Geochemistry of Rare Earth Elements in the Ocean

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Abstract—This work briefly outlines modern ideas on geochemistry of rare earth elements (REE) in the ocean. Sources of REE and chemical properties of these elements, which govern their migration ability in natural processes, are considered. The REE behavior in the river water–seawater mixing zone is analyzed. The fractionation of dissolved and suspended REE in oceanic water in both aerobic and anaerobic conditions is also considered. It is shown that the variability of REE composition in pelagic sediments reflects the fractionation of these elements in the oceanic water as a consequence of material differentiation in the ocean. The REE distribution in terrigenous, authigenic, hydrothermal, and biogenic constituents of sediments, such as clay, bone debris, barite, phillipsite, Fe–Mn oxyhydroxides (ferromanganese nodules and micronodules), Fe–Ca hydroxophosphate, diatoms, and foraminifers, is considered.

As is well known, the REE group includes 15 elements ranging from lanthanum (nucleus charge 57) to lutecium (71). The unique similarity of chemical properties of these elements is related to the filling of their inner 4f electron shell, leading to diminution of the atomic radius (lanthanide compression) in the REE series. In natural chemical compounds, most rare earth elements donate three electrons except for cerium and europium, which change their oxidation state to 4^+ and 2^+, respectively, owing to redox reactions. The decrease in size of atoms and three-charge ions with increasing nucleus charge leads to slow changes in lanthanide properties that are not noted in any other group of elements except actinides. However, the majority of actinides belong to artificially generated elements, and they are not so important in geochemistry as rare earth elements. As a result of the lanthanide compression, last elements of the REE series approach yttrium in the size of their atoms and three-charge ions. Yttrium is concerned the closest analogue of rare earth elements. Being more widely distributed in the nature, yttrium is often replaced by heavy rare earth elements (from gadolinium to lutecium), which are called "yttrium earths". In contrast, light rare earth elements are called "cerium earths". Both terms are now obsolete. In the modern literature, they are denoted as HREE (heavy rare earth elements) and LREE (light earth elements), respectively. The term "middle rare earth elements" (MREE) designates elements from samarium to holmium.

The REE distribution pattern in the nature perfectly supports the Oddo-Harkins rule: even elements have higher Clarke concentrations than odd elements. Moreover, even elements contain a greater number of isotopes (e.g., Ce has four isotopes, Nd, Sm, Gd, Dy, and Yb have seven isotopes, and Er has six isotopes), whereas the majority of odd elements have only one isotope, except for La, Eu, Lu (two stable isotopes) and Pm (no stable isotopes). In order to detect subtle nuances of REE composition variation in natural processes, it is necessary to exclude the influence of their different abundances. This is accomplished by normalization of the studied REE compositions relative to their composition in chondrites or shales. The normalization to chondrite is commonly used for REE composition variations in hypogene processes, because the composition of these elements in chondrites is believed to reflect their composition in the protoplanetary substance. The normalization to shale is applied to study REE variations in hypergene processes. It is assumed that the shale of Precambrian platforms most completely reflects the average REE composition of magmatic, metamorphic, and sedimentary rocks. The Post-Archean Australian Shale (PAAS) or North American Shale Composite (NASC) is commonly used for the normalization, although data on clays from the Russian Platform are preferable today (Table 1).

Rare earth elements are hydrolyzates, because their ions easily undergo hydrolysis in water solutions. In the lanthanide series, pH of hydrolysis varies from 8 for lanthanum to 6.2 for lutecium. Thus, rare earth elements might fractionate as a result of hydrolysis in natural solutions with a wider pH range. However, due to low REE concentrations in rocks and natural waters, the mobility of lanthanides in natural processes is controlled by their ability to form complexes with inorganic and organic ligands rather than the solubility of their compounds. In the trivalent REE, the ability increases with diminution of the ion radius from LREE to HREE, resulting in higher contents of HREE relative to LREE in neutral and alkaline waters, such as river water and seawater. The restricted mobility of REE is related to their adsorption on solid particles due to the formation of ion pairs on the particle surface or their simultaneous precipitation during the formation of

The REE content (ppm) in shales, clays, upper continental crust, and chondrites

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
North American Shale Composite (NASC)	32	73	7.9	33	5.7	1.24	5.2	0.85
Australian Post-Archean Shale (PAAS)	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.774
Clay from the Russian Platform	37.5	74.8	8.6	32.2	6.2	1.30	5.21	0.79
World Shale	41	83	10.1	38	7.5	1.61	6.35	1.23
Upper continental crust	30	64	7.1	26	4.5	0.88	3.8	0.64
Chondrite	0.31	0.808	0.122	0.60	0.195	0.0735	0.259	0.0474
	Dy	Ho	Er	Tm	Yb	Lu	Data source	
North American Shale Composite (NASC)	5.2	1.04	3.4	0.5	3.1	0.48	Gromet et al., 1984	
Australian Post-Archean Shale (PAAS)	4.68	0.991	2.85	0.405	2.82	0.433	McLennan, 1989	
Clay from the Russian Platform	4.88	0.96	2.78	0.41	2.73	0.41	Migdisov et al., 1994	
World Shale	5.5	1.34	3.75	0.63	3.53	0.61	Piper, 1974	
Upper continental crust	3.5	0.80	2.3	0.33	2.2	0.32	Taylor and McLennan, 1988	
Chondrite	0.322	0.0718	0.210	0.0324	0.209	0.0322	Boynton, 1984	

Note: The Dy content in the NASC sample is deduced from Tb and Ho contents in the shale, as well as Tb, Dy, and Ho contents in chondrites.

solid phases owing to the adsorption on the newly formed solid phase and the subsequent isomorphic replacement. Among inorganic complexes, carbonate and phosphate complexes are most significant in sea, river, and lake waters, whereas chloride and fluoride complexes prevail in hydrothermal solutions. Periodicity in changes of stability constants of the REE complexes as a result of the tetrad filling of the 4f layer with electrons (tetrad effect) is described in (Kawabe et al., 1999; Masuda and Ikeuchi, 1979; McLennan, 1994; Ohta and Kawabe, 2001).

Cerium and europium may change the oxidation degree in natural processes and consequently fractionate from other rare earth elements. Cerium has isobaric-isothermic potential of the oxidation reaction close to that of manganese ($Mn^{2+} \longrightarrow Mn^{4+}$). Therefore, it is easily oxidized to 4^+ in river and seawater solutions and reduced (like manganese) in anaerobic conditions (Bau, 1999; Moffett, 1990; Ohta and Kawabe, 2001). The behavior of cerium during its adsorption on oxyhydroxide surfaces in the ocean coincides with the behavior of thorium, which has the oxidation state of 4^+ that does not change in natural processes (Fig. 1). The value of cerium fractionation relative to the trivalent REE is commonly called cerium anomaly and calculated as

$$\text{Ce an} = 2 \times \text{Ce/Ce}^{\text{NASC}}/(\text{La/La}^{\text{NASC}} + \text{Pr/Pr}^{\text{NASC}}),$$

(see the table). This version of cerium anomaly calculation is not unique. Neodymium is used instead of praseodymium if data on its amount are absent. Significance of data on lanthanum is sometimes increased in the second version, and the cerium anomaly is calculated as

$$\text{Ce an}$$
$$= \text{Ce/Ce}^{\text{NASC}}/(2/3 \times \text{La/La}^{\text{NASC}} + 1/3 \times \text{Nd/Nd}^{\text{NASC}}).$$

In any case, the formulas given above suggest that the cerium anomaly is equal to unity for the North American Shale.

Europium is not reduced at common temperatures of hypergene processes. According to calculations (Sverjensky, 1984), europium may also be reduced in the interstitial water of marine sediments under anaerobic conditions at high temperatures (e.g., in the hydrothermal process). Anaerobic conditions probably demonstrate a unique evidence of the anomalous behavior of europium. The positive europium anomaly is noted in the hydrothermal fluid of the basalt–seawater system of the Mururoa Atoll with a high rock/water ratio. This was revealed by the analysis of basalt-percolating water samples taken in boreholes (Guy et al., 1999). The oxidation state 2^+ is common for europium in magmatic, metamorphic, and hydrothermal processes. The equation for the calculation of europium fractionation is similar to that for cerium. However, samarium and gadolinium (neighbors of europium), are used instead of

lanthanum and praseodymium. The Eu/Sm ratio is commonly considered if data on gadolinium are absent.

SOURCES OF RARE EARTH ELEMENTS IN THE OCEAN

Suspended and dissolved river runoff is considered the dominant source of rare earth elements in the ocean. Eolian dust, halmyrolysis of magmatic rocks, hydrothermal activity, and glacier discharge may serve as the subordinate sources (Balashov and Lisitsyn, 1968; Gurvich *et al.*, 1980).

The *suspended it river runoff* may reflect the REE composition in rocks of a river drainage basin. However, the greater the basin dimension and its rock composition variation, the higher resemblance of the suspended matter composition to that of the platformal shale or clay (Dupre *et al.*, 1996; Keasler and Loveland, 1982; Martin *et al.*, 1976; Rachold *et al.*, 1996). The dissolved REE runoff (commonly, less than 0.45 μm) includes both dissolved and colloidal constituents. The latter component mainly consists of organic and inorganic iron colloids. The higher the pH value of river water, the lesser the dissolved REE content and the greater the composition difference relative to the shale. An increase in pH leads to a preferable adsorption of LREE on suspended particles relative to HREE and the subsequent REE composition difference in the dissolved runoff. Chemical properties of REE in solutions, rather than rock composition in a drainage area, govern the composition of dissolved REE in the river water (Elderfield *et al.*, 1990; Goldstein and Jacobsen, 1988; Sholkovitz, 1993, 1995).

Within the seawater and river water mixing zone in estuaries, the dissolved REE content considerably decreases if salinity increases up to 6‰ and the rate of LREE removal from the solution is higher than that of MREE and HREE (Hoyle *et al.*, 1984; Sholkovitz, 1993, 1995). This is related to the adsorption of REE on colloids of organic acids salts and iron oxyhydroxides formed during the mixing with seawater. Meanwhile, cerium oxidizes and the resultant cerium anomaly does not obey the law of conservative mixing.

