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Yttrium and rare earth element contents in seamount cobalt crusts in the Indian Ocean

V. Balam^{1,*}, V. K. Banakar²,
K. S. V. Subramanyam¹, Parijat Roy¹,
M. Satyanarayanan¹, M. Ram Mohan¹ and
S. S. Sawant¹

¹National Geophysical Research Institute (CSIR),
Hyderabad 500 007, India

²National Institute of Oceanography (CSIR), Dona Paula,
Goa 403 004, India

Cobalt-rich Fe–Mn crusts occur on almost all seamounts and plateaus of the world oceans. Fe–Mn crusts are formed through layer-by-layer accretion of colloidal precipitates from cold ambient seawater onto exposed seamount rock substrates. This study reports high concentrations of rare earth elements (REE) and yttrium ranging from 1,727 to 2,511 µg/g in the crust samples collected from the Afanasy Nikitin Seamount (ANS) in the Eastern Equatorial Indian Ocean. The concentrations of REE in the ANS Fe–Mn crusts are much higher than those of the mid-Pacific seamount and nodules (1,180–1,434 µg/g). Ce-enrichment up to 0.17% has been recorded in the present study as against ~0.1% content in global seamount Fe–Mn crusts. This enrichment is attributed to oxidative removal of Ce from seawater to the marine Fe–Mn crust. The negative Ce-anomalies obtained for seawater samples from the ANS region coupled with strong positive Ce-anomalies in Fe–Mn crusts clearly indicate that the source of Ce in ANS Fe–Mn crusts is sea-water. This investigation warrants further detailed exploration studies in order to make an estimate of these highly useful elements in the cobalt enriched Fe–Mn crusts of Indian Ocean.

Keywords: Cobalt crust, rare earth elements, seamount, yttrium.

THE future of India's and the world's enthusiastically envisaged green technologies depends on the availability of several trace and ultra-trace metals, including rare earth elements (REEs) in adequate quantity. REEs are critical constituents to many of the world's most advanced technologies such as defence metallurgy, consumer electronics, medical applications, etc. More than 97% of the world's REE ore production is from mines in China, which have restricted their exports recently for reasons unknown. Other countries with notable production are Brazil, India, Kyrgyzstan and Malaysia. Mainly, monazite from beach placers is mined in India as the principal ore mineral for REE, although xenotime holds out some

*For correspondence. (e-mail: balaram1951@yahoo.com)

prospect for the future. Of India's estimated reserve of 5 million tonnes of monazite, 70–75% occurs in beach placers and the rest in the inland and offshore areas. Monazite content of beach sands may be up to 11 wt%.

Recent studies^{1,2} have indicated that different types of seafloor sediments harbour high concentrations of REE. However, they have not been regarded as REE and yttrium resource so far, because data on the quantitative information on abundance and spatial distribution of these deposits are insufficient. Recently, there have been reports on significant enrichment of REE in over 2,000 seafloor sediments, sampled at depth intervals of around 1 m, from 78 locations covering a vast seafloor area in the Pacific Ocean². Whereas the presently known continental REE deposits world over contain on an average 0.15–0.23% of ΣREE (REE + yttrium), the reported range of $\Sigma\text{REE}/\Sigma\text{REY}$ in the Pacific sediments is of the order of 0.1–0.22%. Estimates suggest that an area of just 1 sq. km, surrounding one of the sampling sites in the Pacific, could satisfy one-fifth of the current annual world consumption of REE. These figures emphasize the importance of marine sediments and other classes of sediments such as seamount Fe–Mn crusts and nodules as possible alternative resources for REY. At places the Pacific mud deposit contain 100–1,000 times more REY than the world's presently known land reserves of 110 million tonnes of REY oxides. Uptake of REY by mineral phases such as dispersed hydrothermal iron-oxyhydroxides and phillipsite was found to be responsible for their high concentration in the Pacific sediments². In addition to its economic importance, the REY as a group plays an important role in geochemical and palaeo-oceanographic studies and helps in understanding its source, distribution and behaviour under different redox conditions (for example Eu and Ce anomalies)^{3,4}.

