

52 **PABA**

Home Report

## DATA ON THE GEOCHEMISTRY OF MANGANESE NODULES FROM THE INDIAN OCEAN

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### (ABSTRACT)

Analyses are given for the core and outer colliform shell of a manganese nodule collected at a depth of 5000 m in the Indian Ocean, and for the red clay that encloses the nodules. Trace elements determined include rare earths, Nb, Ta, Th, and V.

The cores of the nodules were once composed of basaltic rock, but now are phillipsite and nontronite. The outer shell is composed of manganite, with admixed quartz, phillipsite, and some goethite. The correlations established between the redox potentials and the concentration coefficients for 12 elements indicate that Eh plays a greater role in the formation of the manganiferous shells than coprecipitation properties.

### INTRODUCTION

Interest in abyssal oceanic sediments has grown considerably in recent years, and particular attention has been paid to manganese nodules that occur over vast areas of the ocean floor [1-5]. The manganese nodules of the Pacific and Atlantic oceans have been studied in some detail, but there is little information on manganese nodules from the Indian Ocean.

The materials used in this investigation were manganese nodules and red clay collected by L. M. Khitrov at stations 4575 and 4555 in the Indian Ocean during the 1959-1960 cruise of the oceanographic vessel "Vityaz" (see map [6]). The materials were collected from a depth of 5000 meters.

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## MINERALOGICAL DESCRIPTION OF THE SAMPLES

The nodules are flattened ellipsoidal bodies that range from 3 to 20 cm in length. Nodules from station 4575 have a well defined white core and a black outer shell, but nodules from station 4555 have either a very small core or none at all. The outer shell has a well-defined colloform structure.

Mineralogical investigation of the shell shows that it is composed of Fe(III)-manganite and admixed quartz, phillipsite, and a small amount of goethite.

The manganese mineral was identified as Fe(III)-manganite on the basis of the similarity of its X-ray powder pattern (Table 1) to the pattern obtained by Buser from nodules from the Pacific [7].

Table 1

Outer Shell of Nodule from station 4575. Core of Nodule from station 4575.

d/n	l	d/n	l	d/n	l	d/n	l
4,97	1	1,535	3	4,97	3	1,891	0,5
4,28	1	1,416	7	4,46	9	1,833	2
3,73	0,5	1,368	6	4,02	4	1,779	3
3,34	10	1,284	1	3,76	3	1,714	3
3,19	5	1,254	1	3,53	4	1,671	3
2,95	0,5	1,223	0,5	3,34	1	1,628	2
2,46	7	1,195	2	3,19	10	1,605	1
2,27	1	1,179	2	3,00	1	1,506	8
2,13	1	1,077	3	2,95	2	1,473	4
1,986	0,5	1,046	1	2,82	4	1,364	0,5
1,915	0,5	1,031	2	2,71	6	1,343	2
1,876	0,5	1,012	1	2,51	7	1,298	3
1,818	4	—	—	2,39	1	1,257	3
1,727	0,5	—	—	2,07	2	1,216	2
1,664	2	—	—	2,00	3	1,168	1
		—	—			1,152	1

D = 57.3 mm; Fe radiation.

Photographs by K. Fedotova, calculated by A. Volkova.

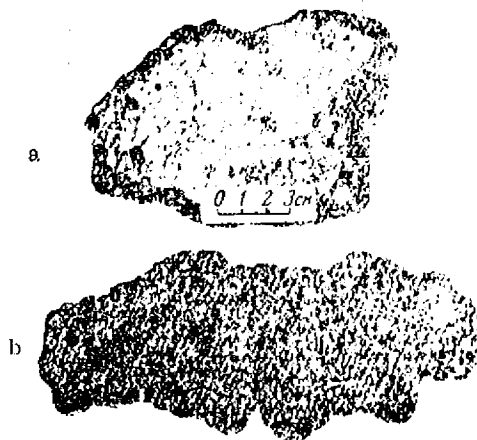
Note: All commas are equivalent to decimal points.

Buser identified his material by comparison with the X-ray powder pattern of synthetic Fe(III)-manganite, which is Mn(II)-manganite ( $Mn_2O_7 \cdot nH_2O$ ) with Mn(IV) partially replaced by Fe(III). This mineral has the structure of lithiophorite. The correctness of this identification of the principal mineral in the Indian Ocean nodules as Fe(III)-manganite is confirmed by the fact that although the mineral contains a considerable amount of iron (~18%  $Fe_2O_3$ ), the powder photographs show only a small amount of free iron hydroxide (goethite).

The core of the nodules is composed mainly of phillipsite mixed with nontronite (Table 1).

