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Ferromanganese Oxides from Mid - Indian Ridge, Seamounts & Abyssal Plains from the Indian Ocean

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Mineralogical and chemical investigations show that todorokite is the only Mn mineral in the Mid-Indian Ridge ferromanganese coatings; δMnO_2 in the seamount crusts, and well crystallised todorokite and minor amounts of δMnO_2 in the abyssal nodules. Enrichment of Mn, Cu, Ni and Mn/Fe ratio is in the sequence, abyssal nodules > seamount crusts > Mid-Indian Ridge samples. Fe is highest in the Mid-Indian Ridge samples followed by seamount crusts and abyssal nodules. Co is enriched (up to 0.47%) in the seamount crusts. The ferromanganese oxides from the Mid-Indian Ridge, seamount crusts and abyssal nodules appear to be of hydrothermal, hydrogenous and early-diagenetic in origin respectively.

Ferromanganese oxides forming at mid-oceanic ridges, seamounts and abyssal plains differ in their composition and mineralogy[1-3]. They occur as stains, coatings or even as dustings and thin encrustations on mid-oceanic ridges and mostly as encrustations on hard substrates on seamounts. Abyssal nodules on the other hand accrete on soft sediments. Ferromanganese oxides from mid-oceanic ridges have been studied earlier[4-6]. Various aspects of abyssal nodules have been documented extensively[7-12] but seamount crusts received less attention till recently[13,14]. Most of these studies are confined to Pacific and Atlantic Oceans, and limited data on Mn nodules and crusts are available from the Indian Ocean[15-18]. This paper presents data on the mineralogy, composition and origin of ferromanganese coatings from the Mid-Indian Ridge, crusts from seamounts and abyssal nodules from the Indian Ocean.

Materials and Methods

Samples were collected during 16th (July 1985) and 20th cruises of *ORV Sagar Kanya* from the Indian Ocean (Fig. 1). During the surveys for hydrothermal mineralization, geophysical data was collected on the Mid-Indian Ridge and the rift valley was identified from the bathymetric profiles (Fig. 2) and magnetic anomalies (unpubl. data). Dredging was carried out on the flanks of the rift valley and on 2 unnamed seamounts with a relief of 700 and 800 m from the base respectively. Nodules from the abyssal plains were collected with free fall grab samplers. The location and water depth of the samples are given in Table 1. Representative samples were selected, washed with fresh water and air dried. With surgical blade ferromanganese oxide layers were separated and powdered. Mineralogy has been determined with Philips X-ray diffractometer using Ni filter, Cu-Kα radiation and scanned at 2° 2θ min^{-1} from 8° to 70°. Part of the same sample was digested in aqua-regia and chemical analysis for Mn, Fe, Cu, Ni, Co and Zn was made by AAS (PE-5000). International rock standards G-2 and AGV-1 as well as the Indian Ocean nodule standard (NIO-2388) were used. Precision was better than ± 5% for the elements determined.

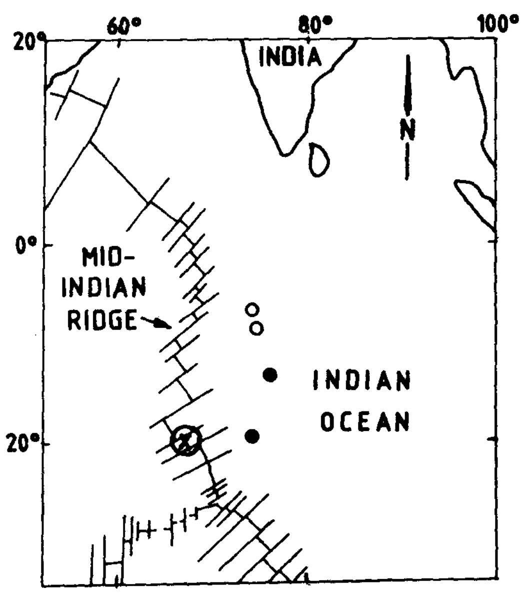

Fig. 1—Map showing the sample locations (⊗ = MIR coatings, ● = seamount crusts, ○ = abyssal nodules)

Table 1—Location and Water Depth of the Samples

Area and sample no.	lat.(S)	long.(E)	Depth (m)
Mid-Indian Ridge			
1681-1685	20°17′	67°39′	3000
Seamount-1			
1711-1714	20°00′	75°00′	4277
Seamount-2			
1731-1735	16°00′	75°57′	4581
Abyssal nodules			
1811, 1812	12°45′	75°50′	5271
1911, 1912	13°45′	75°52′	5256

