

MORPHOLOGY AND GEOCHEMISTRY OF THE POLYMETALLIC NODULES FROM THE CENTRAL INDIAN OCEAN BASIN

G. KUMAR^{*} and S. K. TIWARY^a

BIT Sindri, DHANBAD – 828 123 (Jharkhand) INDIA ^aISRO-EDUSAT Center, UGC-ASC, Banaras Hindu University, VARANASI – 221005 (U. P.) INDIA

ABSTARCT

Polymetallic nodules, also called **manganese nodules,** are rock concretions on the sea bottom formed of concentric layers of iron and manganese hydroxides around a core. The core may be microscopically small and is sometimes completely transformed into manganese minerals by crystallization. When visible to the naked eye, it can be a small test (shell) of a microfossil (radiolarian or foraminifer), a phosphatized shark tooth, basalt debris or even fragments of earlier nodules. They generally range in size from 0.5 cm to 25 cm in diameter but the average diameter being 2 to 4 cm. However, the largest nodule ever recorded weighed about 800 kg.

The shape of nodules vary from spheroidal to oblate, discoidal or prolate. Mostly they are asymmetrical. Truly symmetrical shapes are quite rare. Near spherical shapes have been observed in smaller nodules. It may be said that the shape of the nodules is determined by their growth pattern and is a reflection of gross internal structures and the proximity of the nodules to the mud water interface. The morphology of the nodules depend to a large extent upon the shape of nucleus and is often responsible for the enrichment of the metals. In the present paper, an attempt has been made to classify the most common type of nodules found in the Central Indian Ocean Basin alongwith their genesis and chemistry.

Key words : Polymetallic nodules, Phosphatized shark tooth, Basalt debris, Fragments, Morphology, Genesis.

INTRODUCTION

The ferromanganese deposits in the deep sea represent an important class of authegenic mineral deposits forming at the present time. They result from diverse chemical reactions on the sea floor and can in principle be used to provide information on physical,

^{*}Author for correspondence; E-mail: drgkumar12@gmail.com, Tel.: +91-326-2253425; 2251957; 09431123438; Fax: +91 326 2350729

chemical and biological processes taking place in the ocean as a whole. Significant advances have recently been made in providing information on their geochemistry, an essential prerequisite for understanding their wide compositional variations and their mode of formation. Oceanic ferromanganese deposits occur mainly in two forms, as nodules and as encrustations; while the nodules form a carpet on the deep-sea abyssal plains, encrustations occur as caps on seamounts

Polymetallic nodules are small balls, dark-brown colored and lightly flattened, 5 to 10 centimeters in diameter, which lay on the seabed at 4, 000 to 6, 000 meters deep, i. e. above CCD. However, the reddish brown colour is exhibited by nodules having high Mn content. Hardness of the nodules is variable and ranges from 1 to 4 on Moh's scale of hardness. However, the normal hardness is 2 to 3. Nodules with more than 5 % CaCO₃ are hard and with less than 2 % CaCO₃ are soft and friable in nature. Clays present in them also affect the hardness. They are somewhat porous and thus, light. Their specific gravity varies between 2 to 3 g/cm³, their water-content is 40 % of their dry-weight and their porosity is 50 %.

The nodules occur invariably in almost all the deep-sea basins witnessing low sedimentation rates. But abundant ore grade deposits are limited to Equatorial North Pacific (Clarion-Clipperton fracture Zone), Cooks Island and Central Indian Ocean Basin. The Atlantic Ocean nodule deposits are scanty; probably due to high input of terrigenous sediment relative to its small size, hindering growth of nodules. During 1965, the nodule deposit of the world oceans is between 1.7 to 3 trillion tons.

