation with Co and Pb is weaker.

Sample no.

Element	H4	H8	H9	H13	H17	H18	H23	H27	H35	H37	H40	H42	H43	B2	B5	B7	B14	B15	B349
Fe	7.8	11.1	13	11.8	14.7	11	13.1	10.3	12.4	16.6	9.8	10	5.4	4.32	6.95	5.64	3.92	5.59	8.82
Mn	20.5	21	14.8	12.2	8.2	15.8	18.2	14.3	16.6	16	17	16.1	12	14.6	19	18.4	13.6	10.2	10
Si	0.55	1.07	2.48	1.92	5.7	1.5	1.68	1.37	1.96	2.2	1.68	0.99	0.76	0.12	0.45	0.8	0.4	0.24	3.23
Ti	0.47	0.76	0.72	0.57	0.56	0.59	0.72	0.49	0.71	0.8	0.6	0.49	0.23	0.25	0.4	0.38	0.23	0.28	0.47
Al	0.21	0.22	0.57	0.46	1.87	0.3	0.34	0.35	0.5	0.69	0.49	0.41	0.42	0.05	0.05	0.15	0.24	0.03	1
Ca	10.7	7.7	8.2	13.6	12.1	8.3	6.8	12.4	8.3	8.9	9.2	14.1	21.8						15.55
P	3.6	2.51	2.83	4.9	4.1	2.83	2.18	4.3	2.86	2.92	3.3	5.1	8.2	7.1	4.7	4.6	6.9	8.1	5.61
Co	4100	5300	2500	1400	930	3100	3700	1800	3000	2400	3600	2500	970	2200	2300	2700	1900	1700	2180
Cu	530	720	1000	1000	1700	650	850	730	580	790	780	760	740	1150	870	700	1820	970	1845
Ni	5800	4700	2700	2000	2300	3300	3600	2900	3500	2900	5600	5700	5200	10300	9400	6600	14000	8800	2800
V	420	530	530	470	350	480	620	490	540	640	480	520	320	280	460	400	190	180	340
Pb	1300	1200	910	920	450	1000	1200	980	1300	880	1000	800	770	580	700	850	400	440	840
Zn	740	660	640	540	590	560	670	580	650	700	810	800	920	1030	1210	950	1350	950	480
La	270	230	260	290	460	220	230	220	200	230	230	290	290	292	269	330	356	259	314
Ce	510	560	580	690	190	520	490	470	390	370	430	270	300	610	599	730	222	235	719
Pr	36	36	41	42	66	36	37	32	29	36	31	37	35	32	34.3	47.9	34.9	28.4	62.7
Nd	170	160	190	190	320	170	180	150	140	160	140	180	170	137	147	205	158	126	282
Sm	28	29	34	34	58	30	29	25	24	28	26	29	28	23.6	26	39.5	26.2	22.8	59.1
Eu	7.9	7.4	9	8.4	16	7.9	7.8	7.2	5.6	7.6	6.8	10	8.2	6.01	6.7	10.3	6.66	5.85	12.6
Gd	32	31	36	41	79	33	33	25	28	35	30	43	42	36.3	38.6	56.8	44	26.1	70.6
Tb	5.9	5.3	5.8	5.8	12	4.9	5.5	4.3	4.6	5.4	5.1	6.8	6	4.95	5.46	7.79	5.85	4.85	9.3
Dy	36	32	36	37	77	33	33	30	31	34	35	45	38	36.2	38.4	54.2	44.6	35.6	57
Ho	8.6	7.1	8	8.7	18	6.7	6.6	6.5	5.9	7.3	7.9	10	9.6	9.32	9.7	12.9	11.74	8.97	12.2
Er	27	20	21	25	53	19	19	19	19	21	23	29	28	29.1	30.1	39.8	37.8	28.5	39.5

Note: Data on samples with indexes H and B are based on (Hein et al., 1990) and (Bogdanov et al., 1995), respectively. Data on sample B349 are based on (Baturin and Yushina, 1998).

Table 2. Chemical composition of P- and Ce*-rich ore crusts

Element	Sample no.																							
	H14	H22	H47	H50	H51	H64	H73	H76	H77	H78	H79	H82	H83	H86	B4	B6	B9	B10	B11	B14	B15	B16	B17	B18
Fe	11.5	9.3	9	8.5	7.5	6.7	8.2	7.6	6.6	6.8	8.3	7.8	5.5	8.2	7.57	7.93	6.51	9.33	9.54	7.31	4.6	4.73	6.03	7.39
Mn	12.8	15.5	20.9	23.2	19.9	18	15	17.1	12.2	15.7	16.6	17.5	14.9	21.5	18.6	17.3	20	13.9	11.9	20.4	6	5.6	7.8	9.2
Si	2.9	0.97	0.98	0.64	0.55	0.36	0.85	0.89	1.85	2.31	2	0.72	0.54	0.64	0.59	0.59	0.42	0.63	0.85	0.59	2	1.9	2.2	2.3
Ti	0.78	0.48	0.58	0.38	0.48	0.42	0.51	0.54	0.51	0.59	0.58	0.56	0.43	0.59	0.4	0.42	0.38	0.38	0.38	0.41	0.29	0.27	0.36	0.42
Al	0.78	0.2	0.08	0.14	0.15	0.09	0.19	0.3	0.4	0.25	0.33	0.22	0.16	0.2	0.02	0.1	0.02	0.05	0.17	0.02	0.25	0.23	0.36	0.36
Ca	13.5	13.3	9.5	6.9	8.2	9.6	11.7	9.6	15.2	12	8.9	9	13.8	11										
P	4.8	4.8	3.3	2.11	2.52	3.1	3.8	2.92	5	3.9	2.81	2.88	4.6	3.6	4.2	4.8	4.4	5.1	6.9	4.2	9.9	10.2	9.5	8.3
Co	2200	2300	3500	3900	5000	4000	2500	3200	2000	4100	3800	3400	3000	3800	2400	4000	4300	2000	1600	2900	1100	1000	1400	1600
Cu	1300	660	260	370	460	440	720	1100	710	840	800	970	610	1100	1020	610	780	530	670	310	410	370	500	460
Ni	2300	3600	3900	4300	5600	5300	3500	5400	2600	3400	4100	4900	3400	6300	5400	6000	8700	4000	4000	6000	2000	2200	2500	2700
V	500	450	770	700	450	400	400	430	320	420	420	420	350	440	470	410	420	330	320	430	150	130	210	220
Pb	920	990	1500	2500	1300	990	1100	1000	920	1100	1100	950	1000	1600	1050	750	870	1130	1030	1080	480	360	570	690
Zn	590	590	710	880	740	680	590	730	510	660	630	700	630	740	700	780	1160	720	810	830	100	260	210	430
La	300	220	210	240	270	300	490	280	350	530	270	250	330	390	179	163	154	162	312	213	188	156	188	277
Ce	820	620	1100	1400	1200	1100	2100	1600	1900	2400	1400	1300	2400	2200	1070	532	772	797	911	1236	625	571	793	851
Pr	41	34	32	28	42	44	69	40	44	77	43	39	49	56	32.8	27.4	28.1	32.7	42.5	31.1	24.8	20.7	25.7	36.7
Nd	180	160	140	120	190	190	320	180	210	350	190	170	220	250	128	113	116	134	181	127	102	87	111	156
Sm	33	27	25	19	32	33	52	30	32	57	33	30	36	42	24.2	22.4	21.4	26	32.4	23.4	19.9	15.5	20.1	28.5
Eu	8.3	7.4	6.3	5.4	8.1	6.7	12	6.9	8	13	7.4	7	9.3	10	5.72	5.36	5.4	6.34	8.22	6.3	4.95	4.01	5.19	7.75
Gd	38	32	29	23	35	38	63	37	42	67	38	34	42	53	30.1	26	27.8	31.7	46.8	29	27.9	22.6	29.1	41.8
Tb	6.2	5	5.5	3.7	5.6	6.3	10	5.5	6.3	11	5.8	5.4	6.9	8.5	4.4	4.02	4.18	4.63	6.24	4.48	3.69	3.11	4.05	5.77
Dy	36	33	29	24	36	37	63	36	43	67	36	33	44	53	27.8	25.1	27.8	30.9	41.6	29.2	25.7	22.1	27.2	39.2
Ho	7.9	6.9	6.5	5.8	7.8	9	15	8.1	9.9	15	7.3	6.9	9.2	12	6.42	5.48	6.7	7.04	9.95	6.83	6.15	5.21	6.76	9.61
Er	24	21	20	18	24	25	45	25	30	46	23	22	29	37	19.5	15.6	20.7	26	28.6	21.1	18.5	16.2	20.2	30.2
Tm	3.3	3	3	2.6	3.3	2.6	6.1	3.3	4.4	6.1	3.1	2.8	3.7	4.9	2.69	2.4	2.83	2.92	3.99	3.07	2.47	2.23	2.87	4.09
Yb	23	18	18	18	21	24	38	21	26	38	19	18	24	33	16.6	14.2	18.3	18.8	25.9	18.3	16.7	14.4	18.7	25.9
Lu															2.7	2.33	2.95	3.01	4.01	2.9	2.56	2.53	3.12	4.29
Y	360	210	220	190	220	220	520	240	360	490	210	210	300	570										
Ce*	1.53	1.45	2.8	3.46	2.31	2	2.3	3.1	3	2.4	2.7	2.74	3.9	3.04	3.1	1.71	2.53	2.39	1.64	3.22	1.9	2.08	2.36	1.71
Eu*	1.02	1.1	1.02	1.13	1.06	0.82	0.91	0.9	0.94	0.92	0.92	0.95	1.04	0.92	0.92	0.97	0.97	0.96	0.9	1.05	0.9	0.91	0.92	0.96
Total REE	1521	1187	1623	1907	1875	1817	3283	2273	2706	3677	2076	1918	3203	3149	1550	958	1208	1283	1654	1752	1068	953	1255	1402

