

Ferro-Manganese Encrustation on the Tympanic Bulla of a Minke Whale from Central Indian Ocean Basin

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Ear bone of a minke whale (*Balaenoptera acutorostrata*) was collected from 5200 m water depth with thin coating of Fe-Mn oxide on its surface. The Fe-Mn coating material was similar in nature and ratios Mn/Fe and Cu + Ni/Co were closely comparable to Fe-Mn nodules of Central Indian Ocean Basin. The enrichment of Mn, Co, Ni, Cu within the fresh part of the specimen might be due to the replacement of Ca by Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} in carbonate hydroxy apatite structure and or due to the easy path available for the movement of these metal ions through collagen fibrils and ultimate concentration and deposition within the gaps of collagen.

In the Central Indian Ocean Basin (CIOB) around lat. $12^{\circ}30'S$ and long. $76^{\circ}30'E$, a specimen of tympanic bulla (earbone) of a minke whale (*Balaenoptera acutorostrata*) was collected from 5200 m water depth along with Fe-Mn encrustations and basaltic fragments. The present paper describes the Fe-Mn coating on this specimen.

The specimen weighs 340 g and is highly pitted. The pits are filled with thin layer of Fe-Mn oxide (Fig. 1). The inner part of the specimen on the other hand is quite fresh without any noticeable oxides (Fig. 2).

Sample taken from the inner fresh part was powdered to -230 mesh, packed in an aluminium holder and scanned from $20^{\circ}2\theta$ to $36^{\circ}2\theta$ on a Philips XRD. Samples from inner fresh part and 3 mm thick pitted surface (Fig. 2) on which Fe-Mn coating was found were analysed in duplicate for Mn, Fe, Co, Ni and Cu along with USGS A-1 manganese nodule standard. During the sampling of surface a substantial amount of bone material was mixed up with Fe-Mn oxide coating material. All samples in duplicate were finely ground, dried at $105^{\circ}C$ for 12 h, cooled in desiccator and weighed. Dried samples were dissolved in 3N HCl without destroying the collagen. The residue left over after digestion was filtered through Watman filter paper (no. 42) then dried and weighed. The weight of insoluble residue was deducted from the original dry weight of the sample and used for the metal concentration calculations. The sample solutions were analysed on atomic absorption spectrophotometer (Perkin-Elmer, PE-5000).



Fig. 1 - Tympanic bulla showing tympanic cavity and Fe-Mn oxide thin coating

In order to understand the metal variations, Mn/Fe and Cu + Ni/Co ratios were calculated and compared with those Fe-Mn nodules of CIOB¹.

In the X-ray diffractogram, reflections at 25.7° (002), 31.8° (211) and 32.9° (112) 2θ are of carbonate hydroxy apatite which are poorly resolved

Table 1 – Comparison of Tympanic Bulla Element Concentrations with Fe – Mn Nodules, Mammal bone and Human Dentin (Values are in ppm)

Element	Inner fresh part of tympanic bulla	Outer 3 mm thick surface of tympanic bulla	Fe – Mn nodules from CIOB ¹	Mammal bone (Apatite) ²	Human dentin ³
Mn	29	0.184 *	20.4 *	0.19	0.6
Fe	407	0.086 *	09.6 *	200	93.0
Co	28	41	1400	0.87	1.0
Ni	56	222	8650	3.50	—
Cu	16	256	7450	1.00	—
Ratios					
Mn/Fe	0.07	2.14	2.12		
Cu + Ni/Co	2.6	11.6	11.5		

* Average of 41 analyses

* Values are in percent

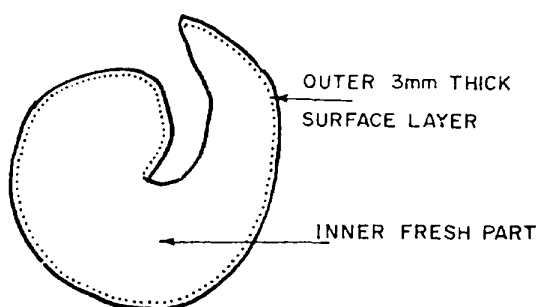


Fig. 2 – Schematic diagram of cross-section of the tympanic bulla

indicating a poor degree of crystallinity. Ratios Mn/Fe and Cu + Ni/Co of tympanic bulla surface coating (Table 1) are closely comparable with those of Fe – Mn nodules of CIOB¹. Inner fresh part of the tympanic bulla shows a relatively manifold enrichment of these metals when compared with mammal bone² and dentin of human tooth³ (Table 1).

Mn/Fe ratio of <2.5 indicates the hydrogenetic growth of Fe – Mn oxides⁴ and this appears to be the case with Fe – Mn oxide coating on the specimen. This is also supported by the more or less similar trends of enrichment of metals in the surface thin layer analysed when compared to those of average compositional values of CIOB nodules; however, the values for the specimen surface are substantially low because of the presence of bone material mixed with Fe-Mn oxide thin coating while sampling and which was unavoidable. As far as the relatively high concentration of these metals within the innermost fresh part of the

specimen when compared to mammal bone two arguments can be advanced to explain this enrichment – a) post depositional replacement of Ca and P by these metals and b) infilling of the gaps within the collagen by these metals.

Though trace metals like Fe, Cu, Zn and Co are necessary for the metabolic processes of animals the concentration of these metals in the inner fresh part of the tympanic bulla are much higher and this can be explained by enrichment from external source only. These metals may enter into the carbonate hydroxy apatite structure on a limited scale⁵. In Fe – Mn nodules, Co is associated with Fe and this may explain the same order depletion of Fe and Co in the inner fresh part of the tympanic bulla when compared to Fe – Mn oxide coating. The gaps within the collagen fibrils might also act as pathways and site of mineralisation in bone⁵.

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