

Abundance of trace and rare earth elements (REE) in ferromanganese nodules of the central Indian ocean basin

Ferromanganese nodules of CIOB contains significant concentrations of Mn, Cu, Ni, Zn, Co and rare earth elements (REEs). To decide occurrence and enrichment processes of those metals in nodules, we carried out excessive-resolution mineralogical and geochemical research on Mn-nodules. Nodules display an excessive average abundance of Mn (avg. 25.63%), slight Fe (avg. 8.91%) and low contents of trace elements and REEs compared to moderate content of nodules from different oceanic areas. Some crucial metals of economic interest, notably Co, Cu, Ni, Mo, and Zn are lower in nodules of CIOB than in nodules from different oceans. They are rich in REEs, Fe, Mn, Cu, Co, Mo, Ni, Zn and other useful metals.

Here, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), an experimental technique with characteristics of correct principle, apparent interference, smooth operation, and reliable results have been used for bulk chemical analyses for trace and REEs of various size nodules. Twenty-nine elements viz. V, Cr, Mn, Co, Ni, Zn, Rb, Sr, Nb, Mo, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, Th and U were measured. The concentrations of these twenty-nine elements in nodules are strategic REEs resource and could be used for resource exploration, environmental assessment and will likely catalyze further advanced analysis investigation of seabed resources in CIOB.

Keywords: Central Indian ocean basin, geochemical analysis, ferromanganese nodules, rare earth elements, XRD, ICP-MS

1.0 Introduction

The marine nodules developed in the various ocean basins of the globe and with varying degree of chemical composition and abundance at the seafloor. The nodules are distributed over a bigger area within the

Pacific than in the Indian and Atlantic oceans. The researches associated with the nodules of the Pacific Ocean is extensive, and numerous works were published, which mentioned several essential problems. (Horn et al., 1972; Glasby, 1977; Burns and Burns, 1977).

There were limited researches on the Indian Ocean nodules (Bezrukov and Andrushchenko 1974; Cronan 1977; Siddiquie et al. 1978; Frazer and Wilson 1980; Cronan and Moorby 1981) before 1982 once serious scientific expeditions started frequently and consistently in the Central Indian ocean basin (CIOB). Since then several researches were published, whereby authors confined themselves with biology (Parulekar et al., 1982), reserves (Siddiquie et al., 1984), morphology (Mukhopadhyay 1987), mineralogy (Rao 1987), topography (Pattan, JN & Kodagali 1988), and geochemistry and formation of variously sized CIOB nodules (Valsangkar, AB, Khadge 1989).

The CIOB show slow rates of sediment accumulation as it is about 1600 km far from the southern tip of the Indian peninsula and also the samples underneath study have been received from the latitude 9.5°S to 12°S and longitude 87°E to 89.5°E; water depth varying between 4,900-5,900m (Fig.1) and as a result, the CIOB is taken into consideration beneficial for Fe-Mn nodules mineralization. As potential economic metal resources, the hydrogenetic Fe-Mn deposits are enriched in Co, REEs, Y, Te and Pt at the same time as hydrothermal deposits are enriched in Mo, Zn and Ba, and the diagenetic deposits are enriched in Mn, Cu, Mo and Ni (Hein et al. 2003; Hein et al. 2013; Hein and Koschinsky 2014; Bau et al. 2014). Terrigenous sources could contribute detritus to marine Fe-Mn deposits, significantly within the marginal ocean Fe-Mn deposits, whose characteristics are different from the ones of the alternative open oceans including CIOB. The marginal sea Fe-Mn deposits are characterized by excessive precipitate growth rates approximately tens mm/Myr from the seawater, and that they usually have comparatively low Co, Ni, Cu, and Zn contents and Mn/Fe ratios (Conrad et al. 2017).

