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GEOCHEMICAL ASPECTS OF FORMATION OF FERROMANGANESE ORES IN SHELF REGIONS OF RECENT SEAS

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INTRODUCTION

Relatively large deposits of Mn and Fe-Mn ores which have been forming during the geological history within the existing continental frontiers are as a rule associated with the deposits of the shelf zones in the paleobasins. This is especially true of the past ore-bearing basins which have preserved fairly enough the initial relationships of the basic facies elements, these being Nikopol, Bolshoy—Tokmak deposits in the South-Ukraine Oligocene Basin, Chiatura and other deposits in Georgia [I. M. VARENTSOV, 1963, 1964; G. A. AVALIANI, 1967; I. M. VARENTSOV, E. S. BASILEVSKAYA *et al.*, 1967].

It is not infrequent that manganese and iron-manganese deposits are still discussed not from the standpoint of the conditions for ore accumulation proper, the obvious evidence for their association with the shelf zone being often the case, but from the standpoint of the nature of sources for ore-forming components. Numerous data have persisted into the recent time which are being used to substantiate either endogenous or, on the contrary, exogenous nature of ore components accumulating in the shelf zone of a basin. The study of the Chiatura Lower Oligocene deposit in Georgia, of the Varna Oligocene deposit in Bulgaria, of the Usin Lower Cambrian deposit in the Kuznetsk Alatau, the Upper Devonian Fe-Mn Deposits of the Atasui Region in the Central Kazakhstan and some others offers the examples of an attempted alternative solution for the problem of the nature of ore-forming components.

Although no recent basins displaying formation of manganese and iron-manganese ores can be directly compared with old ore-forming basins, the study of ore-formation processes is of some interest. Among other factors in such a study, the evaluation of those governing ore-formation stands most prominent: the features of localization of recent ore accumulation, sources for components, nature of solutions, geochemical features of environment, the mechanism governing the formation of ore substance accumulation. To put it another way, the study of formation of iron-manganese and manganese ores in the recent basins may prove to be one of the tools for obtaining knowledge on the past ore formation.

This paper aims at presenting the data of a comparative study of geochemical features involved in formation of iron-manganese ores with the conditions varying as wide as they do in such a basin as the Baltic Sea. The aim has stimulated the selection of the following study objects: the Gulf of Riga, the Gulf of Finland, the Central Baltic (the area of Gdansk and Klaipeda). For purposes of comparison, the data for other shelf basins are given too.

MATERIALS AND METHODS

The investigations are based on the data obtained from thorough work carried out in the ranges specially selected in the Gulf of Finland, the Gulf of Riga, and in the Central part of the Baltic Sea. The investigations were carried out within the joint programme sponsored by the Geological Institute, USSR Acad. Sc., and the Atlantic Division of the Institute for Oceanology in Kaliningrad (A. I. BLAZHCHISHIN). The stations were spaced from one another over the range's network at a distance of 0,5 to 4 km depending on the variations in sediments, the sea floor topography, the features of iron-manganese nodules and other characteristics.

The bottom sediments, the Mn-Fe nodules were sampled by dredging and coring. The water samples were taken by PVC bathometers. The operations performed aboard were as follows: water sample filtration with millipore filters (0,5 μ), pH measurements in the water and sediments with a ППМ—03 potentiometer, squeezing out interstitial waters. The samples were kept in the polyethylene vessels, the water was reduced by distilled acid for pH not to exceed 1,8.

The chemical analysis of iron-manganese nodules, crusts and silts has been performed at the Laboratory of the Geological Institute, USSR Acad. Sc., by the team of analysts M. I. STEPANETS, I. YU. LUBCHENKO, M. A. KANAKINA, E. V. SHURYGINA, headed by E. S. ZALMANZON. The methods applied rank among conventional ones. The content of Mn-Fe in the nodules as well as that of V, Cr, Cu, Ni, Co was estimated colorimetrically, that of Zn polarographically following the chromatographic separation. The elements present in the muds in smaller quantities were found by a quantitative spectral method.

The mineral content of Mn-Fe nodules was studied microscopically and by means of X-ray structural (G. V. SOKOLOVA of the USSR Academy of Sciences; Cr — anticathode, V — filter) and thermal analyses.