The bulk REE composition in *eolian dust* became known rather recently (Greaves *et al.*, 1994, 1999; Sholkovitz *et al.*, 1993). Contents of some individual rare earth elements were reported in (Balashov and Lisitsyn, 1968; Gurvich *et al.*, 1980). Influence of the Sahara dust on the dissolved REE composition in the Atlantic surface water was noted in (Elderfield and Greaves, 1982). From 1% to 3% of the total REE content in eolian particles is transferred to the oceanic water, whereas the proportion is higher for the MREE. Analyses of Pacific surface waters along the Asia–California transect (24°–32° N) showed an influence of the loess-derived eolian dust on the dissolved and suspended REE composition up to the 180° longitude (date line). Based on the comparison of REE fluxes into the
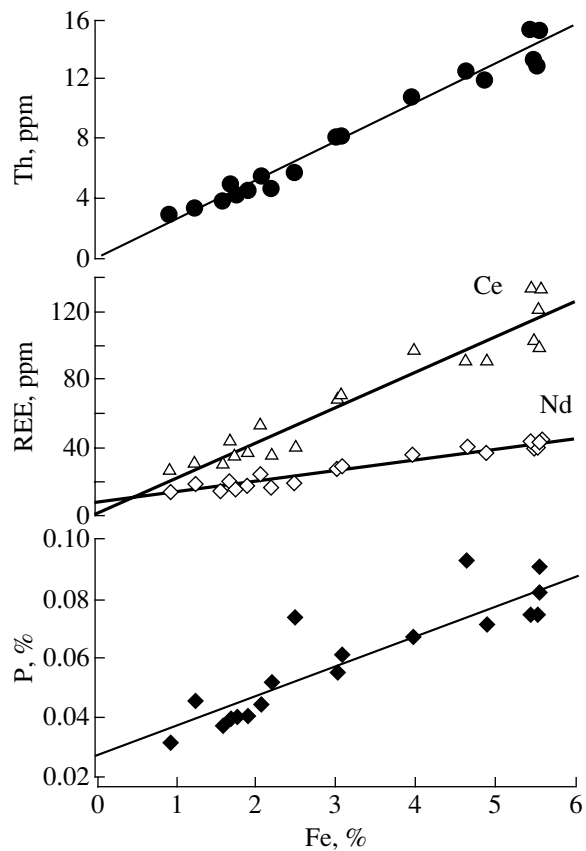

Fig. 1. The P, Ce, Nd, and Th concentrations vs. Fe content relationship in sediments from the Transpacific transect (Dubinin and Rozanov, 2001).

ocean, Greaves *et al.* (1994) suggested that the eolian share possibly makes up 30–130% of the river runoff.

The *glacier runoff* includes the clastic terrigenous material transported by melting ice. Its influence on the composition of dissolved and suspended REE has not been studied.

Data on the scale of REE delivery to the ocean with the *volcaniclastic material* are absent. The volcanogenic material is delivered to the ocean as volcanic ash related to both subaerial and submarine eruptions. The REE signature of volcaniclastics is not inherited by authigenic phillipsite in the case of their complete zeolitization in oxidized sediments (Dubinin, 2000). Phillipsite also does not inherit the REE from deep oceanic waters. The REE composition of phillipsite, similar to that of shales (Fig. 2), is possibly formed under the combined influence of exchange complexes of solid phases (clay minerals and iron oxyhydroxides) in the sediment.

The REE content in hydrothermal fluids of modern submarine hydrothermal systems can reach n μg/1 kg of solution. As is evident from (Fig. 3), they are enriched in the LREE (especially, Eu). Europium occurs in the oxidation state of 2^+ in hydrothermal flu-
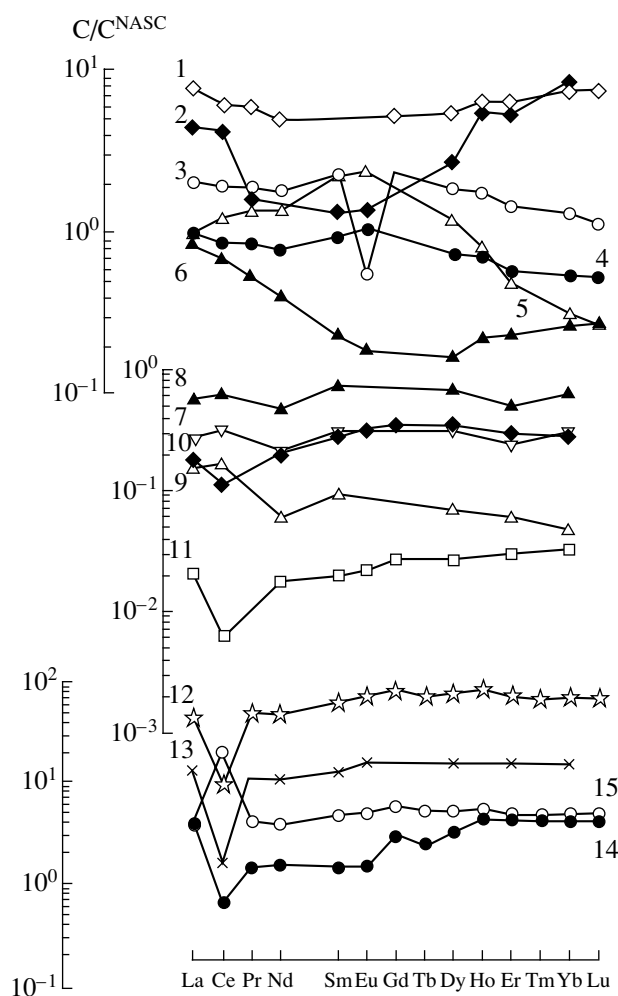
Fig. 2. Shale-normalized REE compositions. (1) Sediment fraction enriched in barite (Ba = 14%) (Fagel, *et al.*, 1997); (2) barite buried in sediments (Guichard *et al.*, 1979); (3–6) clay minerals (Fagel *et al.*, 1997): (3) smectite; (4) illite; (5) kaolinite; (6) chlorite; (7–9) phillipsite from the South Pacific Basin (Dubinin, 2001); (10) diatoms (Elderfield *et al.*, 1981a); (11) carbonate of foraminiferal tests from the Atlantic Ocean (Palmer, 1985); (12) bone debris from the South Pacific Basin (Dubinin and Sval'nov, 2001); (13) Fe–Ca hydroxophosphates (Dubinin, 2001); (14) phosphorite from the Wodejebato Guyot, Pacific Ocean; (15) ferromanganese crust from the Wodejebato Guyot, Pacific Ocean (Bogdanov *et al.*, 1998).
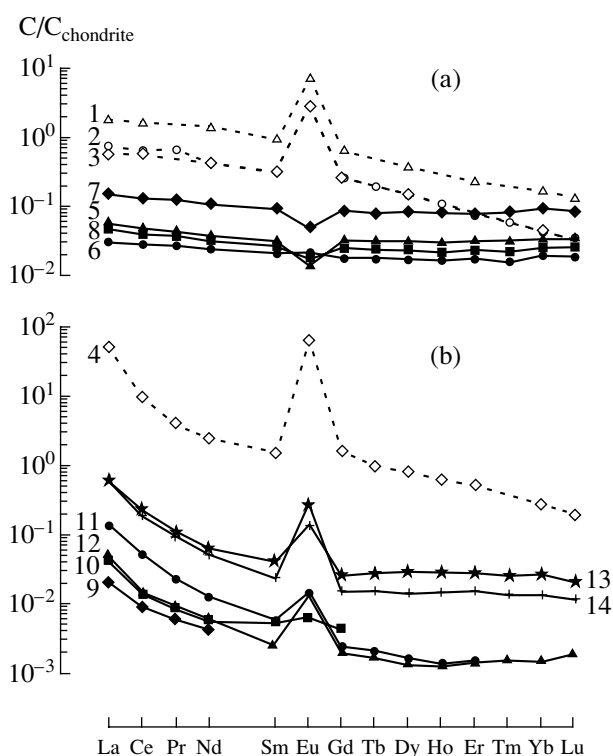

Fig. 3. Chondrite-normalized REE compositions in the hydrothermal fluid and sulfide minerals. (a) TAG and Broken Spur fields; (b) Rainbow field. (1–4) hydrothermal fluids: (1) TAG (Mitra *et al.*, 1994); (2, 3) Broken Spur (Bau and Dulski, 1999; Janes *et al.*, 1995); (4) Rainbow (Douville *et al.*, 2002); (5–14) sulfide minerals (sample nos.): (5) 3348-3-4; (6) 3384-1-2; (7) 3393-2; (8) 3393-7-2; (9) 3840-2-8; (10) 3840-3-3; (11) 3840-4-6; (12) 3844-2-10; (13) 3848-1-9b; (14) 3848-6-13 (Rimskaya-Korsakova and Dubinin, 2003).

ity of chloride and fluoride complexes of LREE relative to those of HREE, as well as the similarity of ion radii of HREE to those of the major rock-forming elements precipitating as hydrothermal sulfides. The REE contents increase in the fluids with temperature increase and pH decrease (Bau and Dulski, 1999; Douville *et al.*, 2002; James *et al.*, 1995; Michard, 1989; Michard *et al.*, 1983; Mitra *et al.*, 1994; Rimskaya-Korsakova and Dubinin, 2003).

RARE EARTH ELEMENTS IN THE OCEANIC WATER

About 93% of the terrigenous material delivered by rivers settles on continental shelves (Lisitsyn, 1978). Loss of the main portion of suspended terrigenous material leads to precipitation of the major part of REE as particulates. Although adsorption (and simultaneous precipitation) on iron oxyhydroxides and salts of organic acids removes a part of dissolved REE from the solution during the mixing of fresh river water with saline seawater, the proportion of dissolved REE invariably increases toward the pelagic area, where the REE
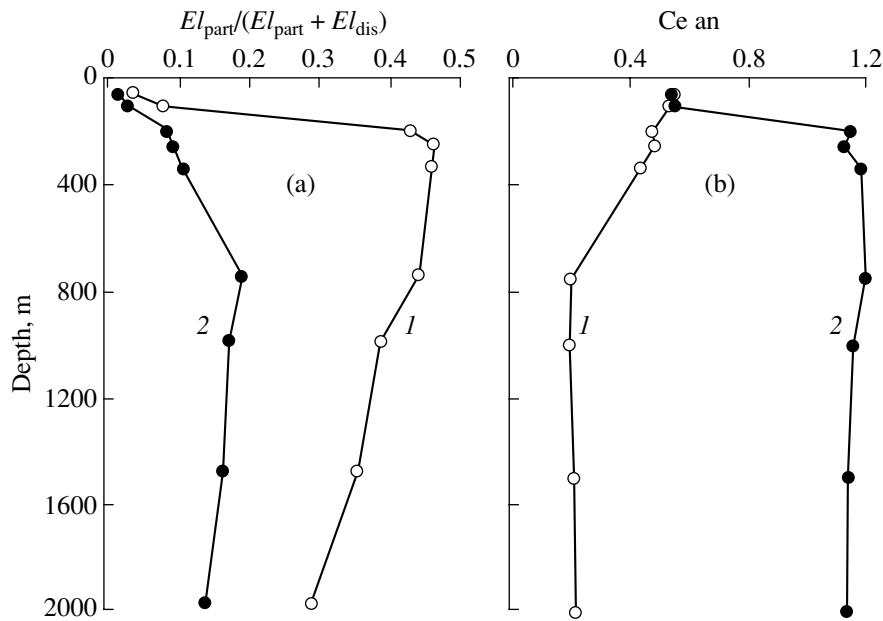
ids at $T = 300°$–$400°C$ and pH ~ 3. Most authors believe that the REE composition of hydrothermal fluids is related to the interaction of oceanic crustal rocks with seawater at high temperatures. During hydrothermal alterations, the stability of rock-forming minerals, which mainly govern the REE composition (especially, in basic rocks) decreases from sodium plagioclase to calcium plagioclase. The stability series for the dark-colored rock-forming minerals is as follows: biotite ⟶ amphibole ⟶ pyroxene ⟶ olivine. Accumulation of LREE relative to HREE in submarine hydrothermal fluids may be related to the REE source, the higher stabil-