The distribution and abundance of nodules is governed by rate of sedimentation, the length of time available for their accretion and availability of nucleating material. In general, the low sedimentation rates lead to higher abundance of nodules. Therefore, the areas receiving low sediment input of the order of 1-5 mm – 1000 Yrs^1 are enriched with abundant nodules. In addition, Banakar et al.² related the erosion of younger sediment in the Central Indian Basin to the occurrence of abundant nodules. They suggested that the sediment erosion activity probably keeps the nodules at sediment water interface facilitating their growth process

Polymetallic nodules from the Central Indian Ocean Basin largely range in size from 2 to 6 cm. The smaller nodules (< 4 cm) are subspheroidal to spheroidal in shape and with the increase in size, nodules become more discoidal and elongated. The size and relief of mammillae vary with the size of nodules. Polynucleate nodules are more abundant in larger size classes (> 6 cm) and in stations closer to the oceanic ridge. Density varies

significantly with shape; less rounded nodules are denser than well-rounded ones.

Description of sample and their location

30 nodule samples of various shapes and sizes were selected for the present study. These samples were raised on board by the Cruise "GA REAY - 1". These samples have been grouped into three categories on the basis of their sizes, namely:

(i) Small nodules : Size less than 2 cm
(ii) Medium nodules : Size 2-4 cm
(iii) Large nodules : Size more than 4 cm

These nodules were raised during the polymetallic nodule exploration programme of the Govt. of India during the year 1985 through several rounds of free fall grab and dredging modes of sampling. These samples were collected by the author (GK) who was one of the Scientists on board during that cruise. The samples are mainly obtained from the latitude $9.5-12^{\circ}$ S and longitude $87-89.5^{\circ}$ E and water depth varying from 4, 500 - 5, 500 m.

Methods of on board sample collection

Various techniques involving sampling devices have been deployed to bring material from water depth of 4500-5500 m. These methods include –

- (i) Free Fall Grab Sampling
- (ii) Dredging
- (iii) Coring etc.

In the present work, sampling by free fall garb and dredging have been employed. Table 1 illustrates the size frequency analysis of nodule recovery during this exploration programme :

Table 1.	Size frequency analysi	s of nodule recovered by	preussag free fall grab
	(Cruise GA REAY - 1)	in the Central Indian	Ocean Basin.

Nodule		No. of sam	ples recovered	
size	Operation I	Operation II	Operation III	Operation IV
00-20 mm	255 (46 %)	211 (37 %)	295 (45 %)	228 (43 %)
				Cont

Nodule	No. of samples recovered						
size	Operation I	Operation II	Operation III	Operation IV			
20-40 mm	128 (23 %)	188 (34 %)	197 (30 %)	145 (28 %)			
40-60 mm	82 (15 %)	96 (17 %)	95 (15 %)	98 (19 %)			
60-80 mm	64 (11 %)	45 (8 %)	49 (7 %)	37 (7 %)			
> 80 mm	28 (5 %)	24 (4 %)	18 (3 %)	17 (3 %)			

It is important to note that the greatest number of individual nodules occur in the smaller size fractions, with rapid decrease in the relative number of nodules with 4 cm or larger diameter. Possible explanations for this decreasing trend include winnowing mechanisms or selective burial of the larger nodules, coalescence of smaller nodules into larger ones, or perhaps improved conditions for nodule nucleation and accretion. It is equally plausible that fewer areas of long-term low sediment accumulation, which are conducive to the continuous accretion of larger nodules, exist on seafloor. However, often nodule samples recovered from single free fall grabs contain many different nodule types and all size ranges.

Nodule morphology

Since the initial description of nodules recovered by the Challenger Expedition, Murray and Renard³, no publication has provided a widely accepted terminology or classification system to deal with the variety of nodules recovered from the deep-sea. A classification scheme provided by Meyer⁴ resulted from nodule recovery operations of the VALDIVIA in the siliceous region. The seven nodule types listed by Meyer are based on size, primary shape, surface texture, intergrowth frequency and internal structure; however, many nodules show examples of transitional features and are inaccurately described by any single category.