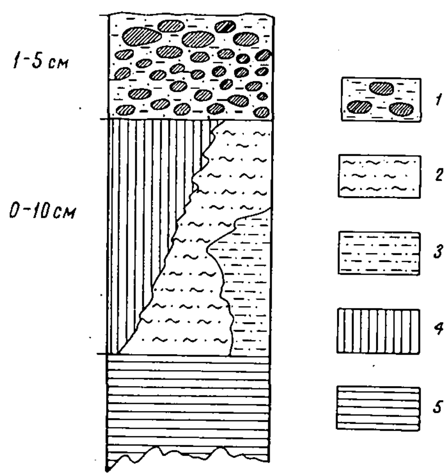

Fig. 1. Core of sediments from ore-bearing regions of the Gulf of Riga:

1 — Pisolitic nodules and their crust-shaped coalescences, of Mn and Fe hydroxides in the brownish watery mud;
2 — Greenish-gray, clayey silts;
3 — sand-clayey black muds frequently with H_2S;
4 — No sediments;
5 — Country deposits: glacial clays, yellow-grey

THE GULF OF RIGA

This region is essentially isolated from the main portion of the Baltic Sea, its sediment distribution being largely dependent upon specific features due to the discharge of the Daugava and, in part, the Lielupa [B. D. Puntas, V. G. Ulst, V. B. Emes, 1968]. The Mn-Fe nodules found in the Gulf of Riga are mainly abundant over the relatively flat Saarema shallow water and over the slopes of the main trough of the 17—39 m depth. They occur in the upper (0—4 cm) layer of brown waterly mud which is frequently underlied by grey silts (0—6 cm), black oozes (0—7 cm) having no nodules *(Fig. 1)*.

The prevailing Mn-Fe nodules are those of spheroidal varieties, their crust-like accretions (2—30 mm on the average), the nucleus being in the form of terrigenous particles, compacted mud, etc. The nodules are mainly in the form amorphous iron hydroxide, hydrogoethite, goethite, birnessite, while manganese carbonate is considerably less abundant. Table 1 lists the chemical composition of the nodules.

The brown watery mud with Mn-Fe is characterized by pH 7,05; Eh +480 millivolts, the underlying dark-grey muds by pH 6,60—7,05; Eh +80—200 millivolts. See Table 2 for the chemical composition.

THE GULF OF FINLAND

The Gulf of Finland can be considered as a marginal-part of the Baltic Sea whose exchange with the main water mass of the basin is rather limited. The main hydrochemical features and sediment distribution are essentially dependent upon the discharge from the surrounding land; first of all upon that of the Neva, Narva and others, and upon an appreciable discharge from smaller channels of the Finland territory [B. Winterhalter, 1966].

The bottom of the Gulf of Finland is remarkable for its dissected topography. The sea hills, moderate elevations with relatively slow sedimentation have accumulated the nodules of manganese and iron hydroxides. The hollows, pockets of the sea relief accumulate black clay-silt muds, not infrequently with hydrogen sulphide (pH 7,60; Eh: −20 millivolts). In the northern and central parts of the Gulf of Finland, the comparatively small but well-pronounced elevations of the sea projections often display large (10×15) globular, compacted (up to 2—3 cm) nodules and crusts occurring over the surface of the basic light-grey morainic clays and sands.

A number of sections display a wide development of black pisolitic pieces (up to 2—5 cm) of a round botryoidal, frequently ellipsoidal shape, with hummocky surface. The nuclei of such nodules often have gravelly terrigenous particles and wood debris. Such nodules fill up (80—85%) the brownish-grey watery mud thick up to 5 cm. Below is black silt (7—10 cm thick) with plentiful fine vegetable remains and scarce nodules decreasing in quantity downwards.

The country grey morainic clays underlie black silts.

Occurring within the Gulf of Finland are also coin-shaped, disk-shaped varieties of nodules, coatings of pebbles, fragments of iron-manganese hydroxides.

The nodules and crusts occur mainly as goethite, hydrogoethite, amorphous iron hydroxides, birnessite, todorokite, with infrequently admixed amounts of manganocalcite. The chemical composition of nodules will be found in Table 1, that of muds in Table 2.

