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GEOCHEMICAL STUDIES ON THE FORMATION OF IRON-MANGANESE NODULES AND CRUSTS IN RECENT BASINS
I. ENINGI-LAMPI LAKE, CENTRAL KARELIA

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ABSTRACT. The processes of formation of iron-manganese nodules and crusts have been studied on an example of the Eningi-Lampi lake, Central Karelia, where the relationships between the source of the ore, sedimentary materials and areas of their accumulation prove relatively simple and apparent. Nodules and crusts are composed mostly by birnessite, amorphous hydrous ferric oxides and hydro-goethite. They occur, as a rule, on the surface of relatively coarse-grained sediments, at the ground-water interface. Considerably in a lesser extent are found the nodules in the upper part (0—5 cm) of the red-brown flooded watery mud covering dark-green, black muds. The nucleus of nodules, or the basis of crusts of iron-manganese hydroxides are various, frequently altered, fragments of rocks, sometimes pieces of wood. Distribution of Mn and Fe in sediments and waters of the lake is considered. It is shown that $\frac{Mn}{Fe}$ ratio considerably decreases in waters, sediments and nodules of the lake with the moving off the source. The main role in the process of formation of iron-manganese nodules belongs to the selective chemosorption interaction (with autocatalytic oxidation) of component-bearing solutions with active surfaces.

INTRODUCTION

The less studied is a certain geological event, the more numerous are points of view on its genetic essence. This is true relative to the problem of formation of sedimentary iron and manganese ores.

The study of the ore formation processes in recent basins has some advantages over investigations of ore formation of the geological past. This concerns the possibility of carrying out direct observations, establishing the main geochemical characteristics controling the ore-forming processes, the relative evidence of interrelation between environmental elements of the basin. In this respect many lakes are characterized by the simplicity of relationships between the sources of ore components and areas of their accumulation, as compared to the mediterranean seas and larger basins.

The formation of iron-manganese ores in the lakes of Central Karelia is rather extensive. However, among many ore-bearing lakes of this region the Eningi-Lampi lake is characterized both by a pronounced manifestation of these processes, and rather simple relationships between the source of the ore, sedimentary material and areas of their accumulation. Such simple and evident relationships between the principal environmental elements of the basin, the possibility of carrying direct observations on the mode of occurrence, ores, sediments, measuring of pH, Eh in waters, muds, the collecting of the necessary ore samples, allow to regard the Eningi-Lampi lake as a certain model of ore-formation in similar basins. The consideration of the specific features of the iron-manganese ore-genesis in other basins, permits to use the materials that serve as a basis of this particular model, for establishing a general model of sedimentary Fe-Mn ore formation.

The principal task of this paper is an attempt to present some fundamental data that characterize geochemical peculiarities of the process of iron-manganese ores formation in the Eningi-Lampi lake, Central Karelia.

GENERAL CHARACTERISTICS

The Eningi-Lampi lake is a relatively narrow (1.0—1.7 km) basin extending over 7 km towards SSE-NNW. The maximum depth of the lake does not exceed 6 m. The Porusta river falling into the lake from the South-South-East is the main feeding artery, its waters being discharged into the Southern depression of the lake *(fig. 1—3)*. In the north-west part the waters of the Eningi-Lampi lake fall via a small channel into the Seletskoe lake, the latter in its turn, is connected with one of the greatest lakes of Karelia, i.e. Seg-Ozero-Lake *(fig. 1—2)*. The tributaries of the Eningi-Lampi lake drain the areas composed of Lower Proterozoic metavolcanites of the basic composition that also make up the bedrocks of the banks and numerous islands of the lake.