Table 3. Coefficients of correlation between elements in P-rich ore crusts of the Ce*-rich (left-hand bottom side) and Ce*-poor (right-hand upper side) varieties

	Fe	Mn	Si	Ti	Al	Ca	P	Co	Cu	Ni	V	Pb	Zn	La	Ce
Fe	1	0.193	-0.070	0.748	-0.139	-0.355	-0.642	0.254	0.006	-0.632	0.781	0.477	-0.486	-0.075	0.068
Mn	0.371	1	-0.767	0.009	-0.768	-0.111	-0.200	0.852	-0.113	0.318	0.671	0.792	0.433	-0.127	0.529
Si	-0.037	-0.670	1	0.428	0.996	-0.351	-0.350	-0.511	-0.325	-0.506	-0.395	-0.572	-0.621	-0.214	-0.455
Ti	0.618	0.341	0.262	1	0.373	-0.904	-0.914	0.279	-0.398	-0.747	0.584	0.317	-0.716	-0.485	-0.015
Al	0.245	-0.467	0.820	0.549	1	-0.318	-0.298	-0.523	-0.342	-0.451	-0.440	-0.600	-0.574	-0.220	-0.484
Ca	-0.049	-0.812	0.433	0.271	0.459	1	0.994	-0.367	0.396	0.317	-0.260	-0.069	0.442	0.499	0.056
P	-0.455	-0.899	0.522	-0.558	0.231	0.986	1	-0.422	0.440	0.620	-0.609	-0.414	0.593	0.442	-0.106
Co	0.143	0.839	-0.484	0.361	-0.333	-0.759	-0.822	1	-0.156	0.118	0.593	0.791	0.113	-0.283	0.445
Cu	0.385	0.136	0.143	0.649	0.455	0.328	-0.306	0.119	1	0.352	-0.230	-0.214	0.328	0.759	0.091
Ni	0.080	0.754	-0.731	-0.007	-0.597	-0.663	-0.562	0.705	0.169	1	-0.371	-0.203	0.942	0.293	-0.018
V	0.581	0.840	-0.371	0.506	-0.189	-0.515	-0.797	0.632	0.101	0.377	1	0.797	-0.179	-0.304	0.400
Pb	0.439	0.761	-0.408	0.257	-0.240	-0.579	-0.696	0.540	-0.019	0.287	0.799	1	-0.096	-0.313	0.542
Zn	0.430	0.834	-0.658	0.216	-0.457	-0.837	-0.742	0.706	0.206	0.825	0.641	0.556	1	0.340	0.033
La	0.108	0.092	0.174	0.519	0.273	0.381	-0.309	0.203	0.340	-0.174	0.085	0.219	0.028	1	-0.039
Ce	-0.095	0.324	-0.093	0.412	0.024	0.259	-0.474	0.350	0.297	0.027	0.210	0.386	0.167	0.820	1
Pr	0.149	0.187	0.061	0.547	0.147	0.333	-0.407	0.310	0.402	-0.037	0.123	0.200	0.138	0.963	0.817
Nd	0.140	0.170	0.081	0.558	0.179	0.378	-0.403	0.300	0.390	-0.070	0.122	0.197	0.110	0.970	0.823
Sm	0.190	0.161	0.087	0.577	0.178	0.352	-0.389	0.294	0.421	-0.049	0.109	0.157	0.121	0.950	0.773
Eu	0.231	0.143	0.112	0.573	0.214	0.452	-0.348	0.239	0.385	-0.100	0.119	0.194	0.120	0.948	0.774
Gd	0.134	0.012	0.164	0.468	0.210	0.404	-0.208	0.121	0.391	-0.122	-0.040	0.073	0.032	0.952	0.735
Tb	0.170	0.152	0.107	0.567	0.175	0.380	-0.344	0.260	0.376	-0.071	0.125	0.173	0.102	0.960	0.786
Dy	0.106	0.070	0.120	0.478	0.178	0.426	-0.264	0.180	0.364	-0.098	0.006	0.121	0.060	0.965	0.789
Ho	0.072	0.024	0.123	0.391	0.155	0.388	-0.189	0.115	0.304	-0.105	-0.040	0.104	0.036	0.952	0.743
Er	0.090	0.026	0.126	0.397	0.146	0.390	-0.198	0.104	0.309	-0.114	-0.044	0.123	0.043	0.930	0.758
Tm	0.114	0.027	0.182	0.422	0.189	0.431	-0.171	0.079	0.300	-0.138	0.002	0.139	0.038	0.924	0.748
Yb	0.107	0.043	0.147	0.417	0.201	0.375	-0.191	0.120	0.307	-0.114	-0.004	0.166	0.041	0.953	0.742
Y	-0.038	-0.222	0.255	0.352	0.192	0.461	0.405	-0.185	0.443	-0.103	-0.323	-0.088	-0.278	0.874	0.682
Ce*	-0.245	0.488	-0.378	0.020	-0.311	-0.171	-0.443	0.316	0.030	0.269	0.343	0.485	0.297	0.097	0.628
Eu*	0.325	0.388	-0.163	0.110	-0.050	-0.043	-0.288	0.225	-0.218	0.054	0.514	0.499	0.299	-0.201	-0.052
Total REE	-0.034	0.281	-0.039	0.462	0.077	0.311	-0.457	0.333	0.333	-0.033	0.186	0.347	0.148	0.899	0.986

Table 3. (Contd.)