The form of the nodules is usually spherical and cauliflower-like. We have studied 29 samples that

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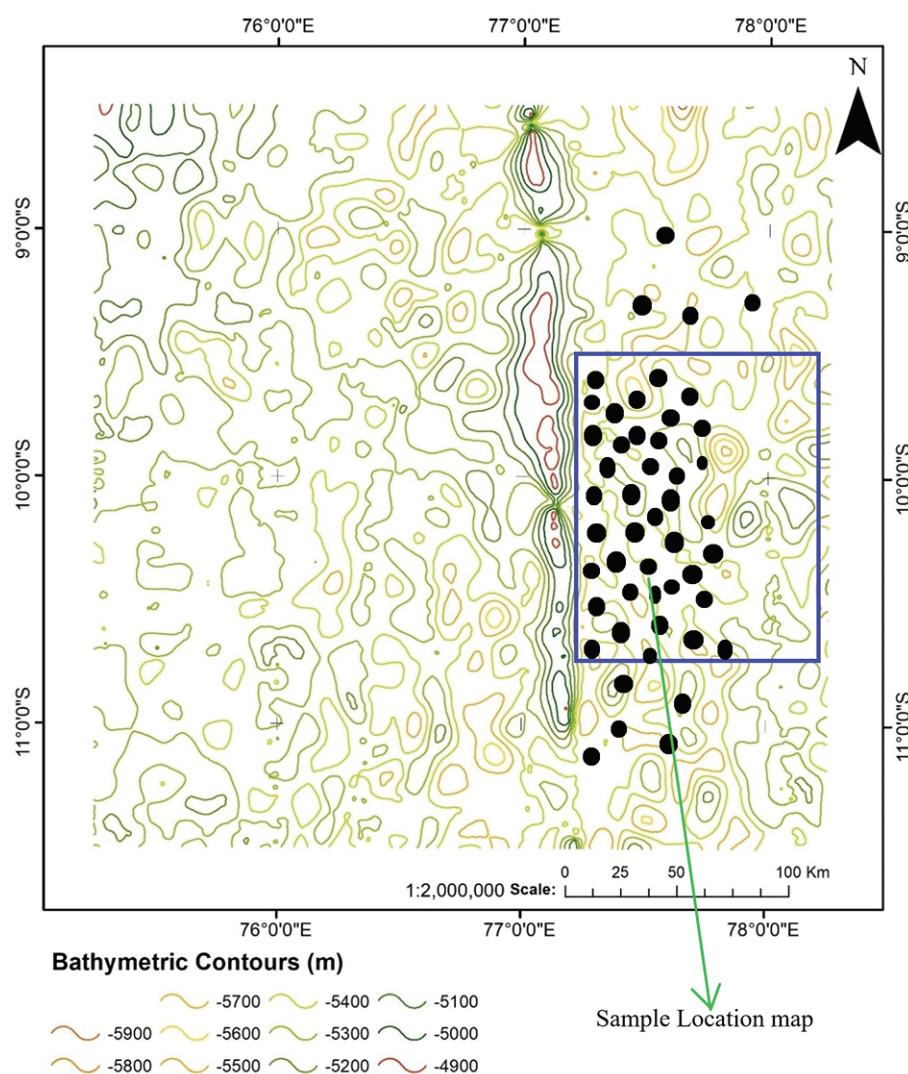


Fig.1: Samples location map (Bathymetry Contour Map)

are categorised into three different size class viz. 09 small size nodules (0 to 3 cm, 8 with rough and 1 with smooth surface), 10 medium size nodules (3 to 6 cm, 8 with smooth and 2 with a rough surface) and 10 large size nodules (+6 cm, 5 with rough and 5 with smooth surface). The primary morphology are [S] = Spheroidal, [E] = Ellipsoidal, [D] = Discoidal, [P] = "Poly" or Coalespheroidal, [B] = Biological (containing tooth, bone, or vertebra), [T] = Faceted (due to angular nucleus or fracturing). The surface textures are: s = smooth (or microgranular), r = rough (or microbotryoidal) b = botryoidal. The examples: 1[D]b = large discoidal nodule with the uniform botryoidal surface; m[D-E]_b^s = medium nodule transitional between Ellipsoidal and Discoidal in shape with a smooth upper surface and botryoidal lower surface and m-1[F]r = medium to massive nodule fragment with a rough surface.

The predominant minerals within the nodules, determined by XRD pattern, are vernadite, todorokite, birnessite, phillipsite, goethite, akaganeite, and the minor minerals within

the nodules embrace montmorillonite, barite, gypsum, a-cristobalite, kaolinite, quartz, feldspar, and others.