## ANALYTICAL METHOD

The rare earths were determined as hydroxides and oxalates after preliminary



Manganese nodules from station 4575  
a--polished surface, b--general view

enrichment by X-ray spectrographic analysis on the DRUS instrument in the X-ray laboratory of the IMGRE [8]. Niobium and tantalum were determined spectrochemically by an improved method described in [9].

Vanadium and thorium were determined by methods described in the literature [10, 11], and the alkalis (Na and K) were determined by flame photometry.

#### DISCUSSION OF RESULTS

As can be seen from Tables 2, 3, and 4, there is a sharp difference between the chemical composition of the core and the outer shell of the manganese nodules. The outer shells are similar in composition to the outer Mn-Fe shells of the nodules from the Pacific Ocean [2, 12, 13, 14].

There is very little information on the contents of RE, Nb, and Ta in the nodules, and for this reason we shall discuss our data in some detail.

The composition of the RE group in the nodules from the Indian Ocean is characterized by a Ce maximum and a small Dy maximum, and may be called selectively cerian. In their cerian character the manganese nodules resemble other deep-sea sediments (for example, see the data on the composition of phosphatic nodules from the Pacific [11] and El Wakeel's data [4]), but they exhibit a greater degree of selectivity.

It was shown by Rankama [16] that manganese nodules are strongly enriched in Nb as compared with other deep-sea sediments.

Our data show that the Indian Ocean nodules are enriched in Nb, and also that niobium and tantalum are separated in the process of formation of the nodules. Two factors are evidently responsible for the separation of these very closely related elements.

First, because of its greater chemical inertness tantalum does not pass into solution as readily as niobium, and second, in aqueous solutions niobium is "masked" by titanium to a greater degree than tantalum [17], as shown by the constancy of the Nb/Ti ratio, and niobium follows titanium during the formation of the nodules (Table 5).

Table 2

Chemical Composition of Manganese Nodules and Red Clay (wt. %)

Components	Nodule, sta. 4575		Red clay, station 4575	Components	Nodule, sta. 4575		Red clay, station 4572
	outer shell	core			outer shell	core	
SiO <sub>2</sub>	15,29	47,11	40,38	MgO	not det.	4,22	3,29
TiO <sub>2</sub>	1,44	1,77	0,74	CaO	not det.	2,21	0,74
Al <sub>2</sub> O <sub>3</sub>	5,77	13,67	17,26	Na <sub>2</sub> O	2,43	3,77	5,72
Fe <sub>2</sub> O <sub>3</sub>	17,78	14,29	6,62	K <sub>2</sub> O	0,47	1,03	2,71
FeO	0,85	0,38	0,52	P <sub>2</sub> O <sub>5</sub>	0,48	0,13	not det.
MnO	22,30	0,46	0,68	Org	0,36	0,45	1,04

N. V. Yeremeyeva, analyst.

Note: All commas are equivalent to decimal points.

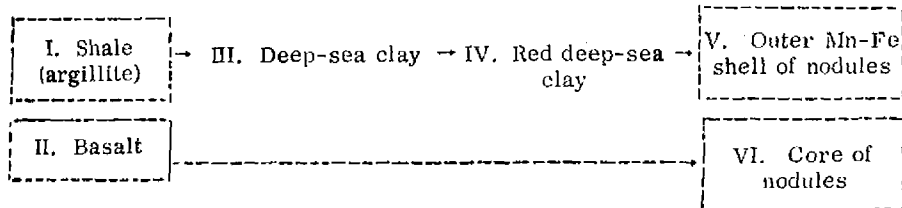
Table 3

Content of Trace Elements (wt. %)

Element	Nodule from sta. 4575		Nodule from sta. 4555		Red clay, station 4572
	outer shell	core	outer shell	core	
Nb <sub>2</sub> O <sub>5</sub>	42,0 · 10 <sup>-4</sup>	11 · 10 <sup>-4</sup>	not det.	not det.	22,6 · 10 <sup>-4</sup>
Ta <sub>2</sub> O <sub>5</sub>	0,21 · 10 <sup>-4</sup>	2,79 · 10 <sup>-4</sup>	"	"	0,85 · 10 <sup>-4</sup>
V	9,0 · 10 <sup>-2</sup>	1,8 · 10 <sup>-2</sup>	6,5 · 10 <sup>-2</sup>	1,0 · 10 <sup>-2</sup>	not det.
Th	20,8 · 10 <sup>-4</sup>	3,7 · 10 <sup>-4</sup>	23 · 10 <sup>-4</sup>	7,7 · 10 <sup>-4</sup>	12,8 · 10 <sup>-4</sup>
ΣRE	0,20	not det.	0,10	not det.	not det.