Another attempt at classification was made to allow for the apparent variability of these nodules Andrews and Friedrich⁵. The primary rational behind this classification system was a need for a brief, unambiguous and yet informative nomenclature for field description of manganese nodules. This classification system, is based on size, primary morphology and surface texture, with no attempt at internal description or inferred genesis. Apart from Meyer⁴, Meylan⁶ classification is also used with marginal modification. During the initial stages of accretion, the shape of nodule generally follows the shape of nucleating material, but on continued growth the shape smoothes out to a nearest spheroid or discoid.

A summary of nodules morphology is given in Table 2. It is important to note that the relative proportions of the major nodule types are fairly constant and that tabular, faceted and biological nodule types are of limited occurrence.

Examples : 1[D]b	=	Large discoidal nodule with 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
m-1[F]r	=	Medium to large nodule fragment with a rough surface

The morphological features of the nodules for this study have been presented in Table 3 and the nodules samples are shown in Plates 1 - 4, while the nucleating matter of some of the nodules are shown in Fig. 1 and 2, i. e. within the nodules polished section.

Table 2 :	Field classification of	f ferromanganese nodules.
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Nodule size	:	0 to 3 cm = small (s); 3 to 6 cm = medium (m) +6 cm = large
Primary morphology		[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)
Surface texture	:	s = Smooth (or microgranular)
		r = Rough (or microbotryoidal)
		b = Botryoidal

Sample numbers	Morphology (Surface texture)	Sample numbers	Morphology (Surface texture)
1	m(S-E)s	16	m(D)s
2	s(S-E)r	17	s(S)r
3	m(P)s	18	s(S)r
4	m(D)r	19	l(E)r
5	s(S)r	20	l(E)s
6	s(S)s	21	l(D)r
7	m(B)s	22	l(S)r
8	m(D)s	23	l(B)s
9	m(B)s	24	l(B)s
10	m(D)r	25	l(B)r
11	s(E)r	26	l(S)s
12	s(B)r	27	l(E)r
13	s(E)r	28	l(P)s
14	s(S)r	29	l(D)r
15	m(B)s	30	l(B)r
Small nodule	s : 09; Medium nodule	es: 09; Large 1	nodules : 12
Thus, Size	class < = 4 cm -	No. of nodule	e samples = 18
. Size	class > 4 cm -	No. of nodule	e samples = 12

 Table 3 : Morphology of the nodule samples

Several generalities may be made regarding primary nodule shape. Size and surface texture which greatly simplifies the seemingly endless variety of nodules recovered from the siliceous region. First is the relationship of nodule type to size. It seems that most larger nodules are of types [D] and [E], though large [S] types have been reported elsewhere⁷ and that these larger types are often transitional (i. e. [D-E]). Upon internal examination, it was discovered that most of these large nodules have nuclei consisting of fragments of pre-existing nodules and that the primary shape is often controlled by the shape of the fragment. Excellent examples of this phenomenon are presented by Sorem⁸,

Sorem and Foster⁹ and Raab¹⁰. Many of the larger, irregularly shaped nodules could have been formed by removal of a portion of a whole nodule and subsequent re-growth over fractured surface by ferromanganese hydroxides. Smaller nodules occur mostly in [S] and [E] types, with uniform thickness of ferromanganese crusts surrounding a nucleus typically consisting of palagonite tuff. However, as in the larger nodules, the overall shape conforms to the shape of the nucleus. Type [P] nodules are probably by the coalescence of small type [S] and [E] nodules and owe their genesis to close contact and subsequent bonding of several nodules by ferromanganese hydroxides.

Nodule chemistry

The samples show considerable higher values for metals like Mn, Ni, Cu, Co and Zn and lower values for Fe, SiO_2 , Al_2O_3 , TiO_2 , P_2O_5 . The alkalis, namely Na₂O, K₂O, MgO also do not have the very significant values. Table 4 represents the compositional ranges of nodules of each size class.

Table 4 clearly indicates that the smaller nodules show higher metal concentrations and also that within the smaller nodules, those with the rough surfaces are exhibiting the higher metal values.