	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y	Ce*	Eu*	Total REE
Fe	0.268	0.341	0.254	0.273	0.037	0.167	0.051	-0.125	-0.222	-0.165	-0.159	-0.115	0.141	0.323	0.092
Mn	-0.243	-0.223	-0.329	-0.388	-0.353	-0.301	-0.267	-0.248	-0.260	-0.222	-0.203	-0.594	0.651	-0.005	0.189
Si	0.085	0.050	0.181	0.299	0.159	0.140	0.036	-0.035	-0.030	-0.081	-0.105	0.219	-0.469	0.252	-0.326
Ti	0.021	0.040	0.073	0.107	-0.166	-0.076	-0.243	-0.429	-0.493	-0.491	-0.487	-0.435	0.121	0.455	-0.180
Al	0.039	0.002	0.133	0.260	0.135	0.109	0.013	-0.042	-0.031	-0.084	-0.106	0.208	-0.495	0.247	-0.364
Ca	0.300	0.335	0.270	0.281	0.396	0.329	0.356	0.441	0.450	0.492	0.481	0.556	-0.186	-0.296	0.362
P	-0.017	-0.033	-0.047	-0.092	0.166	0.076	0.212	0.385	0.438	0.437	0.441	0.564	-0.256	-0.456	0.093
Co	-0.192	-0.178	-0.219	-0.313	-0.362	-0.272	-0.305	-0.351	-0.356	-0.362	-0.325	-0.580	0.575	0.122	0.120
Cu	0.615	0.609	0.573	0.411	0.630	0.578	0.654	0.680	0.694	0.688	0.716	0.685	-0.160	-0.615	0.571
Ni	-0.305	-0.338	-0.377	-0.433	-0.115	-0.189	0.006	0.207	0.280	0.259	0.304	-0.179	-0.024	-0.518	-0.033
V	-0.044	0.011	-0.089	-0.088	-0.255	-0.173	-0.255	-0.385	-0.462	-0.394	-0.388	-0.557	0.542	0.314	0.120
Pb	-0.113	-0.055	-0.139	-0.240	-0.340	-0.255	-0.327	-0.423	-0.446	-0.410	-0.406	-0.603	0.668	0.196	0.206
Zn	-0.262	-0.282	-0.358	-0.392	-0.082	-0.146	0.044	0.242	0.286	0.290	0.331	-0.093	0.028	-0.516	0.019
La	0.725	0.732	0.642	0.663	0.812	0.819	0.899	0.958	0.934	0.968	0.960	0.827	-0.344	-0.461	0.568
Ce	0.210	0.135	0.176	-0.053	0.042	-0.044	-0.060	-0.085	-0.081	-0.085	-0.122	-0.293	0.915	-0.285	0.740
Pr	1	0.985	0.986	0.928	0.937	0.942	0.886	0.785	0.749	0.743	0.723	0.804	-0.128	-0.282	0.781
Nd	0.995	1	0.967	0.938	0.911	0.944	0.881	0.769	0.722	0.736	0.714	0.813	-0.181	-0.205	0.724
Sm	0.995	0.990	1	0.925	0.920	0.922	0.852	0.731	0.704	0.679	0.666	0.813	-0.152	-0.255	0.738
Eu	0.973	0.974	0.977	1	0.900	0.947	0.871	0.759	0.700	0.714	0.690	0.890	-0.356	-0.008	0.549
Gd	0.965	0.958	0.967	0.959	1	0.961	0.951	0.895	0.880	0.857	0.853	0.925	-0.313	-0.427	0.680
Tb	0.987	0.983	0.988	0.974	0.974	1	0.970	0.898	0.864	0.859	0.853	0.896	-0.371	-0.255	0.616
Dy	0.979	0.979	0.977	0.975	0.991	0.985	1	0.966	0.945	0.937	0.941	0.902	-0.384	-0.360	0.607
Ho	0.946	0.943	0.941	0.937	0.984	0.962	0.985	1	0.987	0.986	0.986	0.912	-0.407	-0.440	0.562
Er	0.942	0.937	0.937	0.941	0.975	0.954	0.981	0.988	1	0.978	0.983	0.915	-0.404	-0.515	0.554
Tm	0.908	0.913	0.903	0.934	0.954	0.930	0.962	0.969	0.971	1	0.982	0.901	-0.401	-0.434	0.547
Yb	0.931	0.928	0.924	0.928	0.969	0.952	0.972	0.992	0.981	0.962	1	0.904	-0.435	-0.466	0.519
Y	0.830	0.834	0.829	0.858	0.882	0.875	0.883	0.891	0.901	0.907	0.928	1	-0.646	-0.397	0.468
Ce*	0.109	0.106	0.042	0.050	-0.017	0.057	0.051	0.012	0.057	0.060	0.021	-0.013	1	-0.108	0.441
Eu*	-0.225	-0.196	-0.234	-0.076	-0.328	-0.235	-0.253	-0.312	-0.273	-0.176	-0.272	-0.359	0.204	1	-0.479
Total REE	0.897	0.903	0.862	0.858	0.828	0.871	0.874	0.832	0.839	0.826	0.828	0.775	0.499	-0.104	1

Table 4. Average contents of elements in the P-rich four groups of ore crusts

Element	Group				Element	Group			
	Ce* < 1.3	Ce* > 1.3	P > 5%	P < 5%		Ce* < 1.3	Ce* > 1.3	P > 5%	P < 5%
Fe	9.38	7.60	6.64	9.15	Ce, ppm	449	1237	667	963
Mn, %	14.43	15.48	11.01	16.68	Pr	38.36	39.19	35.16	40.90
Mn/Fe	2.03	1.53	1.66	1.82	Nd	175.7	171.9	156.5	180.0
Si	2.55	1.18	1.39	1.99	Sm	31.46	29.78	27.93	31.64
Ti	0.53	0.46	0.35	0.55	Eu	8.36	7.29	7.26	8.02
Al	0.87	0.21	0.31	0.60	Gd	30.07	36.83	38.76	38.04
Ca	10.88	10.87	16.66	9.95	Tb	6.06	5.68	5.50	6.00
P	4.45	4.90	7.38	3.57	Dy	39.80	36.11	37.39	37.95
Fe/P	1.55	2.11	0.90	2.57	Ho	9.14	8.23	8.96	8.51
(Fe + Mn)/P	4.69	5.35	2.42	7.23	Er	27.49	25.23	27.82	25.61
Co	2415	2875	1860	3069	Tm	3.85	3.41	3.81	3.53
Cu	913	667	840	752	Yb	25.20	21.95	24.72	22.88
Ni	5109	4254	5138	4435	Lu	4.62	3.04	3.89	3.41
V	419	398	270	465	Y	315	309	455	289
Pb	826	1041	693	1048	REE	1134	1887	1321	1639
Zn	751	641	659	704	Ce*	0.91	2.47	1.49	1.88
La	271	268	264	271	Eu*	1.04	0.96	0.94	1.02

Note: Elements from Fe to P (from the top of the column) are given in %; other elements, in ppm.