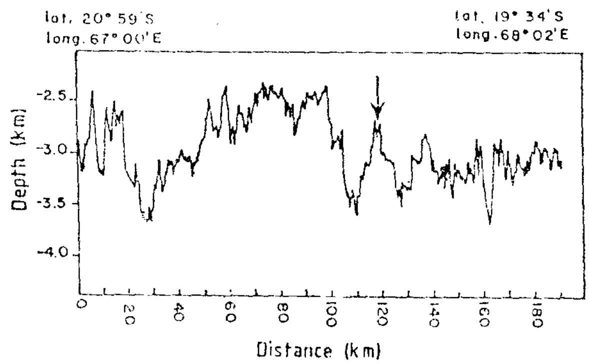

Fig. 2—Bathymetric profile of the Mid-Indian Ridge (arrow points towards the eastern flank of the rift valley and dredge location)

Results and Discussion

Dredge hauls in the rift valley yielded fresh basalts and pillow fragments with (15%) or without (60%) ferromanganese coatings and with (25%) dusting of Mn oxide. The thickness of the coating varies from < 1 to 3 mm. In the curves and pits of the host rock, encrustations reaching thickness of upto 5 mm were observed. The crusts from seamount-1 (SM-1) have 2 to 10 mm thick oxide layer on fresh and partly-altered basalts, mostly smooth, brownish black to black and displaying partly-developed botryoids. Crusts from SM-2 consist of 2-20 mm thick oxide layer on partly-altered basalts. Surface of the thick crust is granular, porous and exhibits cusps. Nodules are earthy black, spheroidal to elliptical, medium size (40-60 mm) and have rough surface texture.

Mineralogy—Samples from the Mid-Indian Ridge, seamount crusts and abyssal plains are characterised by distinctive mineralogy (Fig. 3). Terminalogy and identification of mineral phases are as suggested by Burns & Burns[8]. The Mid-Indian Ridge coatings consist of todorokite with major 9.8 Å and weak 4.8 Å and 2.4 Å reflections. Diffraction pattern also indicates significant quantity of plagioclase feldspar which might be due not only to its presence as an accessory mineral, but also to incorporation of material from the basalt substrate because the oxide coatings were very thin. Diffractograms of