Fig. 4. Variations in manganese and cerium forms and cerium anomaly with depth in the Sargasso Sea (Sholkovitz *et al.*, 1994). (a) Variations in the proportion of the labile particulate fraction relative to the sum of dissolved and labile particulate forms of elements: (*1*) Mn; (*2*) Ce; (b) cerium anomaly value: (*1*) dissolved form; (*2*) labile particulate form.

content accounts for 95% of the total REE in the oceanic water (Balashov and Lisitsyn, 1968; Bertram and Elderfield, 1993; Gurvich *et al.*, 1980; Sholkovitz *et al.*, 1993). The REE content variation in the oceanic water (from 0.*n* to 10*n* ng/l) corresponds to the circumcontinental zonality (Dubinin and Rozanov, 2001; Tachikawa *et al.*, 1999) due to an exchange between the dissolved REE and adsorbed complex of the terrigenous (and eolian) suspended matter. The decrease in terrigenous particulate content toward the pelagic area leads to the domination of dissolved REE phases, whose composition is controlled by the ability of rare earth elements to form complexes. The dissolved REE content increases with water depth by several times in some cases and correlates with the dissolved silica content.

The negative cerium anomaly is formed in surface waters of the ocean as a result of cerium oxidation (Figs. 4, 5). Manganese is also simultaneously oxidized in the upper water layer. The resulting cerium depletion in the dissolved REE composition is compensated by a positive cerium anomaly in the composition of suspended REE (Bertram and Elderfield, 1993; Lerche and Nozaki, 1998; Masuzawa and Koyama, 1989; Sholkovitz *et al.*, 1993; Tachikawa *et al.*, 1999). Cerium is reduced along with manganese reduction within the oxygen minimum zone at the transition from aerobic to anaerobic conditions, e.g., in the Black Sea, salt-rich basins of the Mediterranean, Cariaco Basin, and Saanich Inlet (Bau *et al.*, 1997; De Baar *et al.*, 1988; German and Elderfield, 1989, 1990; Schijf *et al.*, 1991). Cerium oxidation in the aerobic zone leads to its separation from other REE and preferable scavenging by suspended matter (Fig. 6). In the manganese reduction

zone, cerium is also reduced and transferred back to the solution, resulting in an appearance of the positive cerium anomaly in the anaerobic zone.

High concentrations of suspended matter, which is mainly related to the oxidation of reduced iron of hydrothermal fluids in their discharge zone, leads to the extraction of dissolved REE both from the fluid (during its dilution by seawater) and surrounding water (German *et al.*, 1990; Murphy and Dymond, 1984; Rudnicki and Elderfield, 1993; Sherrell *et al.*, 1999). The REE composition of the suspended matter is characterized by a negative cerium anomaly subsequently inherited by hydrothermal metalliferous sediments (Fig. 7). The positive europium anomaly recorded in the suspended matter near the hydrothermal discharge site is also occasionally inherited by metalliferous sediments of the spreading axis.

RARE EARTH ELEMENTS IN OCEANIC BOTTOM SEDIMENTS

Transformation of dissolved and suspended REE compositions is reflected in oceanic sediments. Changes in the REE composition (relative to shales) are minimal in terrigenous sediments from the periphery of the ocean. Only local volcaniclastic material sources may contribute to some specific REE patterns here. The possibility of preservation of the primary REE composition of source rocks directly depends on the proximity to coastline and the amount of coarse-clastic material in sediments (Strekopytov and Dubinin, 1996). In the pelagic realm, the REE composition of volcanogenic material and its weathering products delivered to the
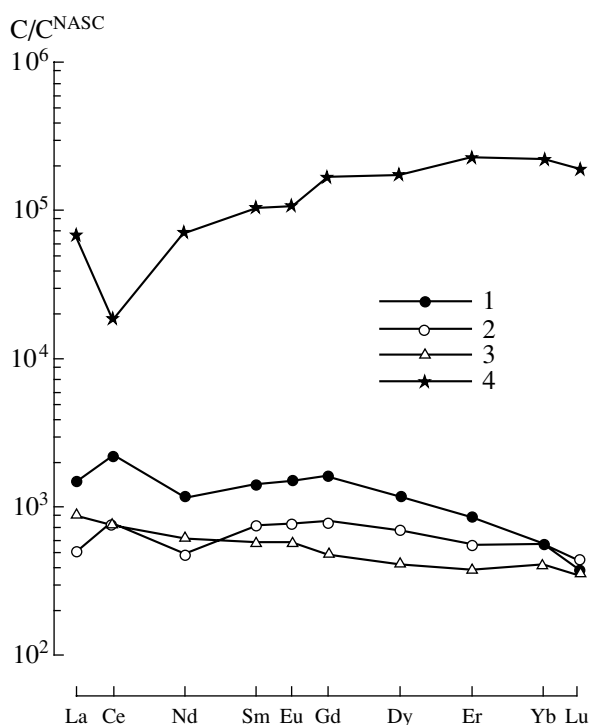
Fig. 5. Shale-normalized REE compositions in the Sargasso Sea water (Sholkovitz *et al.*, 1994). (1–3) REE in suspended matter extracted by: (1) 25% acetic acid, (2) the mixture of 2 M HCl and 1M HNO_3, (3) the mixture of concentrated HCl, HNO_3, and HF at 100°C; (4) REE dissolved in seawater.

Fig. 6. Variations of cerium anomaly $(Ce/Nd)^{NASC} = (Ce/Ce^{NASC})/(Nd/Nd^{NASC})$ in the dissolved REE composition in basins with the anaerobic environment. Horizontal lines show boundaries between aerobic and anaerobic zones in the (a) Cariaco Basin and (b) Black Sea. (1) Cariaco Basin; (2) Black Sea (De Baar *et al.*, 1998; Schijf *et al.*, 1991).

ocean bottom is almost completely inherited by pelagic sediments. In particular, this is noted for sediments from the Hawaiian Islands of the Pacific (Fig. 8). Sediments from the proximal stations 685, 686, and 641 virtually mimic the REE signature of basalts with the characteristic positive europium anomaly. Specific features of the REE composition of basalts are gradually abated in sediments with increasing distance from the volcanic material source (stations 677 and 678) or due to its dilution by biogenic carbonate (station 629, $CaCO_3$ 64%).

The REE content increases in terrigenous sediments in the sand–silt–clay series. First of all, this is related to the increasing adsorption surface of particles in the series. The bulk REE content increases with increase in the proportion of fine fraction in pelagic sediments. The REE behavior in the oceanic lithogenesis has been scrutinized for the transects across the Northwest and Northeast basins of the Pacific (Strekopytov *et al.*, 1995, 1999), the northern equatorial Pacific (Dubinin *et al.*, 1997), the EPR zone of metalliferous sediments (Dubinin and Volkov, 1986, 1988), and the 22° N profile in the North Atlantic (Dubinin and Rozanov, 2001). The obtained results demonstrated that the REE distribution is controlled by the circumcontinental zonality. Increase in the proportion of dissolved REE in the oceanic water is accompanied by increases of both bulk REE and LREE concentrations in sediments during the
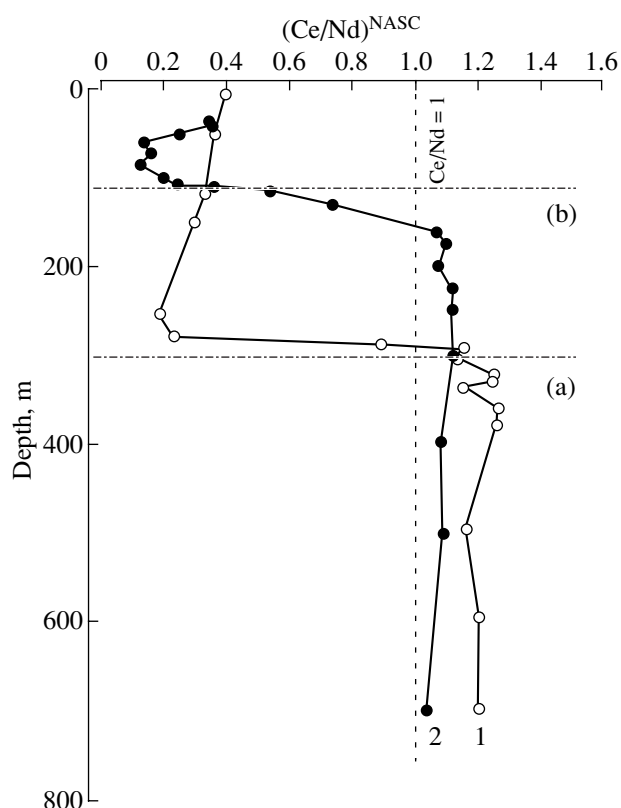
transition from the near-continental zone of terrigenous sediments to the pelagic area. Variations in the proportion of NASC-normalized LREE, relative to HREE, may be expressed as:

$$(LREE/HREE)^{NASC} = (La/La^{NASC}$$
$$+ 2 \times Pr/Pr^{NASC} + Nd/Nd^{NASC})/(Er/Er^{NASC}$$
$$+ Tm/Tm^{NASC} + Yb/Yb^{NASC} + Lu/Lu^{NASC}).$$

The Ce content in sediments increases faster than that of LREE owing to cerium oxidation on the suspended matter. The pelagic red clay is commonly characterized by positive cerium anomalies and elevated MREE contents as a consequence of lanthanide extraction from the oceanic water by hydrogenetic iron oxyhydroxides. Cerium is additionally extracted by manganese oxyhydroxides (Figs. 7, 9). In the Atlantic, the maximum possible Ce and MREE accumulation during pelagic sedimentation is reached in the pelagic red clay of the Canary and North American basins. The further decrease of sedimentation rates, mainly owing to increasing distance from continents, leads to an inversion in the REE composition of sediments. The subse-

quent increase in REE concentration is accompanied by decrease in the LREE proportion and appearance of a considerable negative cerium anomaly.