THE AREA OF GDANSK AND KLAIPEDA

This area can be considered the southern part of the Central Baltic which is a relatively open area of the basin with no pronounced localized source of sediments. Mn-Fe nodules, crusts occur mainly over the slopes of the plateau of the Gdansk—Gotland Rise, 60—104 m deep. They are associated with gravelly sands, sandy silts from 0 to 7 cm thick. As a rule the nodules, crusts, are found over the surface of these sediments or immediately on eroded rocks of country substratum represented by recent glacial clays, morainic loams *(Fig. 2)*. The depressions, pockets of the sea relief accumulate greenish-grey black muds, silts of up to 1,0 m thick [I. M. VARENTSOV, A. I. BLAZHCHISHIN, 1970].

The nodules, crusts occur as Mn-Fe hydroxides building up over the surface of altered clays, pebbles, terrigenous grains. Widely spread are crust-like formations over altered clays, coin-shaped, disk-shaped, less often pisolitic, buck-shot nodules, their aggregate, coallescences. They are represented by hydrohematite, hematite, amorphous iron hydroxides, todorokite, birnessite, rather seldom with manganocalcite. The chemical compositions of nodules, crusts are to be found in Table 1.

Dark-green, dark-grey muds filling in the depressions of substrata and black muds of the Gdansk and Gotland troughs vary rather moderately with respect to their compositions, although their Eh vary in a wide range (from −25 to +430 millivolts) with pH 6,70—7,70 (Table 2).

In spite of rather shallow depths, the bottom waters of this Baltic area display appreciably higher concentrations of Mn, Fe, Co, Ni, Zn, Pb (Table 3).*

The comparison between total concentration in the bottom water and the content of these elements in the water filtrated through the millipore filter of 0,5 μ pores allows a conclusion that a considerable part of these metals is found in the form which should be considered as dissolved.

DISCUSSION

The formations of iron-manganese nodules in the Gulf of Riga and the Gulf of Finland, and the Gdansk-Klaipeda area of the Baltic vary considerably, their major distinctions being as follows.

Mode of occurrence. The Mn-Fe nodules found in the Gulf of Riga and often those found in the Gulf of Finland are mostly present in the brownish watery mud (up to 5 cm) which spreads over rather thin (up to 7—10 cm) dark-grey silts, black muds with hydrogen sulphide. In most cases the brownish watery mud contains appreciable amounts of Mn-Fe nodules, up to 80% of the volume *(Fig. 1)*.

The nodules found in the Gdansk-Klaipeda areas occur as a rule over coarse clastic sediments, not infrequently upon the eroded surface of the main rock represented by glacial clays *(Fig. 2)*.

*) The analyses have been carried out by S. I. NEIMAN and D. L. ZALEV using Techtron AA-4 atomic absorber made by Varian Co. (at the Department for Analytical Chemistry of Moscow University). For this kind of water the limit of the method's sensitivity for the elements have been found in the following range (in μg/l), the figures in brackets show variation coefficients (in %): Mn 0,2 (22); Fe 1,5 (3,3), Co 0,6 (3,6), Ni 0,6 (2,8); Zn 0,4 (2,5); Pb 2,6 (5,0), Cu 0,5 (4,8).

TABLE 1

Chemical Composition of iron-manganese nodules, crusts of the Gulf of Riga, the Gulf of Finland, and the Gdansk-Klaipeda areas in the Baltic

