# Application of $k_0$ -based INAA Method in the Studies of Rare Earth and Other Elements in Manganese Nodules from Indian Ocean

# R. K. Dutta,<sup>a,b</sup> R. Acharya,<sup>b</sup> A. G. C. Nair,<sup>b</sup> S. N. Chintalapudi,<sup>c</sup> V. Chakravortty,<sup>a</sup> A. V. R. Reddy,<sup>\*,b</sup> and S. B. Manohar<sup>b</sup>

<sup>a</sup>Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751004, India <sup>b</sup>Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India <sup>c</sup>IUC for DAE facilities, Calcutta Centre, III/LB-8, Bidhan Nagar, Calcutta 700 091, India

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Five manganese nodules obtained from different locations with varying water depths of the Indian Ocean were analysed by  $k_0$ -based instrumental neutron activation analysis ( $k_0$ -INAA) method. A total of 22 elements were estimated including nine rare earth elements (REE). The accuracy of the method has been evaluated by analysing USGS manganese nodule reference material NOD P1. The nodules have been classified into hydrogenous and diagenetic on the basis of their Mn/Fe ratios. Data on elemental concentrations were used to explain the possible differences in the trace element distribution. The minor elements were found to be enriched in the hydrogenous nodules compared to the diagenetic one. An attempt was made to characterise the distribution of these minor elements in the light of known geochemical evidences of Pacific Ocean nodules. The dissimilarity of the geochemistry of Ce and Mn in the Indian Ocean nodules has been discussed. The manganese nodules under investigation exhibit a positive cerium anomaly, indicating an oxidising environment. The possible mechanism of incorporation of elements like REE into the iron oxyhydroxide phase has been discussed.

#### 1. Introduction

Manganese nodules are small, dark, potato-shaped mixtures containing sources of useful metals such as Mn, Fe, Cu, Ni, Co, and Zn, making them a potential ore of these valuable elements. These nodules are built of onion like layers of manganese and iron oxides. The mineral content varies from place to place and the nodules in some areas contain about 30% manganese, 15% iron, 1.25% nickel, 1% copper, and 0.25% cobalt, much higher concentrations than are usually found in the land ores. The chemical composition of manganese nodules are reported to vary from ocean to ocean.<sup>1-3</sup> The variation in the chemical composition of these nodules might be due to mineralogical effects<sup>4, 5</sup> as well as different metal sources.<sup>6</sup> The nodules were discovered by the Challenger expedition (1873-76) and since 1950s, mining of manganese nodules has been the subject of study and experimentation. Although the nodules grow at an estimated rate of 0.1 mm/1000 years, they are already present in vast quantities. They are found in the areas of slow sedimentation, usually five millimetres per thousand years or less. The North and South Pacific Oceans hold the greatest concentration of manganese nodules; in some places 90% of the surface of the Ocean floor is covered by nodules. Similar high coverage of ocean floor is also found in the southernmost South Atlantic. The Indian Ocean floor is largely devoid of manganese nodules. Because seawater is supersaturated in manganese, the direct precipitation of the element onto an available surface is the most likely mode of nodule formation.

The characterisation of manganese nodules may provide important information on physical, chemical, and biological activities taking place in the Ocean as a whole. The knowledge on the elemental concentration levels is relevant in understanding the inter-elemental relationship and the distribution of the elements in the manganese and/or iron oxyhydroxide phases.<sup>7</sup> This helps in differentiating the deposits into hydrogenous or diagenetic types. The diagenetic nodules occur at the sediment-sea water interface, at a depth of about 5000 m and are formed by the upward supply of the elements from the underlying sediment column. These types of nodules are mostly formed on siliceous zones and their Mn/Fe ratios are high (> 2.5). On the contrary, the hydrogenous types are the ones where the metal constituents are obtained by direct precipitation from the seawater in favourable oceanic condition. The Mn/Fe ratios of these deposits are low (1-1.5). Such deposits are mostly formed on red clays where  $\delta$ -MnO<sub>2</sub> is the major phase.

