Quantitative Determination of Rare Earth Elements in Marine Sediment Samples by ICP-MS and NAA Technique

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INTRODUCTION

The crustal contents, distribution patterns, and isotopic signature of rare earth elements (REEs) have been widely employed as geochemical tracers in the marine environment (1,2). REEs reflect their continental sources and transport pathways by preserving the imprints of erosion and weathering history from source to sediment (3). REEs are useful for determining the petrogenetic history of rock suites (4).

Marine sediment samples have been generated by the Geological Survey of India over the past 40 years. The samples are being analyzed for major, minor, and a few trace elements for various studies. However, the analysis of REEs in marine sediment samples is yet to be done. The reason for not undertaking the analysis of REEs is due to non-availability of reasonable numbers of marine sediment reference samples.

One of the major techniques for REE studies is ICP-MS (5,6). The important criteria for precise and accurate determination of REEs by ICP-MS is the complete dissolution of the samples (7,8). Marine sediment samples contain highly resistant minerals, particularly zircon, which is the carrier of heavy rare earth elements (HREEs). Roje (9) used microwave digestion, employing several combinations of acids for digestion of MESS-3 Marine Sediment (National Research Council,

ABSTRACT

This paper reports a simple method for the determination of REEs in sea sediment samples by $\text{LiBO}_2\text{-Li}_2\text{B}_4\text{O}_7$ fusion, followed by inductively coupled plasma mass spectrometry (ICP-MS) measurement at ppm and sub-ppm levels. A comparison of ICP-MS and neutron activation analysis (NAA) data shows that except for La, the results for all other REEs agree between the two techniques. The ICP-MS data for one SRM MESS-1 Marine Sediment agree very well with the certified values. Two other sea sediment reference samples, MESS-2 Marine Sediment and NIST1646a Estuarine Sediment, were also analyzed by our method, and we report the REE data for the first time. NIST 1646a has certified values for La, Ce, and Nd which also agree with our ICP-MS data. Comparison of our sea sediment data with those of sea crustal abundance data and other sea sediments has been made. The quantification limit (10σ) for lanthanides varies from 20 to 100 ppb.

Canada), a reference sample, and determined several trace elements by ICP-MS. Nath et al. (10) in their studies utilized a Teflon® bomb heated at 245 °C for 96 hours for decomposition of USGS MAG-1 Marine Sediment reference sample. Dieger et al. (11) employed a high pressure dissolution technique for three marine sediment reference samples, BSK-1 Sediment (USGS), MESS-2 Marine Sediment (NRCC), and PACS-1 Marine Sediment (NRCC). They achieved dissolution

of the samples in more than 3 days. Antonina et al. (12) employed microwave digestion for the dissolution of marine sediment samples for the estimation of REEs. They observed that the recoveries for all of the REEs ranged between 78-93%. Begum et al. (13) in their study of marine sediment samples utilized both open and closed vessel digestion techniques and found that the closed vessel technique is preferable for precise and accurate estimation of trace and REEs.

All of the above methods used a combination of several acids for digestion of the samples, which is very time-consuming but also does not produce complete decomposition. An alternative method to acid digestion is the use of the fusion technique employing various alkali mixtures. Alkali fusion ensures rapid and complete decomposition of rock-forming minerals, including highly resistant minerals (14,15). Bayon et al. (16), using NaOH and Na_2O_2 as the fusion mixture, dissolved several geological samples including one marine sediment sample, GSMS-2 Geochemical Marine Sediment. They found results in reasonable accuracy with the published working values.

In our laboratory, we are using $\text{LiBO}_2\text{-Li}_2\text{B}_4\text{O}_7$ fusion, followed by ICP-MS, for the determination of REEs in a large number of stream sediment samples generated through our National Geochemical Mapping (NGCM) Programme (17). Although marine sediment samples are being analyzed for several trace elements by atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission

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spectrometry (ICP-AES) techniques, the development of a methodology for REE estimation in such samples is yet to be established. We apply the fusion methodology for the estimation of REEs in marine sediment samples by ICP-MS. Since there are few standards available for marine sediment samples, we checked our data by NAA. The aim of this study are as follows:

- (a) Establish a simple, rapid method for the estimation of REEs in marine sediment samples.
- (b) Determine the REE pattern in marine sediment samples collected from Car Nicobar and the Bay of Bengal.
- (c) Make a comparative study of ICP-MS and NAA.