Components	Gulf of Finland			Gulf of Riga			Gdansk-Klaipeda area			Black Sea (average)	Atlantic Ocean (average)	Pacific Ocean (average)
	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average			
1	2	3	4	5	6	7	8	9	10	11	12	13
SiO_2	14.59	27.36	19.60	16.99	34.21	23.35	13.27	60.92	33.67	—	—	—
TiO_2	0.35	0.59	0.47	0.33	0.60	0,49	0.34	0.72	0.51	—	—	—
Al_2O_3	1.65	5.03	3.43	1.15	6.96	3.57	0.37	7.08	3.68	—	—	—
Fe_2O_3	14.65	40.03	28.02	17.95	52.30	32.41	16.29	35.15	26.17	—	—	—
FeO	0	0.55	0.10	0	0.64	0.12	0	0.71	0.19	—	—	—
CaO	1.85	2.92	2.38	1.25	2.84	1.90	1.21	1.84	1.50	—	—	—
MgO	0.11	0.71	0.35	0	1.10	0.71	0.88	1.43	1.07	—	—	—
MnO	1.63	5.15	3.29	0.40	7.60	2.84	0.13	6.05	1.98	—	—	—
MnO_2	2.93	28.06	17.06	1.04	24.01	11.90	1.38	21.33	11.26	—	—	—
Na_2O	1.14	1.74	1.41	0.60	1.92	1.05	0.81	1.48	1.18	—	—	—
K_2O	1.27	2.10	1.72	1.11	2.44	1.75	1.22	2.60	1.98	—	—	—
P_2O_5	0.56	4.58	2.85	0.57	2.98	1.59	1.13	3.78	2.53	—	—	—
CO_2	1.74	3.42	2.73	0.54	3.39	2.39	0.36	1.86	0.93	—	—	—
C_{org}	0.64	3.22	1.29	0.43	1.93	1.06	0.23	0.91	0.56	0.60	—	—
Fe_{total}	10.30	28.43	19.68	12.55	36.66	22.76	11,88	25.58	18.45	26.27	15.50	14.00
Fe^{2+}	0	0.43	0.08	0	0.50	0.10	0	0.55	0.15	—	—	—
Fe^{3+}	10.25	28.00	19.60	12.55	36.58	22.67	11.39	24.58	18.30			
Mn_{total}	7.06	21.72	13.32	0.97	20.69	9.70	0.97	15.88	8.65	6.90	13.55	24.20
Mn^{2+}	1.26	3.99	2.54	0.31	5.88	2.21	0.10	4.68	1.53	—	—	—
Mn^{4+}	1.85	17.73	10.78	0.66	15.17	7.52	0.87	13.48	7.11	—	—	—
Mn/Fe	0.685	0.764	0.677	0.077	0.564	0.426	0.082	0.646	0.468	0.26	0.87	1.73
P	0.24	2.00	1.24	0.25	1.30	0.70	0.49	1.65	1.02	—	—	—
Cr	12	28	17	12	36	23	14	43	30	—	—	10
V	34	90	68	32	134	98	123	157	134	—	—	540
Cu	3	20	9	1	65	17	9	100	42	40	1600	5300
Ni	5	106	35	3	150	47	40	250	148	280	3300	9900
Co	70	130	96	10	120	64	60	130	91	60	2400	3500
Zn	63	239	113	44	257	135	66	204	137	—	—	470
Pb	5	16	9	7	55	24	10	19	15	—	1200	900
Number of samples	—	—	9	—	—	19	—	—	7	—	—	—

NOTE. Content of main components is shown in weight %, that of minor constituents in n. 10^{-4}%
11. acc. to V. R. SEVASTYANOV, I. I. VOLKOV, [1966]. 12. acc. to F. T. MANHEIM [1965]. 13. acc. to J. MERO [1965].

*Content of Mn, Fe, P, V, Cr, Ni, Co, Cu, Pb, Mo, Ga, Ge in muds of the Gulf of Finland, the Gulf of Riga and the Gdansk-Klaipeda area of the Baltic**

TABLE 2

Components	Content**					
	Brownish watery muds	Black muds				Dark-green muds
	Gulf of Finland	Gulf of Riga	Gulf of Finland	Gulf of Riga	Gdansk-Klaipeda area	Gdansk—Klaipeda area
Fe_{total}	4.37—6.51 (5.25)	2.59—5.18 (3.78)	2.07—4.66 (3.74)	2.66	2.55—5.51 (4.39)	3.40—4.43 (3.93)
Mn_{total}	0.06—0 93 (0.37)	0.04—0.17 (0.10)	0.07—0.13 (0.10)	0.14	0.01—0.04 (0.03)	0.02—0.05 (0.04)
P	0.12—0.40 (0.24)	0.06—0.12 (0.09)	0.05—0.09 (0.07)	0.06	0.04—0.11 (0.07)	0.04—0.08 (0.06)
V	65—87 (76)	38—68 (59)	29—65 (51)	49	51—86 (68)	57—72 (68)
Cr	56—92 (71)	25—68 (48)	22—49 (39)	39	40—57 (50)	47—63 (54)
Ni	22—32 (27)	7—25 (17)	10—28 (21)	17	20—34 (26)	22—27 (24)
Co	12—20 (15)	6—11 (9)	7—19 (14)	7	9—11 (10)	8—13 (10)
Cu	48—66 (58)	10—29 (19)	13—32 (20)	21	3—26 (22)	25—35 (30)
Pb	66—93 (81)	18—39 (35)	16—58 (35)	30	32—99 (77)	40—78 (60)
Ge	1.9 —2.9 (2.10)	1.1 —2.2 (1.7)	1.1—16 (10.4)	1,6	15—20 (18)	1.2 —17.0 (10.4)
Mo	1.0 —108 (40)	1.0 —2.3 (1.4)	2.1—69 (52.4)	1.7	21—69 (35)	2.3 —46.0 (23.1)
Ga	23—28 (25)	9—26 (18)	12—21 (17.3)	16	17—32 (28)	22—24 (23)
Number of samples	3	6	3	1	5	5

