

## Ferromanganese oxides on sharks' teeth from Central Indian Ocean Basin

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The mineralogy, composition and growth rates of ferromanganese (Fe-Mn) oxides over the sharks' teeth from the Central Indian Ocean Basin are presented. The trends of metal enrichment (Mn, Ni, Cu and Zn) and depletion (Fe and Co), the Mn/Fe ratio and the growth rates, basically indicate a hydrogenous source; in contrast, limited role of diagenesis. Furthermore, the nucleus does not seem to significantly affect the nature and bulk chemistry of the Fe-Mn oxides.

Ferromanganese (Fe-Mn) oxides in the form of nodules, micronodules and encrustations are common on the seafloor. Together with the Fe-Mn oxides, the other economically important metals which accrete on and around the nucleus are Co, Cu and Ni. The Central Indian Ocean Basin (CIOB), a prime mine site for manganese deposits, has been explored quite thoroughly by the National Institute of Oceanography and various aspects of these deposits have been published<sup>1</sup>. The samples recovered from the basin includes, volcanics, encrustations, sharks' teeth and the ubiquitous manganese nodules. The present communication concerns with the occurrence of sharks' teeth in the CIOB, the source of the encrusting Fe-Mn oxides, and the influence of the teeth on the bulk chemistry of the Fe-Mn oxides.

### Materials and Methods

Sharks' teeth have been recovered in different samplers during manganese nodules collection from the CIOB. Normally sharks' teeth occur in sizes <1 cm to few cm long as individual entities. In many instances, the teeth are encrusted with Fe-Mn oxides. At the locations, lat. 12°33'S and long. 78°12'E (water depth=5210 m) and lat. 13°15'S and long. 77°30'E (water depth=5270 m) number of sharks' teeth were dredged together with manganese nodules and rocks from the siliceous sediment ooze. Altogether 45 teeth were examined from both the locations.

The sharks' teeth were separated from other recovered materials, and their dimensions and the thickness of the Fe-Mn oxides on the enamel were measured. X-ray diffractometry (XRD) was carried out of 5 samples using a Philips system, to deduce the

mineral phases. The samples were scanned from 5 to 40° and 60-70°2θ at 0.05°2θ sec<sup>-1</sup> with nickel filtered Cu Kα radiation. The minerals were identified following established criteria<sup>2</sup>. The bulk composition of the samples was determined using an Inductively Coupled Plasma-Atomic Emission Spectroscopy. Of the five samples, #sts 1, 3 and 7 are Mn-rich encrustations, # st. 6A is the altered basaltic material surrounding the base of the tooth and # st. 6B is the Fe-Mn oxides over the basaltic substrate (Fig. 1). Growth rates of the Fe-Mn oxides were calculated from the chemical composition adopting the methods of Lyle<sup>3</sup> and Sharma & Somayajulu<sup>4</sup>.

### Results

**Nucleus**—It is commonly observed that the accretion of Fe-Mn oxides requires presence of a suitable nucleus<sup>5,6</sup>. The nucleus could be a sediment clast, rock fragment, older nodule, shark tooth, whale bone and biogenic fragment<sup>7</sup>. In general, deep-sea Fe-Mn deposits have volcanics of various kinds like basalts and pumice as the most important nuclei especially in the CIOB<sup>8,9</sup>. In the present instance, sharks' teeth have acted as nuclei for the oxides (Fig. 1). In all the samples, the cavity of the teeth is filled by the siliceous sediments.

**Morphology**—Various descriptive terms such as oblate, discoid, prolate spherical, tabular, ellipsoidal and polygonal are used to define the shape of Fe-Mn concretions<sup>10</sup>. Predominantly the teeth are triangular in shape. The base of the teeth vary between 2 to 6.5 cm in length while from the base to the apex the dimension is between 1 to 5.5 cm. In most of the 45 teeth the basal portions are not well preserved as compared to the apical and dentine parts. This is



Fig. 1—a) Representative specimens of sharks' teeth recovered from the Central Indian Ocean Basin, of varying shapes, sizes and thickness of Fe-Mn oxides. b) Two large sharks' teeth with the one on the left substantially encrusted while the basal part of the tooth at the right is filled with altered basaltic material. Scale in cms.

similar to the observation made of sharks' teeth recovered from other locations in the CIOB<sup>11</sup>.