ELEMENTAL COMPOSITION OF CRUSTS WITH DIFFERENT CONTENTS OF PHOSPHORUS

Tables 1 and 2 present compositions of samples of groups 3 and 4 with high and moderate P contents (>5 and 2–5%, respectively). Therefore, the further description will be based on average contents of elements in these groups (Table 4).

Relative to P-poor samples of group 4 (P_{av} 3.57%), P-rich samples of group 3 (P_{av} 7.38%) are depleted in lithogenic elements (Si, Al, and Ti), as well as Fe, Mn, Co, Pb, V, and Ce. However, they are slightly enriched in Cu, Ni, and Y. At the same time, contents of La, Pr, Nd, Sm, Eu, and Tb are lower; contents of Gd, Dy, and

Ho are similar; and contents of Er, Tm, Yb, and Lu are higher (Fig. 2).

Table 5 (upper side) shows correlations between elements in crusts of group 3 characterized by the maximal P content. Fe correlates with the following elements (in decreasing order): Pb, Ti, V, Co (less prominent), two LREEs (Pr, Nd), all MREEs, and Eu*. Mn correlates with Co, V, Zn, La, and all HREEs. Correlation with LREE and MREE is less significant. Correlation of Ca is strong with P ($r = 0.986$) and moderate with Zn ($r = 0.617$). However, both Ca and P lack any correlation with any REE. La correlates with all REEs (except Ce), Cu, and Zn. It has a weaker correlation with Co, Zn, and V. Correlation of Ce is strong with Ti, moderate with Si

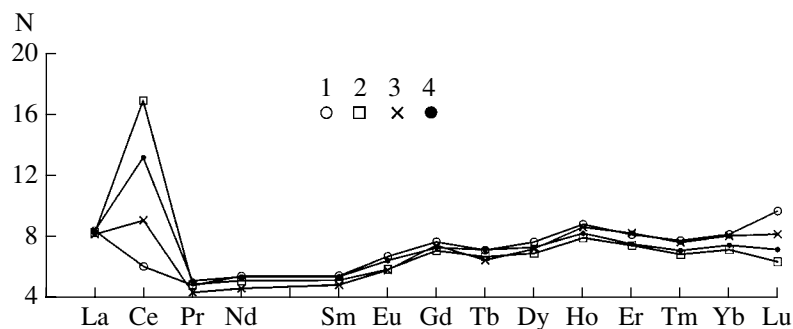


Fig. 2. The shale-normalized (N) average REE contents in P-rich ore crusts. (1, 2) Varieties with decreased and increased Ce anomaly values, respectively; (3, 4) varieties with maximum and moderate phosphorus contents, respectively.

Table 5. Coefficients of correlation between elements in ore crusts with the phosphorus content >5% (right-hand upper side) and <5% (left-hand bottom side)

	Fe	Mn	Si	Ti	Al	Ca	P	Co	Cu	Ni	V	Pb	Zn	La	Ce
Fe	1	0.364	0.187	0.771	0.302	-0.797	-0.628	0.486	-0.086	-0.393	0.746	0.814	-0.071	0.075	0.207
Mn	-0.143	1	-0.613	0.189	-0.128	-0.322	-0.810	0.752	0.380	0.560	0.748	0.480	0.773	0.555	-0.081
Si	-0.054	-0.827	1	0.518	0.761	-0.422	0.169	-0.161	-0.075	-0.740	-0.100	0.032	-0.800	-0.146	0.400
Ti	0.626	-0.424	0.450	1	0.510	-0.982	-0.611	0.547	-0.064	-0.516	0.616	0.625	-0.334	0.225	0.598
Al	-0.101	-0.803	0.995	0.409	1	-0.192	-0.222	0.151	0.410	-0.370	0.320	0.180	-0.296	0.315	0.144
Ca	-0.026	-0.102	-0.333	-0.332	-0.347	1	0.986	-0.981	-0.214	0.310	-0.527	-0.551	0.617	-0.387	-0.343
P	-0.192	-0.070	-0.249	-0.452	-0.253	0.975	1	-0.846	-0.417	-0.183	-0.788	-0.715	-0.444	-0.543	-0.293
Co	-0.206	0.798	-0.601	-0.192	-0.586	-0.248	-0.298	1	0.507	0.353	0.663	0.382	0.419	0.478	0.108
Cu	0.449	-0.139	-0.200	0.170	-0.240	0.452	0.294	-0.209	1	0.630	0.131	-0.106	0.583	0.642	-0.261
Ni	-0.448	0.708	-0.558	-0.629	-0.515	-0.076	0.233	0.536	-0.029	1	-0.041	-0.352	0.890	0.461	-0.515
V	0.489	0.590	-0.517	0.145	-0.537	-0.168	-0.251	0.342	-0.041	0.046	1	0.706	0.267	0.385	0.078
Pb	-0.001	0.747	-0.555	-0.207	-0.544	-0.122	-0.309	0.582	-0.201	0.191	0.679	1	0.039	0.177	0.480
Zn	-0.240	0.698	-0.599	-0.570	-0.576	-0.025	0.259	0.443	0.051	0.906	0.274	0.275	1	0.596	-0.410
La	-0.023	-0.136	-0.075	-0.010	-0.109	0.508	0.166	-0.060	0.422	-0.152	-0.226	0.017	-0.116	1	0.146
Ce	-0.479	0.306	-0.328	-0.295	-0.324	0.324	0.068	0.333	0.007	0.135	-0.060	0.407	0.073	0.569	1
Pr	-0.029	-0.217	0.002	0.045	-0.037	0.452	0.140	-0.074	0.425	-0.209	-0.307	-0.099	-0.208	0.971	0.563
Nd	0.059	-0.241	0.004	0.094	-0.038	0.459	0.105	-0.089	0.447	-0.261	-0.275	-0.093	-0.247	0.967	0.502
Sm	0.060	-0.348	0.116	0.126	0.072	0.428	0.140	-0.185	0.473	-0.288	-0.362	-0.224	-0.280	0.940	0.402
Eu	0.145	-0.475	0.272	0.181	0.229	0.385	0.132	-0.339	0.455	-0.383	-0.386	-0.306	-0.338	0.854	0.213
Gd	0.018	-0.357	0.158	0.038	0.121	0.404	0.218	-0.277	0.490	-0.181	-0.400	-0.283	-0.157	0.904	0.329
Tb	0.040	-0.294	0.108	0.083	0.068	0.424	0.167	-0.176	0.456	-0.209	-0.322	-0.191	-0.190	0.940	0.386
Dy	0.034	-0.283	0.070	0.011	0.034	0.447	0.219	-0.206	0.485	-0.143	-0.355	-0.213	-0.114	0.931	0.351
Ho	-0.014	-0.236	0.043	-0.080	0.013	0.451	0.268	-0.208	0.472	-0.054	-0.350	-0.201	-0.022	0.921	0.333
Er	-0.082	-0.215	0.043	-0.114	0.017	0.463	0.282	-0.195	0.443	-0.019	-0.369	-0.177	0.005	0.920	0.379
Tm	0.005	-0.216	0.026	-0.104	-0.007	0.487	0.328	-0.240	0.491	-0.047	-0.300	-0.168	0.009	0.888	0.305
Yb	0.023	-0.200	0.015	-0.072	-0.013	0.463	0.269	-0.199	0.487	-0.033	-0.296	-0.145	0.019	0.913	0.306
Y	0.021	-0.387	0.229	0.014	0.199	0.414	0.395	-0.361	0.558	-0.206	-0.408	-0.268	-0.213	0.817	0.298
Ce*	-0.531	0.520	-0.433	-0.493	-0.410	0.149	0.041	0.415	-0.145	0.331	0.128	0.531	0.278	0.076	0.820
Eu*	0.275	-0.205	0.304	0.258	0.306	-0.183	-0.217	-0.175	-0.274	-0.406	0.139	0.043	-0.322	-0.362	-0.447
Total REE	-0.395	0.193	-0.273	-0.238	-0.280	0.396	0.104	0.243	0.133	0.060	-0.131	0.313	0.016	0.750	0.970

Table 5. (Contd.)