* The figures in brackets show the average values.

** The main elements are given in weight percent; the minor ones in $n \cdot 10^{-4}$%.

TABLE 3

Content of Mn, Fe, Co, Ni, Zn, Pb, Cu in sea water of the Gdansk-Klaipeda area of the Baltic, Station 1762 (depth 103 m)

Nos	Depth (m)	Brief description	pH	Eh	Concentration (μg/l)						
					Mn	Fe	Co	Ni	Zn	Pb	Cu
1	0.0	Natural	8.20	+560	0.2	14.8	0.8	1.0	8.9	2.9	1.4
2	0.0	Filtrated through 0.5 μ filter			0.2	—	0.8	1.4	—	—	0.5
3	50.0	Filtrated through 0.5 μ filter	7.85	+560	0.3	19.1	1.25	2.0	41.5	3.9	2.80
4	75.0	Natural	7.10	+560	0.2	36.1	1.20	1.5	14.5	3.2	0.5
5	75.0	Filtrated through 0.5 μ filter			—	22.7	1.4	—	—	2.0	—
6		Bottom, filtrated through 0.5 μ filter	7.05	+490	4.1	28.9	1.0	1.7	37.7	8.6	0.6

Sources of ore-forming components. The sediments of the Gulf of Finland are supplied mainly by the Neva, Narva, Luga and other rivers. Special mention sould be made of the discharge from the territory of Finland and the Karelian Isthmus which brings considerable amounts of dissolved heavy metals, mainly humates. It should be pointed out that the peculiarities in the distribution of the continental discharge within the Gulf of Finland essentially govern the main features of hydrochemistry and distribution of sediments.

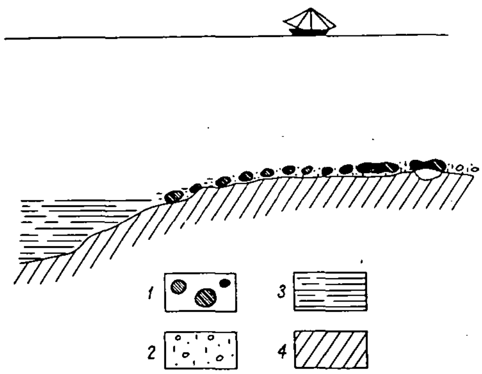

Fig. 2. Schematic representation of occurrence of Mn-Fe nodules, crusts at the bottom of the Gdansk-Klaipeda area of the Central Baltic:

1 — Mn, Fe nodules, crusts;
2 — Sandy-gravel;
3 — Black, dark-green clayey muds, frequently with H_2S;
4 — Country deposits: morainic clay, loams, etc.

The sediments of the Gulf of Riga are supplied mainly by the Daugava and, less so, by Lielupa and other rivers. The open part of the Baltic which is connected with the Gulf of Riga mainly through the Irben Strait influences its sedimentation but moderately.

The Gdansk-Klaipeda area can be considered an open part of the Baltic Sea which displays no clear-cut localized source for ore-forming components. In addition to the supplying of sediments from the mouths of the neighbouring rivers (the Vysla, the Neman) and the erosion of the country sea-floor rocks, the ore-forming elements are to a large extent supplied by currents whose mass contains Atlantic water incoming via the Danish Straits. There are some reasons suggesting that enrichment of the bottom waters with heavy metals can also be due, to a large extent, to the processes of their diffusion inflax from the sections of accumulation of dark, organic-rich muds neighbouring the concentration fields and from the stagnation zones of the area.

Morphology. The following varieties of nodules are widespread in the Gulf of Riga: pisolitic, buck-shot and their aggregate coalescences.