EXPERIMENTAL

Instrumentation

The present study was done with a PerkinElmer® ELAN® DRC™-e inductively coupled plasma mass spectrometer and an RSX-11/MCA-85/90/SPEC-RAN-F Instrumental NAA system (Canberra Industries, USA). An Apsara reactor was used for sample irradiation. The instrumental operating parameters for ICP-MS analysis are shown in Table I.

A comparative study was made with the help of NAA model RSX-11/MCA-85/90/SPEC-RAN-F Instrumental NAA system (Canberra Industries, USA). The instrumental operating parameters are given in Table II.

The isotopes used for analysis of the REEs by ICP-MS are listed in Table III.

Reagents

All reagents used were of AnalR® grade (Sigma Aldrich, Germany).

- (a) Lithium metaborate
- (b) Lithium tetraborate
- (c) Concentrated nitric acid: 4% Nitric acid was prepared by appropriate dilution of concentrated distilled nitric acid.
- (d) 500 ppb indium solution: 100 ppm indium solution was prepared by digestion of 0.0302 g indium oxide (278 g/mol) with 1:1 nitric acid, made up to 250-mL volume, and maintaining 4% HNO₃ concentration. This solution can be used as stock solution. 500 ppb indium solution was prepared by appropriate dilution of 100 ppm stock solution.

High purity Milli-Q® water (18 mΩ-cm) was used in all of the sample preparation procedures. All glassware and digestion vessels were acid-washed and rinsed with Milli-Q water.

Standard Reference Materials

Two standard reference samples, MESS-1 and MESS-2 Marine Sediments (National Research Council, Canada) and one NIST1646a Estuarine Sediment (National Institute of Standards and Technology, USA) were chosen for this study.

Sample Digestion

ICP-MS

In the sample dissolution procedure, accurately weighed 0.1 g marine sediment sample, 0.2 g lithium metaborate, and 0.15 g lithium tetraborate were taken in a platinum crucible, mixed well, and fused in a muffle furnace at a temperature of 1050 °C. The temperature was maintained for 15 minutes. The furnace was allowed to cool to 200 °C, the Pt-crucible was taken out and placed in a 100-mL beaker. A magnetic needle and 25 mL of 8% nitric acid were added into the Pt-crucible and the beaker containing

Table I
ICP-MS Instrumental and Data Acquisition Parameters

Instrumental Parameters			
RF Power	1125.00 W	Plasma Gas Flow	15.00 L/min
Nebulizer Gas Flow	0.85 L/min	Lens	Auto Lens
Auxillary Gas Flow	1.20 L/min	Sample Uptake Rate	1.0 mL/min
Data Acquisition Parameters			
Measuring Mode	Peak Hopping	Integration Time	2500 ms
Points per Peak	1	Replicates	3
Number of Sweeps	20	Internal Standard	¹¹⁵ In
Dwell Time	50 ms		

Table II
NAA Instrumental Operating Parameters

Efficiency	20%	Resolution	2.0 KeV
Applied Electric Field	3500 Volts	Irradiation Time	7 hrs

TABLE III
Isotopes for ICP-MS Analysis

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Isotope	139	140	141	143	147	151	158	159	163	165	167	169	172	175

the Pt-crucible was placed in a magnetic stirrer. The magnetic stirrer was switched on for 30 minutes, and the needle rotated at 700 revolutions per minute. The fused mass of the Pt-crucible was dissolved and the solution transferred to a 250-mL volumetric flask. The volume was made up to the mark with high purity Milli-Q water, distilled nitric acid, and 10 mL of 250 ppb indium solution (as an internal standard). The mixture was thoroughly shaken and kept standing overnight. The final solution contained 2% acid and 0.18% salt, maintaining total dissolved solids at less than 0.2%, suitable for aspiration. This solution was stored in 100-mL high density polythene bottles for ICP-MS measurement.

