

Ferro-Manganese Oxide Growth on Shark Teeth from Central Indian Ocean Basin

V K BANAKAR & M SUDHAKAR

National Institute of Oceanography, Dona Paula, Goa 403 004, India

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Study of ferro-manganese oxide growth on apatitic substrates like shark teeth enamel from siliceous sediment environment (lat. 10°S and long. 75°E) suggests the changes in depositional environments within the sediment layer through the growth history of these oxides. Though the nature of substrates does not have any control over the mineralogy and chemistry of Fe-Mn oxides, an active sink like loose sediment or altered basaltic coat appears to be the primary requirement before ferric hydroxide coat on hard nucleating agent.

Fe-Mn oxide growth as nodules or encrustations around or on substrates like basaltic fragments, clay lumps and basaltic outcrops is well known and studied in detail¹. Eventhough shark teeth have frequently been recovered as nuclei for Fe-Mn oxide growth and reported², their detailed study is sparse. This paper describes the Fe-Mn oxides on shark teeth from the Central Indian Ocean Basin (CIOB) and the fate of shark teeth during post depositional diagenetic processes.

Materials and Methods

During several cruises to CIOB, under the programme 'Surveys for Polymetallic Nodules', three shark teeth (samples A, B and C) and one associated nodule (sample D) were collected from 5200 m depth around lat. 10°S and long. 75°E. All these samples were from siliceous sediments. In these shark teeth, Fe-Mn oxide growth was more pronounced around the basal portion of the enamel. In samples A, B and C oxide deposition covered the entire lingual enamel and only partly the labial enamel. Wherever the oxide growth was not progressed on labial enamel a thin film of Fe-Mn oxide was observed (Fig. 1). The lingual outer oxide had a distinct rough surface (presumed bottom) which was in contact with underlying sediments. The labial outer oxide had a distinct smooth surface (presumed top) which was in contact with overlying water column.

The lingual outer, lingual inner, labial outer, labial inner parts of Fe-Mn oxide of sample A and the smooth and rough surfaces of associated nodule (D) were uniformly scraped considering

the oxide surfaces as zero depth, which successively increased towards the nucleus or enamel. The subsample depth of each scraping was determined indirectly with weight, density and area relation³. Shark teeth B and C were sampled in bulk at various parts with characteristic features (Fig. 1).

Finely ground and dried subsamples were leached in 6M HCl in the presence of a few drops of H₂O₂. The insoluble residue was removed by filtration and the dried weight of residue was re-

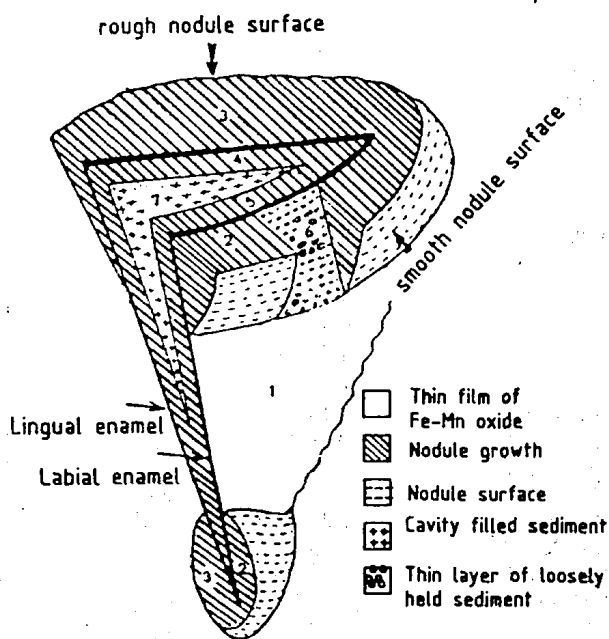


Fig. 1—Schematic diagram of a ferro-manganese oxide deposition on shark tooth (numbers indicate subsamples)

corded. Clear leachate finally made to volume, and analysed for Mn, Fe, Co, Ni and Cu on Perkin-Elmer 5000 AAS. The accuracies of the results were checked by analysing the USGS-A-1 and NIO-2388 nodule standards at regular intervals and were within $\pm 6\%$ for all the elements analysed. A few selected samples were scanned from $8^\circ-70^\circ 2\theta$ on a Phillips XRD using Ni filtered Cu-K (α) radiations at a speed of $2^\circ 2\theta \text{ min}^{-1}$. The SEM photographs of the thin sediment coat which forms the foundation for ferromanganese oxide growth were taken on CAME-BAX-MICRO.571.