Such transformations in the REE composition are related to the accumulation of phosphorus (mainly as bone debris) in sediments (Strekopytov *et al.*, 1999; Toyoda *et al.*, 1990; Volkov and Yagodinskaya, 1979). The bone debris at the water–bottom interface accumulates significant amounts of REE (Fig. 2) dissolved in deep oceanic water (Baturin *et al.*, 1986; Dubinin and Sval'nov, 2001; Elderfield and Paggett, 1986). Such sediments are found on the Marcus-Necker Rise in the Pacific (Fig. 9). Oceanic biogenic sediments, such as carbonate and siliceous oozes, also show compositional features typical of the REE dissolved in the oceanic water (Fig. 2). They are characterized by a very low REE content owing to the diluting effect of biogenic carbonate and silica (Dubinin and Rozanov, 2001; Elderfield *et al.*, 1981a; Palmer, 1985).

Input of material related to the origination of new oceanic crust in mid-oceanic spreading zones, intraplate magmatism, and subduction is superimposed on the normal oceanic sedimentation (circumcontinental, climatic, and vertical zonalities). The influence of volcaniclastic material delivery on REE distribution has been discussed above with the Hawaiian Islands region as example. In addition, material supply from hydrothermal sources directly related to volcanic activity also plays an important role in the REE geochemistry of oceanic sediments. Sulfide ore deposits mainly composed of pyrite, chalcopyrite, sphalerite, and pyrrhotite are formed at sites of the hydrothermal fluid discharge onto the bottom surface. Despite a considerable REE content in acid (pH ~ 3) hot (300–360°C) fluids, sulfides do not accumulate REE (Fig. 3) Thus, sulfides do not probably play any considerable role in the REE accumulation in oceanic sediments.

The influence of suspended iron oxyhydroxides related to the oxidation of iron delivered by hydrothermal fluids on the REE geochemistry in the ocean is much more important. Precipitation of suspended iron oxyhydroxides from solutions is accompanied by the REE adsorption from deep oceanic waters. The REE composition in the suspension is characterized by negative cerium anomaly and depletion in LREE (German *et al.*, 1990; Murphy and Dymond, 1984; Rudnicki and Elderfield, 1993; Sherrell *et al.*, 1999). Metalliferous sediments are formed as a result of the settling of such suspension onto the ocean bottom in the course of pelagic sedimentation. They are defined as sediments containing more than 10% iron (calculated on the carbonate-free basis) represented by X-ray amorphous oxides and goethite. The metalliferous sediments are characterized by enrichment in Mn and some other transitional metals and depletion in Al, Ti, Th, Ga, and others. Metalliferous sediments cover especially large areas on the East Pacific Rise (Gurvich, 1998; Migdisov *et al.*, 1979). In the Indian Ocean, metalliferous sediments are known from
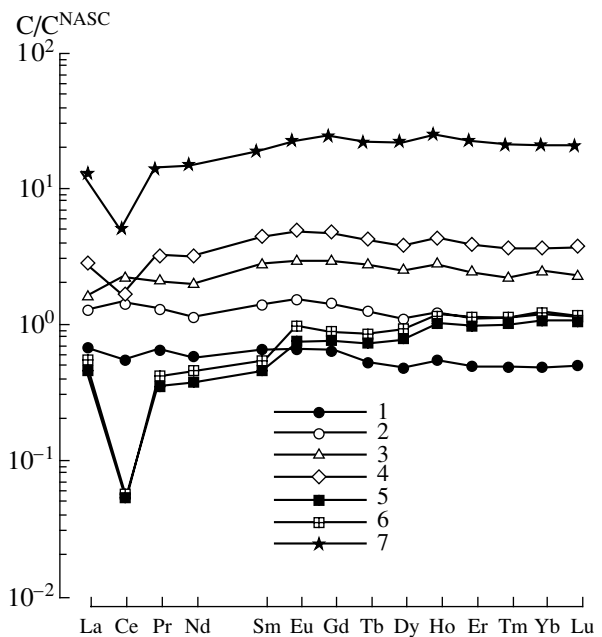
Fig. 7. REE compositions in oceanic sediments. (1) Carbonate-terrigenous mud from the Atlantic Ocean, St. 3840, 0–2 cm; (2) pelagic red clay from the northeastern Pacific, St. 6175, 0–1 cm; (3) pelagic red clay from the South Pacific Basin, St. 34, 0–2 cm; (4) pelagic red clay enriched in bone debris from the Pacific, St. 6177, 0–2 cm; (5, 6) metalliferous sediments from the East Pacific Rise, St. 45: (5) 0–10 cm, (6) 365 cm; (7) clay with an admixture of hydrothermal material from the South Pacific Basin, St. 35. Based on (Dubinin and Rozanov, 2001; Dubinin and Sval'nov, 2001; Strekopytov *et al.*, 1999; and our unpublished data).
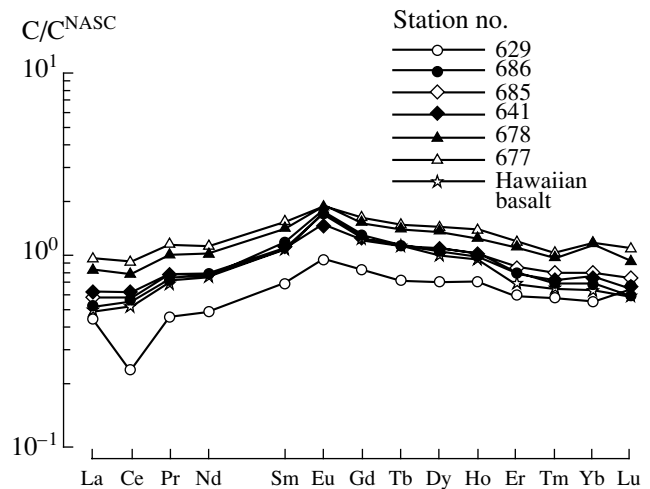
Fig. 8. REE compositions in sediments from the Hawaiian Islands (Strekopytov and Dubinin, 1996).

the triple junction area. In the Atlantic, they only occur in the narrow axial valley of the Mid-Atlantic Ridge, although the influence of hydrothermal material supply
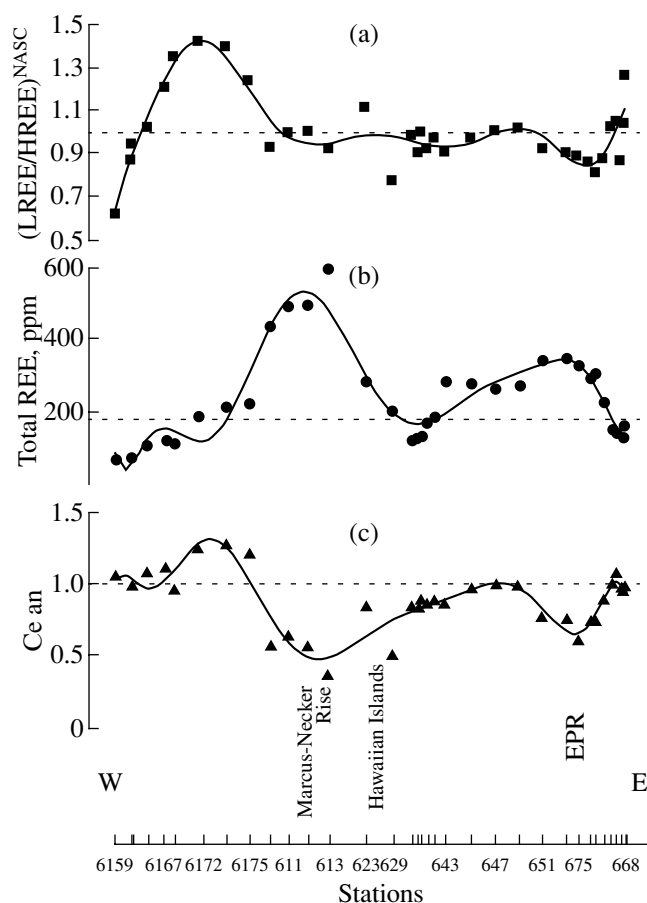
Fig. 9. Variations in the REE composition of sediments along the transect from the Japan Islands to the Gulf of California (Strekopytov *et al.*, 1999). (a) (LREE/HREE)^{NASC}; (b) total REE (calculated on the carbonate-free base); (c) cerium anomaly value. NASC values are shown by the dotted line.

is recorded in the entire axial zone (Cronan, 1980; Dubinin and Rozanov, 2001).

Since the amount of REE adsorbed from oceanic waters by iron oxyhydroxides depends on the interaction time and, consequently, distance from hydrothermal sources, the REE content in metalliferous sediments is a variable value (Dubinin and Volkov, 1986, 1988). The closer to the source, the lower is the REE content and the higher is the probability of finding positive europium anomaly in the REE composition of metalliferous sediments (Fig. 7).

The REE distribution between different phases of pelagic sediments provides a better understanding of the REE behavior in the ocean. Oceanic pelagic sediments are polygenetic formations including terrigenous, biogenic, hydrogenetic, volcanogenic, and hydrothermal components with specific REE compositions (Fig. 2). Moreover, diagenetic processes produce new mineral formations, such as barite, zeolites, ferromanganese micronodules, and apatite. General regularities

established by correlation analysis for sediments of the Pacific (Strekopytov *et al.*, 1999) and Atlantic (Dubinin and Rozanov, 2001) oceans show that rare earth elements are mainly related to phosphorus and iron (Fig. 1). Iron occurs in sediments as oxyhydroxides and terrigenous or volcanogenic Fe-containing aluminosilicates. Phosphorus can occur as biogenic apatite, component of organic and terrigenous materials, adsorbate on iron oxyhydroxides, or Fe–Ca hydroxophosphates. Mobility of REE in postsedimentary conditions depends on the stability of various parental sediment phases.