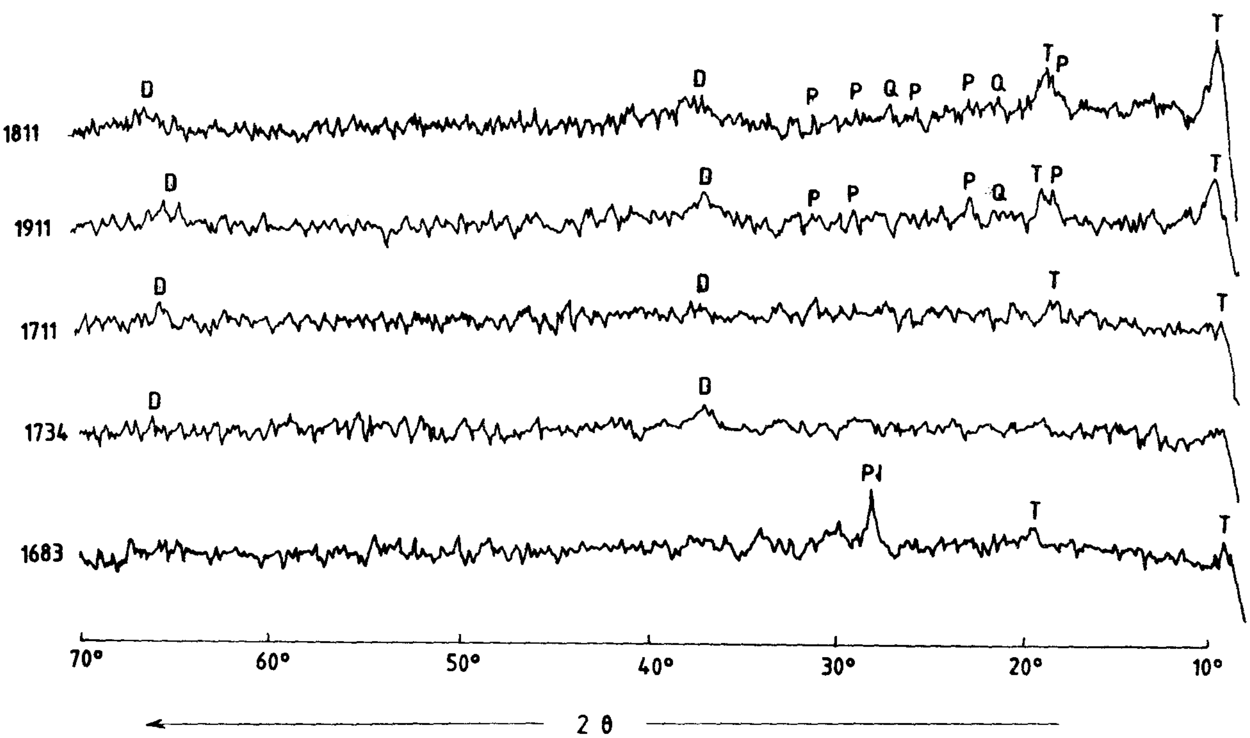

Fig. 3—X-ray diffraction of ferromanganese oxides (1683, Mid-Indian Ridge coatings; 1711 and 1734 seamount crusts; 1811 and 1911 abyssal nodules, T = Todorokite, D = δ MnO_2, P = Phillipsite, Q = Quartz, Pl = Plagioclase)

ferromanganese crusts from the seamounts exhibit weak and broad 2.4 Å and 1.42 Å reflections indicating δ MnO_2. Abyssal nodules have well crystallised todorokite with primary 9.8 Å and weak 4.8 Å, 2.4 Å and 1.42 Å reflections and also minor amounts of δ MnO_2. Ratios of 9.8 Å/1.42 Å (1.5 to 1.8) indicate that todorokite is dominant in nodules whereas δ MnO_2 is the predominant mineral (ratio 0.5 to 0.6) in seamount crusts. None of the diffraction patterns show identiafible reflections of iron oxides due to their amorphous nature.

Composition—The results of chemical analysis (Table 2) show that Mn varies from 7.79 to 14.41 % in the Mid-Indian Ridge samples, 12.23 to 23.89 % in seamount crusts and 26.1 to 30.51 % in abyssal nodules. The Mn/Fe ratio (0.6) is less than unity in Mid-Indian Ridge samples, 1-2 in crusts and > 5 in abyssal nodules. Cu and Ni concentrations are highest in the nodules (1.27-1.31, 0.87-1.02 %) followed by crusts (0.10-0.59, 0.29-0.55 %) and least in Mid-Indian Ridge samples (0.03-0.04, 0.06-0.11%). Zn was present in higher concentrations (0.10-0.12 %) in abyssal nodules and in similar quantities (0.4-0.5 %) in both the Mid-Indian Ridge and seamount samples. Co has its highest concentration in the seamount crusts (0.47%).

Mid-Indian Ridge samples—Ferromanganese coatings formed on fresh basalts are similar in composition to the ferromanganese coatings of Mid-Atlantic Ridge[19]. Their similarity in locations (mid-oceanic ridges), composition (higher major and low trace element concentration compared to other ferromanganese oxides such as abyssal nodules and seamount crusts) indicate a common origin. The ternary diagram[20] of Fe, Mn and (Cu + Ni + Co) × 10 shows that the ferromanganese coatings of the MIR samples fall in the hydrothermal field (Fig. 4). This field is towards Fe-end member and away from the diagenetic field. It is due to enrichment of Fe and depletion of Mn and trace metals. Average Mn/Fe ratio (0.6) also suggests the enrichment of iron in these coatings. The relatively rapid accumulation of hydrothermal deposits[4] from the solutions with low trace metals compared to high Mn and Fe concentrations may restrict the minor element enrichment. Marine hydrothermal deposits are characterised by extreme Fe and Mn values and low trace metal concentrations. In an environment of increasing *p*H and oxidation potential as would be encountered upon mixing of hydrothermal solutions with oxygenated bottom water, fractionation of Fe and Mn takes place due to lower solubility of Fe species compared to Mn[21]. Hydrothermal deposits may therefore represent Fe enrichment at one end and Mn on the other. It is possible that Fe precipitates first as X-ray amorphous material followed by Mn in the form of

Table 2—Chemical Analysis of Ferromanganese Oxides from the Mid-Indian Ridge, Seamount Crusts and Abyssal Nodules from the Indian Ocean

(Values, are in %)