Results and Discussion

Observations were made on forty shark teeth

Fe-Mn oxides, a few nodules and encrustations. In most of the samples, a thin layer of loosely held sediment or altered basaltic material with considerable amount of mixed Fe-Mn oxides is present directly above the hard nucleating materials. Fe-Mn oxide to a considerable thickness has accreted at places where loosely adhering sediment provides a foundation. Absence of such sediment foundation material on the nucleating agents restricts Fe-Mn oxide growth to a thin layer (of few μm). SEM studies of this foundation forming sediment layer show clay lumps, siliceous ooze and in certain cases the altered mineral fragments.

Analytical results for Mn, Fe, Co, Ni and Cu are presented in Tables 1 and 2. Except for the

Table 1 - Trace Metal Concentrations of Ferro-Manganese Oxide as per the Depth within Oxide

Sample	Subsample interval (mm)	Concentration					Mn/Fe
		Mn (%)	Fe (%)	Co (ppm)	Cu (ppm)	Ni (ppm)	
A	0* -0.19	22.8	10.0	2124	2792	5508	2.3
Labial outer oxide (presumed top)	0.19-0.38	34.3	8.1	1713	3920	8811	4.2
	0.38-0.70	30.1	6.5	1106	5416	12041	4.6
	0.70-0.95	28.7	6.9	1019	5828	11636	4.2
	0.95-1.24	25.9	6.8	1132	6975	12708	3.8
	1.24-2.09	29.8	6.2	1200	9702	10139	4.8
	2.09-2.44	30.7	5.7	989	11222	9680	5.4
A	2.44-2.67	27.5	4.0	616	12031	11124	6.9
	0* -0.33	31.9	4.5	1117	8470	12358	7.1
	0.33-0.59	29.1	5.1	1341	7816	11692	5.7
	0.59-0.83	26.0	8.5	1322	7100	11008	3.1
	0.83-1.02	33.1	8.7	1977	5318	8974	3.8
	1.02-1.56	29.4	8.9	1312	5231	9220	3.3
A	1.56-3.06	17.2	9.1	1224	5626	7981	1.9
	3.06-4.40	30.5	8.0	969	9162	8335	3.8
	0* -0.19	15.8	4.2	920	8006	8540	3.8
	0.19-0.37	16.7	3.3	936	6900	7009	5.1
	0.37-0.52	17.1	4.5	909	6822	7910	3.8
	0.52-0.68	20.8	4.4	990	6418	7137	4.7
A	0.68-1.34	21.9	5.8	1123	4835	5416	3.8
	0* -0.27	23.1	3.0	968	8440	7400	7.7
	0.27-0.51	18.5	3.9	714	7300	7541	4.7
	0.51-0.69	15.8	5.0	808	7031	7002	3.2
	0.69-0.86	13.5	3.5	792	6624	6680	3.9
	0.86-0.98	20.4	4.3	784	6210	6720	4.7
D	0.98-1.61	17.5	5.8	1071	4742	5366	3.0
	1.61-1.67	8.4	5.5	826	2309	3112	1.5
	0* -0.13	22.3	14.5	2090	7358	9496	1.5
	0.13-0.48	25.7	15.3	1925	6272	9308	1.7
	0.48-1.26	20.3	12.4	1168	6616	7730	1.6
	1.26-1.55	19.4	12.4	1281	6218	8589	1.6
D	0* -0.23	33.7	8.4	1210	13094	13202	4.0
	0.23-0.49	33.5	5.0	820	6730	15086	6.7
	0.49-0.65	37.7	4.3	790	10910	14194	8.8
	0.65-0.79	37.2	4.2	768	11562	14316	8.9
	0.79-1.22	36.4	4.8	981	10280	10503	7.6
	1.22-1.56	31.3	6.2	1310	12314	10717	5.0

*Corresponds to surface of Fe - Mn oxide.