In marine mineral analysis and development, geochemical evaluation is one of the key technologies. The polymetallic nodules are among the most important potential deep-sea mineral resources. These deep-sea nodules are formed in completely unique surroundings and are rich in Cu, Co, Ni and REEs in addition to water and salts (Yao et al., 1993; Yao et al., 1996; Wiltshire et al. 2010; Xia et al., 2001). Earlier, the composition of ferromanganese nodules were used to be analyzed through conventional methods, interelemental interferences were severe.

ICP-MS is turning into one of the useful elemental analytical technology since it was invented two decades ago, having excessive sensitivity, low detection limits and modern and simultaneous evaluation of multielement. Within the standard series of U.S. Environmental Protection Administration (EPA), ICP-MS has been indexed as the desired technique of evaluation of inorganic metals in environmental samples. At present, more than 60 elements found in maximum rocks, minerals, soils, sediments, and water are being decided the use of ICP-MS, and its

reliability is established worldwide. Jarvis et al. (1991) systematically added the history, principle, and applications of ICP-MS technology. ICP-MS was successfully applied in the determination of multielement in numerous land-based geological and environmental samples. With the development and current advances in analytical technology, the International Seabed Authority (ISA) has conjointly instructed that the concentrations of micro and trace elements in Fe-Mn nodules would be decided by the use of ICP-MS.

Minerals of deep-sea Fe-Mn nodules are fine, the scale of maximum authigenic ferromanganese oxyhydroxide minerals are much less than 300 Å (Shan and Yao 1993). The mineralogical characteristics confirm that dissolution of Fe-Mn nodules is comparatively easy, and ICP-MS technique will overcome the interelemental interference. Therefore, this technology has an unique predominance over different techniques within the determination of elements in Fe-Mn nodules. In the present study, we have used this analytical

TABLE 1: TRACE AND REE DATA ANALYSED BY ICP-MS
(VALUES IN PPM)

Elements	Small (ppm)	Medium (ppm)	Large (ppm)
51 V	330.5897	329.3378	312.4833
52 Cr	10.0504	50.37876	17.22575
55 Mn	214661.1	185995.4	194807.7
59 Co	1224.243	1247.172	1162.814
60 Ni	9753.826	6389.456	8521.592
66Zn	1064.298	808.1615	925.1541
85 Rb	13.96983	13.67957	14.40114
88 Sr	566.0252	623.7994	563.5099
93 Nb	10.59904	11.68329	12.67091
95 Mo	295.0816	264.6688	286.8595
133 Cs	0.593327	0.597298	0.639837
137 Ba	1108.119	1197.054	1401.958
139 La	98.09463	137.6102	99.32144
140 Ce	462.168	647.4192	497.1779
141 Pr	27.2587	34.93257	27.34803
146 Nd	109.6557	142.0971	110.9054
147 Sm	28.60107	32.63617	25.74193
153 Eu	6.497669	8.221376	6.52056
157 Gd	27.33126	35.71322	26.68173
163 Dy	21.25498	29.07438	21.07813
165 Ho	3.973193	5.653612	3.902705
166 Er	10.48849	15.53923	10.60373
169 Tm	1.556964	2.264289	1.61723
172 Yb	9.881653	15.01184	10.079
175 Lu	1.490469	2.320323	1.549698
178 Hf	2.222095	2.267515	3.077054
208 Pb	615.3371	734.1352	670.6896
232 Th	26.175	27.92025	27.05569
238 U	3.724045	4.135673	3.640038
Total Value	230494.21	198808.35	209574.00
Mean	7948.076	6855.46	7226.69
SD	39797.49	34474.32	36111.69

method for V, Cr, Mn, Co, Ni, Zn, Rb, Sr, Nb, Mo, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, Th and U present in the ferromanganese nodules. The data shown in Table 1 indicates positive and negative correlation matrix between elements.