Sample no.	Mn	Fe	Cu	Ni	Co	Zn	Mn/Fe	Co/Zn	Cu + Ni + Co
Mid-Indian Ridge									
1681	8.89	17.65	0.03	0.06	0.06	0.04	0.50	1.50	0.15
1682	14.41	20.50	0.04	0.11	0.06	0.04	0.70	1.50	0.21
1683	10.68	18.50	0.04	0.08	0.05	0.04	0.57	1.25	0.17
1684	7.79	14.70	0.03	0.07	0.04	0.05	0.53	0.80	0.14
1685	10.85	19.70	0.03	0.07	0.06	0.04	0.55	1.50	0.16
Seamount-1									
1711	23.89	21.50	0.12	0.37	0.45	0.04	1.11	11.25	0.94
1712	23.73	19.10	0.19	0.39	0.26	0.04	1.24	6.50	0.84
1713	22.37	20.10	0.23	0.33	0.36	0.04	1.11	9.00	0.92
1714	22.37	20.30	0.10	0.36	0.47	0.04	1.10	11.75	0.93
Seamount-2									
1731	16.67	11.75	0.37	0.43	0.36	0.04	1.41	8.48	1.16
1732	12.23	7.50	0.26	0.29	0.31	0.04	1.63	7.75	0.86
1733	18.89	9.20	0.18	0.39	0.34	0.06	2.05	5.66	0.91
1734	22.23	12.45	0.59	0.55	0.42	0.04	1.78	10.62	1.56
1735	12.37	9.70	0.24	0.29	0.30	0.04	1.27	7.50	0.83
Abyssal nodules									
1811	26.10	4.80	1.27	0.87	0.03	0.10	5.43	0.32	2.17
1812	27.25	4.61	1.28	0.88	0.03	0.11	5.91	0.27	2.19
1911	30.51	5.80	1.31	1.02	0.07	0.12	5.26	0.58	2.40
1912	29.80	5.62	1.28	1.01	0.05	0.11	5.30	0.45	2.34

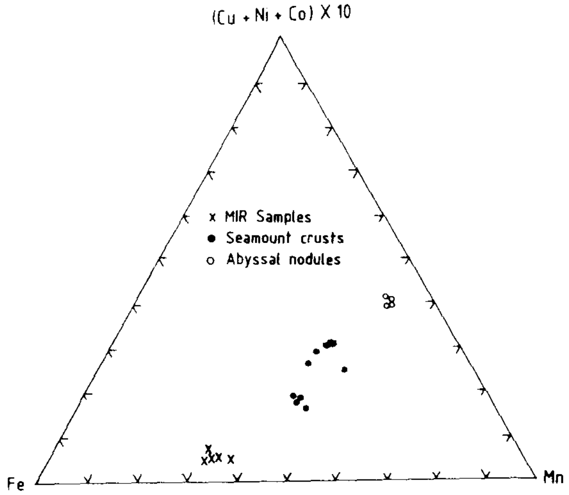

Fig. 4—Ternary diagram of Fe, Mn and [(Cu + Ni + Co) × 10]

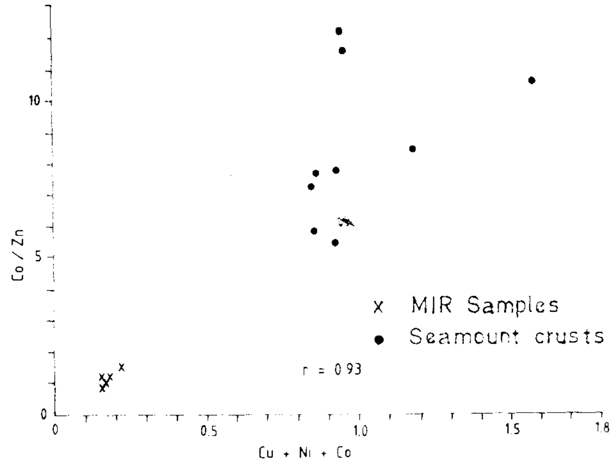

Fig. 5—Co/Zn vs (Cu + Ni + Co) concentrations of the Mid-Indian Ridge coatings and seamount crusts

todorokite as the only identifiable mineral phase. A strong correlation (r = 0.93) exists between Co/Zn and Cu + Ni + Co concentration. The ratio of Co/Zn may be used as an indicator of hydrothermal versus normal authigenic deposition where Zn is directly linked to hydrothermal source and Cu, Ni and Co to hydrogeneous[6]. The Co/Zn ratio in the Mid-Indian Ridge samples (Fig. 5) is very low (0.8 to 1.5) indicating low concentrations of seawater derived Cu, Ni and Co confirming that major source is hydrothermal.