Table 2—Trace Metal Concentration in Different Features of Ferro-manganese Oxide on Shark Tooth

Sample location*	Description	Concentration					Mn/Fe	Specimen details
		Mn (%)	Fe (%)	Co (ppm)	Cu (ppm)	Ni (ppm)		
1	Thin film of ferro-manganese oxide directly on the enamel of shark teeth.	23.8	11.6	919	1414	3466	2.1	B labial outer enamel
		25.8	10.0	931	2820	3718	2.6	B labial inner enamel ^f
		31.6	6.9	942	3135	6723	4.6	B lingual inner enamel ^f
		20.8	10.8	1406	2180	2904	1.8	C labial outer enamel
		25.0	10.5	870	4671	5021	2.4	C labial inner enamel ^f
2	Ferro-manganese oxide growth on labial enamel.	27.9	11.0	1422	2480	7184	2.5	B bulk nodule
		23.9	8.7	1306	4512	9430	2.8	C bulk nodule
		26.6	9.3	1766	3710	7772	2.9	C nodule surface scraped
		23.3	8.9	1521	5816	11258	2.6	C bulk nodule on tip of tooth
3	Ferro-manganese oxide growth on lingual enamel	38.0	6.0	1100	10136	10832	6.3	C nodule surface scraped
		30.1	9.4	1425	4100	7084	3.2	C bulk nodule
		29.6	7.8	1502	5813	9868	3.8	C bulk nodule on tip of tooth
4	Ferro-manganese oxide growth on lingual inner enamel	25.7	6.8	1030	4860	9218	3.8	B bulk nodule
5	Ferro-manganese oxide growth on labial inner enamel.	16.0	7.4	1092	3500	4696	2.2	B bulk nodule
6	Thin loosely held sediment layer forming base for Fe-Mn oxide growth	8.2	3.9	468	825	712	2.1	A
7	Tooth cavity filled sediment	3.1	1.6	121	307	216	1.9	B
		3.1	1.7	94	412	530	1.9	A
8	Tooth enamel after thorough cleaning	2.2	0.6	106	474	318	3.8	B

* As in Fig. 1.

^f Portion of enamel on which thick ferro-manganese nodule (encrustation) growth is present.

presumed top of the associated nodule (D) and a few sections of labial Fe-Mn oxide, rest of the subsamples from A, B, C and D fall in the mixed type nodule (type AB) field of modified three component diagram⁴. Lingual outer and lingual inner Fe-Mn oxide of sample A show decreasing Mn, Ni, Cu and Mn/Fe ratio (Table 1) towards their nucleating surface of lingual enamel, while labial outer oxide shows the same increasing towards its nucleating surface of labial enamel. Labial inner Fe-Mn oxide does not show any significant trend in metal variation (Fig. 2). In case of samples B and C, Fe-Mn oxide growth restricted to a few microns thickness on labial outer and inner surfaces of enamel have the Mn/Fe ratio 1.9 and 2.6 respectively. The lingual inner thin Fe-Mn oxide has the ratio 4.6 (Table 2). Thick Fe-Mn oxide growth on lingual enamel has the higher Mn/Fe ratio than the oxide on labial enamel (Table 2, see Fig. 1).

The heterogeneity in the composition of Fe-Mn oxide with depth in samples A and D (Table 1), Fe-Mn oxide from various parts and features of B and C which are from the same location, and large variation in their genetic behaviour indicate changes in depositional environ-

ments through time. Presuming the accretion of Fe-Mn oxide around a nucleus both from overlying water column and from underlying sediments⁵ the large variation in Mn/Fe ratio in samples A and D may be due to the shifting of zero Eh boundary line⁶ within the sediment layer. The decrease in Eh by a few millivolts increases the solubility of Mn²⁺ to a greater extent. It has been calculated⁷ theoretically an increase in Mn²⁺ solubility by a factor of 10 with decreasing Eh by only 50 mv. Thus changes in Eh may have occurred frequently through the growth history of Fe-Mn oxides in this biologically high productive equatorial zone.

Mn/Fe ratio in the oxide material varies between 2 and 9 and the combined Ni+Cu content increases with increasing Mn/Fe ratio and varies between 8000 and 26000 ppm. The higher Ni+Cu contents are associated with higher Mn/Fe ratio and do not show any point of reversal⁴ at Mn/Fe ratio 5. The decreasing Mn/Fe ratio towards the lingual enamel of sample A (Fig. 2) can be attributed to the increasing diagenetic influence during oxide accretionary sequence through time. Since these samples are from below the biologically high productive zone and well below car-