The rare earth elements (REE), La to Lu, are widely utilized as tracers for a range of geological processes because of their strikingly similar electronic configurations that give rise to subtle, predictable chemical behaviour along the series. Studies have revealed that REE patterns in sedimentary systems are both influenced by depositional environment and diagenetic processes.8 The shale normalised REE pattern are useful for understanding the geochemical aspects of the formation of manganese nodules and the prevailing local oceanic physicochemical environment. Investigations on the REE behaviour and particularly cerium anomaly give an idea about the redox condition at the depositional environment.9 Extensive studies on the REE content of ferromanganese nodules of Pacific Ocean have been carried out for understanding their accretionary processes.9-12 Similar studies are available on the Atlantic Ocean nodules.<sup>13, 14</sup> A few reports are available on the characterization of the elements namely, Sc, Sb, W, Hf, and Th in the Pacific Ocean nodules.9, 15 Studies on REE of Indian Ocean manganese nodules are rare and are mostly concentrated on the nodules of the Central Indian Basin.<sup>16-19</sup> To the best of our knowledge, such detail studies including characterization of elements like that in Pacific Ocean nodules have not been carried out on the Indian Ocean nodules.

The success of such studies and interpretation of the data solely depend on accurate and precise analysis of concerned samples by a good, matured, and reference analytical technique. One such technique is the instrumental neutron activation

<sup>\*</sup>Corresponding author. E-mail: avreddy@magnum.barc.ernet.in. FAX: +91-22-2550 5151.

analysis (INAA). It has been extensively used for non-destructive multielement determination in various fields like geology, environmental science, and biology. The INAA method is capable to determine major, minor, and trace elements simultaneously. This is one of the best methods for analyzing REE as well as other elements like Sc, Sb, Cs, W, Hf, and Th due to their favourable nuclear properties.<sup>20</sup> The method of INAA does not require special sample preparation and chemical pretreatment, and experiences negligible matrix interferences due to high penetration power of neutron, activating source, and yrays, the measured radiation. The advent of high-resolution gamma ray spectrometer with multichannel analyzer (MCA) using high efficiency HPGe detector has increased the potential of this technique. The use of the single comparator method of INAA, generally known as  $k_0$ -INAA method<sup>21</sup> is versatile for multielement analysis and is easy to adopt. The most important advantage of this method over relative method is that it uses a single comparator instead of multielement standards. The  $k_0$ technique has been evolved over the years by De Corte et al.<sup>21, 22</sup> to achieve better precision and accuracy of the results. It provides an opportunity to determine all elements that are amenable to INAA. The  $k_0$ -INAA method was adapted at Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India and in use since 1995 for the analysis of varieties of samples including manganese encrustations.<sup>23</sup> As a part of standardization of this method in our laboratory, the  $k_0$ -factors for prominent gamma lines of 38 nuclides with respect to gold single comparator were experimentally determined using elemental standards. A good agreement between the determined and the literature  $k_{0,Au}$ -factors was observed.<sup>24</sup> The developed method of  $k_0$ -INAA was validated using several certified reference materials.24 Kunzendorf and Gwozdz estimated W, Th, and U contents in the US Geological Survey (USGS) nodule standards NOD A1 and NOD P1 for the first time by INAA method.<sup>25</sup>

In this paper, we report the results of elemental concentrations of five manganese nodule samples of Indian Ocean by  $k_0$ -INAA method. Gold was used as the single comparator. Data on elemental concentrations were used to understand the possible differences in the trace element distribution. An attempt has been made to characterize the Indian Ocean nodules by correlating the distributions of Sc, Sb, W, Hf, Th, and REE, especially the Ce anomaly in the light of known geochemical evidences of those of the Pacific Ocean nodules. The USGS manganese nodule reference material NOD P1 was used as a control for evaluating the accuracy of the method.

#### 2. Experimental

**Sample Description.** The samples, which were obtained from National Institute of Oceanography, Goa, India, were collected from different locations in the Indian Ocean during cruises of the Scandi Surveyor and the 35th Sagar Kanya. The geographical locations and water depths of these manganese nodules are given in Table 1.