Seamount crusts—The rarity of todorokite in the seamount crusts is in contrast to its abundance in the abyssal nodules. The formation of todorokite is generally associated with Mn/Fe ratios exceeding about 2.5 (ref. 22) and such values were not found in the seamount crusts. The reflections indicate that δ MnO_2 is more prominent in SM-2 samples compared to SM-1. Fe does not form any crystalline oxide mineral as no distinct peak related to Fe oxides was observed. The composition of the crusts show little variation from both the seamounts. Ni values are similar to those reported for the seamount nodules, whereas average Co content is less than the seamount nodules and the crusts but higher than the deep - sea nodules[1]. On the other hand, Cu content is above the average seamount crusts and nodules and lower than the deep-sea nodules[1]. Mn contents range from 12.23 to 23.89 % and are higher than the average value for the seamount Fe - Mn oxides. Fe varies from 7.5 to 21.5% and the average is similar to the values reported for seamounts. The marginal increase in Ni and Cu values from SM-1 and SM-2 may be related to the increase in average Mn/Fe ratio. The variability in thickness and chemical composition of ferromanganese crusts may reflect complex interaction of sediment influx, bottom current velocity and redox potential[5]. Co varies from 0.21 to 0.47 % and the average of SM-2 is higher than SM-1 crusts. Co concentration may be related to δ MnO_2 since low spin Co^{3+} may substitute for Mn^{4+} in the δ MnO_2 matrix[23]. High values of Co/Zn (Fig. 5) ratio indicate higher concentrations of seawater-derived Cu, Ni and Co compared to hydrothermally - derived Zn content. Adsorption of minor and trace metals from seawater by the colloidal Fe and Mn during transport and deposition accounts for the higher concentrations of these elements compared to Mid-Indian Ridge samples. The ternary diagram also shows that crusts fall in the hydrogenous field (Fig. 4).

Abyssal nodules—Todorokite is the major mineral with minor amount of δ MnO_2 in the nodules from the plains. Todorokite-rich nodules form at a lower Eh (+ 0.465 V) compared to δ MnO_2-rich nodules and crusts (+ 0.562 V) (ref. 2). The redox potential is influenced by the rate of sedimentation and organic carbon accumulation which in turn depend upon the depth and biological productivity of surface waters[24]. Abyssal nodules are from the area that lies in the region of equatorial currents where biological productivity is higher. The sediments in this area are siliceous ooze[25] and water depth (5271 and 5256 m) well below the carbonate compensation depth (CCD). Metals such as Mn, Fe, Cu and Ni increase with decreasing carbonate flux[24]. The metals incorporated in the carbonate organisms will become liberated below the lysocline as the organisms dissolve. The maximum increase in their concentration in ferromanganese oxides will therefore coincide with the maximum rate of dissolution[17] of $CaCO_3$. The enrichment of Cu, Ni and Zn in todorokite is possible because the crystal lattice of todorokite can take up divalent ions of transition metals such as Cu^{2+}, Ni^{2+} and Zn^{2+} which have suitable ionic radii in place of octhedrally coordinated[7,26] Mn^{2+}. Heath and Dymond[27] suggested that biogeneic silica (opal) reacts with ferromanganese oxyhydroxides and forms Fe-rich smectite allowing Mn to be incorporated in the nodule as todorokite which also accepts Ni, Cu and Zn. Release of metals during the decomposition of organic material and dissolution of hard parts and the reaction between Fe-Mn oxyhydroxides and biogenic silica therefore play a major role in diagenetic nodule formation. The Mn/Fe ratio of the nodules is an useful index of diagenetic influence. The higher the ratio the stronger the diagenetic signature. Mn/Fe ratio (> 5) and Mn, Fe and $(Cu + Ni + Co) \times 10$ when plotted on the ternery diagram (Fig. 4) indicate that nodules were formed during early diagenesis. Ore microscopic and scanning electron microscopic observations also revealed that the nodules from the abyssal plains have columnar structure suggesting early diagenetic origin[28].

To conclude, ferromanganese oxide coatings from the Mid-Indian Ridge have hydrothermal origin, seamount crusts formed due to hydrogeneous precipitation and abyssal nodules are of early diagenetic nature.

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