NAA

The marine sediment samples and SRMs (0.1000 g) were accurately weighed and taken in a polythene bag, which was then sealed. All of the polythene bags containing samples and SRMs were then wrapped together in aluminum foil, making a small strip of 2 cm wide and 4 cm long. These samples were irradiated simultaneously in an Apsara Reactor for 7 hours. After irradiation, the samples were cooled and taken out of the reactor chamber for measurement of γ -radiation using the HpGe-detector system.

RESULTS AND DISCUSSION

Sea sediment samples usually contain zircon which is a highly resistant material for acid decomposition. Alkali fusion, employing lithium metaborate and lithium tetraborate mixtures, ensures complete digestion of the samples. Although alkali fusion increased the salt concentration in the solution, it is still below the permissible limit of the ICP-MS measurement. Any instrumental drift was corrected for by using 10 ppb indium as an internal standard.

The analytical data of three reference samples, MESS-1, MESS-2, and NIST1646a, including 10 marine sediment samples (5 each from the Bay of Bengal and the Car Nicobar Island) are presented using ICP-MS and NAA techniques. Out of three SRMs, only one sample, MESS-1, has certified values for REEs. Hence, a comparison of the ICP-MS data has been made using the NAA technique. However, the comparison of the data is restricted to only eight REEs due to the inherent limitations of the NAA technique.

SRM Data

The data from the SRMs is presented in Table IV. For MESS-1, the ICP-MS data are in very good agreement with the certified values. However, the La value by NAA is slightly higher compared to the certified value. The ICP-MS data obtained for MESS-2 and NIST 1646a agree well with the NAA data, except La. NIST 1646a has certified values for La, Ce, and Nd, which show good agreement with the ICP-MS data. This study provides comprehensive REE data for the two SRMs, and these data may be taken as recommended values. The values are the mean of 5 determinations. The precision achieved is <5% RSD.

Sea Sediment Samples

The samples were collected from the Ganga Prodelta area of the Bay of Bengal and the Car Nicobar Island during the study cruises ST-189 and SM-195. Longitude and latitude of cruise ST-189 is between 88°15' E to 88°35' E and 20°47' N to 21° N, respectively. The depth varies from 20 to 90 m. Location of cruise ST-195 is longitude in between 92°18' E to 93°02' E and latitude from 9°15' N to 9°07' N. The data for the samples obtained from the Bay of Bengal are presented in Table V and those for the Car Nicobar Island in Table VI.

From these data it is observed that except for La, all other available values by the NAA technique compare favorably with the ICP-MS values. The La values obtained by the NAA technique are always in the higher side in most of the samples. We could not explain the trend by the NAA technique. However, the ICP-MS value is more accurate than the NAA value considering that the ICP-MS data agree well with the SRM data.

In the Bay of Bengal, the REE pattern for three samples, 1, 2 & 3, is distinctively different from 4 & 5 (Table V). In case of the former, the total REE is about 150 ppm, whereas in case of the latter it is about 70 ppm. In case of the Car Nicobar samples, the total REE content for the five samples is about 80 ppm. The comparison of our data with those of the oceanic crustal value shows that the total REE value for all samples, except the samples 1, 2, and 3 from the Bay of Bengal, are in the range of the crustal value. For comparison, the data from the other sea samples are also given in Table VII (18,19). It was further observed that the abundance of La and Nd was about 60% and 50%, respectively, in comparison to Ce. The variations of the concentrations of Er and Yb and Tm and Lu are similar to each other. This is the common trend for the majority of the soil and sediment samples.

The % variation between the ICP-MS and NAA results are as follows: lanthanum 1.5–11%, cerium 1–5%, neodymium 2–13%, samarium 1–5%, europium 2–8%, terbium 5–17%, ytterbium 12–22%, and lutetium 5–15%.