2.0 Materials and methods

2.1 SAMPLE, REAGENTS

In this study trace and REEs were analysed. Approximately 30 mg powdered of every representative sample was taken to perform Trace and Rare Earth Element analyses. The digestion of the sample was finished in a Teflon tube using a two-step digestion method. In the primary step, an aggregate of hydrofluoric acid and nitric acid ($\text{HF}+\text{HNO}_3$ in 2:1 ratio) along with 1 ml perchloric acid (HClO_4) was added in the sample. The tube was tightly capped and heated to

$\sim 120^\circ\text{C}$ for 7 hr (Q-Block operating system). Afterwards, the lid of the Teflon tube was loosened to permit evaporation of acid fumes and persisted till the acid fumes stopped evaporating from the tube, and the sample dried utterly. In the next step, the same method was repeated with the opposite ratio aggregate of hydrofluoric acid and nitric acid ($\text{HF}+\text{HNO}_3$ in 1:2 ratio) along with 1 ml perchloric acid (HClO_4). Subsequently, the tube was checked for complete digestion of nodules sample by adding 2 ml of 5% HNO_3 and observing the clarity of the solution. If any part was still left, the method was repeated till its complete digestion. After that, 2% HNO_3 solution was used to rinse every tube, and the sample was transferred in a volumetric flask to make the final volume of 50ml. The digested samples and blanks have been analyzed using the Agilent Quadrapole 7700 ICP-MS facility established on the Birbal Sahni Institute of Paleosciences, Lucknow, India for trace element concentrations. All the dataset suggests results within the limit of 5% error (Table 2). The reproducibility of repeated samples turned into the error.

3.0 Results and discussion

3.1 CHARACTERISTICS OF REEs IN POLYMETALLIC NODULES

REEs are strategic substances important for the improvement of high-tech, advance cutting-edge defence technology. They will transform conventional industries, and hence, are believed to be a massive key useful resource in the twenty-first century. On land, rare earth natural resources are declining, however rich deposits of REEs may be found in marine Fe-Mn nodules. They endure massive financial cost in mining. Usually, industrial analysis of land rare-earth minerals takes the shape of measuring oxide content. The current activity of REEs examines a single element that is then transformed into an oxide stage and possibly nearer to industrial grade.

Since the improvement of submarine technology, studies in Fe-Mn nodules has become extra refined. Now, higher techniques of keeping apart the related minerals Fe, Mn, Cu, Co, and Ni from those nodules would undoubtedly increase the human capacity to expand and use REEs. Enhancements in rare earth ore processing and smelting technology have and can still cause quality necessities to decrease; however, this most effective make ocean polymetallic nodules with REEs more attractive.

The REEs are very stable, in surface environments. The REEs sediment composition and their distribution patterns depend on source rock composition. The elements are rarely affected by weathering or erosion, transport, hydrodynamics, sedimentation, diagenesis or metamorphism that may normally be used to trace deposits.

The REEs content is incredibly low in ocean water. The content in surface water is the lowest, and the whole quantity of REEs increase with depth (Dubinin and Shirshov 2004; Elderfield H et al., 1988; Baar et al. 1985; Alibo

TABLE 2: TRACE & REE DATA ANALYZED BY ICP-MS (VALUES IN PPM)TABLE 1: CORRELATION MATRIX OF ELEMENTS ANALYZED BY ICP-MS OF MANGANESE NODULES FROM PARTS OF CENTRAL INDIAN OCEAN BASIN (MINOR, TRACE & REE)