The Mn/Fe ratio of the nodules is an important criterion to distinguish between the diagenetic and hydrogenetic source for their formation. The diagenetic nodules have this ratio > 5; while the hydrogenetic nodules have this ratio < 2.5. In the present studies, this ratio varies from 2.38 to 3.66 (Fig. 3). Although, it is not possible to establish, what fraction of the ferromanganese oxyhydroxide was derived directly from sea water and what fraction was accreted during transformation and early diagenetic reactions within the sediments, Lyle et al.¹¹. Pattan¹² showed that the contribution of interstitial water to the outer diagenetic layer was about 75 % and that of sea water about 25 % based on a mixing model.

In order to compare the nodule compositions with the other metalliferous deposits, the ternary diagrams act as important tools. For this purpose, the ternary diagram (Ni + Cu + Co) x 10 - Mn - Fe is quite useful (Fig. 4). The variations in nodule chemistry seen over short seafloor distances could thus be explained by the episodic growth of various fraction of the nodule population responding to burial and erosion by sedimentary processes. The observed characteristics of both internal and external nodule structure are population parameters suggest the "episodic" nature of nodule development.

The most important nucleation mechanism for increasing the weight and coverage

of the nodule deposit is its "fragmentation". Fragments serving as nucleation sites have been recognized by a number of authors including Raab¹⁰ and Horn et al.¹³. Many bottom photographs show the effect of this fragmentation process on both the population size structure and density of coverage. It seems that the areas of dense nodule cover consist of irregularly shaped nodules of generally smaller size (probably fragmented larger nodules), while the lower coverage areas showed typically varied whole nodule populations. However, most bottom photographs show the mixing of fragmented and whole nodules of all sizes within a small area. As a localized nucleation mechanism, the fragmented process would produce a substantial increase in the surface area available for ferromanganese accretion, provide a compatible surface for this accretion, i. e. the "catalytic effect" discussed by Burns and Brown¹⁴; Fein and Morgenstein¹⁵ and increase the surficial coverage.



Fig. 1 : Polished section showing 03 nucleus (1st one is rounded, while the 2nd and 3rd being scattered



Fig. 2: Polished section of the nodule with distinct rounded uncles and 02 other elliptical (one complete and another incomplete on) with irregular fractures.

Values	S	ize class	(<2-4 cm)			Size class	(> 4 cm)		Sam	ples of al	ll size cla	sses
v alues	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD
						(in %)						
Mn	24.42	28.92	26.50	1.43	22.94	25.72	24.34	0.98	22.94	28.92	25.63	1.66
Fe	7.92	10.11	8.64	0.78	9.09	10.15	9.72	0.38	7.92	10.11	9.07	0.86
SiO_2	13.41	16.51	14.63	0.94	13.73	15.98	15.09	0.67	13.41	16.51	14.81	0.89
Al_2O_3	2.92	3.55	3.16	0.19	2.98	3.68	3.33	0.27	2.92	3.55	3.22	0.74
CaO	2.11	2.62	2.37	0.17	2.23	2.82	2.53	0.17	2.11	2.62	2.43	0.19
MgO	1.68	1.99	1.83	0.11	1.44	2.04	1.75	0.02	1.44	1.99	1.80	0.16
Na_2O	1.22	1.75	1.44	0.17	1.41	1.78	1.67	0.10	1.20	1.75	1.53	0.18
K_2O	0.89	1.19	1.03	0.10	1.04	1.21	1.11	0.05	0.89	1.19	1.06	0.09
Cu	1.02	1.22	1.13	0.07	1.01	1.11	1.05	0.03	1.02	1.22	1.10	0.07
Ni	0.98	1.24	1.09	0.09	0.97	1.08	1.00	0.03	0.97	1.24	1.05	0.08
						(in ppm)						
TiO_2	6800	8300	7694	390	7400	8400	7917	276	6800	8400	7783	372
${\rm P_2O_5}$	2200	3800	2906	486	2700	3600	2625	375	2200	3800	3003	468
Zn	1400	1900	1633	160	1400	1700	1525	92	1400	1900	1500	149
Co	1600	2800	2100	245	1600	2100	1783	134	1600	1983	1846	218
Pb	006	1800	1244	313	1100	1800	1244	313	006	1800	1357	310
Sr	600	1400	906	321	006	1600	1350	189	009	1600	1103	308