**TABLE 1: Sample Locations and Descriptions** 

Sample Code	Latitude (S)	Longitude (E)	Water Depth (m)
N1	9.88°	64.25°	4120
N2	11.05°	63.63°	3600
N3	14.5°	75.73°	5175
N4	14.56°	75.5°	5200
N5	NA	NA	>5000

NA - not available

Note: Geographical location is not available for the nodule N5, which is originated from Central Indian Basin.

**Irradiations.** The samples were powdered separately in an agate mortar and were heated in an air oven at 105 °C for about 24 h and cooled for 8 h before sample preparation. Samples weighing in the mass range of 75–100 mg were sealed in a polypropylene tubes (2 mm i.d.). The sealed tubes containing the samples together with the accurately weighed gold standard (5  $\mu$ g), prepared from a standard gold solution, were doubly sealed in polythene. The manganese nodule control sample (NOD P1) was also sealed in the similar way to that of samples. Samples and standards were irradiated at the E8 position of APSARA reactor at BARC, Trombay, Mumbai. The neutron flux at E8 position of APSARA reactor is ~ 10<sup>12</sup> cm<sup>-2</sup>s<sup>-1</sup>. The duration of irradiation was varied between 5 min to 7 h depending on the half-life of the radionuclide of interest.

Radioactive assay. After an appropriate cooling period, the samples were mounted on standard Perspex plates and assayed for gamma activity using a 16% HPGe detector coupled to a PC based 4K channel analyser in an efficiency calibrated position with reproducible sample-to-detector geometry. The resolution of the detector was found to be 2.0 keV at 1332 keV. A multi gamma ray standard of <sup>152</sup>Eu source was used for efficiency calibration of the detector. A 5 min irradiation time and a longer cooling period of about 8-10 h were selected for the determination of Mn using <sup>56</sup>Mn (half-life 2.58 h). The irradiation time in most of the cases was 7 h. The elements e.g. Na, K, As, La, Lu, Sb, Sm, W, Yb, and Ho were determined with an experimental condition of 7 h irradiation time and 3-7 days of cooling, while Ce, Nd, Co, Eu, Fe, Hf, Sc, and Tb were determined after 12 days of cooling. Half-life of the activation product of Mn, <sup>56</sup>Mn is 2.58 h and the measurements were made after allowing it to decay. On the other hand the activation product of Fe, 59Fe has a half-life of 44.5 days and therefore did not contribute to dead time for the radioactive measurement and also its y-rays did not interfere in the spectrum. Therefore, it was not difficult for measurement of other nuclides/elements in the presence of high amounts of Mn and Fe. The sample to detector distance was maintained between 8 and 15 cm depending upon the level of radioactivity in the sample to avoid any coincidence effects. Peak areas under the full energy peaks were evaluated via peak fit software PHAST, developed at our institute.<sup>26</sup> The software has features for energy calibration and determination of peak shape parameters. A second order polynomial in energy was used to calibrate the full width at half maximum (FWHM) of the individual peaks and is used for deconvolution of multiple peaks in the gamma ray spectrum.

**Calculations.** The concentration of an element,  $C_i$ , was calculated using the following formula of  $k_0$ -INAA method.<sup>21,24</sup>

$$C_{i}(\mu g \cdot g^{-1}) = \frac{\frac{N_{p}/LT}{SDCW}}{\left(\frac{N_{p}/LT}{SDCw}\right)^{*}} \cdot \frac{1}{k_{0}} \cdot \frac{f + Q_{0}(\alpha)^{*}}{f + Q_{0}(\alpha)} \cdot \frac{\varepsilon^{*}}{\varepsilon}$$

where  $N_p$  is the net counts, *S* is the saturation factor  $(1-e^{-\lambda t_i})$ , *D* is the correction factor for decay during cooling  $(e^{-\lambda t_d})$ , *C* is the correction factor for decay during counting  $((1-e^{-\lambda LT})/\lambda LT)$ ,  $t_i$ is the duration of irradiation,  $t_d$  is the cooling time, LT is the live-time of counting, *W* is the mass of the sample, *w* is the mass of the comparator,  $k_0$  is the literature recommended  $k_0$ -factor,<sup>22</sup> and  $Q_0(\alpha)$  is the ratio of cross sections and is equal to  $I_0(\alpha)/\sigma_0$ , where  $I_0(\alpha)$  is the infinitely dilute resonance integral corrected for the non-ideal epithermal neutron flux distribution. The symbol "\*" refers to the corresponding parameters of the comparator. The determined values of *f* and  $\alpha$  for the E8 position of APSARA reactor are 52.2 ± 2.7 and -0.016 ± 0.004 respectively.<sup>24</sup> The relevant nuclear data were taken from Reference 22.