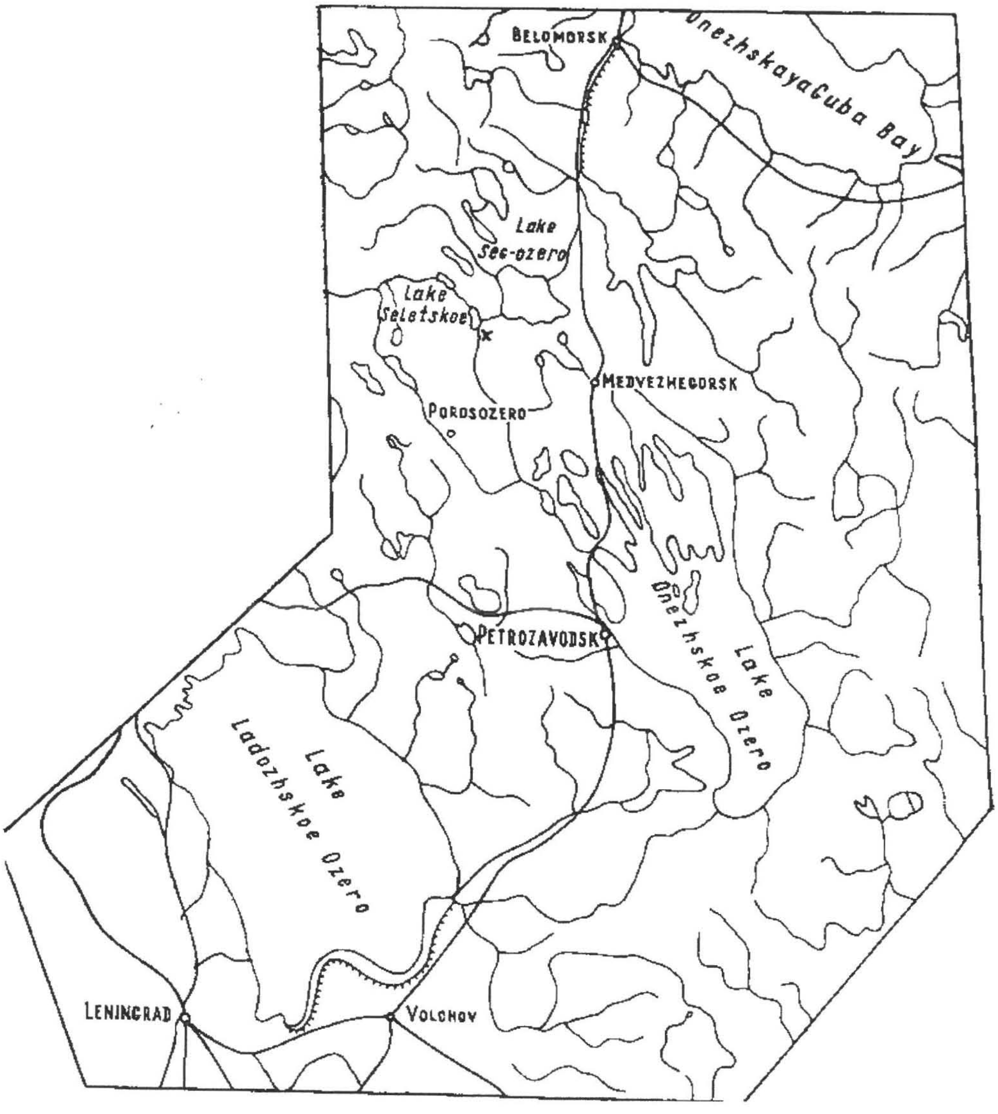


Fig. 1. Index map of the lakes of Central Karelia. x-Region of the Lake Eningi-Lampi.

Mineralization and ionic composition of waters, the Lake Eningi-Lampi (see fig. 2) TABLE 1

Analyst: M. I. STEPANETS

№	№ Station	Depth (m)	Date of sampling (1967)	Sample №	Measurement at the sampling: pH	Measurement at the sampling: Eh	CONTENT p.p.m: Dry res.*)	Dry res.**)	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^-	ion sum.	CONTENT mg/equ: Ca^{++}	Mg^{++}	Na^{+}	K^{+}	cat. sum	HCO_3^-	Cl^-	SO_4^-	anion sum.
1.	—	0,0	28/7	101	5.90	+490	56,00	36,00	3,60	3,28	0,73	0,40	21,96	0,74	2,88	33,59	0,18	0,27	0,03	0,01	0,49	0,36	0,02	0,06	0,44
2.	—	0,0	29/7	105	4,45	+440	68,00	44,00	5,40	2,19	1,09	0,72	29,28	0,74	0,96	40,38	0,27	0,18	0,05	0,02	0,52	0,48	0,02	0,02	0,52
3.	2a	0,0	31/7	122	7,25	+510	48,00	32,00	2,80	3,89	0,73	0,40	21,96	1,17	1,92	32,87	0,14	0,32	0,03	0,01	0,50	0,36	0,03	0,04	0,43
4.	2b	2,70	31/7	131	6,75	+510	48,00	32,00	3,60	2,19	0,86	0,41	21,96	1,10	0,96	31,07	0,18	0,18	0,04	0,01	0,41	0,36	0,03	0,02	0,41
5.	2g	1,50	1/8	139	7,10	+440	44,00	24,00	2,80	1,70	0,73	0,40	14,65	0,35	3,35	23,98	0,14	0,14	0,03	0,01	0,32	0,24	0,01	0,07	0,32
6.	2s	3,80	1/8	147	6,80	+405	60,00	28,00	1,80	2,80	0,73	0,40	19,76	0,21	1,44	27,14	0,09	0,23	0,03	0,01	0,36	0,32	0,01	0,03	0,36

1. The sample No. 101, Porusta-River, 1,5 km upstream the mouth of the river.

2. The sample No. 105. Truckling out of ground waters near the bank ledge of the lake's bay, to south-east from the cape Shuavan-Degi. The area of trickling out 10×5 m, the sand is stained by reddish-brown and black Fe—Mn hydroxides, on the water one can distinctly see the black films of Mn hydroxides. Near the area of trickling out the lake's water pH 6.000.