	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y	Ce*	Eu*	Total REE
Fe	0.549	0.518	0.528	0.647	0.467	0.538	0.441	0.254	0.251	0.194	0.203	0.214	0.089	0.422	0.312
Mn	0.343	0.390	0.226	0.430	0.343	0.452	0.538	0.586	0.585	0.614	0.606	-0.578	-0.373	0.330	0.096
Si	0.360	0.328	0.443	0.307	0.350	0.253	0.118	-0.064	-0.066	-0.104	-0.121	0.581	0.418	-0.228	0.417
Ti	0.606	0.610	0.555	0.630	0.480	0.558	0.486	0.279	0.258	0.265	0.222	-0.229	0.365	0.311	0.682
Al	0.736	0.759	0.804	0.765	0.780	0.738	0.624	0.468	0.435	0.430	0.430	0.878	-0.087	-0.085	0.388
Ca	-0.373	-0.395	-0.278	-0.414	-0.233	-0.392	-0.551	-0.349	-0.330	-0.560	-0.502	0.189	-0.324	-0.145	-0.402
P	-0.686	-0.706	-0.592	-0.677	-0.587	-0.689	-0.716	-0.629	-0.676	-0.632	-0.599	0.283	0.062	-0.215	-0.509
Co	0.537	0.540	0.475	0.552	0.479	0.579	0.651	0.587	0.639	0.597	0.606	-0.068	-0.179	0.206	0.307
Cu	0.598	0.600	0.618	0.512	0.667	0.648	0.737	0.786	0.843	0.777	0.817	0.875	-0.573	-0.358	0.069
Ni	-0.081	-0.053	-0.130	-0.085	0.011	0.053	0.243	0.454	0.486	0.507	0.551	-0.111	-0.664	-0.093	-0.377
V	0.549	0.606	0.484	0.732	0.529	0.642	0.590	0.469	0.403	0.458	0.454	-0.182	-0.193	0.565	0.266
Pb	0.570	0.543	0.492	0.550	0.452	0.483	0.391	0.259	0.272	0.201	0.141	-0.416	0.299	0.176	0.559
Zn	0.152	0.189	0.067	0.176	0.207	0.284	0.435	0.610	0.620	0.643	0.659	-0.132	-0.671	0.067	-0.218
La	0.659	0.712	0.534	0.619	0.685	0.732	0.838	0.921	0.828	0.934	0.890	-0.387	-0.411	-0.062	0.436
Ce	0.306	0.287	0.195	0.087	0.129	0.105	0.070	-0.024	-0.031	-0.029	-0.161	-0.503	0.828	-0.243	0.925
Pr	1	0.985	0.976	0.926	0.961	0.959	0.916	0.801	0.800	0.738	0.707	0.674	-0.131	-0.136	0.625
Nd	0.990	1	0.952	0.947	0.951	0.976	0.937	0.828	0.804	0.782	0.748	0.649	-0.182	-0.039	0.616
Sm	0.978	0.981	1	0.917	0.949	0.937	0.869	0.732	0.751	0.658	0.649	0.802	-0.174	-0.150	0.516
Eu	0.888	0.909	0.951	1	0.930	0.977	0.916	0.788	0.747	0.739	0.737	0.814	-0.326	0.186	0.413
Gd	0.929	0.923	0.966	0.944	1	0.962	0.925	0.842	0.821	0.781	0.774	0.864	-0.284	-0.176	0.470
Tb	0.957	0.959	0.980	0.945	0.977	1	0.974	0.884	0.853	0.840	0.831	0.807	-0.359	0.052	0.455
Dy	0.938	0.943	0.966	0.943	0.984	0.984	1	0.958	0.931	0.931	0.924	0.684	-0.431	0.019	0.428
Ho	0.910	0.906	0.934	0.911	0.973	0.966	0.986	1	0.965	0.989	0.979	0.806	-0.538	-0.047	0.323
Er	0.904	0.896	0.919	0.893	0.967	0.959	0.981	0.993	1	0.953	0.948	0.776	-0.491	-0.134	0.306
Tm	0.868	0.871	0.896	0.901	0.946	0.933	0.961	0.975	0.977	1	0.987	0.643	-0.543	-0.002	0.305
Yb	0.880	0.881	0.906	0.889	0.952	0.949	0.973	0.992	0.986	0.971	1	0.741	-0.636	0.022	0.184
Y	0.813	0.818	0.873	0.891	0.918	0.900	0.906	0.909	0.907	0.909	0.918	1	-0.547	-0.461	-0.302
Ce*	0.066	-0.007	-0.097	-0.256	-0.126	-0.092	-0.121	-0.112	-0.057	-0.108	-0.131	-0.042	1	-0.275	0.588
Eu*	-0.381	-0.310	-0.316	-0.073	-0.380	-0.331	-0.327	-0.354	-0.374	-0.279	-0.339	-0.313	-0.362	1	-0.263
Total REE	0.744	0.694	0.609	0.433	0.540	0.595	0.564	0.544	0.581	0.512	0.518	0.474	0.680	-0.469	1

Table 6. Coefficients of correlation of REE with Fe, Mn, Ca, and P in four groups of P-rich samples

Correlation	Group			
	Ce* < 1.3	Ce* > 1.3	P > 5%	P < 5%
Fe-La	—	—	—	—
Fe-Ce	—	—	0.21	-0.48
Fe-REE	Pr-Eu: 0.25–0.31	—	Pr-Dy: 0.44–0.65 Ho-Yb: 0.19–0.25	—
Mn-La	—	—	0.55	—
Mn-Ce	0.53	0.32	—	0.31
Mn-REE	—	—	Pr-Tb: 0.23–0.45 Dy-Yb: 0.54–0.61	Pr-Yb: -(0.21–0.47)
Ca-La	0.50	0.38	-0.39	0.51
Ca-Ce	—	0.26	-0.34	0.32
Ca-REE	Pr-Dy: 0.27–0.40 Ho-Yb: 0.36–0.49	Pr: 0.26 Nd-Yb: 0.35–0.45	Pr-Yb: -(0.28–0.56)	Pr-Yb: 0.39–0.49
P-La	0.44	-0.31	-0.54	0.17
P-Ce	—	-0.47	-0.29	—
P-REE	Dy-Yb: 0.21–0.44	Pr-Yb: -(0.17–0.40)	Pr-Yb: -(0.59–0.61)	Gd-Yb: 0.22–0.33
Fe-P	-0.62	-0.45	-0.63	-0.19
Mn-P	-0.20	-0.90	-0.81	-0.07

and Pb, and weak with Pr and Nd. Like the Ce content, the Ce* value has a weak correlation with Si and Ti.

In crusts of group 4 characterized by a lesser P content (average 3.57%), Fe correlates only with Cu and V, whereas Mn correlates with all nonferrous metals, Ce (to a lesser extent), and Ce* (Table 5, lower side). Like in previous cases, P correlates with Ca ($r = 0.975$), while Ca correlates with all REEs, including Ce (although very weakly). The Ce* value shows correlation with Mn, Co, and Pb.