Although considerable work has been carried out on the Fe–Mn crusts in the different oceans of the world, studies on Indian Ocean Fe–Mn crusts are limited^{5–9}. An attempt was made in 2002 by the National Institute of Oceanography (NIO), Goa, to explore the seamount crust at the Afanasy Nikitin Seamount (ANS) in the Indian Ocean⁶. Subsequently, the study was extended to detailed multi-beam swath bathymetric and geochemical investigations of seamount cobalt crust in collaboration with the National Centre for Antarctic and Ocean Research (NCAOR), Goa and National Geophysical Research Institute (NGRI), Hyderabad, to understand the cobalt–REY–platinum group metals (PGE) enrichment processes in the ferromanganese crusts of the ANS deposits in the eastern Equatorial Indian Ocean. The Fe–Mn crust samples were collected by dredging along short tracks of ~100 m length on the slopes of ANS during the cruise of *R. V. Academic Boris Petrov-37 (ABP-37)* during June–July 2009, by scientists of NIO, NCAOR and NGRI for studying REY and PGE enrichment along with several other trace elements in these crusts. In fact, the collection of

samples was so difficult that in a one-month long cruise, about 25 dredges were tried along with other continuous on-board experiments, out of which six attempts were successful in grabbing sizeable quantities of cobalt crust samples from depths of 3,000 to 5,000 m, leaving only six samples for these studies. Here we present preliminary results of REY concentrations observed in these cobalt-rich Fe–Mn crusts from ANS.

Oceanic ridges are the primary sites of volcanic activity where a new oceanic crust is generated. The ANS (~3°S and 83°E, eastern Indian Ocean) is an old volcanic seamount formed ca. 65 m.y. ago (Figure 1). Subsequent

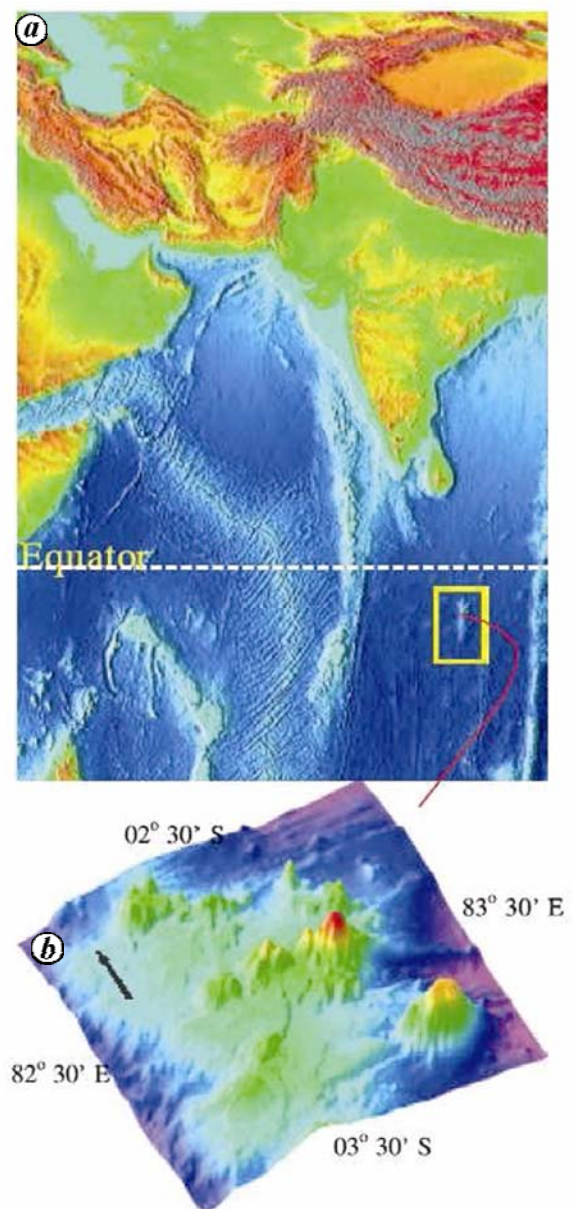


Figure 1. *a*, Location of the Afanasy Nikitin Seamount (ANS) (enclosed by a box) in the Eastern Equatorial Indian Ocean. *b*, 3D colour-coded multibeam swath bathymetric map of the northern part of the seamount (100 × 100 km). Pink colour indicates shallowest (<1,700 m) region and red colour indicates shallowest (<1,700 m) region. North shown by arrow in lower panel (Source: Banakar *et al.*⁸).