V	Cr	Mn	Co	Ni	Zn	Rb	Sr	Nb	Mo	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb	Lu	Hf	Pb	Th	U	
V	1																												
Cr	0.29	1																											
Mn	0.277	-0.839	1																										
Co	0.947	0.583	-0.0471	1																									
Ni	-0.0911	-0.979	0.932	-0.407	1																								
Zn	0.112	-0.919	0.986	-0.214	0.979	1																							
Rb	-0.89	-0.694	0.191	-0.989	0.535	0.354	1																						
Sr	0.478	0.979	-0.711	0.736	-0.918	-0.819	-0.826	1																					
Nb	-0.883	0.193	-0.696	-0.685	-0.387	-0.565	0.572	-0.00997	1																				
Mo	-0.196	-0.995	0.888	-0.501	0.994	0.953	0.621	-0.955	-0.287	1																			
Cs	-1	-0.275	-0.292	-0.942	0.0761	-0.127	0.883	-0.465	0.89	0.181	1																		
Ba	-0.972	-0.0565	-0.495	-0.844	-0.146	-0.342	0.758	-0.258	0.969	-0.0403	0.975	1																	
La	0.421	0.99	-0.755	0.691	-0.942	-0.855	-0.788	0.998	0.0542	-0.972	-0.407	-0.195	1																
Ce	0.729	1	-0.845	0.573	-0.982	-0.923	-0.686	0.977	0.204	-0.996	-0.265	-0.0452	0.989	1															
Pr	0.436	0.988	-0.744	0.703	-0.936	-0.845	-0.798	0.999	0.0371	-0.968	-0.423	-0.212	1	0.986	1														
Nd	0.415	0.991	-0.759	0.686	-0.944	-0.858	-0.784	0.997	0.0609	-0.974	-0.401	-0.189	1	0.99	1	1													
Sm	0.775	0.829	-0.392	0.937	-0.7	-0.541	-0.978	0.925	-0.388	-0.771	-0.766	-0.605	0.899	0.823	0.907	0.896	1												
Eu	0.435	0.988	-0.745	0.702	-0.936	-0.846	-0.798	0.999	0.0385	-0.968	-0.421	-0.211	1	0.986	1	1	0.906	1											
Gd	0.502	0.973	-0.692	0.754	-0.907	-0.803	-0.841	1	-0.0376	-0.946	-0.489	-0.285	0.996	0.971	0.997	0.995	0.936	0.997	1										
Dy	0.463	0.983	-0.724	0.724	-0.925	-0.829	-0.816	1	0.00755	-0.96	-0.449	-0.241	0.999	0.98	1	0.999	0.919	1	0.999	1									
Ho	0.477	0.979	-0.712	0.735	-0.919	-0.82	-0.825	1	-0.00865	-0.955	-0.464	-0.257	0.998	0.977	0.999	0.998	0.925	0.999	1	1	1								
Er	0.427	0.989	-0.75	0.696	-0.939	-0.851	-0.792	0.998	0.0469	-0.97	-0.414	-0.203	1	0.987	1	1	0.902	1	0.996	0.999	0.998	1							
Tm	0.375	0.996	-0.787	0.654	-0.957	-0.879	-0.756	0.994	0.104	-0.982	-0.361	-0.147	0.999	0.995	0.998	0.999	0.876	0.998	0.99	0.995	0.994	0.998	1						
Yb	0.415	0.991	-0.759	0.686	-0.944	-0.858	-0.784	0.997	0.0608	-0.974	-0.401	-0.189	1	0.99	1	1	0.896	1	0.995	0.999	0.998	1	0.999	1					
Lu	0.387	0.995	-0.779	0.664	-0.953	-0.873	-0.765	0.995	0.0908	-0.98	-0.373	-0.159	0.999	0.993	0.999	1	0.883	0.999	0.992	0.997	0.995	0.999	1	1	1				
Hf	-1	-0.304	-0.263	-0.951	0.106	-0.097	0.897	-0.491	0.876	0.21	1	0.968	-0.434	-0.293	-0.45	-0.428	-0.784	-0.448	-0.515	-0.476	-0.49	-0.441	-0.389	-0.428	-0.401	1			
Pb	-0.0226	0.95	-0.967	0.301	-0.994	-0.996	-0.435	0.867	0.489	-0.976	0.0378	0.257	0.897	0.954	0.89	0.9	0.614	0.89	0.853	0.876	0.868	0.894	0.918	0.9	0.913	0.00792	1		
Th	-0.0672	0.935	-0.977	0.258	-0.987	-0.999	-0.395	0.844	0.528	-0.965	0.0823	0.3	0.877	0.939	0.868	0.88	0.578	0.869	0.829	0.853	0.845	0.873	0.9	0.88	0.894	0.0525	0.999	1	
U	0.582	0.947	-0.62	0.813	-0.863	-0.743	-0.888	0.993	-0.132	-0.912	-0.569	-0.374	0.983	0.943	0.986	0.981	0.965	0.985	0.996	0.99	0.992	0.984	0.972	0.981	0.975	-0.593	0.8	0.773	1

and Acta 1999). Marine sediments collect REEs over time, soaking up them from seawater. In general, the REEs content in ocean sediments is about 468.26×10^{-6} (Xu et al., 2007; Sholkovitz 1988; Sholkovitz 1990; Sholkovitz et al. 1994). This value is much higher than those recorded in Earth's continental crust and sedimentary rocks. This REEs enrichment is specially controlled by the absorption of Fe-Mn oxides and clay minerals in the nodules and therefore the high levels of REEs in seawater and sediments. High cerium enrichment in nodules could result in the more effective exploitation of REEs in future (Zhang et al. 2012).