3. The sample No. 122, Porusta River, 20 m upstream the mouth.

4. The sample No. 131. The middle of the mouth part of the Porusta River, bottom water.

5. The sample No. 139. Estuary of Porusta-River, bottom water.

6. The sample No. 147. Centre of the Southern part of the lake, bottom water.

*) Dry residue, not ignited.

**) Dry residue, ignited.

A noteworthy feature of the cliffs, accumulations of rocks and boulders is the black crust of manganese, and to a lesser extent ferric hydroxides, that cover their surface above the water line. Such growths of Mn- and Fe- hydroxides on the surface of the rocks are frequently characterized by a lineation that seemed to correspond to the higher water levels; similar coatings of Mn and Fe hydroxides have been observed below the water-level.

GEOCHEMICAL CHARACTERISTICS OF THE LAKE WATER

The waters of the Eningi-Lampi lake are brown coloured due to the presence of dissolved humic substances and suspended organic material. Their mineralization varies from 23.98 to 40.38 mg/l; among anions predominant are HCO_3^{-1} (14.65—

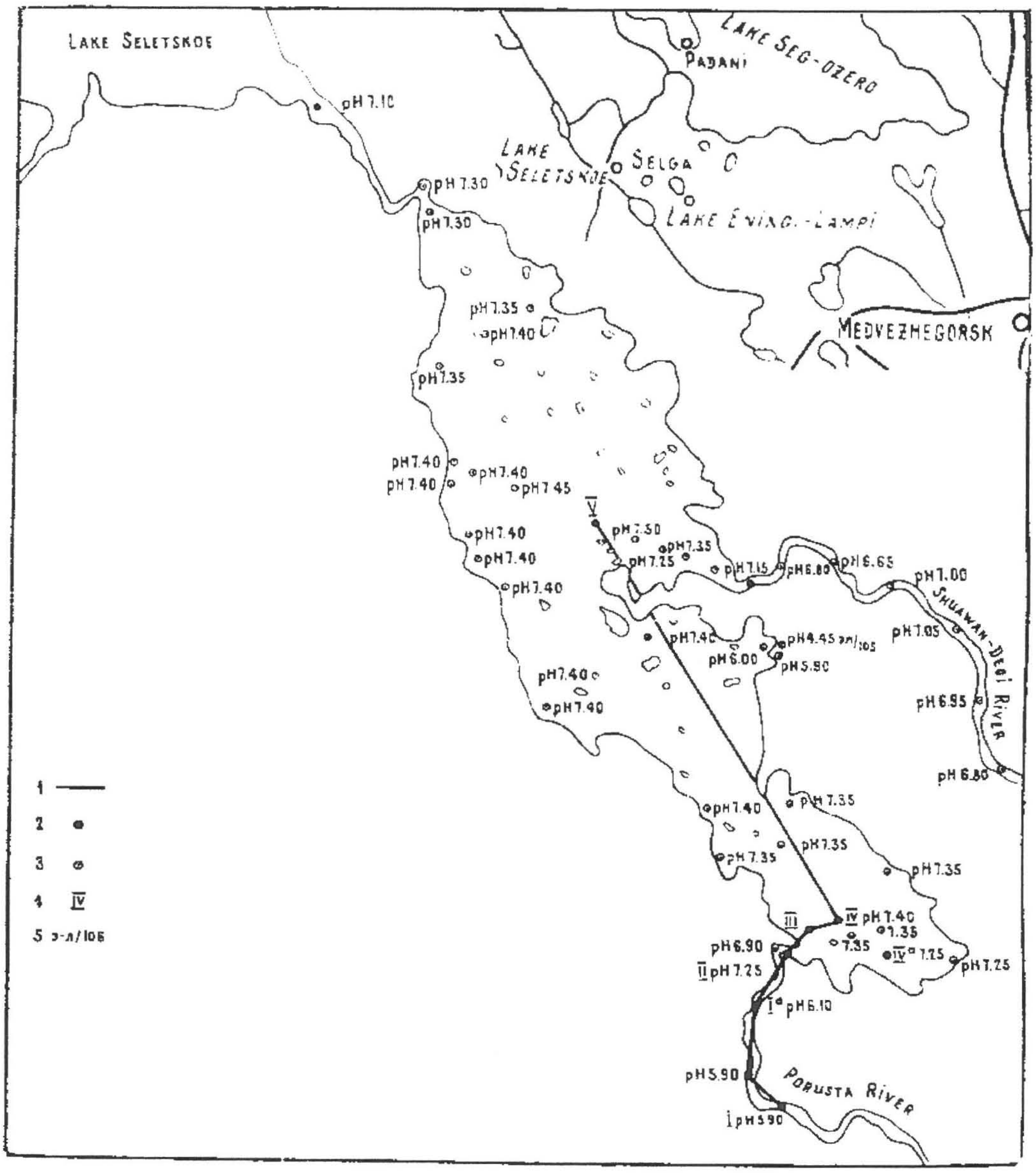


Fig. 2. The schematic map of stations where collected water-samples, measured pH, Eh, the Lake Eningi-Lampi. *1.* The line of geochemical section. *2.* The stations of water sampling, characterized by chemical analysis. *3.* The stations where pH, Eh were measured. *4.* Index on geochemical section and on the schematic map. *5.* Sample number. Note: the pH values shown on the schematic map for surface water.

29.28 ppm), among cations — Ca^{++} (1.80—3.60 ppm); Mg^{++} (1,70—3.89 ppm), the organic matter content reaching 32.86 ppm. In Table 1—2 *(fig. 2)* the pH, Eh values for the surface and bottom waters are given. Worth attention is the increasing of the pH values from the main tributary of the lake — the Porusta river (5.90). At the mouth of this river pH of the surface water increases up to 7.25, this value is typical to the surface waters of the southern depression, whereas in the northern depression pH increases up to 7.45 (see *fig.* 2).

Manganese and iron in the lake waters. The determination of the total Mn- and Fe contents was carried out by M. I. STEPANETS in the chemical laboratory of the Geological Institute of the USSR Academy of Sciences by colorimetric methods. The samples were fixed by adding 25% H_2SO_4 for obtaining pH less than 2. Before an analysis the samples had been treated with an acid for obtaining the reliable total contents. Just on the spot of sampling the