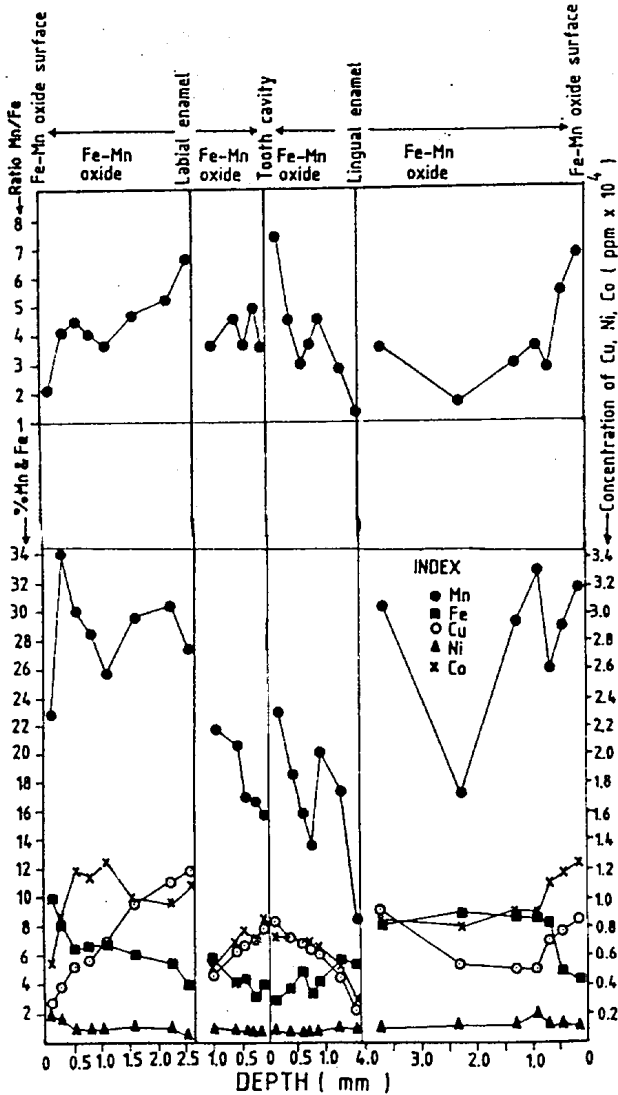


Fig. 2 - Metal variations vs depth plots of sample A (arrows on the top indicate growth direction of Fe - Mn oxide).

bonate compensation depth (CCD), the trace metals incorporated into the skeletal parts of the settling organisms are released to the bottom waters and this release varies inversely with carbonate flux⁸. These trace metals eventually get incorporated into the accreting nodule matrix or removed to the bottom sediments. Decreasing Mn/Fe ratio with decreasing trace metal content in the Fe - Mn oxide towards the lingual enamel may indicate the increasing biological activity since the beginning of oxide accretion around this lingual enamel. Todorokite is formed⁹ at lower Eh than δ -MnO₂ and is more conspicuous in lingual oxide than in labial oxide (Fig. 3). This indicates that, the lingual oxide has been accreting under the diagenetic influence. Nevertheless, the intensity of diagenetic influence may have varied through its growth period due to the fluctuations in the depositional microenvironments like shifting of zero Eh line frequently through the sediment layer. The top of the associated nodule (D) does not show any significant variations in its mineralogy (Fig. 3) and chemistry (Table 1) and is similar to the labial oxide growth on samples B and C (Table 2) indicating that the labial oxides and the presumed top of the nodule have been accreting under uniform hydrogenetic influence.

The loosely held sediment layer on the hard nucleating agents provides a foundation for oxide accumulation and may be acting as an active sink for the expelled electrons during the oxidations of Mn²⁺ and Fe²⁺. Observations on various Fe - Mn oxides and Fe - Mn oxides of shark teeth suggest the necessity of an active sink like sediment layer before the ferric hydroxide coating on incipient nucleating materials¹⁰, which forms the beginning of oxide accretion.