The surface texture of Fe-Mn concretions can be either smooth or rough, the latter being a result of the mammillated appearance<sup>10</sup>. The morphological features are determined by factors such as the source of the elements, type and age of the nucleus and environment of deposition<sup>12</sup>. The Fe-Mn oxides on the CIOB sharks' teeth are a few mm to 1.5 cm thick (Fig. 1). Most of the samples exhibit a rough texture due to the presence of small mammillae and botryoids.

**Mineralogy**—The three Mn-phases identified<sup>13</sup> in Fe-Mn oxides are 7A<sup>0</sup> manganite (todorokite), 10A<sup>0</sup> manganite (birnessite) and  $\delta$ -MnO<sub>2</sub>. In contrast, the Fe-phases occur in an amorphous form<sup>14</sup> in which there is a dominant presence of hydrated ferric oxyhydroxide<sup>2</sup>. Besides these, goethite is one of the most important while the presence of maghemite, hematite and akaganeite have also been noted<sup>2</sup>. In addition to the Mn- and Fe-phases, the minor and accessory minerals are quartz (most common), feldspars, clay

and zeolites<sup>2</sup>. XRD of # sts 1, 3, and 7 shows occurrence of ferric oxyhydroxide and some todorokite while # st. 6 has  $\delta$ -MnO<sub>2</sub> and ferric oxyhydroxide. In addition, the samples have minor amounts of silicate minerals (quartz and plagioclase) palagonite and montmorillonite.

**Composition**—The Fe-Mn oxides and the associated Co, Cu and Ni vary in concentrations. The variations could be intra- and inter-oceanic and also within individual samples. The other elements which co-occur with Fe-Mn deposits are Si, Ti, K, Zr, Pb, V and Zn and the rare earth elements. There is a manifold increase in the contents of these elements in the Fe-Mn deposits relative to their crustal abundance<sup>12</sup>. The composition of sharks' teeth and of nodules from the CIOB are shown in Table 1 and the elemental variations are hereunder.

**Major and minor element variations**—The SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents are low in sts 1, 3 and 7 as compared to st. 6A and st. 6B and Al<sub>2</sub>O<sub>3</sub> has similar values as the CIOB nodules (Table 1). TiO<sub>2</sub> is generally <1% in all the samples. The high value of 1.49% P<sub>2</sub>O<sub>5</sub> in # st. 3, could reflect the presence of minor amounts of apatite. In general, Mn ranges between ~9% to ~30% and Fe from 1% to 8%. Mn/Fe ratios range between 1.76 to 3.83 with an high value of 29 for # st 1. For comparison, the average and range of the composition of the present study are made with earlier values of sharks' teeth<sup>15</sup> and nodules<sup>16</sup> (Table 2). The table depicts that the average Mn value of the present samples is close to the nodules and that Fe is slightly impoverished. The altered basaltic matrix (# st. 6A) has the lowest CaO (1.47%) and highest K<sub>2</sub>O (2.31%) and Na<sub>2</sub>O (5.91%) and Mn is ~9% and Fe ~5% in # st. 6A as compared to 14.7% and 8.3% in # st. 6B (Table 1).