Table 6 presents summary data on the pair correlation of REE with Fe, Mn, and P in all four groups of ore crusts. The table also shows a wide range of relationships between these elements. In general, P lacks any correlation with Fe or Mn in these groups. Hence, the phosphate and hydroxide phases of ore crusts are genetically different.

Dendrograms presented in Fig. 3 show that the elements mentioned above have more complicated interrelations.

In Ce*-depleted samples of group 1, all REEs, except Ce, make up a complex stepwise association including three subgroups: (Tb + Gd) + Eu + La + Y, [(Er + Yb) + Dy](Ho + Tm), and (Pr + Nd) + Sm. Ce and Ce* correlate with two metal groups: (Mn, Pb, V) and (Ni, Zn, Co). P and Ca have significant correlation with Cu and total REE and insignificant correlation with three associations, including twelve REEs (Fig. 3a).

In Ce*-rich samples of group 2, all REEs, including Ce, also make up a complex stepwise association [(Gd +

Dy)(Pr + Nd) + Tb + Sm + Eu + (Ho + Er) + La] + Tm + Yb + Y (Fig. 3b). This association is conjugated with Ce, total REE, and Ce*. The REE association is linked with the manganese association that also includes Zn, Co, and Ni. The assemblage of elements associated with Fe includes Ti, Pb, V, Cu, Si, and Al. It is worth mentioning that REEs are absent and both P and Ca are alien in this association.

In the P-rich (>5% P) samples of group 3 (Fig. 3c), the common association includes six REEs: (Pr + Sm) + Gd + Dy + (Er + Yb). Ce and Nd make up a separate subgroup associated with V and Pb. The latter association can also include Co. Eu and Ho associate with Fe and P. La is associated with Mn. Tb and Tm also make up a separate subgroup. The Ce* value correlates with Si and Ti, while the Eu* value correlates with P and Fe.

In P-poor samples of group 4 (<5% P), the correlation pattern is similar: association of six REEs (Pr–Yb), separate [(Eu + Ho) + Fe] and (Tb + Tm) associations, as well as correlation of Ce* with Si and Ti (Fig. 3d). However, this group is characterized by close La–Nd–V and Ce–Pb correlations. When considering the influence of P on the REE behavior in ore crusts, it is also expedient to analyze their distribution in samples with the minimal content of the phosphate phase (<1% P). We divided the data on 40 such samples presented in (Hein et al., 1990) into three groups (Table 7) depending on the Ce* value: >3, 2–3, and 1–2 (average 4.12, 2.55, and 1.34, respectively). According to this subdivision, the three groups are virtually similar in average contents of Mn (20.4–21.7%) and P (0.36–0.39). How-

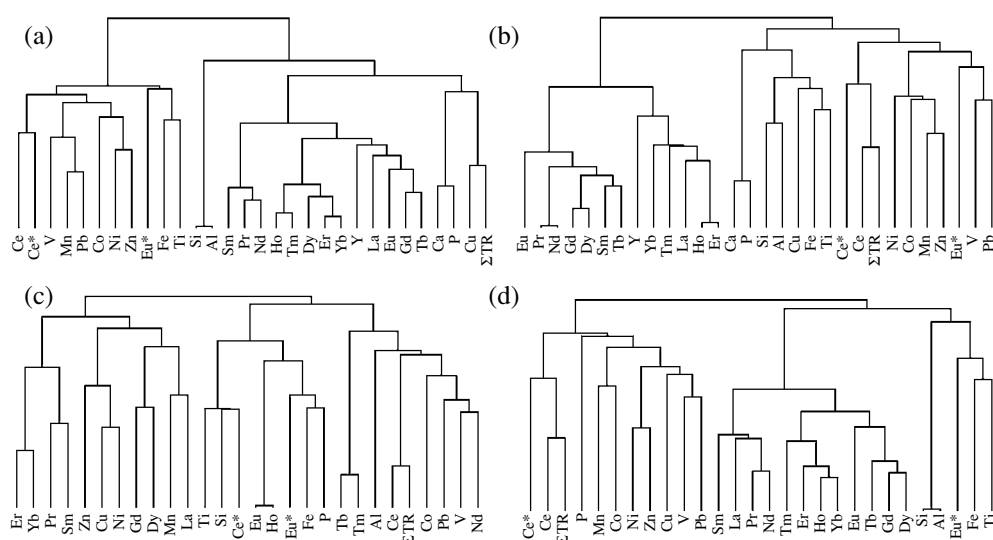


Fig. 3. Plots showing multiple correlation of REE with trace elements in P-rich ore crusts. (a, b) Varieties with decreased and increased Ce anomaly values, respectively; (c, d) varieties with maximum and moderate phosphorus contents, respectively.

ever, the average Fe content increases from 11.4 to 15.4%. Correspondingly, the Mn/Fe ratio decreases from 1.91 to 1.37. Simultaneously, one can see decrease in Co (7500–5530 ppm) and Pb (1530–1330 ppm), but a slight increase in Cu (770–900 ppm) and V (540–610 ppm).

The REE composition of these groups exhibits the decreasing trend of contents of Ce (from 1750 to 617 ppm) and total REE (from 2262 to 1226 ppm). At the same time, contents of other REEs increase slightly (Fig. 4).

FACTORS INFLUENCING THE CONTENT AND COMPOSITION OF RARE EARTH ELEMENTS IN ORE CRUSTS

The facts presented above indicate that the REE content and composition in ore crusts are characterized by a wide variation range due to several factors.

If the ore crusts contain abundant phosphate phase, the latter can significantly control the REE behavior. This is evident from the appearance of negative Ce anomaly, which is virtually universal in phosphorites of seamounts that often serve as substrate for the crusts

Table 7. Average contents of elements in three groups of P-poor ore crusts

Element	Group			Element	Group		
	Ce* > 3 N = 8	Ce* = 2–3 N = 15	Ce* = 1–2 N = 17		Ce* > 3 N = 8	Ce* = 2–3 N = 15	Ce* = 1–2 N = 17
Fe	11.4	13.6	15.5	Nd	99	175	175
Mn	21.7	20.4	21.1	Sm	18	33	33
Mn/Fe	1.91	1.50	1.37	Eu	4.6	7.9	8.5
P	0.36	0.365	0.39	Gd	18	33	35
Fe/P	35	37	39	Tb	3.1	5.4	5.8
Co	7500	6053	5535	Dy	18	32	35
Cu	770	810	899	Ho	3.9	6.7	7.2
Ni	4600	4237	4460	Er	12.0	18.7	20.3
V	540	561	609	Tm	1.7	2.6	2.9
Pb	1530	1433	1330	Yb	13	17	19
Zn	640	640	692	REE	2262	1809	1226
La	147	225	225	La/Yb	13.82	13.82	
Ce	1496	1200	617	Ce*	4.12	2.55	1.34
Pr	25	43	38	Eu*	0.994	0.976	

Note: Elements from Fe to P (from the top of the column) are given in %; other elements, in ppm.