to its formation, a series of volcanic mounts north of ANS were formed in the equatorial Indian Ocean⁵. Though cobalt-enriched ferromanganese encrustations (Fe–Mn crust) were reported long ago from the Pacific seamounts, only a decade ago enrichment of cobalt metal was reported in ANS⁵. Cobalt-enriched Fe–Mn crusts of ANS and volcanic rocks have been studied to understand the evolution of the seamount-forming basalts apart from locating any possible hydrothermal vent sites.

Cobalt-rich Fe–Mn crusts occur on old seamounts and plateaus in almost all world oceans as precipitates from cold ambient sea-water onto rock substrates, forming pavements up to 250 mm thick (Figure 2). The mixed Fe–Mn oxyhydroxide phases accumulate slowly on the substrate rocks on the seafloor at rates of the order of a few millimetres per million years forming the crust. The Fe–Mn crusts containing > 1% of cobalt metal can be designated as the cobalt crust. The cobalt crust accrete at shallow water depths (generally <2,500 m) as slabs capping the seamounts. They are 3–6 times more enriched in cobalt metal than the abyssal polymetallic nodules. Crusts are composed of the minerals vernadite (manganese oxide) and ferrosiderite (iron oxide). Moderate amounts of carbonate–fluorapatite occur in thick crusts representing hiatus in the growth of cobalt due to reduced oxygenation. Also, it has been observed that most of the seamount Fe–Mn crusts contain minor fraction of intimately inter-mixed terrigenous minerals such as quartz and feldspar. Compared to sea water, the seamount Fe–Mn crusts exhibit several times more enrichment of metals^{10–13}. The most dominant metals are the transition group elements (Mn, Fe, Co, Ni, Cu, V, Pb, Zn), REY followed by PGE.

The REY on six cobalt crust samples were determined by ICP–MS following the procedure described by Balaram *et al.*¹⁴. The precision obtained for these measurements is better than 5% RSD with comparable accuracies. The minimum, maximum and average data of each



Figure 2. An example of cobalt crust formation as a thick layer over marine basalt at ANS¹⁹.

REE and yttrium are presented in Table 1. The REE patterns of ANS Fe–Mn crust show large positive Ce-anomalies (Figure 3a). The average concentration of Ce is 1,209 µg/g, which is much higher than that of mid-Pacific seamount nodules (718 µg/g). In addition, very high enrichment of a few elements such as Co (up to 0.66%), Ni (up to 0.47%), Cu (up to 0.10%), V (up to 0.1%), Sr (up to 0.16%) and Mo (up to 0.08%) in the crusts has been attributed to the surface oxidation processes. For example, under oxidizing conditions Co II can be oxidized to Co III and Ce III can be oxidized to Ce IV and these oxidized, undissolved phases get incorporated into the crust with time. The dissimilarities in enrichments observed between the present Fe–Mn crusts and the Pacific seamount crusts in Co and Ce associations with major mineral phases indicate inter-oceanic heterogeneity and region-specific conditions responsible for their enrichment⁶. Table 2 presents comparative data of Σ REY from different marine sediments of world oceans, including cobalt crusts from ANS. Σ REY in the Fe–Mn crust samples from the Indian Ocean ranges from 1,727 to 2,511 µg/g, which is much higher than that of the mid-Pacific seamount nodules (1,180–1,434 µg/g)¹⁵. The concentration of Ce (1,003–1,668 µg/g) is also much higher than that of mid-Pacific seamount nodules (718 µg/g). Ce-enrichment of up to 96% of Σ REE is also reported from the mio and hemipelagic muds of Brazil basin, Atlantic Ocean¹⁶. This Ce-enrichment in particular is noteworthy in the ANS deposits. Ce content up to 0.17% has been recorded in the present study as against ~0.1% content in global seamount Fe–Mn crusts. Ce alone ranges from 62% to 73% of Σ REE. The North American shale composite (NASC) normalized REE distribution patterns show a large positive Ce anomaly (Figure 3a). This enrichment is attributed to oxidative removal of Ce from