**Trace element variations**—The concentrations of trace elements in samples #ST 1 and 7 show low Ba and elevated Cu, Ni, V and Zn (Table 1). Sample # st. 3, although similar, has enhanced Ba, Co, Cr and Pb. Among the 2 samples # st. 6A and B, the former has higher Ba, Cr, Ni, V and Zn vis-a-vis st. 6B which has higher Co, Cu and Pb. The trace elements attain high values in the different samples for e.g., Ba is 2565 ppm in # st. 6A, Co is 1347 ppm in # st. 6B, Cr is 168 ppm in # st. 3 and Cu, Ni and Zn respectively are 10, 820 ppm, 11,000 ppm and 1122 ppm, in # st. 7. Such differential enrichments suggest intra-oceanic variations. Cr contents in the CIOB sharks' teeth are substantially higher than the average value of the Indian Ocean nodules (Table 1) which might reflect

Table 1—Chemical composition of sharks' teeth from the Central Indian Ocean Basin

[Oxides in weight% and trace elements in ppm). Stations 1, 3 and 7 are encrustations, st. 6A is altered basaltic materials (dominant) from the base and cavity of the tooth admixed with FeMn oxides and st. 6B is FeMn oxides (dominant) on st. 6A. GR (A) and GR (B) are the growth rates (mm/10<sup>6</sup> yr) calculated based on  $R=16.0 (\Sigma_{Mn}/[\Sigma_{Fe}]^2)+0.448^{(ref.3)}$  and  $R=8.33 [\Sigma_{Mn}/(\Sigma_{Fe})^2]+2.16^{(ref.4)}$ , respectively. CIB=average of 22 nodules from the Central Indian Basin<sup>12</sup>. Ni value for the CIB is of Cronan and Moorby<sup>16</sup>. na=not available.]

Oxides	St 1	St 3	St 6A	St 6B	St 7	CIB
SiO <sub>2</sub>	16.06	22.03	35.64	35.50	14.64	na
Al <sub>2</sub> O <sub>3</sub>	4.35	5.00	10.52	8.60	4.10	5.19
Fe <sub>2</sub> O <sub>3</sub>	1.47	11.27	6.76	11.88	9.18	10.87
MnO	38.47	21.34	11.57	18.91	31.73	28.54
MgO	2.05	0.94	1.87	1.30	2.33	na
CaO	3.21	3.73	1.47	2.33	2.28	1.86
Na <sub>2</sub> O	4.08	3.04	5.91	3.67	2.90	na
K <sub>2</sub> O	1.20	0.88	2.31	1.28	1.11	na
TiO <sub>2</sub>	0.49	0.50	0.53	0.64	0.39	0.54
P <sub>2</sub> O <sub>5</sub>	0.42	1.49	0.20	0.43	0.29	na
Total	71.80	70.22	76.78	84.54	68.95	na
Mn/Fe	28.93	2.10	1.87	1.76	3.83	2.90
GR(A)	449.88	4.71	6.72	3.84	9.99	6.57
GR(B)	236.14	4.38	5.43	3.93	7.13	5.35
Ba	1103	1614	2565	1033	1425	na
Co	1156	1256	764	1347	1042	1130
Cr	67	168	85	53	70	36
Cu	7245	5815	4390	4584	10820	9910
Ni	10290	7035	5060	4948	11000	8650
Pb	496	645	210	581	522	650
V	373	239	203	175	335	na
Zn	1056	697	391	370	1122	1190

Table 2—Average composition of sharks' teeth and manganese nodules from the Central Indian Ocean Basin  
[1=Present work, 2=Average of 14 sharks' teeth<sup>15</sup>, 3=Average of 44 nodules<sup>16</sup>. Values in brackets are the ranges]

	1 (Sharks' teeth)	2 (Sharks' teeth)	3 (Nodules)
Mn	18.90 (9-30)	26.29 (16-38)	20.40 (3.6-32)
Fe	5.68 (1-8.3)	8.27 (6-11.6)	9.64 (4.2-19.7)
Co	1113 (764-1347)	1160 (870-1766)	1400 (570-2750)
Cu	6571 (4390-10,820)	4403 (2180-10,136)	7450 (590-17,700)
Ni	7666 (4948-11,000)	6827 (2904-11,258)	8650 (750-15,700)
Pb	491 (209-645)	na	650 (210-1320)*
Zn	727 (390-1122)	na	1180 (210-1810)*
Mn/Fe	2.39 (1.76-3.83)**	2.84 (1.8-6.3)	2.12 (0.59-6.7)
GR(A)	6.32 (3.84-10)**	6.60 (3.28-17.34)	3.96
GR(B)	5.22 (4-7)**	5.36 (3.63-11)	3.99

\* average of 38 samples, \*\* average of 4 analyses, GR=growth rates in mm/10<sup>6</sup> yr

the presence of detrital silicate phases derived from the surrounding altered basalts.