### 3. Results and Discussion

The determined concentrations of various elements in the USGS NOD P1 and the nodule samples are presented in Tables 2 and 3, respectively. The measured elemental concentrations in the tables are the mean values from four independent mea-

TABLE 2: Determined Elemental Concentrations (in mg kg<sup>-1</sup> unless % is indicated) of the USGS Manganese Nodule Reference Material, NOD P1 by  $k_0$ -INAA

Element	This work	Certified, (info)	
Na %	$1.7 \pm 0.1$	1.63	
К %	$(9.8 \pm 0.4) \times 10^{-1}$	1.0	
Mn %	$29.3 \pm 0.1$	29.1	
Fe %	$5.8 \pm 0.1$	5.82	
Sc	$(49.6 \pm 0.3) \times 10^{-1}$	NA	
Co	$(2.26 \pm 0.05) \times 10^3$	2240	
As	$37.9 \pm 1.8$	NA	
Sb	$38.3 \pm 1.6$	NA	
Cs	$(2.14 \pm 0.06) \times 10^3$	NA	
Hf	$1.4 \pm 0.1$	NA	
W	$31.7 \pm 2.1$	NA	
Th	$27.1 \pm 1.7$	NA	
La	$(1.03 \pm 0.04) \times 10^2$	(104)	
Ce	279 ± 19	(290)	
Nd	$(1.26 \pm 0.06) \times 10^2$	(120)	
Sm	$27.9 \pm 1.2$	(30)	
Eu	$7.2 \pm 0.4$	(7.5)	
Tb	$1.4 \pm 0.1$	NA	
Но	$(12.3 \pm 0.8) \times 10^{-1}$	NA	
Yb	$12.3 \pm 0.4$	(13)	
Lu	$2.0 \pm 0.1$	(1.8)	

surements of samples with their standard deviations  $(\pm 1\sigma)$ . The determined values of the elemental concentration in the reference material (Table 2) are in good agreement with those of the certified values,<sup>27</sup> which reflects the accuracy of the method for analysing manganese nodules. In addition to the elements certified in the USGS Reference material NOD P1 other minor elements e.g. Sc, As, Sb, Cs, Tb, Ho, Hf, W, and Th, which are not available in the certificate, have been estimated.

The Mn/Fe ratio, frequently used as an indicator for hydrogenous or diagenetic nodules.<sup>7, 28</sup> were found to be in the range of 0.9-1.5 for nodules N1-N4 and may thus be considered to be hydrogenous nodules. The higher Mn/Fe ratio for the Central Indian Basin nodule N5 (3.1) may be due to early diagenetic influence mixed with hydrogenous contribution. From Table 3, it is seen that the classification of the nodules on the basis of their Mn/Fe ratios is well reflected from their minor elemental composition. Most of the minor elements, namely, Sc, Co, As, Sb, Hf, W, Th, and REE are observed to be enriched in the hydrogenous nodules (N1-N4) compared to the diagenetic one (N5). On the other hand, the Na and K contents are mostly unaffected by the variation in the Mn/Fe ratio whereas the Cs content is found to be higher for the nodule whose Mn/Fe ratio is high (3.1). These observations are in good agreement with the corresponding elemental profiles of the Pacific Ocean nodules.9