Distribution of REE between different mineral phases of sediments based on the grain size analysis has been reported in (Tlig, 1982; Tlig and Steinberg, 1982; Toyoda *et al.*, 1990; Volkov and Yagodinskaya, 1979). Sediments from the Indian Ocean are subdivided into eight size fractions. The coarser fractions (>35, 35–20, and 20–5 μm) are mainly composed of biogenic opal and calcite and characterized by negative cerium anomaly, which is transformed into a positive one in the fine-grained fractions (2–5, 1–2, 0.5–1, 0.2–0.5, and <0.2 μm) containing clay minerals and oxyhydroxides. Sediments with a hydrothermal component in fine fractions are characterized by negative cerium anomaly and their REE composition is similar to that of metalliferous sediments (Tlig, 1982; Tlig and Steinberg, 1982). Analysis of pelagic fractions (>10 and <10 μm) from the Pacific revealed the REE accumulation in fractions containing biogenic apatite (Volkov and Yagodinskaya, 1979). Division of pelagic clays into six fractions showed that the maximum REE content appears in the 38–100 μm fraction enriched in biogenic phosphorus (Toyoda *et al.*, 1990).

Selective leaching is another method often used for the study of REE distribution between mineral phases in sediments. Difficulties in the interpretation of data obtained by the extraction with chemical reagents are caused by an insufficient selectivity of extracts relative to the easily soluble authigenic minerals of sediments. Results of the chemical analysis of labile (soluble) fractions in sediments depend on the concentration of acid (or salt) in the applied extraction method, redox properties of the reagent, the relationship between liquid and solid phases, the treatment duration, and the grain size of the analyzed material (Dubinin and Strekopytov, 2001). Despite such constraints, we can determine conventionally reactive (labile) REE, which can participate in diagenetic processes, by the extraction method. Study of the compositions of ferromanganese nodules and micronodules, as well as the reactive part of associated sediments, may serve as example (Dubinin, 1996; Dubinin and Strekopytov, 1994; Dubinin and Sval'nov, 1996; Dubinin *et al.*, 1997; Elderfield *et al.*, 1981a; and others). Study of the cerium behavior in clays with a downward increasing admixture of hydrothermal material (Fig. 10) represents another example. Irrespective of extraction type, 88–98% of the trivalent REE are transferred into solution. The high REE yield
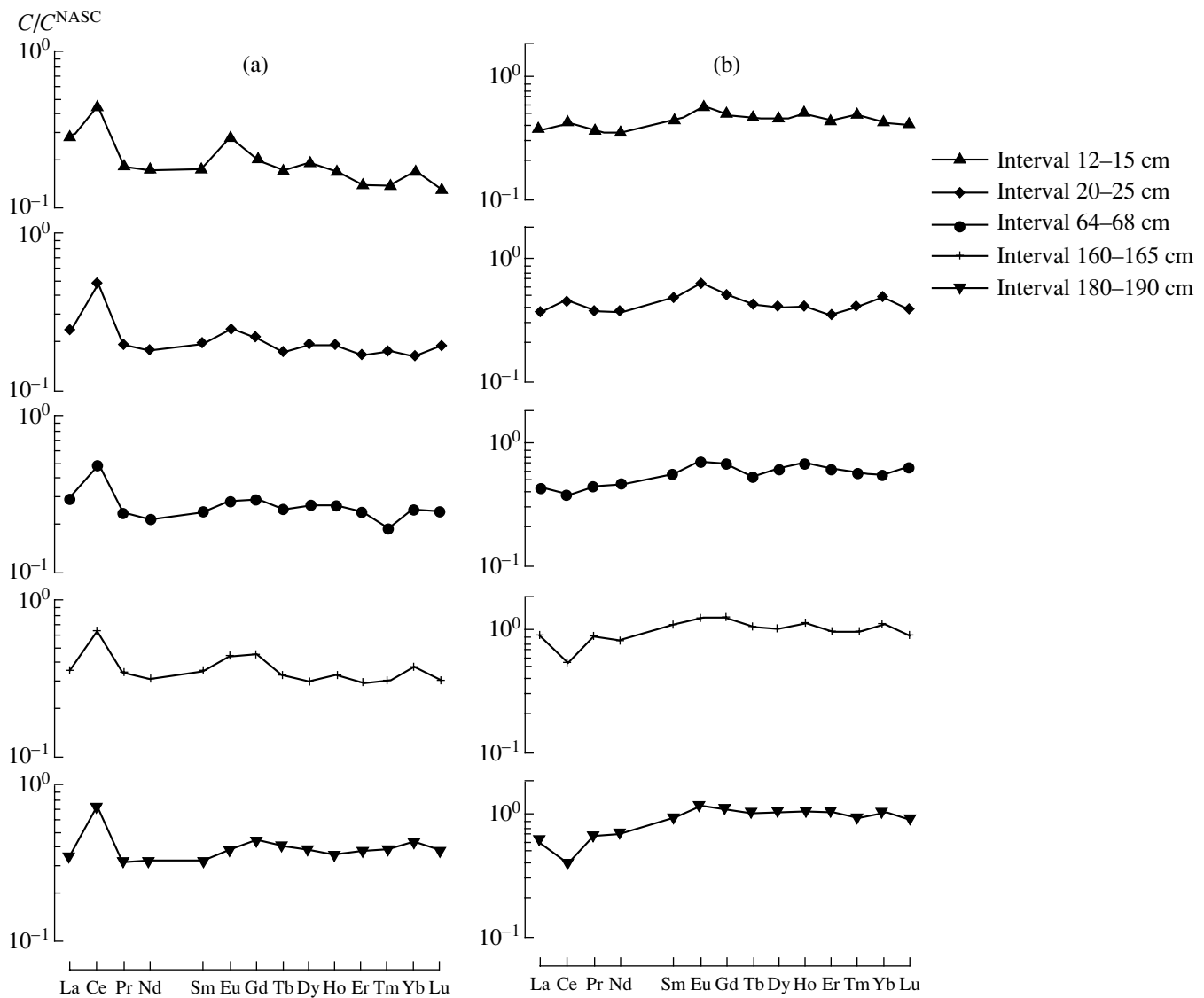
C/C^{NASC}

Fig. 10. Shale-normalized REE compositions in sediment residues after extraction by: (a) 3.5N H_2SO_4; (b) 1M $NH_2OH \times HCl +$ 25% CH_3COOH. Station 35, South Pacific Basin (Dubinin and Sval'nov, 2000b).

into the extracts indicates the prevalence of adsorbed forms in their composition. In addition to aluminosilicates, iron oxyhydroxides are also preserved in sediments as a result of the complete removal of manganese oxyhydroxides and low-crystalline iron oxyhydroxides by the Chester reagent. A negative cerium anomaly is recorded in bulk sediments at intervals 12–15 cm and 20–25 cm, but the anomaly is positive in the Chester residue. In the lower part of the core, increase in the admixture of hydrothermal material is accompanied by the negative cerium anomaly of the residue, indicating the domination of crystalline forms of hydrothermal iron oxyhydroxides in sediments.

The positive cerium anomaly appears in residues after extraction by 3.5N H_2SO_4 (Volkov *et al.*, 1980) as a result of the presence of Mn(IV) oxyhydroxides dis-

tinguished from iron oxyhydroxides by insolubility in this leachate. Hence, a part of cerium is probably associated with manganese oxyhydroxides because of conjugate oxidation processes $Mn^{2+} \longrightarrow Mn^{4+}$ and $Ce^{3+} \longrightarrow Ce^{4+}$ in oceanic surface waters (Dubinin and Sval'nov, 2001).

Investigation of the REE behavior in reducing diagenesis of oceanic sediments may serve as another example of the extraction method application (Dubinin, 1998). The behavior of rare earth elements in interstitial waters of sediments from nearshore areas of the Buzzards and Chesapeake bays and Saanich Inlet was studied earlier (German and Elderfield, 1989; Elderfield and Sholkovitz, 1987; Sholkovitz *et al.*, 1989, 1992). The REE concentrations in the interstitial water are 10–50 times higher than those in the bottom water and
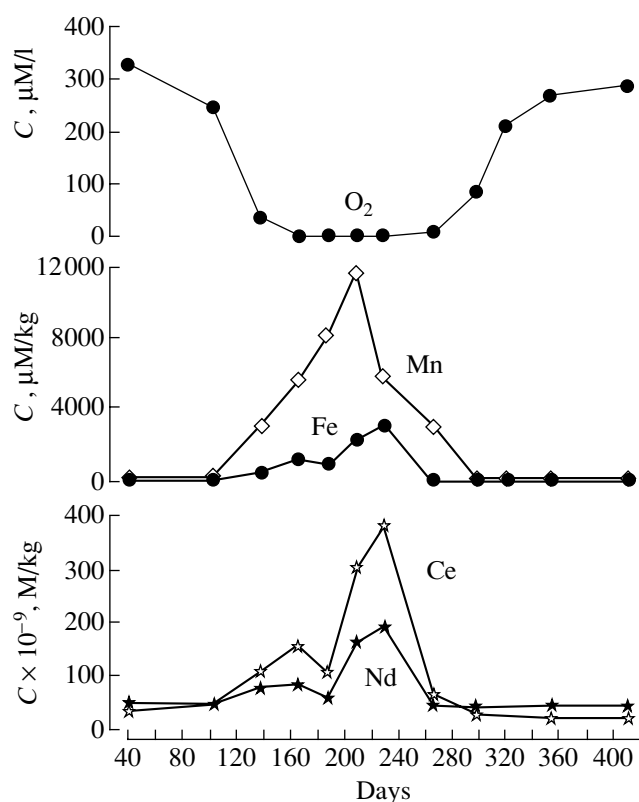
Fig. 11. Variations of dissolved oxygen, Fe, Mn, Ce, and Nd contents in the Chesapeake Bay bottom waters (Sholkovitz *et al.*, 1992).

depend on the redox conditions in sediments. Variations of REE concentrations in interstitial (and bottom) waters display seasonality. It is evident from Fig. 11 that they coincide with the development of oxidizing and reducing conditions in sediments (Sholkovitz *et al.*,1992). Variations of the REE content are related to Fe content variations in the interstitial water. The development of reducing conditions in sediments leads to a preferable increase in Ce and LREE contents. The replacement of reducing conditions by oxidizing ones promotes a more prominent decrease in Ce and LREE contents relative to the HREE. The more rapid rise of the Ce content is related to its reduction and transfer from solid sediment phases into the interstitial water.

Study of the possible influence of seasonal REE changes in the interstitial water on sediment composition revealed that REE composition variations in the interstitial water do not change the reactive part of sediments if the distribution coefficient in the sediment–interstitial water system is about 10^6 (Elderfield and Sholkovitz, 1987; Sholkovitz *et al.*, 1989).