From Table 2 it is observed that Co is slightly depleted, Cu and Ni are enriched with respect to the earlier studied teeth. Again, with respect to the nodules, Cu, Ni, Pb and Zn are depleted. Nonetheless, all the values are within the reported ranges. The individual plots of Cu, Ni and Zn against Mn and Co against Fe show positive correlations (Fig. 2).

*Growth rates*—The growth rates of Fe-Mn oxides on a substrate could provide significant clues to the processes which control their formation. It is generally believed that for accretion of 1 mm or less of Fe-Mn oxides it requires a million years. Few factors which conceivably control the growth rates are, the source of the metals, duration of exposure of the nucleus to the accretionary processes and morphoforms of the seafloor. There exists different techniques to determine the growth rates of the oxides, such as radiometric methods, paleomagnetism, racemization of amino acids and palagoniti-

sation of basaltic glass encrusted with Fe-Mn oxides<sup>17</sup> and the use of microfossils and thermoluminescence<sup>12</sup>. In addition to these methods, a simple method to calculate the growth rates was proposed by Lyle<sup>3</sup> (method A) and Sharma & Somayajulu<sup>4</sup> (method B). In these calculations, the Mn and Fe contents of the oxides are considered. Based on the given formulae of those authors, the growth rates of the CIOB sharks' teeth were obtained (Table 1). The results indicate that for slowly accreted Fe-Mn oxides, both these methods are comparable, but not for faster accretion rates. For instance, st. 1 has a growth rate of ~450 mm/10<sup>6</sup> yr by the former method which is an order of magnitude more than that obtained by the latter method (236 mm/10<sup>6</sup> yr). The growth rates for the CIOB samples (Table 2) indicate that the values for the sharks' teeth are quite comparable (from both the methods) and are slightly faster than those of the nodules. An exception to the slow growth rates is # st. 1 which has the highest value (Table 1).