Table 1. Average concentrations of yttrium and rare earth elements (µg/g) in cobalt crust from the Afanasy Nikitin Seamount, Indian Ocean

Analyte	Minimum	Maximum	Average
Y	129.7	251.4	198.0
La	199.6	324.7	245.2
Ce	1003.2	1667.6	1342.0
Pr	26.6	54.9	38.1
Nd	115.2	234.5	163.0
Sm	22.4	49.0	33.5
Eu	5.6	11.2	7.9
Gd	32.2	58.7	43.5
Tb	4.8	9.3	6.6
Dy	26.8	48.7	35.5
Ho	7.4	11.9	9.1
Er	15.2	23.5	18.2
Tm	2.8	4.4	3.4
Yb	17.0	28.1	21.5
Lu	2.7	4.4	3.4
Σ REY	1726.6	2511.1	2169.0

No. of samples = 6.

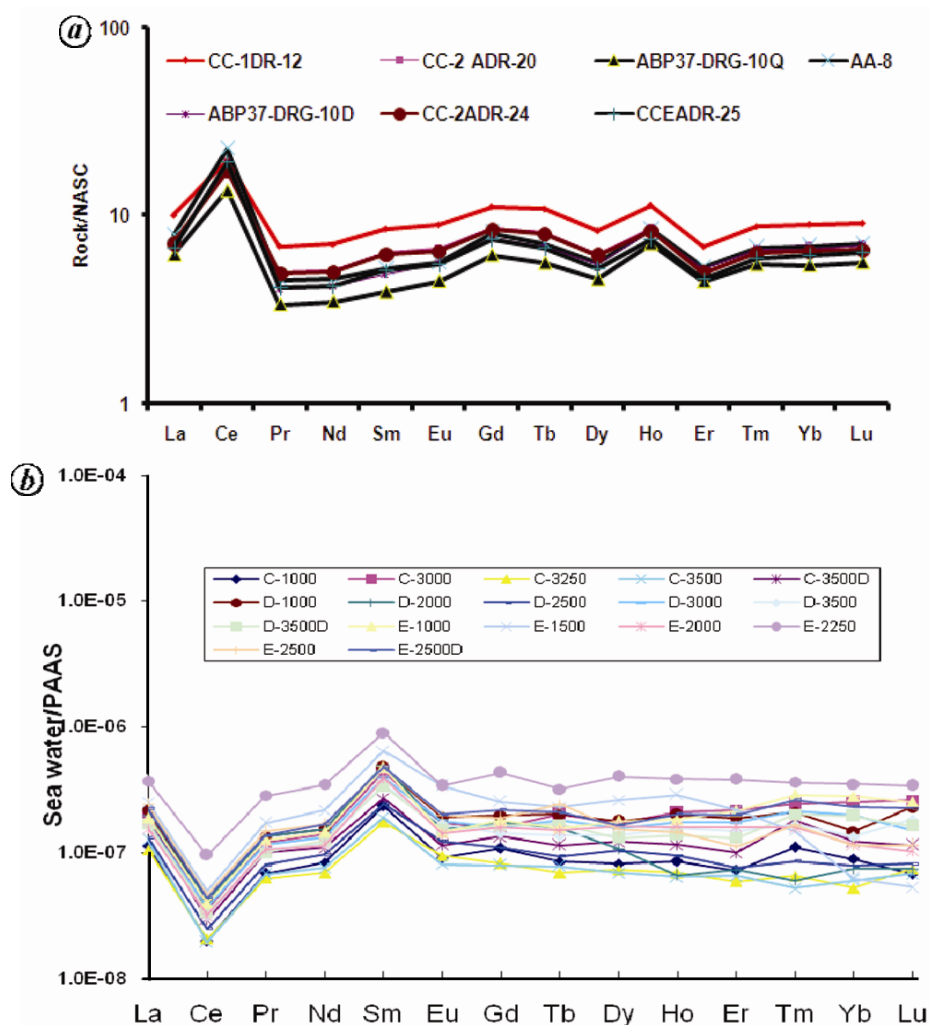


Figure 3. *a*, North American Shale Composite (NASC) normalized REE patterns of the ANS Fe–Mn crusts collected during the ABP-37 cruise. *b*, The Post Archean Australian Shale (PAAS) normalized REE distribution patterns of sea-water samples collected from ANS show characteristic features such as Ce-negative anomaly.

Table 2. Overview of $\Sigma\text{REE}/\Sigma\text{REY}$ range ($\mu\text{g/g}$) in marine sediments from different oceans

Sl. no.	Ocean	$\Sigma\text{REE}/\Sigma\text{REY}$ range ($\mu\text{g/g}$)	Matrix	Reference
1	Central Indian Ocean (ANS)	1,727–2,511	Cobalt crust	Present study
2	Mid-Pacific Seamount	2,084	Cobalt-rich crust	20
3	Indian Ocean	928–1,570	Ferromanganese crust	3
4	Scotia Sea	3,400	Ferromanganese crust	1
5	Eastern South Pacific	1,000–2,230	Deep-sea mud	2
6	North Pacific (east and west of Hawaiian Islands)	400–1,000	Deep-sea mud	2
7	Mid Pacific Ocean	1,178–1,434	Fe–Mn nodules	15
8	Pacific Ocean	1,326	Deep nodules	21
9	Pacific Ocean	1,398	Shallow nodules	21

Sl. nos 1–4, Cobalt crust; 5, 6, Deep-sea mud; 7–9, Ferromanganese nodules.

sea water to the marine Fe–Mn deposits and crust in the marine environment³. Also, changes in Eh, pH and temperature were found to be the cause for Ce mobility¹⁷.