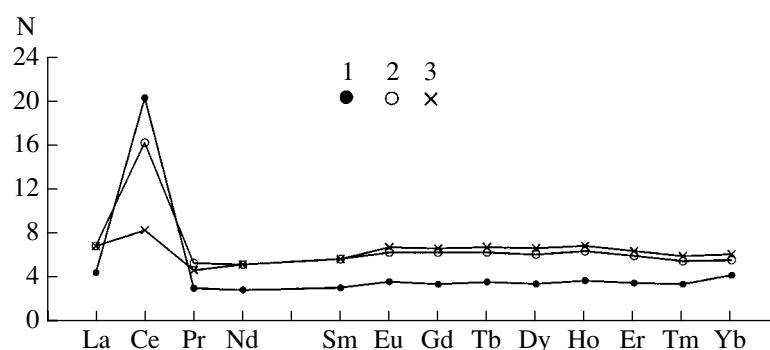


Fig. 4. The shale-normalized (N) average REE contents in P-poor ore crusts with (1) increased, (2) moderate, and (3) decreased Ce anomaly values based on (Hein et al., 1990).

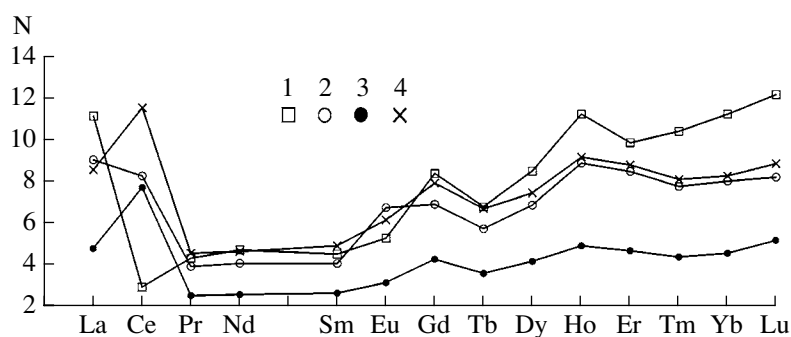


Fig. 5. REE distribution in samples of P-rich ore crusts with positive and negative Ce anomaly values from the Wodejebato Guyot, Pacific. (1, 2) Hole 874A; (3, 4) Hole 878A. The phosphorus content in samples 1–4 is 6.9, 7.1, 10.2, and 8.3%, respectively (Bogdanov et al., 1995).

(Baturin, 2004). However, the REE distribution in crusts of the mixed composition is more complicated owing to the rivalry between two (phosphate and ferromanganese) mineral phases that can concentrate REE. The role of these phases is ambiguous.

For example, the P-rich (>2% P) mixed crusts with the maximal and minimal Ce* values (2.47 and 0.91, respectively) have virtually similar average P contents (4.45 and 4.90%, respectively). In the P-poor variety, this element does not appreciably influence the Ce* value. For example, the Ce* value in the groups varies from 1.34 to 4.12, while the P content remains virtually constant (0.36–0.39%). However, if we divide the samples into four groups with the average P content ranging from the maximal (7.30%) to high (3.57%), moderate

(1.49%), and low (0.37%) values, the correlation becomes more definite. The Ce* value in these four groups is equal to 1.49, 1.88, 2.27, and 2.35, respectively. The relationship with phosphorus is irregular, because the REE distribution in the ore crusts is often independent of the relationship between the phosphate and ferromanganese phases. For example, the REE distribution follows the phosphate trend instead of the hydroxide trend in some crust samples recovered by boreholes drilled at the Wodejebato Guyot with the P content ranging from 8.2 to 10.2% and the Fe/P ratio varying from 0.46 to 0.89 (Fig. 5). According to (Bogdanov et al., 1995), four samples of the Wodejebato series exhibit the following contrast composition (macrocomponents are given in %; REE, in ppm):

Sample no.	Fe	Fe ₂ O ₃	Mn	MnO ₂	P	Apatite	La	Ce	Nd	Ce/La	Ce*	Apatite/Hydroxides
1	3.9	5.58	13.6	21.5	6.9	35.9	356	222	158	0.27	0.39	1.32
2	4.3	6.15	14.6	23.1	7.1	36.9	292	610	137	0.91	1.27	1.26
3	4.7	6.76	5.6	8.8	10.2	53.0	156	571	87	1.60	2.09	3.40
4	7.4	10.57	5.2	15.5	8.3	43.0	277	851	156	1.34	1.74	1.70

As is evident, the REE distribution shows the hydroxide trend in the phosphate-rich samples 3 and 4. Samples 1

and 2 with nearly similar contents of the phosphate phase exhibit the phosphate (or intermediate) trend.

The detailed (layer-by-layer) investigation of ore crust from the MacKin Guyot in the central equatorial Pacific also demonstrated that the REE distribution shows the phosphate trend in the lower portion of the crust (horizon 60 mm, Fe 7%, P 1.8%). At the same time, the adjacent layer (horizon 58 mm) of the same composition shows the hydroxide trend (De Carlo et al., 2000). Thus, relationship between the major REE-concentrating mineral phases is not always the main regulator of REE distribution in the ore crusts.

The aggregate state and mineral and chemical compositions of the major mineral phases in the ore crusts are among the reasons responsible for such peculiarities in the behavior of REE. For example, phosphate can occur in these phases as holocrystalline aggregates, phosphatized biogenic carbonates, apatite interlayers and veinlets, and fine-dispersed particles (Baturin and Dubinchuk, 1979, 1989). At the same time, phosphate phases can be composed of different minerals ranging from apatite to carbonate-apatite. This is evident from the wide range of CO₂ (from <0.3–0.5 to *n*%) in the relatively pure phosphorites (*Gaioty zapadnoi...*, 1995).

In the hydroxide phase, phosphorus can probably occur not only in apatite, but also in the inferred ferrophosphate. This fact is evident from the correlation detected by Indian scientists (Pattan and Banakar, 1993) between Fe, P, and REE in the ferromanganese nodules from the Indian Ocean. In addition, the REE-rich iron hydroxophosphates have been detected in Pacific pelagic sediments (Dubinin, 2001, 2004). Presumably, phosphates mentioned above have different capacities of REE concentration. This is demonstrated, for example, by the behavior of these elements in the different-aged biogenic phosphates on the Namibia shelf (Baturin, 2004, 2005).

The ferromanganese phase of ore crusts has no less diverse composition than the phosphate phase, although Fe-vernadite and iron hydroxides are the major ore minerals (Baturin, 1986; Baturin and Dubinchuk, 1989; Burns and Burns, 1979; Chukhrov et al., 1989). The degree of difference between the ferromanganese phases in terms of their capacity to accumulate REE remains a controversial issue. The content of Co, which is similar to Ce in terms of distribution pattern, can provide an indirect solution.

According to previous investigations of the elemental composition of the major minerals in ocean ferromanganese nodules and crusts (Andrushchenko, 1976; Burns and Burns, 1979; Burns and Fuerstenau, 1966; Chukhrov et al., 1978), the cobalt oxide content is approximately one order of magnitude higher in Fe-vernadite (1.53–3.41%) than in todorokite (0.2–0.5%) and birnessite (0.13–0.25%). Probably, this trend is also valid for Ce. Correlations presented above and relevant data reported by many researchers indicate that other REEs do not exhibit stable correlation with the Fe- or Mn-rich phase. Nevertheless, experimental data on the leaching of several polyvalent metals from the

ore crusts testify to their correlation mainly with the Fe-rich phase (Hein et al., 2003; Nath et al., 1994).

The composition and concentration of REE in phosphates and Fe–Mn hydroxides are also governed by the rate of their accumulation on seamounts, more precisely, the duration of their contact with the bottom water, which is the source of metals. This dependence is evident for phosphorites at the Mid-Pacific seamounts (Baturin, 2004; Baturin and Yushina, 1998). The accumulation rate also significantly controls the deposition of Co, Ce, and Te in the ore crusts (Halbach et al., 1983; Hein et al., 2003; Manheim and Lane-Bostwick, 1988, 1989).