The Gulf of Finland contains spheroidal nodules and, occasionally, relatively large compacted varieties (10×15×2 cm), there are also disk- and coin-shaped nodules as well as fragments coated with Mn and Fe hydroxides.

The Gdansk-Klaipeda area is known for its comparatively widespread crusts and coatings ranging from pigmentation of boulder-and-pebble fragments with Mn and Fe ydroxides to disk- and coin-shaped nodules. There are also rather numerous crust-like formations, mainly Fe hydroxides developing over the altered clays of he basic substratum. The spheroidal nodules, as a whole, are rather scarce in the dansk-Klaipeda area.

Mineral and chemical composition. While the mineral composition of Mn and e nodules, crusts, of the territories under study varies but slightly, their chemical composition testifies strongly to the particular conditions of their formation. Among ther factors these include the influence of the Atlantic waters (in the case of the dansk-Klaipeda area) and the effects due to the continental discharge in the bays hich brings fresh water.

One can, obviously, consider that, of the territories investigated, the most ronounced sea condition is found in the Gdansk-Klaipeda area while it is relatively oderate in the Gulf of Finland which is appreciably influenced by the river discharge. This can be illustrated by a relative comparison between the average content of nodule components over the three territories: the Gdansk-Klaipeda, he Gulf of Riga, the Gulf of Finland. The nodule components in the Gdansk-laipeda area is assumed to be a conventional unit. Then an increase in the relative content of CaO (1—1,27—1,59), Na_2O (1—0,89—1,19), CO_2 (1—2,57—2,94), $_{org}$ (1—1,89—2,30) testifies to the increasing effect of the river discharge upon he conditions of nodule formation. Conversely, the same order of a decrease in he relative content: MgO (1—0,64—0,33), K_2O (1—0,88—0,87), Cr (1—0,77—0,57), V (1—0,73—0,51), Cu (1—0,41—0,21), Ni (1—0,32—0,24), Zn (1—0,98—0,82) can e taken to account for a decrease in factors typical of the sea condition.

FORMATION OF Mn—Fe NODULES

The opinion on the process of formation of Mn-Fe nodules, the crusts in the dansk-Klaipeda area is based upon quite obvious and simple observations of their occurrence, structure, composition and the results obtained from the experiments by a number of authors [J. MORGAN, W. STUMM, 1965; G. MICHARD, 1969], s well as by our work on simulation of such phenomena. The data obtained allow judgement to the effect that Mn-Fe hydroxide nodules form due to selective chemisorption accumulation of transition elements followed by autocatalytic oxiation when active surfaces interact with bottom waters. Such surfaces can, to a ertain extent, be found in the altered terrigenous particles which have been leached-out, in the fragments of the country glacial clays which often make up a nodule core or a base of crusts. When Mn and Fe hydroxides forming on such surfaces interact, during subsequent cycles, with bottom water, they show up as even more active sorbents as compared with the nucleus substance, the base. In other words, the products of such interaction promote the subsequent cycles of the process which leads to its autocatalytic nature. Each cycle of such a process includes several stages: the early stages cover a highly-selective ion exchange, molecular sorption ollowed by catalytic oxidation, formation of hydroxides, while the relatively more recent stages seem to include dehydration, transformation of the formed hydroxides. Apart from the formation of the hydroxide phases of Mn, Fe and other transitional metals, there also form authigenic silicates, rather complex spinel-like compounds.

This process can be contributed to by relatively slow terrigenous sedimentation or no sedimentation at all (the terrigenous clayey particles block the active surfaces), by bottom currents which carry considerable masses of component containing solutions over the active surfaces, by positive values of Eh. Such a process can take place in a wide range of the concentrations of the accumulated components: 10^{-2}—10^{4} μg/l.

The Mn-Fe nodules found in the Gulf of Riga and, to a large extent, in the Gulf of Finland, as shown above, differ from the nodules found in the open sea as to their conditions of occurrence, morphology, structure and composition.