The development of reducing conditions in sediments is related to the oxidation of organic matter with the successive application of the following oxidants: dissolved oxygen, nitrates of interstitial water, Mn (IV) oxyhydroxides, Fe (III) oxyhydroxides, and sulfates of interstitial water (Stumm and Morgan, 1981). Increase

of Fe–Mn oxyhydroxides toward the oceanic pelagic area is accompanied by decrease in the organic matter content and ultimate elimination of the possibility of reducing diagenesis. Meanwhile, extraction of trace elements from the oceanic water by Fe–Mn oxyhydroxides during pelagic sedimentation leads to increase of their content in pelagic sediments. During the reducing diagenesis, Fe–Mn oxyhydroxide compounds may partially be dissolved, resulting in the redistribution of REE and other associated trace elements. These processes most intensely develop in hemipelagic sediments, which contain a sufficient amount of buried organic matter for the development of reducing diagenesis and considerable amounts of hydrogenetic Fe–Mn oxyhydroxides. Iron and manganese redox processes control the REE behavior at the boundary between oxidized and reduced waters in the Cariaco Basin, Saanich Bay, and Black Sea. Rare earth elements are adsorbed on the suspended Fe–Mn oxyhydroxide particulates under oxidizing conditions and transferred to water due to their reduction of Fe and Mn under reducing conditions (De Baar *et al.*, 1988; German and Elderfield, 1989; Schijf *et al.*, 1991). Similar processes may develop within sediments.

We studied the REE redistribution REE during early diagenesis in hemipelagic sediments from Station 6171 located in the Northeast Basin of the Pacific (Dubinin, 1998). The upper core interval (0–40 cm) is oxidized. The diagenetic redistribution of Fe and Mn as accumulations of their oxyhydroxides is noted in sediments at 40–57 cm (Mn up to 13%) and 57–67 cm (Fe up to 6.4%). Sediments are reduced below 67 cm. The 40-cm-thick oxidized layer hindered the transfer of reduced Fe and Mn (and related trace elements) to the bottom water. In order to separate the reactive part of sediment, we used the Chester reagent that almost completely reduces Mn(IV) oxyhydroxide and partially dissolves low-crystalline Fe (III) oxyhydroxides. About a half of the total MREE content was transferred into leachate. Lanthanum dissolved less than any other REE, but even its proportion was about 25% in the leachate. Aluminum is the least mobile element in the early diagenetic reduction. Rare earth elements (except lanthanum and praseodymium) accumulate in Fe- and Mn-rich sediment layers. Light rare earth elements display the lowest mobility during the diagenesis. Cerium accumulates in Fe- and Mn-rich layers where the Ce anomaly reaches 1.50 against the background value of 1.34–1.41 (Fig. 12). Accumulation of phosphates from the interstitial water on the diagenetic iron oxyhydroxide led to additional extraction of the HREE.

In order to characterize the REE behavior in polygenetic oceanic sediments, it is necessary to study the REE distribution between their different phases. Owing to low crystallinity of many authigenic minerals and abundance of admixtures in them, their separation is a hardly solvable problem. For example, the REE content in phillipsite is strongly affected by iron oxyhydroxide and bone debris admixtures, which were entrapped dur-
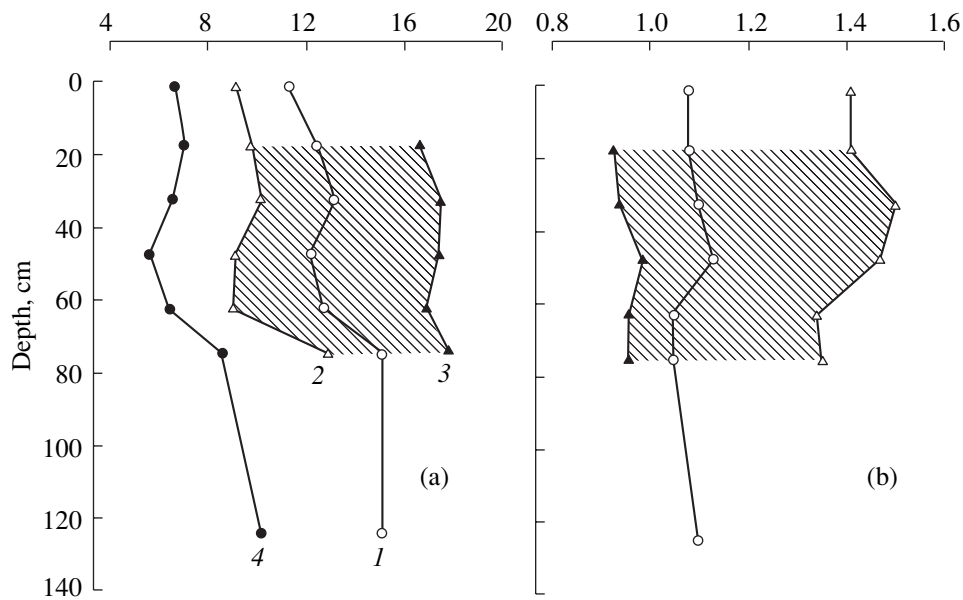
Fig. 12. Variations in values of (a) (LREE/HREE)^{NASC} (×10) and (b) cerium anomaly with depth in sediments at St. 6171 (Dubinin, 1998) (*1*) Bulk sample; (*2*) leachate; (*3*) residue; (*4*) (Fe/P)/10. The shaded area reflects difference between values of (LREE/HREE)^{NASC} and Ce an for the leachate and residue.

ing the growth of phillipsite crystals and cannot be removed by mechanical or chemical methods (Dubinin, 2000; Piper, 1974).

Authigenic (chemogenic or partially biogenic) minerals are formed during the diagenesis as a result of approaching equilibrium in the sediment–bottom water–interstitial water system. They include two paragenetic associations: (1) minerals related to the reduced zone in the near-continental oceanic areas and inland seas; (2) minerals related to oxidized pelagic sediments of oceans. The first association is formed in terrigenous and terrigenous–carbonate sediments, where the REE composition is similar to that of the shale. Therefore, the REE composition in shelf phosphorites does not differ from the shale composition (McArthur and Walsh, 1984).

The REE composition in sediments from the pelagic regions is formed as a result of the combined contribution of polygenetic sediment components. The clay mineral composition of pelagic sediments from the Indian Ocean is shown in Fig. 2. Phosphate phases in pelagic regions of oceans are represented by bone debris, seamount phosphorites, and Fe–Ca hydrophosphates (Baturin *et al.*, 1986; Dubinin, 2001; Dubinin and Sval'nov, 2001; Elderfield and Paggert, 1986; McArthur and Walsh, 1984). Their REE compositions are characterized by a minor fractionation under the direct influence of elements dissolved in the oceanic water, as indicated by the persistent depletion in Ce and LREE (Fig. 2). In addition to bone debris, which accumulates rare earth elements at the postsedimentary stage, foraminiferal tests, diatom frustules, and other biogenic components in sediments are also character-

ized by the Ce deficit and the trivalent REE composition of the oceanic water type (Fig. 2). Barite is depleted in the MREE (Fig. 2). According to (Guichard *et al.*, 1979), the above composition is a consequence of the similarity of LREE and barium (in terms of ionic radius) and elevated HREE content in the oceanic water.

The REE composition of hydrogenetic and hydrothermal Fe–Mn oxyhydroxides is already developed during their suspension state (Fig. 5). Hydrogenetic Fe–Mn oxyhydroxides probably governed the dissolved REE composition in the ocean, including the origin of negative cerium anomaly. The specific REE composition (positive cerium anomaly) of the dispersed hydrogenetic Fe–Mn oxyhydroxides is recorded in subcolloidal fractions of pelagic sediments, as well as ferromanganese crusts, micronodules, and nodules (Fig. 13). Ferromanganese micronodules—common authigenic mineral aggregates in the pelagic sediments—are formed during postsedimentary diagenetic processes. They are similar to nodules in their morphology and chemical and mineral composition (Addy, 1979; Dubinin and Sval'nov, 1995, 1996, 2000a, 2000b, 2003; Pattan, 1993; Pattan *et al.*, 1994; Sval'nov *et al.*, 1991a, 1991b). The REE composition in four size fractions of sediments from the South Pacific Basin and northern equatorial Pacific is presented in Fig. 13. The diagram shows that the REE composition gradually changes with increasing size of micronodules in both cases. The trivalent REE content decreases with increasing size of micronodules. The cerium behavior is strongly variable (Fig. 13). In the case typical of low-productivity regions of the ocean, increase in micron-
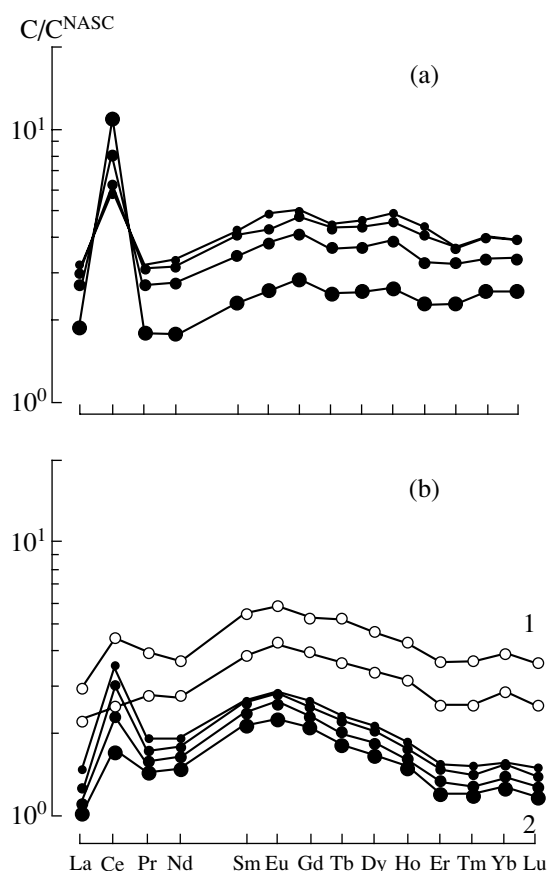
Fig. 13. Shale-normalized REE compositions: (a) Ferromanganese micronodules from the South Pacific Basin representing a low-productivity region; (b) ferromanganese nodules and micronodules from the northern equatorial Pacific representing a high-productivity region (Dubinin and Sval'nov, 2000b, 2003). (1) Nodules; (2) micronodules. Symbol size corresponds to the micronodule fraction size of 50–100, 100–250, 250–500, and >500 μm, respectively.

diagenetic processes (Fig. 14). The finest micronodule fractions are most affected by diagenesis in the low productivity regions. The composition of micronodules approaches that of the hydrogenetic macronodules with an increase of their size (Dubinin and Sval'nov, 2000a, 2000b, 2003).