Concentration of elements in hydroxide phases is also fostered by the motion of water masses. This is evident from the preferential growth of crust on the windward slopes of seamounts noted in several complex investigations of ore genesis on seamounts (Shkol'nik et al., 2001).

Concentration of elements can also be fostered by the additional supply of material from hydrothermal sources. The detailed investigation of morphology of seamounts and guyots revealed that their summits often include volcanic cones, indicating a significant postvolcanic hydrothermal activity (Mel'nikov, 2005).

Numerous investigations have shown that hydrothermal springs in the oceanic rift zones are strongly enriched in REE relative to the oceanic water. The hydrothermal solutions are also characterized by the absence of Ce anomaly, the development of prominent positive Eu anomaly, and the excess of LREE relative to the HREE (Bau and Dulsky, 1999; Douville et al., 1999; James et al., 1995; Klinkhammer et al., 1984; Michard et al., 1983, 1984; Mitra et al., 1994). Therefore, bottom sediments of all types with the hydrothermal admixture are characterized by differently manifested positive Eu anomaly related to the precipitation of hydrothermal Fe and Mn. These metals are transformed into hydroxides that entrap REE derived from both hydrothermal solutions and oceanic waters.

The typical hydrothermal signature of REE in the ferromanganese crusts (reduced positive Eu anomaly) has been reported from several regions of the Pacific (Baturin and Yushina, 1991a, 1991b; Hein et al., 1990, 1993) and Atlantic oceans (Varentsov et al., 1989). The contribution of hydrothermal component to the crustal composition has also been estimated quantitatively for the first region.

In the studied material, the hydrothermal contribution to the REE composition is noted only for some samples with the Eu* value ranging from 1.08 to 1.16. Like the general chemical composition of ore crusts from seamounts in the northwestern Pacific, the REE composition is generally close to the average chemical composition of hydrogenetic ferromanganese crusts in the World Ocean (Anikeeva and Kazakova, 2002; Baturin, 1993; Usui and Someya, 1997).

The REE composition in the studied ore crusts can also be influenced by their occurrence mode. It is usually believed that REEs are in the sorbed state in the hydroxide phase of crusts, while they are mainly confined to the crystal lattice of apatite in phosphorites. However, natural minerals of REE (monazite, xenotime, bastnasite, cerianite, and parasite) have been detected in both shelf phosphorites and seamount phosphorites associated with ore crusts (Baturin and Dubinchuk, 1999, 2004, 2005). Such minerals are so far unknown in the hydroxide phase. However, their development in the phosphate phase of ore crusts undoubtedly influences the bulk composition of REE in the P-rich crusts. Since cerianite is the major REE mineral in the phosphate phase of crusts, the above influence is obviously expressed in the relatively high Ce content, which compensates to some extent the negative Ce anomaly related to the extraction of REE from the oceanic water by phosphates.

Mechanism and constraints of REE accumulation in the hydroxide phase of ore crusts have remained debatable issues for many years. According to the initial assumption, REEs are absorbed by manganese hydroxides. In contrast to other REEs, Ce is oxidized by the manganese hydroxides and, therefore, is more intensely accumulated, resulting in the positive Ce anomaly (Goldberg et al., 1963). According to the currently popular alternative hypothesis based on various experiments with the leaching of metals from crusts, the REEs are absorbed by iron hydroxides and then Ce is oxidized (Nath et al., 1994). Co, Te, and probably Pt are absorbed by the tetravalent Mn (Hein et al., 2003).

The validity of the last assumption is unclear so far. According to the commonly accepted notion, manganese hydroxides have a strong negative charge, while iron hydroxides have a weak positive charge. At the same time, all REEs dissolved in the oceanic water are mainly located in the form of positively charged carbonate complexes (Bruland, 1983). The cationic occurrence mode of metals is subordinate. Therefore, the REEs are preferentially connected with manganese hydroxides. Nevertheless, some samples of the Pacific hydrogenetic crusts show a significant correlation with all REEs ($r = 0.657$) except Ce (Dubinin, 2004).

This peculiarity can at least partially be related to the following experimental fact. If the pH value of sea water is ~ 8.3 , it can contain negatively charged REE carbonate complexes of the $\text{Ln}(\text{CO}_3)_2^-$ type (Byrne and Sholkovitz, 1996).

According to experimental data reported in (De Carlo et al., 2000), the synthetic iron hydroxide can extract $>90\%$ of the dissolved REE at seawater pH equal to >8 . Moreover, the REE distribution in some layers of the ore crusts depends on the state of carbonate system in the oceanic water; e.g., the Sm/Yb ratio is inversely proportional to the carbonate compensation depth, which repeatedly changed in the Cenozoic.

CONCLUSIONS

According the conventional opinion, ferromanganese crusts and phosphorites on seamounts drastically differ in terms of REE composition. The crusts are characterized by the positive Ce anomaly, whereas the phosphorites are marked by the negative Ce anomaly. In the first case, the positive anomaly is related to the following process: the trivalent Ce dissolved in seawater is oxidized up to the tetravalent insoluble oxide and precipitated. This process is particularly active at the surface of ferromanganese sediments on the seafloor (Goldberg et al., 1963). This process is responsible for the negative Ce anomaly in the oceanic (particularly, benthic) water. In contrast to the ore crusts, phosphorites at seamounts extract the REE from the oceanic water without fractionation and inherit the oceanic negative Ce anomaly.

Since the phosphate phase is significant in many polymetallic crusts on seamounts, the influence of this factor on the total REE content in them becomes an interesting issue. In order to elucidate this issue, we compared the bulk and microelement compositions of ore crusts with the Ce anomaly value and the content of phosphate phase therein. Our work was based on the comprehensive analysis of published data on the composition of 84 crust samples recovered from the surface of seamounts and DSDP holes drilled in the northwestern tropical Pacific.

In P-rich ($>2\%$ P) crust samples with high (>1.3) and low (<1.3) Ce^* values, the average P content appeared to be virtually similar. At the same time, samples with the maximal and moderate P contents (>5 and $2-5\%$, respectively) are characterized by significantly different Ce^* values (1.49 and 1.88, respectively).

If we divide the P-poor ($<1\%$ P) samples into three groups with high, moderate, and low Ce^* values (4.12, 2.55, and 1.34, respectively, on the average), they are characterized by decrease in the total content of REE and average contents of Co and Pb; insignificant increase in contents of Cu, V, and Zn; and almost similar content of P (0.33–0.39%).

Pair and multiple correlations between the elements in the ore crusts indicate that virtually the whole amount of P, Ca, and CO_2 in them is confined to apatite. However, the groups show weak and fragmentary correlations in the phosphate-REE and hydroxide phase-REE systems owing to the rivalry between two phases-carriers, instability of their sorption properties, variability of their aggregate state and mineral composition, and the formation of authigenic REE minerals in the phosphate phase. The REE accumulation in the ore crusts is also governed by the following factors: their growth rate, circulation of water masses around the seamounts, sporadic and local hydrothermal activity, and probably variations in the carbonate compensation depth in the Cenozoic ocean. Interplay of these factors was responsible for occasional disturbances in the correlation between the REE distribution and the dominant

mineral phase of crusts, leading to mismatch of their bulk chemical composition and REE composition.

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