For Mn-Fe nodules found in the Gulf of Riga and those in a number of areas of the Gulf of Finland their occurring conditions are of importance. Let us consider them using a respresentative example of the Gulf of Riga. In many cases, though far from all of them, the nodule-containing brownish watery mud (3—5 cm) is underlain by the grey silts (up to 5—7 cm) with black clayey organic-rich muds having H_2S usually being below it *(Fig. 1)*. In interstitial waters of such black, grey clayey silts there are, according to T. I. Gorshkova [1970], relatively high concentrations of Mn (up to 8,46 mg/l) and Fe (up to 2,28 mg/l). A high gradient of concetration of Mn and Fe in interstitial and bottom water in the accumulation areas of these sediments suggests a question on the likely role of Mn and Fe diffusing upwards, from the relatively concentrated interstitial solutions into the layer of watery mud, containing the nodules of Mn, Fe hydroxydes.

To estimate a relative share of Mn and Fe diffusing upwards from the relatively reduced layers of the sediment in the total balance of these elements during formation of nodules, the calculations were made wherein the part of the factors favouring diagenetic processes was purposefully exaggerated. For detailed substantiation of such calculations, taken as a reference was a representative station No. 1788 in the Gulf of Riga (depth 22,0 m, lat. 58°00′2, N long 22°30′7 E), water-depth 0,0 m, pH 8,35; Eh +560 mV, depth 22,0 m, pH 7,20; Eh +560 millivolts. The water core of this station is represented as follows: 0—3 cm of brownish watery mud, containing up to 70% of spheroidal nodules (1—3 mm) of Mn, Fe hydroxides which frequently form accretions; 3—8 cm of greenish-grey mud, silty, having no hydroxide Mn-Fe nodules; 8—10 cm of black mud, silty-clayey, organic-enriched, stinking of H_2S. Below are pale-grey, thin, glacial clays.

The calculations have been based on the following assumptions: the content of manganese-iron hydroxide nodules in the brownish watery mud — 10%, thickness of mud — 1 cm. The nodules contain Mn — 10%, Fe — 20%, the specific gravity of nodules — 2,5 g/cm³ (*i. e.* these characteristics are taken to be somewhat higher than actual ones). The thickness of grey silts is 10 cm, that of black clayey muds containing H_2S is also 10 cm. The humidity of the two types of muds is assumed to be 80%, the concentration of Mn in the solution of mud is 20 mg/l, that of Fe is 5 mg/l. It is admitted that all the quantities of Mn and Fe present in the solution diffuse entirely upwards to take part in the formation of nodules.

The calculations show that the quantities of Mn and Fe present in the solution of mud comprise but 1,28% of the quantity of Mn and 0,16% of Fe found in the nodules. Thus to provide the accumulating amounts of Mn and Fe in the hydroxide nodules according to the above assumptions and with a mere diffusion inflow o these components from the mud solutions of lower sediments, the thickness of the latter must have been 17 m for the case of Mn, and 125 m for Fe.

However, the rate of sedimentation within the areas of Mn-Fe nodule formation in the Gulf of Riga and the Gulf of Finland is relatively slow, not more than 20 cm of sedimentation column has accumulated since the recent glaciation (about 10 000 years).

Thus, the diffusion supply of Mn and Fe due to diagenetic phenomena in relatively reduced sediment layers in the Gulf of Riga and the Gulf of Finland is practically within one per cent of the Mn and Fe amounts accumulated in the nodules.

The estimations of the relative share of Mn in the total balance of supply of this element in the formation of oceanic abyssal nodules [M. L. BENDER, 1971] also testifies to a negligent role of the Mn diffusion influx from the lower layers of sediment.

The above data and estimations suggest that Mn-Fe nodules in the Gulf of Riga and the Gulf of Finland were formed due to the selective and chemosorptive mechanisms and that of autocatalytic interaction between the solution and the active surfaces. In the cases under consideration, the feature of Mn-Fe nodule formation is that, along with the solute-state metals, the gulf is supplied with their suspension-state varieties as humates, organic and mineral particles. These metal-containing suspensions decompose both in the water mass proper of the gulfs and in the upper horizons of the sediment where Mn and Fe came into the solution. This is testified to by their high concentrations in the interstitial waters of the brownish muds: Mn up to 18 mg/l, Fe up to 1,33 mg/l [T. J. GORSHKOVA, 1970].

BRIEF REVIEW OF GEOCHEMICAL ASPECTS OF FORMATION OF Mn—Fe NODULES, CRUSTS IN THE SHELF REGIONS OF SEAS

The works of F. T. MANHEIM [1965] and T. I. GORSHKOVA [1967] contain an extensive review of the conditions of formation of manganese-iron nodules in relatively shallow seas.