Grades of few critical metals of economic interest extensively Co, Cu, Ni, Mo, and Zn are slightly lower in the nodules of CIOB than in the nodules from Pacific prime mineralization zones. Concentrations of Mn, Pt, Mo, Co, Te, and Bi, however, show comparatively high concentrations relative to the continental crust (González et al., L 2010).

3.2 MINERALS IN POLYMETALLIC NODULES

Todorokite and delta MnO_2 are the two essential minerals present within the nodules. Generally, nodules rich in manganese have todorokite, and those rich in iron have $\delta\text{-MnO}_2$. The major Mn minerals, namely todorokite, $\delta\text{-MnO}_2$ (vernadite) and quartz occur as a vital mineral (Fig.2). In smaller nodules incidence of phillipsite and feldspars is much less and that of birnessite is rare. The important mineral occurring in the medium size nodules are todorokite, $\delta\text{-MnO}_2$ (vernadite), Feldspar, phillipsite and Quartz (Fig.3). It has been observed that the profile peaks of todorokite decrease from small to large size nodules with few exceptions as seen in the XRD profile of large nodules (Fig.4). These mineral phases are intergrown with the X-ray amorphous Fe oxides/hydroxides, which may also have been crystallized to goethite (Hein and Koschinsky 2014).

Additionally, detrital aluminosilicate minerals which include quartz and minor

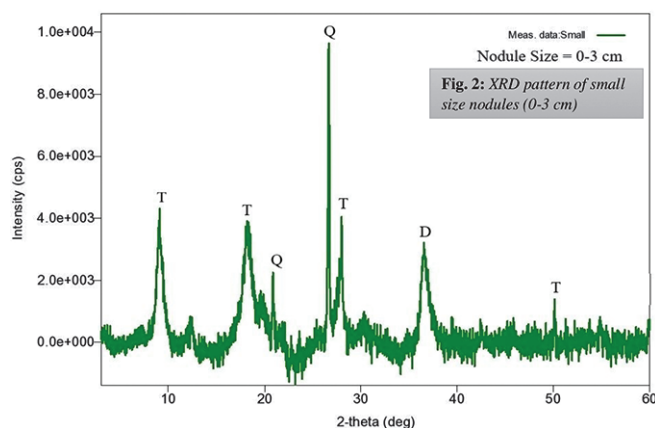


Fig.2: XRD pattern of small size nodules (0-3 cm)

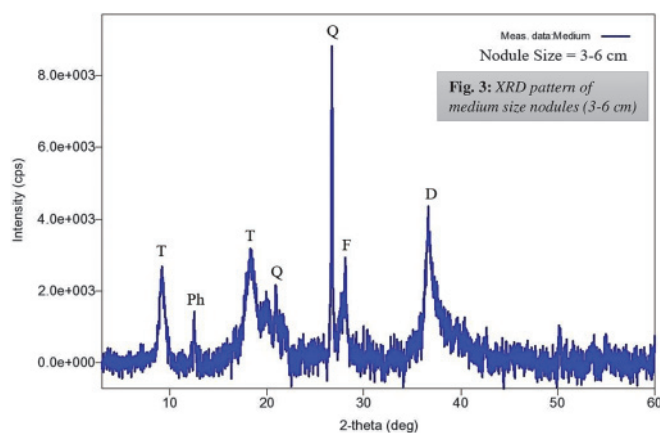


Fig.3: XRD pattern of medium size nodules (3-6 cm)

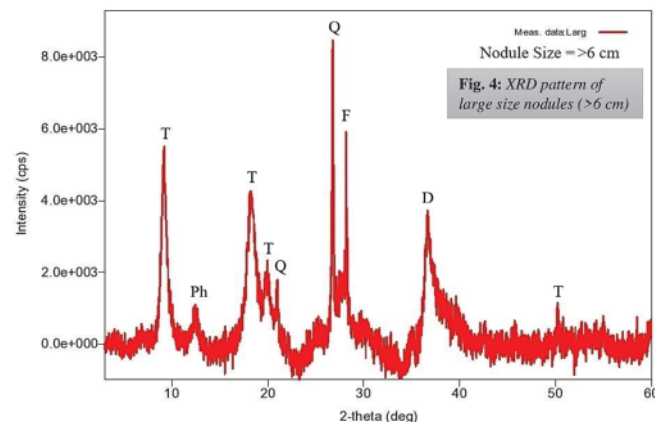


Fig.4: XRD pattern of large size nodules (>6 cm)

feldspars are present within the nodules. Fe-Mn oxides and oxyhydroxides are usually >70 wt% of the nodular mass. Silicates (particularly in detrital layers) and carbonates distributed in the oxide layers and the nuclei represent approximately 30 wt% of the nodular mass.