The colloidal precipitates of the Mn-oxide and Fe-oxyhydroxide provide large surface area with abundant negatively charged particles, which effectively scavenge

large amounts of dissolved trace metals from ambient sea water.

The interaction of sea water with the seafloor and the terrigenous materials delivered to the oceans at the seamounts affect the chemical composition of sea water. Also, seamounts are usually associated with hydrothermal vents, which contribute to the physico-chemical exchange between the seamounts and the ocean water¹⁸. Hence, the sea-water chemistry is useful to understand the processes operating at the mid-oceanic ridges and seamount systems. Therefore, the sea water REE chemistry was studied along ANS at different water depths to assess the interaction between sea water and ANS cobalt crust¹⁴. The Ce-negative anomalies (Figure 3 b) obtained for sea-water samples in ANS coupled with strong positive Ce-anomalies in Fe–Mn crusts clearly indicate that the source of Ce in ANS Fe–Mn crusts is sea water.

There is a growing recognition that the cobalt-rich Fe–Mn crusts deposited on the seamounts are potential resources for several strategic metals such as REE and cobalt. Preliminary data presented here point out that the cobalt crusts of ANS are found to be enriched in REE (in particular, Ce) and yttrium and the abundance levels appear to be much higher than those of the mid-Pacific seamount nodules. The Ce-negative anomalies obtained for sea-water samples in ANS coupled with strong positive Ce-anomalies in Fe–Mn crusts clearly indicate that the source of Ce in ANS Fe–Mn crusts is sea water. The reported high concentration of REE (Ce in particular) from ANS Fe–Mn crusts warrants further detailed exploration studies in order to make an estimate of these elements in the cobalt crusts of ANS.

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