TABLE IV
Standard Reference Materials (in ppm)

Ele- ments	MESS-1			MESS-2			NIST 1646a		
	Observed Value		Certified Value	Observed Value		Certified Value	Observed Value		Certified Value
	ICP-MS	NAA		ICP-MS	NAA		ICP-MS	NAA	
La	37.20	42.06	36.80	40.04	45.00	N.A.	19.70	26.05	(17)
Ce	75.15	74.21	75.90	67.33	67.00	N.A.	34.40	35.10	(34)
Pr	8.68	N.D.	8.74	8.40	N.D.	N.A.	4.30	N.D.	N.A.
Nd	36.25	37.15	36.00	32.76	38.00	N.A.	16.57	14.85	(15)
Sm	6.78	6.45	6.90	5.62	5.40	N.A.	2.90	2.80	N.A.
Eu	1.27	1.21	1.31	1.56	1.30	N.A.	0.81	0.64	N.A.
Gd	5.61	N.D.	5.45	5.21	N.D.	N.A.	2.76	N.D.	N.A.
Tb	1.08	0.85	0.99	0.73	0.60	N.A.	0.40	0.53	N.A.
Dy	4.37	N.D.	4.43	4.18	N.D.	N.A.	2.44	N.D.	N.A.
Ho	1.02	N.D.	0.91	0.85	N.D.	N.A.	0.50	N.D.	N.A.
Er	2.41	N.D.	2.52	2.57	N.D.	N.A.	1.51	N.D.	N.A.
Tm	0.47	N.D.	0.45	0.43	N.D.	N.A.	0.24	N.D.	N.A.
Yb	2.48	2.83	2.42	2.55	3.20	N.A.	1.50	1.60	N.A.
Lu	0.36	0.30	0.37	0.43	0.47	N.A.	0.27	0.25	N.A.

N.D. - Not detected.

N.A. - Not available.

TABLE V
Samples From Bay of Bengal (in ppm)

Sample ID	MS-2		MS-5		MS-8		MS-12		MS-16	
	ICP-MS	NAA	ICP-MS	NAA	ICP-MS	NAA	ICP-MS	NAA	ICP-MS	NAA
La	40.95	42.00	40.07	41.70	42.64	43.50	16.24	16.00	14.87	14.00
Ce	70.16	72.10	68.07	70.20	67.96	70.00	27.23	26.00	24.09	23.00
Pr	8.61	N.D.	8.36	N.D.	8.36	N.D.	3.62	N.D.	3.27	N.D.
Nd	34.05	36.00	33.53	35.00	33.29	34.00	11.43	11.00	10.97	10.40
Sm	5.86	5.60	5.92	6.20	5.63	5.60	2.63	2.70	2.29	2.10
Eu	1.64	1.68	1.67	1.70	1.38	1.30	0.75	0.69	0.57	0.49
Gd	5.76	N.D.	5.57	N.D.	5.67	N.D.	2.60	N.D.	2.25	N.D.
Tb	0.83	0.82	0.82	0.86	0.84	0.83	0.41	0.47	0.37	0.39
Dy	4.91	N.D.	4.81	N.D.	4.86	N.D.	2.62	N.D.	2.26	N.D.
Ho	1.00	N.D.	0.97	N.D.	0.99	N.D.	0.55	N.D.	0.47	N.D.
Er	2.91	N.D.	2.82	N.D.	2.93	N.D.	1.66	N.D.	1.42	N.D.
Tm	0.47	N.D.	0.46	N.D.	0.47	N.D.	0.27	N.D.	0.23	N.D.
Yb	2.99	3.10	2.98	3.20	2.96	3.10	1.57	1.68	1.40	1.50
Lu	0.50	0.60	0.54	0.60	0.45	0.44	0.26	0.20	0.23	0.23

N.D. - Not detected.