Table 4 : Compositional variations among nodules of different size classes

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Fig. 3 : Si – Mn – Fe diagram to show the various sdiments phases¹⁶



Fig. 4 : (Ni+Cu+Co) x 10 – Fe – Mn diagram showing the field of hydrogentic and diagnostic nodules

The mechanism(s) by which nodules are fractured on the seafloor is not apparent at this time. The role of relatively sluggish bottom water movement and the influence of benthonic organisms as fracturing agents are considered negligible compared to the impact strength of unaltered whole nodules. Nodule fracturing during the grab sampling process is relatively common (evidenced by freshly fractured nodules); however, it is suggested that the fracturing processes is initiated by internal stressed created by diagenesis involving ferromanganese mineral recrystallisation and/or hydration/dehydration reactions and requires little or no outside force to occur.

Governing factors for nodule morphology

Initially, the governing factor for nodule morphology is the nucleating size and shape and thus, nodules may be:

(i)	Mononodule	:	Simple nodule, spherical or ellipsoidal,
(ii)	Polynodule	:	A nodule with several cores,
(iii)	Composite nodule	:	Several joined nodules.

During the initial stages of accretion, the shape of nodule generally follows the shape of nucleating material, but on continued growth, the shape smoothes out to a nearest spheroid or discoid. The rough surface nodules are less enriched in the metal content and indicate an earlier stage of nodule formation whereas the rounded and smooth source nodules are more enriched in metal content as a result of growth pattern from the Hydrogenous as well as sea bottom interface¹⁶. In section, most nodules show concentric layers called "cortex" that correspond to the successive step of growth around a "core", often microscopic. The core can be a fragment of an old nodule, a shark tooth or a rock fragment (basalt, limestone, etc...). The layers are formed of hydroxides of manganese and iron more or less crystallized. The more crystallized are (todorokite, birnessite), the richer in Mn, Ni and Cu, while cryptocristallized structures (vernadite) are richer in Fe and Co. The growth rate of the nodules is one of the slowest phenomenon (in the order of a centimeter by several millions years). The age of Pacific Ocean nodules is 2 to 3 millions years. A complex interplay of factors like the degree of oxidation of the depositional environment, abundance of nucleating agents, proximity of source elements, sedimentation rates in the areas, bottom current activity, existence of benthic organisms, biological productivity in surface waters and many other as yet unidentified phenomena determine nodule density¹⁷.







CONCLUSIONS

The Central Indian Ocean Basin is the most promising zone of nodule occurrence. In this basin, the nodules with different morphological features are present. The nodules are not monomineralic. Instead they composed of several phases intimately intergrown leading to a complex mineral composition. The nodules contain detrital grains, Fe-Mn oxide phases, organic matter and biogenic skeletons of microfauna. The major component is the authigenic Fe-and Mn-oxides. The observed characteristics of both internal and external nodule structure are population parameters suggest the "episodic" nature of nodule development. The most important nucleation mechanism for increasing the weight and coverage of the nodule deposit is its "fragmentation" and that is the most important deciding factor for the morphology of the nodule. However, the morphology of the nodule is also decided by the accretion process, which accounts for nodule formation as inorganic precipitation of metal oxides. According to this hypothesis, the nodule accretion takes place mainly due to hydrogenetic and or diagenetic processes. In hydrogenetic process, the source of the metals is the sea-water, while in diagenetic process, the main source of metals is the interstitial water trapped within the sediment column. The variation of Mn/Fe ratio from 2.38 to 3.66 of these nodules is mainly attributed to the Hydrogenetic Phase.

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