In general the mechanism of incorporation of elements like REE into iron hydroxide/oxyhydroxide precipitate is governed by co-precipitation. The two principal ways in which the coprecipitation takes place are adsorption and occlusion. Foreign ions are brought down to the surface of the iron hydroxide precipitate by adsorption and also by occlusion within the crystal structure of the precipitate. All precipitates even colloidal, gelatinous and curdy ones show crystalline structure and the surface area plays a major role on the extent of adsorption of ions. Thus elements like REE, Th, Hf, As, Sb, and W that form either hydroxide or oxyanions are easily brought down by iron

NA - not available; (info) - Information value

Elements	N1	N2	N3	N4	N5
Na %	$2.44 \pm 0.12$	$2.56 \pm 0.13$	$1.75 \pm 0.12$	$2.08 \pm 0.14$	$2.32 \pm 0.11$
К %	$0.57 \pm 0.03$	$0.58 \pm 0.04$	$0.40 \pm 0.03$	$0.50 \pm 0.03$	$0.48 \pm 0.03$
Mn %	$15.3 \pm 0.5$	$19.1 \pm 0.7$	$18.6 \pm 0.6$	$16.9 \pm 0.5$	$17.2 \pm 0.4$
Fe %	$16.5 \pm 0.7$	$21.2 \pm 0.8$	$13.9 \pm 0.7$	$11.3 \pm 0.4$	$5.5 \pm 0.3$
Sc	$15.7 \pm 0.3$	$22.9 \pm 0.8$	$13.7 \pm 0.4$	$15.3 \pm 0.8$	$10.9 \pm 0.4$
Co	$3220 \pm 163$	$5362 \pm 214$	$2180 \pm 96$	$2174 \pm 106$	$1128 \pm 49$
As	$76 \pm 8$	$110 \pm 9$	$77 \pm 6$	61 ± 5	$39 \pm 4$
Sb	$18.9 \pm 0.7$	$21.6 \pm 0.8$	$19.5 \pm 0.8$	$17.9 \pm 0.6$	$12.2 \pm 0.6$
Cs	$321 \pm 7$	$379 \pm 16$	$216 \pm 12$	$267 \pm 9$	$718 \pm 24$
Hf	$6.52 \pm 0.37$	$6.61 \pm 0.35$	$8.54 \pm 0.46$	$7.14 \pm 0.49$	$3.40 \pm 0.22$
W	$67.1 \pm 4.3$	$77.8 \pm 6.8$	$49.2 \pm 3.9$	$46.6 \pm 4.5$	$42.5 \pm 4.4$
Th	$42.5 \pm 2.4$	$50.5 \pm 3.3$	$48.5 \pm 2.9$	$47.2 \pm 2.9$	$24.6 \pm 1.4$
La	$142.2 \pm 6.4$	$257.5 \pm 10.2$	$204.8 \pm 7.9$	$184.4 \pm 8.6$	$98.6 \pm 8.2$
Ce	951 ± 34	$1862 \pm 83$	$1246 \pm 48$	948 ± 39	$502 \pm 23$
Nd	$137.4 \pm 7.2$	$196.6 \pm 9.8$	$167.7 \pm 7.6$	$138.4 \pm 9.7$	$88.3 \pm 7.2$
Sm	$28.2 \pm 1.1$	$42.8 \pm 2.1$	$42.1 \pm 2.1$	$34.4 \pm 1.1$	$20.3 \pm 0.9$
Eu	$6.74 \pm 0.56$	$11.14 \pm 0.66$	$8.70 \pm 0.83$	$7.55 \pm 0.72$	$4.76 \pm 0.38$
Tb	$3.24 \pm 0.33$	$4.82 \pm 0.34$	$3.31 \pm 0.37$	$3.09 \pm 0.29$	$2.62 \pm 0.33$
Но	$4.78 \pm 0.64$	$6.89 \pm 0.91$	$6.53 \pm 0.87$	$5.78 \pm 0.64$	$2.97 \pm 0.32$
Yb	$19.32 \pm 0.59$	$32.43 \pm 1.08$	$24.22 \pm 1.03$	$21.41 \pm 0.98$	$9.85 \pm 0.63$
Lu	$3.48 \pm 0.13$	$6.22 \pm 0.24$	$4.62 \pm 0.13$	$3.82 \pm 0.13$	$1.58 \pm 0.11$
Ce*	+0.48	+ 0.54	+0.46	+ 0.39	+ 0.37
Mn/Fe	$0.93 \pm 0.05$	$0.90 \pm 0.05$	$1.3 \pm 0.1$	$1.5 \pm 0.1$	$3.1 \pm 0.2$
(La/Lu)*	0.61	0.62	0.66	0.72	0.94
ΣREE	$1296 \pm 35$	$2420 \pm 84$	$1708 \pm 49$	$1347 \pm 41$	731 ± 25
Ce/La	$6.7 \pm 0.3$	$7.2 \pm 0.5$	$6.1 \pm 0.3$	$5.1 \pm 0.3$	$5.1 \pm 0.3$