These parts of nodules (Fe and Mn minerals: todorokite: $[(\text{Na}, \text{Ca}, \text{K}, \text{Ba}, \text{Sr})_{1-x}(\text{Mn}, \text{Mg}, \text{Al})_{6\text{O}_{12}} \cdot 3\text{-}4\text{H}_2\text{O}]$, goethite: FeOOH and a few clay minerals), have larger specific surface

areas and strong adsorption of colloids. They promote the accumulation of REEs within the close medium (Yasuo et al., 2006; Ran and Liu 1992; Liu et al. 2002; Wan and Liu 2004). Besides, organic matter in polymetallic nodules additionally has a positive impact on REEs enrichment (Meng and Fu 2006; Li et al. 2005).

3.3 ORIGIN AND ENRICHMENT OF REES IN POLYMETALLIC NODULES

In nodules from Central Indian ocean basin, Jauhari and Pattan (2000) discovered Fe and Co concentrated close to the nucleus (hydrogenetic in origin), and Mn more concentrated in the exterior layers (early diagenetic). Zero to negative Ce anomaly in the studied nodules shows that they had been formed at a lower redox level in the neighbourhood of the redox boundary and the settlement with a diagenetic growth and later exhumation process. Therefore, the low Ce contents and low Ce anomalies suggest that the CIOB nodules could have formed in much less oxidized environments than those of the Pacific (González et al., 2010).

During the long growth method of nodules, and through the adsorption of REEs from seawater and sediment, the nodules become rich in REEs and their content material may also exceed tens of times that of traditional marine sediments. There are two primary sources of REEs in sediments viz weathered terrigenous material and submarine volcanoes (Zhang et al., 2012; Piper 1974). The enrichment process is also affected by physical, chemical, biological, and different factors (Murray and Margaret 1993; Bruno et al. 1999; Karem et al. 2010; Greta ME, 1987).

The REEs enrichment of Fe-Mn nodules is managed through a complicated structural set up. The enlargement of the 90°E Ridge supported the era of submarine volcanic rock and active hydrothermal regions. The submarine basalt weathering and hydrothermal fluids provide plenty of source material for the expansion of nodules and the minerals therein. The volcanic eruptions and the hydrolysis of submarine rock improve levels of Fe, Mn, Cu, Co, Ni, different metals and REEs in water and sediment, prompting the growth of nodules. The mineralization of polymetallic nodules within the REEs enrichment process. The REEs content in crust is better than that of nodules. This is carefully associated with seabed volcanic activity within the areas wherever crusts occur (Sholkovitz et al. 1999; Zhang et al., 2008; Klinkhammer et al., 1994; Mascarenhas et al., 2010). The REEs content is rich in nodules at sea margins, that is relevant to the adequate supply of terrestrial sediments.

REEs enrichment in marine nodules is a complex process, affected by the type of substance forming, sediments type, oceanic environments, and mineral characteristics (C Yingchun et al., 2009; Ren et al., 2010; Jiang et al. 2011). Manganese oxides and hydroxides in nodule adsorb REEs very well, promoting REEs enrichment. The, Ce enrichment in nodules causes a lack of calcium carbonate, barite, apatite, silica, and different sediments. The idea is that nodules occur

in oxidizing environments. The Ce indicates different geochemistry as compared to other trivalent REEs, and it is easier to precipitate than other REEs. It exists in two valence states: Ce³⁺ and Ce⁴⁺. In strongly oxidizing environments, the Ce⁴⁺ ion with a better valency can be simply and firmly adsorbed through a solid material in seawater, and therefore more easily absorbed through the nodules. It is due to this characteristic, Ce is not only strongly present in nodules; however it is additionally often used to suggest the level of oxidation within the seawater environment.