Note: All commas are equivalent to decimal points.

To determine the origin of the manganese nodules we examined the content and proportions of certain elements in the following series of rocks:



In this series of rocks, two members (I and II) are apparently the principal source of deep-sea sediments. Member I is terrigenous material (clay suspension) with the average composition of argillaceous sediments (argillite or shale according to Turekian and Wedepohl [18]) and member II is a product of submarine volcanism (basalt).

The rest of the members represent a single genetic series of deep-sea deposits that reflect successive stages of alteration of the initial material. The

Table 4  
Content of the Rare  
Earths (% of  $\Sigma$  RE = 100)

Element	Outer shell, sta. 4575	Core, station 4555
La <sub>2</sub> O <sub>3</sub>	7,71	3,67
Ce <sub>2</sub> O <sub>3</sub>	55,67	67,43
Pr <sub>2</sub> O <sub>3</sub>	6,86	1,38
Nd <sub>2</sub> O <sub>3</sub>	6,42	8,73
Sm <sub>2</sub> O <sub>3</sub>	1,71	2,75
Eu <sub>2</sub> O <sub>3</sub>	0,43	0,91
Gd <sub>2</sub> O <sub>3</sub>	0,43	2,29
Tb <sub>2</sub> O <sub>3</sub>	0,22	0,46
Dy <sub>2</sub> O <sub>3</sub>	14,13	3,67
Ho <sub>2</sub> O <sub>3</sub>	1,28	0,91
Er <sub>2</sub> O <sub>3</sub>	1,28	2,29
Tm <sub>2</sub> O <sub>3</sub>	0,43	0,46
Yb <sub>2</sub> O <sub>3</sub>	3,00	4,59
Lu <sub>2</sub> O <sub>3</sub>	0,43	0,46
$\Sigma$	100,00	100,00

Note: All commas are equivalent to decimal points.

manganese nodules are the final product of this process.

Examination of the chemical analyses given in Table 5 leads to a number of conclusions.

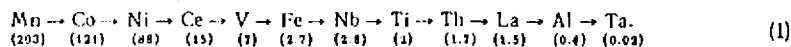
1. The similarity between the contents and ratios of some of the elements (Mn, Fe, Ti, Th, Ti/Al, K/Na) in basalts and in the cores of the nodules suggests that the cores were formed mainly from volcanic material.

2. In the other members of the series (from shale to the outer shell of the nodule), there are regular increases in the contents of Ni\*, Co\*, Mn, and Ce while the contents of Fe, V, Ti, Th, and Nb remain constant through the whole series except in the outer shell of the nodules, and then rises abruptly. The content of lanthanum is constant throughout the series, and the contents of Al and Ta decrease in the outer shell of the nodules.

3. An interesting feature of the series is the tendency of chemically related elements to separate.

For instance, the Nb/Ta ratio which is 13.8 in the shales increases in the abyssal red clay to 22.6, and reaches 170.5 in the outer shell of the nodules. Some other ratios behave in the same way.

4. The elements are concentrated to different degrees in the outer shell of the nodules. Arranged in the order of decreasing concentration coefficients, the elements fall into the following sequence:\*\*



As can be seen from this sequence, elements with variable valence have the highest concentration coefficients.

The concentration coefficient of iron may have a higher value because the nodules analyzed are relatively low in iron as compared with the Fe-Mn nodules described in the literature\*\*\*.

If the same elements are arranged in the order of diminishing redox potential, they give the following series:\*\*\*\*

\* Data from reference [18].

\*\* The coefficient of concentration =  $\frac{\text{content of the element in the outer shell of the nodules}}{\text{content in shale}}$ . If the content of an element in the red clay is taken as the numerator the values of the coefficients decrease but the general tendency is preserved.

\*\*\* It should be noted that since the average Fe content in clays is (~4.7%) its concentration coefficient cannot be higher than ~15.

\*\*\*\* Values of Eh are given for pH = 8 [20, 21].