 $Ce^* = Magnitude of cerium anomaly, calculated using the relation log [3Ce/(2La+Nd)], as given by Elderfield and greaves.<sup>9</sup> (La/Lu)<sup>*</sup> = (La<sub>sample</sub>/La<sub>NASC</sub>) / (Lu<sub>sample</sub>/Lu<sub>NASC</sub>)$ 

hydroxide precipitate. Adsorption is dependent on the pH of the zero point charge ( $pH_{zpc}$ ) of the sorbing medium. The  $pH_{zpc}$  of ferrihydrite is 8.0 and that for manganese oxides is 2.2.<sup>29</sup> Since the pH of the sea water is ~ 8.0, the anionic species in the sea water environment are thus expected to be adsorbed on positive surface charge of the ferric oxyhydroxide while the cationic species would adsorb on the negative surface charge of the  $\delta$ -MnO<sub>2</sub> phase.

It may be observed from Table 3 that higher Co content was observed for the hydrogenous nodules originating at relatively shallower depth, i.e. on the elevated areas (nodules N1 and N2) compared to the hydrogenous nodules originating at greater water depths (N3 and N4). Such a negative correlation between Co content in nodules and water depth is consistent with the earlier report by Cronan and Tooms.<sup>30</sup> The Na and K contents do not vary appreciably with the variation in their corresponding Mn/Fe ratio and their contribution could be due to sea salt component and terrigenous input as described by Kunzendorf et al.<sup>31</sup> It may be assumed that these mono-valent species are deposited in the nodules as a separate phase and are not taken up by either Fe or Mn oxide phases. However, it could be observed from Table 3 that the Cs content is significantly larger in the Central Indian Basin nodule (N5) compared to the hydrogenous nodules. Caesium, which exists as Cs<sup>+</sup> in the seawater environment may have been adsorbed on the negatively charged surface of  $\delta$ -MnO<sub>2</sub>. The W content is found to be higher in the nodules originated at elevated areas, i.e. nodules N1 (67.1 mg kg<sup>-1</sup>) and N2 (77.8 mg kg<sup>-1</sup>) than in the nodules occurring at greater depth  $(43-49 \text{ mg kg}^{-1})$ . The information on the distribution of W in the Indian Ocean manganese nodules are rare compared to the Pacific Ocean nodules.<sup>9, 31</sup> Tungsten exists as an oxyanionic species (WO<sub>4</sub><sup>2-</sup>) in seawater<sup>32</sup> and are thus adsorbed on the surface of the positvely charged ferric oxyhydroxide phase. Kunzendorf and Glasby suggested that tungsten is not deposited by direct precipitation from seawater rather the oxyanionic species are adsorbed on the charged surface of the sorbing colloids.<sup>31</sup>

The distribution pattern observed for As and Sb, too, are in close resemblance to that of the distribution of W in the Indian Ocean nodules. This is well expected as these elements also form oxyanionic species and are thus sorbed on the ferric oxyhydroxide phase. The Sb concentration in Indian Ocean nodules are found to be less compared to those of equatorial and SW Pacific Ocean nodules.9 It should be mentioned here that the correlation of Sb with Mn as previously reported by Moore et al. in Pacific Ocean nodules<sup>33</sup> could not be observed. It is interesting to note here that the Th concentrations for the hydrogenous nodules (N1-N4) are of nearly similar values in spite of the variation in their Fe and Mn contents. However, the Th concentration in the iron depleted nodule of the Central Indian Basin (N5) is significantly low. This indicates the affinity of Th towards iron oxyhydroxide phase. Thorium hydroxide may have been co-precipitated with ferric oxyhydroxide phase. Our finding gets support from the reports of Shaw and Francois,34 who explained the co-precipitation of Th with Fe and Al hydroxide.