The oxidation of Fe²⁺ to Fe³⁺ requires lower redox potential than that of Mn²⁺ to Mn³⁺ in seawater (Brian and Moore 1982). Iron is preferentially concentrated inside Fe-Mn precipitates formed in ambient seawater (that is highly more significant oxidized), and Mn at the seafloor wherein the bottom seawater is less oxidized. In marine polymetallic nodules, Fe oxyhydroxides and Mn oxides are epitaxially intergrown to stabilize the latter's structure (Burns and Burns 1977). The overall deep-sea nodules formation is a complicated succession of various steps of material state changes (Halbach et al. 2017). Chemical compositions of those nodules replicate the enrichment of ore elements associated with the Fe and Mn mineral phases (Glasby 2006), which had been formed by hydrogenetic or diagenetic processes under different redox conditions. Meanwhile, the chemical and mineralogical compositions of the nodules may additionally change by post-depositional diagenetic processes, and thus may lead to Mn-rich redistribution or mineralization and textural alteration (Halbach et al. 2017).

The metal enrichment processes within the hydrogenetic components are an inorganic colloidal chemical/interface-chemical mechanism (Stumm 1992). The Mn and Fe oxides in the seawater can form hydrous ions with massive surface electrostatic adsorption capacity, and the surface energy (charged surface) of Mn-Fe oxides/oxyhydroxides have interaction with the hydrous metallic ions (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003; Bau et al. 1996; Bau and Koschinsky 2009; Hein and Koschinsky 2014). The interface effect among Fe-Mn minerals and seawater may also give an explanation for the trace elements enrichments in hydrogenetic processes of nodule formation (Guan et al. 2017). Metals related to δ -MnO₂ (vernadite) consist of Mn, Co, Ni, Zn, REE, W, Mo, Pb, Sr, , Pt, Te and Tl, which may also be carried through the mixed Fe (-Ti) oxyhydroxides (Halbach et al. 2017). The diagenetic processes, however, can lead to the remobilization and recrystallization of primary Fe-Mn minerals. Sediment porewater is the predominant source of Mn²⁺, Ni²⁺, Cu²⁺ and Zn²⁺. The phyllosulfates (todorokite, birnessite and buserite) occurring in polymetallic nodules might cause enrichment of trace elements, such as Ni, Cu, Zn, Ba, Mg, and Li (Nedjatpoor et al., 1985; Usui et al. 1995 Koschinsky and Hein, 2003; Hein and Koschinsky 2014) within the Fe-Mn nodules (excessive Mn enrichment) (Guan et al. 2019).

4.0 Conclusions

In the present study, nodules display an excessive abundance of Mn (avg. 25.63%), slight Fe (avg. 8.91%) and occasional contents of trace elements and REEs in comparison with the common content material of deep-seabed polymetallic nodules from different oceanic areas. Investigation for the deep-sea mineral resource has at least two purposes, one is resources exploration, and therefore the other is advance scientific analysis. For both resources exploration and scientific research, accurate, precise geochemical analysis is one of the key elements of the study. The present study involving the determination of V, Cr, Mn, Co, Ni, Zn, Rb, Sr, Nb, Mo, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, Th and U in deep-sea Fe-Mn nodules proved that membrane desolution ICP-MS is an effective multielement determination methodology in each exploration and research of deep-sea Fe-Mn nodules. This method, primarily based totally on correct principle, with apparent interference, easy operation procedure, and reliable results, each decides the concentrations of elements with potential economic value (Cr, Mn, Co, Ni and Zn) and therefore the elements with important environmental significance (REE, U, Th, Rb, Sr and V), and becomes a powerful geochemical method for measuring micro and trace elements in Fe-Mn nodules. The nodules could thus represent a strategic REEs resource and will possibly catalyze further additional investigation of seabed resources within the CIOB.

5.0 Acknowledgements

We are thankful to the Council of Scientific and Industrial Research (CSIR) for providing fellowship and Head of the Department of Geology, Institute of Science, BHU, Varanasi, India for providing necessary facilities for conducting the research. We thank Central Instrumental Facilities (CIF) IIT-BHU, Varanasi for supporting in analyzing the samples using XRD; and Birbal Sahni Institute of Palaeosciences (BSIP), Lucknow for analyzing the samples using ICP-MS.

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