The nodules found in the shelf zone of the Black Sea, near the Crimean coast, south of Tarkhankut have been described by V. R. SEVASTYANOV and I. I. VOLKOV [1966], those in the Rumanian coast littoral near Constanţa and Sulin (depth of 40 to 60 m) by LU. GEORGESCU and S. LUPAN [1971].

Comparison of the data obtained by these authors with the characteristics available for the nodules in the Gulf of Finland, the Gulf of Riga, the Gdansk-Klaipeda area of the Central Baltic goes to prove that they share some common features: the conditions of occurrence, localization, structure, mineral and chemical composition. For instance, the mean composition of Mn-Fe nodules in the Black Sea [V. R. SEVASTYANOV, I. I. VOLKOV, 1966] differs but slightly from that of Mn-Fe nodules in the Gdansk-Klaipeda area of the Central Baltic (Table 1). At the same time, the chemical composition of Mn-Fe nodules in the shelf basins differs markedly from that of the nodules in the Atlantic and the Pacific (Table 1). As stated above, with a decrease in the continental discharge, in particular in the river discharge, the relative content of Mg, K and especially of minor elements — V, Cu, Ni, Zn — increases appreciably. However, in one studies the changes in the chemical composition of Mn-Fe nodules in a succession reflecting a decrease in the continental discharge: the Gdansk-Klaipeda area of the Baltic — the Atlantic — the Pacific (Table 1), one cannot help noticing a marked growth of the Mn/Fe ratio and the contents of V, Cu, Ni, Co.

It was stated earlier [I. M. VARENTSOV, 1972], that the formation of Mn-Fe oxide ores in the existing basins can be considered to depend upon the reactive mechanism of the selective, chemosorptive interaction, along with autocatalytic oxidation, between the active surfaces and the component containing solutions. In the oceanic basins, such a mechanism of formation seems to be no less obvious and possible than in the shelf waters. As to the differences in chemical composition of manganese-iron nodules in these basins, they can be accounted for proceeding from the study of the composition of interacting waters, sources (in particular of endogenic ones), the conditions of dissolved oxygen, pH, Eh, sedimentation rates, etc.

An analysis of paleogeographic conditions acting in formation of relatively large manganese and iron-manganese deposits within the existing continental boundaries strongly testifies to their formation in the shelf basins.

Though direct extrapolation would be unacceptable, the knowledge of the processes involved in formation of Mn-Fe ores in the shelf regions of modern seas can be made use of when studying ore formation in old basins.

CONCLUSIONS

1. The main factors have been considered which govern formation of Mn-Fe ores in the Gulf of Riga, the Gulf of Finland, the Gdansk-Klaipeda area of the Central Baltic. The formation of Mn-Fe ores takes place within the sites of weaker sedimentation, such as slopes, peaks of submarine elevations, localities of submarine erosion of the country bottom rocks, etc.

2. The chemical composition of the ores regularly changes following the looser connection with the open sea basin and stronger influence of the river discharge (the Gdansk-Klaipeda area — the Gulf of Riga — the Gulf of Finland). This succession displays a regular decrease in the content of Mg, K, Cr, V, Cu, Ni, Zn while the amounts of Ca, Na, CO_2, C_{org} rise.

3. The processes involved in formation of oxide ores can be considered to depend upon highly selective, chemosorptive accumulation of Mn and Fe and other transition metals with their autocatalytic oxidation while the active surfaces interact with the bottom waters.

4. The calculation of the diffusion inflow of Mn and Fe from the reduced muds when they underlie Mn and Fe nodules (the Gulf of Riga) shows that this is responsible for as little as 1—2% of Mn and Fe accumulated in nodules.

5. The study of ore formation in shelf regions of other seas allows a conclusion to be drawn that the ores forming in such conditions are rather similar in their composition but differ greatly from Fe-Mn nodules found in the open sea containing, as they do, an essentially poorer minor elements associations, and essentially smaller concentrations and values of Mn/Fe ratios.

6. Though direct extrapolations would be unacceptable, the knowledge of the processes involved in formation of Mn-Fe ores in shelf regions of modern seas can be made use of in studying ore formation in old basins.

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