As the micronodules grow and, consequently, their surface area increases, the composition of Fe–Mn oxyhydroxides changes due to an increasing role of diagenesis or hydrogenetic particulate flux after the segregation of micronodules from the sediment. Evolution of the micronodule composition and nodule type depend on the productivity of surface waters, i.e., the amount of organic matter delivered to sediments after its oxidation in the water column. Compositional variations of nodules from the northern equatorial Pacific are related to bottom currents and hilly bottom topography (Dubinin *et al.*, 1997).

Since cerium accumulates on Fe–Mn manganese oxyhydroxide particulates (Fig. 5), one can expect that oceanic ferromanganese nodules would bear a positive cerium anomaly. Actually, in addition to hydrogenetic crusts, only hydrogenetic nodules with Mn/Fe < 2.5 are characterized by this anomaly (Uspenskaya and Skornyakova, 1991).

Hydrothermal Fe–Mn oxyhydroxides are incorporated into nodules in the hydrothermal-sedimentary deposit zones, such as the Bauer and Guatemala basins (Dubinin, 1996; Elderfield and Greaves, 1981; Murphy and Dymond, 1984). The REE composition of these deposits is developed during the adsorption of dissolved REE with a negative cerium anomaly and depletion in the LREE from deep waters (German *et al.*, 1990; Murphy and Dymond, 1984; Rudnicki and Elderfield, 1993; Sherrell *et al.*, 1999). Although these processes result in the preferential accumulation of Ce and LREE, the fractionation factor is insufficient to create a positive cerium anomaly in the shale-normalized REE composition of the hydrothermal-sedimentary deposits. The bone debris in pelagic sediments leads to an inversion of the cerium anomaly. However, it can hardly produce the negative cerium anomaly observed in ferromanganese nodules, because the bone debris only sporadically occurs in their composition.

Variations in the REE composition (especially, the cerium anomaly values) in nodules, micronodules, and crusts might be explained in terms of the REE adsorption on hydrogenetic and hydrothermal iron oxyhydroxides from initially different (surface and deepwaters) dissolved REE compositions (Dubinin and Volkov, 1988). However, considerable variations in the REE composition of oceanic ferromanganese deposits are also known beyond the hydrothermal influence zone. Differences in the REE composition of ferromanganese nodules and micronodules are recorded even at a single station with identical conditions of suspended matter flux onto the bottom (Dubinin and Sval'nov, 1996, 2000a, 2003).

odule size is accompanied by increase in the Ce content and the consequent positive cerium anomaly. In the second case typical of the high-productivity equatorial zone, the Ce content and cerium anomaly decrease. Moreover, the Ce decrease trend is more rapid than that of the trivalent REE. Thorium and cobalt behave like cerium in processes of the ferromanganese ore formation (Dubinin and Sval'nov, 2000a, 2003). During adsorption processes taking place in the water column, the behavior of thorium is similar to that of cerium at oxidation state 4+. Cobalt is oxidized in the upper part of the water column together with manganese and cerium (Moffett, 1990; Moffett and Ho, 1996).

The composition of ferromanganese nodules and micronodules considerably differs in similar sedimentation conditions (e.g., at the same station). As the micronodules grow in the high bioproductivity regions of the ocean, their composition gradually approaches that of macronodules and the reactive part of associated sediments, reflecting an increasing influence of early
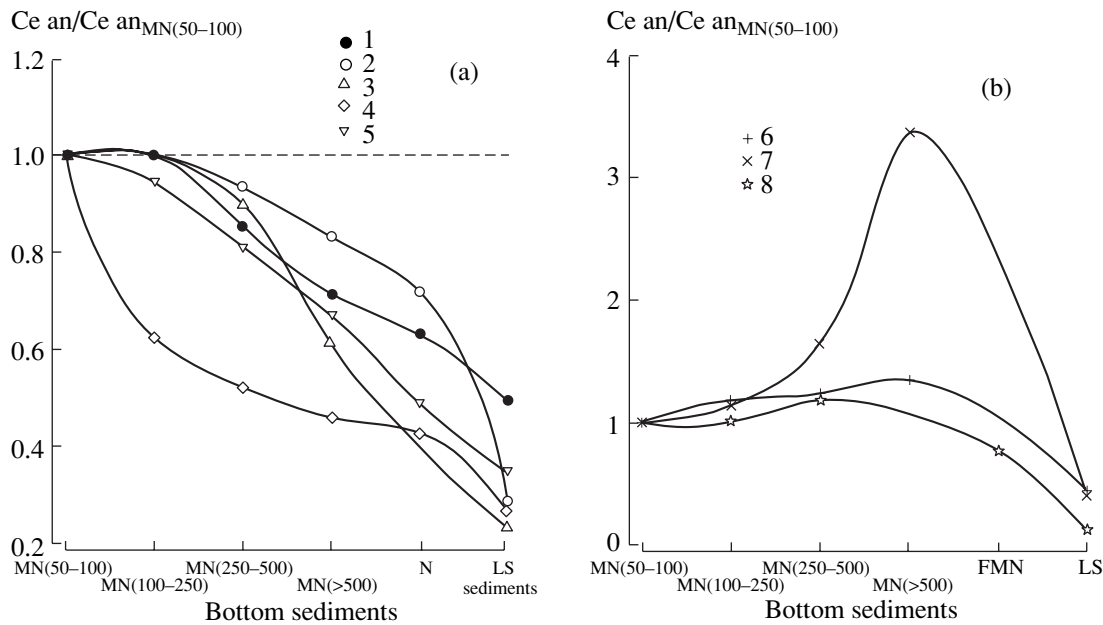
Fig. 14. Ce anomaly values in ferromanganese micronodules (MN) of different size fractions (normalized by Ce an in the finest fraction 50–100 μm), ferromanganese nodules (FMN), and the labile part of enclosing sediments (LS): (a) high-productivity regions; (b) low-productivity regions (Dubinin and Sval'nov, 2000a, 2003; and our unpublished data). (1–8) Station nos.: (1) 3874; (2) 56; (3) 3834; (4) 3911; (5) 3915; (6) 35 (interval 37–40 cm); (7) 35 (interval 105–110 cm); (8) 2492.

Lanthanides are present in the adsorbed iron oxyhydroxide complex of authigenic ferromanganese aggregates in the ocean. Diagenetic compositional changes in the adsorbed complex are possible during exchange reactions (e. g., with proton during acidification) or dissolution of the associated phase. Dissolution owing to the Fe(III) reduction by organic matter does not occur in the pelagic environment if Mn(IV) oxyhydroxides are available. The pH value of bottom and interstitial waters insignificantly differs from that of the adsorbed complex formation on suspended particles of hydrogenetic Fe–Mn oxyhydroxides in oceanic surface waters. Therefore, the variability of REE composition in authigenic ferromanganese aggregates is related to diagenetic processes, which lead to the dissolution of Mn(IV) oxyhydroxides owing to their reduction by organic matter, rather than REE desorption. The diagenetic Mn enrichment of the upper sediment layer, micronodules, and nodules (increase of Mn/Fe) supports the above conclusion.

The variability of REE composition in oxyhydroxide aggregates, which formed in identical conditions, depends on the P/Fe ratio that increases during diagenesis (Fig. 15). As a result of the diagenetic alteration of hydrogenetic Fe–Mn oxyhydroxide intergrowths, manganese passes into the pore solution. Manganese is reduced by organic matter in suspension. Figure 4 demonstrates a relative decrease of Mn content in suspended matter with depth. Processes of Mn reduction

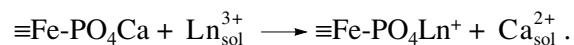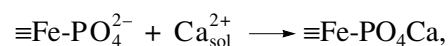essentially coincide with those in early diagenesis within sediments:

$$\equiv Fe\text{-}O\text{-}Mn\text{-}(OH)_3 + C(H_2O) \longrightarrow \equiv Fe\text{-}OH$$
$$+ Mn_{sol}^{2+} + CO_2 + 2H_2O,$$
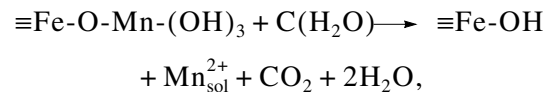
where $\equiv Fe–OH$ reflects the composition of the surface of iron oxyhydroxide particulates.

As a result of the removal of manganese oxyhydroxides, the newly formed surfaces of iron oxyhydroxides adsorb anions and cations to form their own sorption complexes. Iron oxyhydroxides irreversibly adsorb phosphate-ion from oceanic water and pore solution, leading to increase in the P/Fe ratio according to the reaction:

$$\equiv Fe\text{-}OH + HPO_4^{2-} \longrightarrow \equiv Fe\text{-}PO_4^{2-} + H_2O.$$
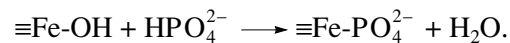
Such processes take place during the reducing diagenesis and the formation of hydrothermal iron oxyhydroxides. The same reaction occurs on iron oxyhydroxides formed by the submarine weathering of igneous rocks. Calcium is adsorbed to compensate the charge and partially replaced by the trivalent REE, leading to a significant relationship between the REE and phosphorus (Dubinin and Sval'nov, 2003):

$$\equiv Fe\text{-}PO_4^{2-} + Ca_{sol}^{2+} \longrightarrow \equiv Fe\text{-}PO_4Ca,$$

$$\equiv Fe\text{-}PO_4Ca + Ln_{sol}^{3+} \longrightarrow \equiv Fe\text{-}PO_4Ln^+ + Ca_{sol}^{2+}.$$

Additional adsorption of phosphate-ion promotes transfer of the trivalent REE into the solid phase. The
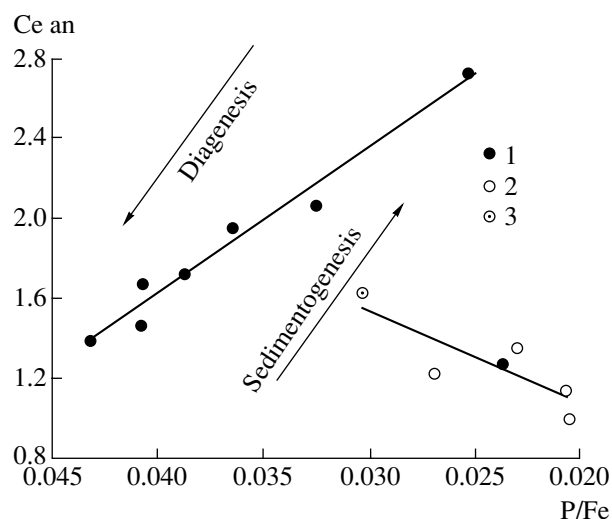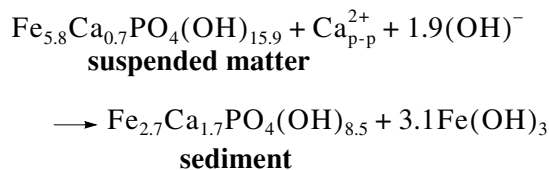
Fig. 15. Relationship between cerium anomaly (Ce an) and P/Fe ratio in ferromanganese micronodules and nodules from stations 3911/76, 3915, and 3913-3 (Dubinin and Sval'nov, 2003). (1) Micronodules; (2) nodules; (3) nucleus of a large nodule from St. 3915.

rare earth elements, in turn, decrease the positive cerium anomaly or increase the negative one. These chemical reactions are responsible for the local variability of REE composition in ferromanganese nodules from the northern equatorial Pacific (Dubinin *et al.*, 1999; Elderfield *et al.*,1981). Increasing influence of the diagenetic source leads to rise of the P/Fe value in micronodules and decrease in the positive cerium anomaly (Fig. 15).