TABLE VI
Samples From Car Nicobar Island (in ppm)

Sample ID	MS-22		MS-34		MS-50		MS-65		MS-71	
Elements	ICP-MS	NAA	ICP-MS	NAA	ICP-MS	NAA	ICP-MS	NAA	ICP-MS	NAA
La	19.45	20.00	16.79	18.00	14.00	15.00	19.09	20.00	14.99	16.00
Ce	32.05	30.00	26.10	27.00	20.07	21.00	30.57	31.00	25.18	25.00
Pr	4.29	N.D.	3.32	N.D.	2.68	N.D.	3.98	N.D.	3.33	N.D.
Nd	13.93	13.00	12.62	12.00	10.32	9.80	15.09	14.00	12.70	11.00
Sm	2.97	3.03	2.30	2.50	2.06	2.20	2.73	2.70	2.34	2.40
Eu	0.85	0.89	0.65	0.77	0.54	0.65	0.79	0.85	0.68	0.54
Gd	2.85	N.D.	2.17	N.D.	1.86	N.D.	2.77	N.D.	2.32	N.D.
Tb	0.46	0.56	0.36	0.41	0.30	0.39	0.43	0.49	0.39	0.47
Dy	2.73	N.D.	2.20	N.D.	1.83	N.D.	2.52	N.D.	2.38	N.D.
Ho	0.58	N.D.	0.46	N.D.	0.54	N.D.	0.52	N.D.	0.49	N.D.
Er	1.72	N.D.	1.39	N.D.	1.12	N.D.	1.57	N.D.	1.48	N.D.
Tm	0.28	N.D.	0.23	N.D.	0.17	N.D.	0.25	N.D.	0.24	N.D.
Yb	1.87	2.00	1.53	1.60	1.24	1.30	1.66	1.80	1.40	1.80
Lu	0.28	0.32	0.23	0.24	0.20	0.22	0.25	0.23	0.24	0.25

N.D. – Not detected.

TABLE VII
Comparison of REEs With Other Areas (South China, Oceanic Crust, Redang Island, Malaysia)

Elements	South China Sea	Oceanic Crust	Redang Island, Malaysia	Car Nicobar Island*
La	165.80	16.00	16.34	16.86
Ce	917.00	28.00	24.48	26.79
Pr	41.00	4.70	4.30	3.52
Nd	132.60	21.00	12.85	12.93
Sm	44.00	5.30	4.20	2.48
Eu	12.76	1.40	3.39	0.70
Gd	48.00	5.90	2.47	2.40
Tb	9.74	0.90	0.65	0.39
Dy	53.00	4.90	1.54	2.33
Ho	7.30	-	0.59	0.58
Er	22.12	3.10	1.04	1.46
Tm	5.44	-	0.42	0.23
Yb	19.60	2.70	1.20	1.54
Lu	4.98	-	0.66	0.24

All concentrations are in ppm.

* Average of this study.

Fig. 1. CI-chondrite normalized REE determined by this study of the samples collected from the Bay of Bengal.

Fig. 2. CI-chondrite normalized REE determined by this study of the samples collected from Car Nicobar Island.

The REE pattern in our samples (ICP-MS analysis) normalized to the concentration of chondrite is shown in Figures 1 and 2. Normalization shows that fractionation has taken place which was characterized by a significant enrichment of light REEs (La to Sm) over heavy REEs (Gd to Lu). The chondrite normalized REE pattern of marine sediments collected in this study area was similar with the results obtained by Khadijah Sarace et al. (18) from the East Coast of the Peninsular Malaysia region and by Sultan and Shazili (19) from the Terengganu river basin, Malaysia.

CONCLUSION

A simple method for the determination of rare earth elements in marine sediment samples using inductively coupled plasma mass spectrometry with $\text{LiBO}_2\text{-Li}_2\text{B}_4\text{O}_7$ fusion sample preparation at ppm and sub-ppm level has been developed. The ICP-MS data were verified by comparing the results with the SRM values and NAA. The REE data by ICP-MS agree well with those of the SRM as well as by the

NAA technique, except for La. This paper also reports REE data for the first time for two SRMs, MESS-2, and NIST 1646a. Sea sediment data are also compared with crustal sea sediment and also with samples from other marine areas. Rare earth data obtained from the Car Nicobar Island are very close to those of the oceanic crust and the Redang Island, Malaysia.

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