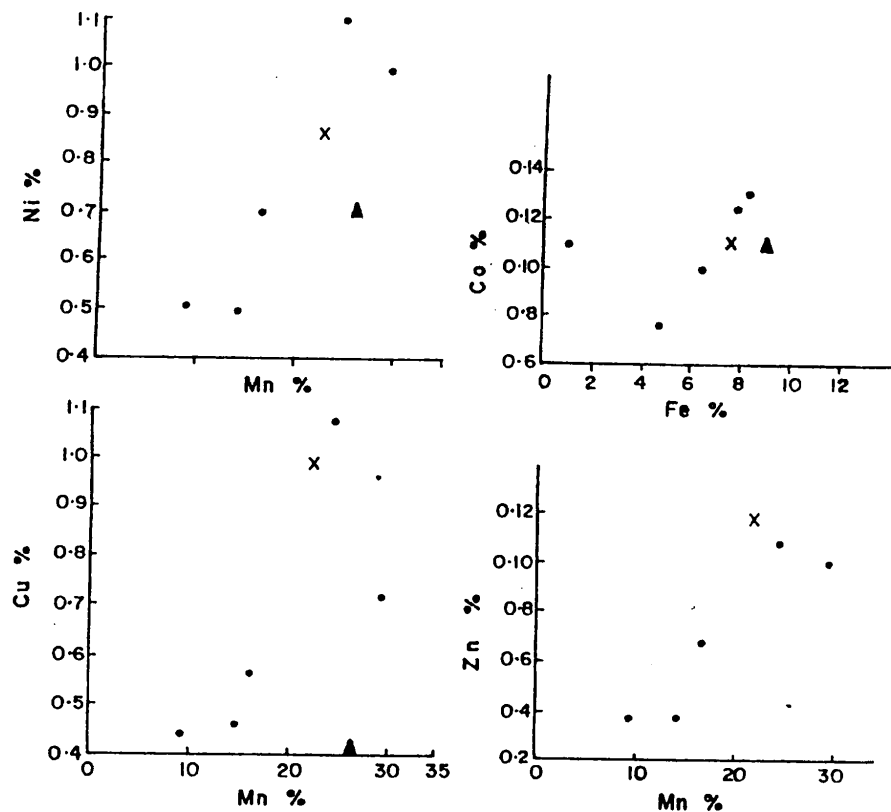


Fig. 2—Plots of Mn vs Cu Ni and Zn and Fe vs Co. Darkened circles are present samples, cross is CIB value<sup>12</sup> and filled triangle is of sharks' teeth<sup>15</sup>.

## Discussion

The essentialities for formation of Fe-Mn deposits are a relatively oxidising environment, a low rate of sedimentation, influence of the local topography, volcanics, sediment type, mineralogy and currents. Bonatti *et al.*<sup>18</sup> classified Fe-Mn deposits on the basis of different potential sources of elements, into hydrogenous, diagenetic, hydrothermal and halmyrolytic. These processes respectively correspond to the derivation of the elements from: the seawater, post-depositional redistribution within the sediment column, hydrothermal activity and submarine alteration (halmyrolysis) of volcanics. The resultant deposit may have signatures of one or more of these processes<sup>18</sup>. To account for the transportation of elements from these sources, mechanisms such as oceanic circulation and mixing, adsorption<sup>14</sup>, biological removal<sup>19</sup> and the role of bacteria<sup>20</sup> have been suggested.

To decipher the source of the elements of the CIOB sharks' teeth, the elemental values (Tables 1 and 2) are plotted on a triangular diagram of Mn-Fe - (Cu+Co+Ni)×10 (ref.18). It can be noted that all the samples congregate in the hydrogenous field, while # st. 1 is little closer to the diagenetic field.

Evidences exist to show that the crystal structure of iron and manganese minerals in Fe-Mn deposits plays a major role in the accretion of the minor metals. Divalent substitution for Mn by Cu, Ni and Zn in the structure of todorokite has been known<sup>2</sup>. The strong positive relation between these elements in the present samples (Fig. 2), implies such a mechanism of divalent cations substitution.  $\delta$ -MnO<sub>2</sub> reaches its greatest abundance in Fe-Mn oxides occurring as nodules and encrustations in areas of elevated topography<sup>23</sup> since there is an accretion of iron from both volcanic sources and seawater, vis-a-vis Fe-Mn oxides with todorokite which additionally accretes manganese from interstitial waters<sup>12</sup>. Further, enrichment of Co in Fe-Mn oxides rich in  $\delta$ -MnO<sub>2</sub> (# st. 6B) may be due to the ability of Co in its higher oxidation state to substitute for Mn<sup>4+</sup> or as Co<sup>3+</sup>OOH for Fe<sup>3+</sup>OOH (ref.22). If this is the case, a prerequisite for its enrichment in nodules would be the oxidation of Co<sup>2+</sup> to Co<sup>3+</sup> under highly oxidizing conditions which also favour the formation of  $\delta$ -MnO<sub>2</sub> (ref. 2).

Palagonitisation of the basaltic glass in st 6A has resulted in an enrichment of Na over K and formation of a Ca-poor and a K- and Mg-rich smectite. This composition probably reflects development of incipient phillipsite<sup>23</sup>.