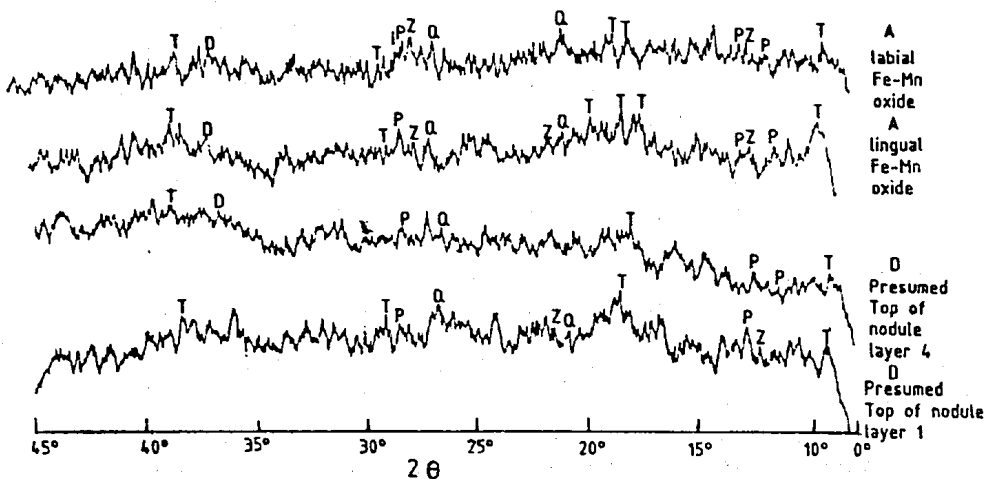


Fig. 3 - X-ray diffractograms of a few selected sections of ferro-manganese oxides (T = todorokite, D = delta MnO₂, P = phillipsite, Q = zeolite)

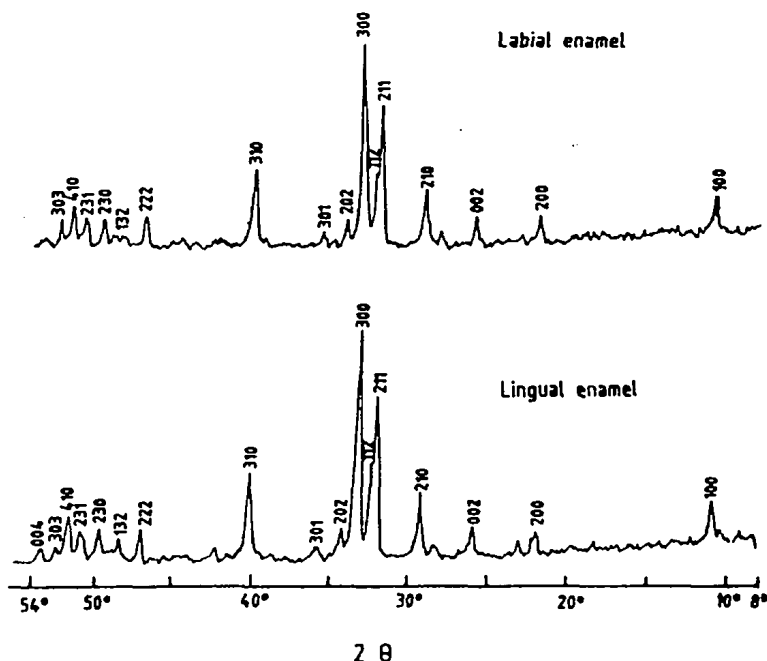


Fig. 4 - X-ray diffractograms of shark tooth enamel (all peaks numbered are hkl indices of carbonate hydroxy apatite).

Manifold enrichment of trace metals in the analysed enamel (in ppm: Mn, 22340; Fe, 6010; Co, 106; Ni, 474; and Cu, 318) which is of the similar order of tooth cavity filled sediments (Table 2 and Fig. 1), compared to mammal bones¹¹ (in ppm: Mn, 0.19; Fe, 200; Co, 0.87; Ni, 3.5 and Cu, 1) and human dentin¹² (in ppm: Mn, 0.6; Fe, 93 and Co, 1) suggests the possible replacement of Ca by Mn^{4+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} in carbonate hydroxy apatite (enamel) structure or the infilling of the gaps within the collagen fibrils of bone structure¹³ or the volume by volume replacement of apatitic material by Fe-Mn oxide as evident¹⁴ from the hard tubes of protozoans being totally replaced by Fe-Mn oxides during post depositional processes. Thus the post depositional decay of collagen and the replacement of apatite components by Fe-Mn oxide components during diagenetic processes may be responsible for the well crystallised carbonate hydroxy apatite i.e. enamel structure (Fig. 4). Similarity in the chemistry and mineralogy of Fe-Mn oxides on enamel to those on basaltic material or clay particles suggest that the nucleating material does not have any control over the mineralogy and chemistry of Fe-Mn oxides.

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