**Rare Earth Elements (REE).** It is evident from Figure 1 that the Fe enriched nodules of Indian Ocean are associated with higher sum of the rare earth elements ( $\Sigma REE$ ) (Table 3), which indicate that the REE are preferentially distributed in the iron oxyhydroxide phase. Significantly large  $\Sigma REE$  contents in the hydrogenous nodules are attributed to slow growth rate of these deposits and thereby favorable for co-precipitation/adsorption from seawater and are preferably carried by the ferric phosphate phase.<sup>35</sup> The depletion of  $\Sigma REE$  in the nodule N5 is thought to reflect the diagenetic influence.<sup>28</sup> The North American Shales Composite (NASC) data, taken from the reference by Henderson,<sup>36</sup> have been used for normalizing the REE contents of nodules, i.e. [REE<sub>sample</sub>/REE<sub>NASC</sub>]. It is evident



Figure 1. Scatter plot showing variation of total REE content with Fe content in hydrogenous nodules of Indian Ocean.



Figure 2. North American Shales Composite (NASC) normalised REE patterns of manganese nodules of Indian Ocean.

from Table 3 that the  $\Sigma REE$  of the nodules vary inversely with the Mn/Fe ratio. Such a phenomenon could be attributed to the adsorption process and is in good agreement with reports by Glasby and Thijssen.<sup>35</sup> The nodules under investigations exhibit a positive cerium anomaly (Figure 2), which is calculated by using the formula, log [3Ce/(2La+Nd)], where, Ce, La, and Nd are NASC normalised values.<sup>10</sup> The positive Ce anomaly indicates the oxidising bottom environment at the depositional sites. In the oxidising condition, Ce<sup>3+</sup> is oxidised to Ce<sup>4+</sup> and are precipitated as Ce(OH)<sub>4</sub>, preferentially on the ferric hydroxide colloidal particles.<sup>9, 18</sup> Further, a negative correlation between Ce/La and Mn/Fe was observed in our studies as evident from Table 3. The highest Ce/La ratio (7.2) is observed for the lowest Mn/Fe ratio (0.90) and our observation is consistent with the earlier observations from Pacific Ocean nodules.9, 12, 37 This indicates the dissimilarity of the geochemistry of Ce and Mn. The fractionation of light REE (LREE) and heavy REE (HREE) has been obtained from the (La/Lu)\* ratio, i.e. [(La<sub>sample</sub>/La<sub>shale</sub>)/(Lu<sub>sample</sub>/Lu<sub>shale</sub>)]. The magnitude of the (La/Lu)\* ratio was found to be less than one (Table 3), which suggests marginal enrichment of HREE over LREE. The enrichment of HREE might be due to small ion size, whereby they can be incorporated more easily into iron oxyhydroxide matrix than the LREE.

#### 4. Conclusions

INAA using  $k_0$ -method has been successfully used to determine many elements in manganese nodules in presence of high amounts of Fe and Mn. The Fe-enriched hydrogenous nodules were associated with higher concentration of minor elements. The Co content was found to vary inversely with the depth of the occurrences of hydrogenous nodules. The nodules under investigations showed a positive Ce anomaly, which indicated an oxidising bottom environment at the depositional sites. The present work describes characterization of elements in Indian Ocean manganese nodules. It has been observed that there are many similarities in the elemental concentration profiles of our samples with the nodules of Pacific Ocean. The similar observations are (i) the REE and minor elements namely Sc, Co, As, Sb, Hf, W, and Th are enriched in hydrogenous nodules, (ii) the REE abundances increase with the increase in the Fe content, and (iii) there is a dissimilarity of the geochemistry of Ce and Mn which is conjectured with a negative correlation between Ce/La and Mn/Fe.

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