The process of nucleation in Fe-Mn deposits has been suggested to be brought about by the epitaxial intergrowths of  $\delta$ -MnO<sub>2</sub> and FeOOH.xH<sub>2</sub>O (ref.2). Apparently an active hydrous ferric oxide surface like clay minerals, a shark's tooth or a rock fragment is needed before precipitation of divalent Mn is initiated<sup>25</sup>. A local increase in the pH produced in seawater trapped in cavities during solution and hydrolysis of the substrate<sup>2</sup>, could have helped precipitate the FeOOH.xH<sub>2</sub>O phase on the CIOB sharks' teeth. According to Arrhenius<sup>25</sup>, most of the refractory solid organic matter consists of the original and decomposed organic molecule interstratified with, and protected by, the apatite crystallites in the ubiquitous fish-bone debris. Higher fatty acids form much of the decomposition products precipitated by salt formation with Zn, Cu, Ni, Pb and Ag, adsorbed from seawater, which are fixed by the proteinaceous residue in the bone debris.

It has been suggested that faster grown nodules have lower Ni contents and birnessite as the dominant mineral, even though they accumulate Ni at a higher rate<sup>25</sup> but the present samples do not show these characteristics. This is exemplified by samples st. 1 which has the fastest growth rate and st. 7 which is orders of magnitude less yet, both have todorokite and > 10,000 ppm of Ni (Table 1). One notable aspect is the high growth rate of # st. 1, which is orders of magnitude more than for the other samples. Despite the limitations of Lyle's formulae, which can predict growth rates up to rates between 50 and 100 mm/10<sup>6</sup> yr, it however, correctly predicts that Mn-enriched deposits, hydrothermal crusts and near-shore growing nodules, have faster accretion rates<sup>3</sup>. It is recognised that shallow-water Fe-Mn deposits have high and variable growth rates (mm to cm per 1000 years)<sup>17</sup>. However, it is worthy to note that rapid growth also has been recorded from a deep-sea nodule from the Peru Basin<sup>26</sup>. This nodule, with an average Mn of 43.3% (range 36.2 to 55.2%) and Fe 0.63% (range 0.56 to 1.58%), has been radiometrically dated to have grown at 168±24 mm/10<sup>6</sup> yr. According to

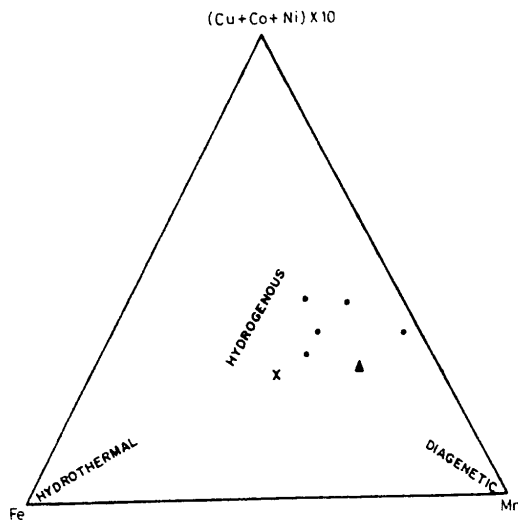


Fig. 3—Triangular diagram<sup>18</sup> to decipher the source of the metals to the FeMn oxides of nodules and encrustations on the sharks' teeth. Source of data and symbols as in Fig. 2.

them<sup>26</sup> such high growth rate indicates significant contributions from diagenetic source. Similarly, based on the conclusion, that nodules with a high Mn/Fe ratio grow faster than those with lower ratio<sup>27</sup>, it was proposed that such nodules represent precipitates that have accreted metals via diagenetic process in addition to a hydrogenous source<sup>28</sup>. All these facts, viz., high values of Mn, Mn/Fe ratio and growth rate and low Fe, are present in # st. 1. Furthermore, this sample plots nearer to the diagenetic field (Fig. 3). Hence, it is suggested that the slow deposition of Mn from proximal sources, prolonged contact of the teeth with the seawater and ambient physico-chemical conditions and diagenetic contributions have resulted in an high growth rate.

Thus, it is inferred that the Mn/Fe ratios, the growth rates, enriched Mn, Ni, Cu and Zn and depleted Fe and Co in the CIOB sharks' teeth, indicate that metal accretion was primarily through hydrogenous process while diagenesis was largely restricted. Secondly, the influence of the nucleus on the bulk composition of the FeMn oxides seems to be minimal.

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