Table 5

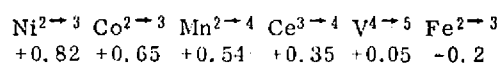
The Table is Based on Our Data (for Red Clay and Nodules) and on the Data of Turekian and Wedepohl [18]

Elements and ratios	Shale (I)	Deep-sea clay (III)	Red clay (IV)	Outer shell of Nodules (V)	Basalt (II)	Core of Nodules (VI)
Mn	0,085	0,67	0,52 0,94*	17,25	0,15	0,35
Fe	4,72	6,5	5,04	12,7	8,65	10,3
Mn/Fe	0,02	0,1	0,1	1,3	0,017	0,03
Co·10 <sup>-2</sup>	0,19	0,74	0,90	23	0,48	not det.
Ni·10 <sup>-2</sup>	0,68	2,25	2,60	60	1,3	»
Co/Ni	0,28	0,33	0,35	0,30	0,37	»
V·10 <sup>-2</sup>	1,3	1,2	1,3	9,0	2,5	1,8
Al	8,0	8,4	9,15	3,04	7,8	7,24
Ti	0,46	0,46	0,44	0,86	1,38	1,01
Ti/Al·100	5,7	5,4	4,8	28,2	18,0	14,2
Nb·10 <sup>-4</sup>	11,0	14,0	15,6	29,0	19,0	7,6
Nb/Ti·10 <sup>-4</sup>	24	30,0	35,4	33,7	13,8	7,3
Ta·10 <sup>-4</sup>	0,80	—	0,69	0,17	1,10	2,33
Nb/Ta	13,8	—	22,6	170,5	1,3	3,28
La·10 <sup>-3</sup>	9,2	12,0	5,5—13,0**	13,0	1,5	not det.
Ce·10 <sup>-3</sup>	5,9	13,0	14,0	89,5	4,8	»
Th·10 <sup>-4</sup>	12,0	7,0	12,8	20,6	4,0	3,7
K/Na	2,77	0,63	0,53	0,22	0,46	0,48

\* Landergren's data [19].

\*\* Data for the Indian Ocean after El Wakeel et al [4].

Note: All commas are equivalent to decimal points.



(2)

A comparison of series (1) and (2) shows that the sequence of the first three elements is reversed, while the sequence of the other three elements remains the same. This can be explained in the following way. The values of Eh and pH in the ocean measured by several investigators [22-25] are as follows:

Near-bottom sea water	pH 8, Eh +0.4
Red abyssal clays	pH 8, Eh +0.4; +0.6
Abyssal ooze beneath red clay	pH 7-8, Eh up to -0.2

When the boundary between the oxidizing and reducing zones rises, the sediments enter a zone with lower Eh values and their constituent elements are reduced and pass into solution [26]. Elements with high redox potentials are more easily reduced, their concentrations in the pore solutions increase, and they diffuse towards the surface of the sediments where their concentrations are lower. As the elements move upwards, those with the higher potentials are precipitated first, and the result of these two processes is a strong fractionation of the elements. Manganese, for example, has a higher redox potential than iron and will pass into solution more readily in the reducing

zone. At the same time, during the upward movement iron because of its lower potential will be precipitated sooner than manganese.

Thus, solutions near the surface of the sediments will be enriched in manganese as compared with iron. The fractionation of the elements is enhanced as this process is repeated again and again with gradual burial of the sediments\*.

The maximum value of Eh in the bottom environment is +0.6 (approximately equal to the redox potential of Mn), and elements with higher potentials are difficultly oxidized. Therefore, the high concentrations of Ni and Co in the nodules are only partially explained by oxidation. A definite role is played here by their coprecipitation with Mn hydroxides [27, 28]. Elements with redox potentials closer to the redox potential of Mn will be coprecipitated to a greater degree.

In view of all this, series (1) and (2) may be considered identical for elements with variable valence.

Thus, the clear correlation between the redox potentials and the concentration coefficients of Mn, Co, Ni, Ce, V, and Fe in the manganese nodules indicates that Eh plays the most important role in their concentration.

The concentration of the elements which do not change their valence in the deep sea environment (Th, Nb, Ti)\*\* evidently is caused by sorption on Mn hydroxides [28, 29].

#### Summary

1. New data have been obtained on the contents of some rare elements (RE, Nb, Ta) in manganese nodules from the Indian Ocean.
2. The data obtained suggest a genetic relation between the core of the nodules and volcanic material.
3. The correlation established between the redox potentials and the concentration coefficients for some elements in the manganese nodules indicates that Eh plays the dominant role in the formation of the nodules.

In conclusion the authors express their thanks to L. M. Khitrov for providing material for this investigation, to all their associates who helped in the research, and to A. B. Ronov for reading the manuscript and making a number of valuable comments.

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\* If a thick oxidizing zone were present, some elements might pass into pore solutions in the oxidized form and diffuse into the upper part of the sediments and the bottom water as a result of the formation of a concentration gradient.

\*\* In this environment Nb and Ti exist only in the higher valence state because their redox potentials are considerably lower than the lower Eh limit in the sediments.

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