The phosphorus concentration is higher relative to iron in diagenetic, hydrothermal, and halmyrolytic iron oxyhydroxides (the latter variety is produced during the submarine weathering of volcanic rocks). This leads to an additional accumulation of calcium and trivalent REE, which are more associated with phosphorus than with iron. Relationship between the trivalent REE and the phase mainly composed of Fe–Ca phosphates was repeatedly observed in sediments, nodules, and micronodules (Dubinin and Strekopytov, 1994; Dubinin *et al.*, 1997; Elderfield *et al.*, 1981a). The Fe–Ca hydroxophosphates were found in the >50 μm fraction of pelagic clays from the South Pacific Basin with an extremely high REE content and negative cerium anomaly (Dubinin, 2001). The composition of the Fe–Ca hydroxophosphates is shown in the Fe–Ca–P ternary diagram (Fig. 16). The P/Ca ratio in hydroxophosphates is close to 0.6. Such relationship between phosphorus and calcium corresponds to the molar (atomic) ratio of these elements in apatite $Ca_{10}(PO_4)_6(OH)_2$. The composition of hydrothermal suspension collected from the East Pacific Rise at 19° S is shown in the same diagram (Feely *et al.*, 1996). The suspension composition changes along the line corresponding to the molar ratio P/Fe = 0.25. This maximum possible value was

obtained in experiments of phosphorus accumulation by its simultaneous precipitation on iron hydroxides in seawater (Savenko, 1995). Suspended matter with the highest hydrothermal contribution is marked by the maximal Fe content. The composition field of hydrothermal suspension is located on the line corresponding to P/Ca = 0.6 and this suspension may serve as the source of Fe–Ca hydroxophosphates in sediments.

The molar ratio Fe/Ca/P is equal to 5.8/0.7/1 in the hydrothermal suspension and 2.7/1.7/1 in sediments. During **sedimentation**, calcium is adsorbed from the seawater and a part of calcium may subsequently be replaced by the trivalent REE:

$$Fe_{5.8}Ca_{0.7}PO_4(OH)_{15.9} + Ca_{p\text{-}p}^{2+} + 1.9(OH)^-$$
suspended matter

$$\longrightarrow Fe_{2.7}Ca_{1.7}PO_4(OH)_{8.5} + 3.1Fe(OH)_3$$
sediment

Analyses of the composition of hydroxophosphates from sediments show that the obtained phase is unstable (Fig. 16). The Fe–Ca hydroxophosphates are decomposed into iron hydroxide and apatite during **diagenesis** according to the reaction:

$$6Fe_{2.7}Ca_{1.7}PO_4(OH)_{8.5}$$
sediment

$$\longrightarrow 16.2Fe(OH)_3 + Ca_{10}(PO_4)_6(OH)_2$$
sediment
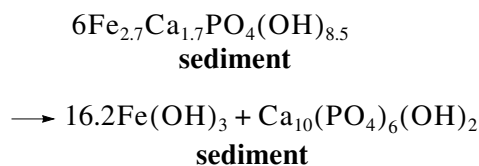
CONCLUSIONS

The main chemical properties, sources, and behavior of REE in the oceanic water are considered. We preferred the data obtained after 1980 when methods of the thermic ionization mass spectrometry were introduced in the analytical chemistry of REE. Data obtained after 1987 were based on the ICP mass spectrometry that allows one to record complete spectra of REE, including monoisotopic elements Pr, Tb, Ho, Tm. The refinement of analytical methods made it possible to determine extremely low REE concentrations in seawater, suspended matter, hydrothermal fluid, and sulfide minerals with a high reproducibility.

However, it is worth noting that the refinement of analytical methods only widened the knowledge on REE geochemistry of the ocean. Investigations carried out from in the 1950s–1970s revealed for the first time the REE contents and compositions in oceanic sediments, oceanic and river waters, ferromanganese nodules, metalliferous sediments, and phosphorites (Goldberg *et al.*, 1963; Høgdahl *et al.*, 1968; Martin *et al.*, 1976; Ostroumov, 1953; Piper and Graef, 1974; Wildeman and Haskin, 1965). First conclusions on the REE behavior in the ocean were made in (Balashov, 1976; Balashov and Lisitsyn, 1968; Gurvich *et al.*, 1980; Piper, 1974).
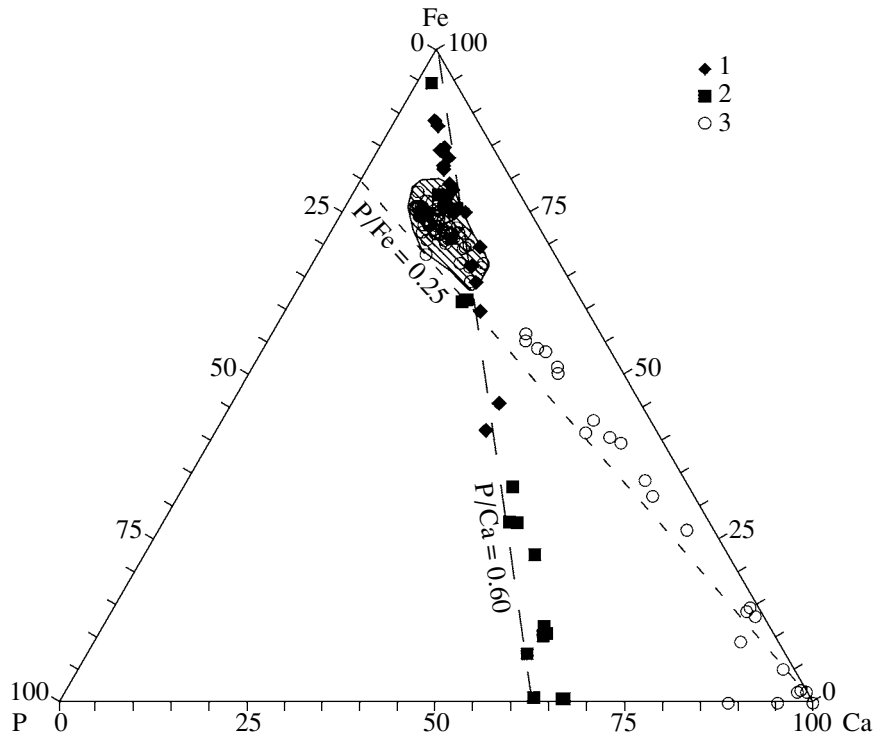
Fig. 16. Compositions of Fe–Ca hydroxophosphate plotted in the P–Ca–Fe diagram. (1, 2) Sediments from the South Pacific Basin, St. 35: (1) interval 37–40 cm; (2) interval 105–110 cm; (3) hydrothermal suspension from the East Pacific Rise, 19° S (Feely *et al.*, 1996). Lines show molar ratios P/Ca = 0.6 (apatite) and P/Fe = 0.25 (the maximal value obtained in experiments of the precipitation of phosphate-ion by iron oxyhydroxide from seawater (Savenko, 1995). Shaded area indicates the composition field of hydrothermal suspension with the maximal Fe content.

Further studies on the geochemistry of rare earth elements confirmed that river runoff and eolian transport deliver the major part of these elements to the ocean. The composition of suspended REE in river waters reflects the rock composition of drainage areas, whereas the composition of dissolved REE is controlled by the stability of their complex compounds. The dissolved REE content and pH value show an inverse correlation. Terrigenous sediments from the oceanic margins are similar to the shale or dominant rocks of the drainage area in terms of their REE content and composition. Fractionation of dissolved REE in the ocean commences in the river–sea mixing zone after the settling of the major part of the terrigenous suspended matter. The dissolved REE composition is characterized by a deficit in Ce and LREE. As the hydrogenetic component increases, the suspended matter is enriched in Ce (mainly due to oxidation) and LREE (owing to adsorption). The dissolved REE content in the ocean increases with water depth as a result of desorption of suspended REE and other processes.

The REE fractionation in oceanic waters is reflected in the composition of bottom sediments. The REE content and positive cerium anomaly increase in sedimentary processes with a higher contribution of reactive iron and manganese. Increase of the bone debris content in the pelagic clay as a result of low sedimentation rates leads to inversion of the REE composition. Depletion in Ce and LREE becomes stronger, because the bone debris accumulates considerable amounts of REE dissolved in the oceanic water probably without any noticeable fractionation. The pelagic clay with high bone debris content represents the terminal member in the series of sediments formed during the oceanic material fractionation. Such sediments occur in the Pacific beneath the cyclonic gyres, and they are absent in the Atlantic Ocean. Biogenic sediments (carbonate and siliceous oozes) dilute rather than accumulate REE. Thus, they inherit features of REE dissolved in the oceanic water. Delivery of the hydrothermal-sedimentary material to sediments leads to the inheritance of rare earth elements dissolved in the oceanic water owing to their adsorption by suspended iron oxyhydroxides.

Problems of the REE distribution between mineral phases of sediments are not yet completely solved. First of all, this is related to a poor crystallinity of the authigenic minerals, their intergrowth, and entrapment of other mineral phases during crystallization. Reliable data on the REE composition have been obtained for zeolites, barite, and clay minerals. The Fe–Ca hydroxophosphates have been discovered and their REE composition has been determined. This mineral phase is unstable in oceanic sediments, but it persists to form in products of the halmyrolysis of volcaniclastic material

and diagenesis of sediments and on hydrothermal iron oxyhydroxides. The incorporation of this phase into ferromanganese nodules and micronodules promotes the negative cerium anomaly and increase of the trivalent REE content.

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