study of relationships between a suspended and dissolved Mn and Fe forms was carried out. The analysis of the filtrate that passed through a membrane filter with pores size — 0,5μ, and that of the suspension on the filter show that 92% of Mn and 48% Fe of the total contents respectively were present in a dissolved form. Table 2 presents the total contents of Mn and Fe in the water of the lake according to the main profile *(fig. 2)*. The higher Mn and Fe contents were observed in the tributaries of the lake; they can be correlated, as a rule, to the lower pH values of the water. Thus, in the Porusta river there have been observed relatively high Mn and Fe contents that were considerably decreasing towards its mouth estuary (mg/l) for Mn: 871 → 110 → 68 → 48, for Fe: 420 → 400 → 300 → 200, the pH values increasing from 5.90 to 7.10. Differences in the rate of decreasing of Mn and Fe concentrations in this part of the Porusta river have been reflected in the $\frac{Mn}{Fe}$ values ($n \times 100$): 216.88 → 27.25 → 22.66 → 24.00. These data show that on the given part of the Porusta river a noticeable separation of Mn and Fe takes place, a considerable part of Mn is released from solution and not supplied into the lake.

The difference between the Mn and Fe contents in the surface water of the southern and northern parts of the lake is insignificant. In the centre of the northern basin the Mn and Fe contents (ppb) in the surface water are 35 and 200 respectively. Despite a small depth of the lake and possible wind mixing, the bottom waters still differ considerably in higher Mn and Fe concentrations, as well as in lower pH values, as compared to the surface waters (see Table 2).

SEDIMENTS

A relatively wide range of sediments is being accumulated in the Eningi-Lampi lake, from boulder-pebble to silt-clay sapropel-like muds. Each type is characterized by a certain localization, clear specific character of the chemical composition *(fig. 3.)*. In general, terrigenous components of the sediments of the lake are products of destruction, mostly of the Lower Proterozoic volcanogenic series of the basic composition that underwent a greenstone alteration. It means that the clastic sediments of the lake have a distinct greywacke composition: quartz, irregularly angular grains (up to 75%), feldspars, mostly plagioclases of the series albite-labradorite (up to 15%) fragments of siliceous rocks, hornfels (up to 20%), fragments of chloritic, epidotitic, biotite schists, amphibolites, gneisses and other rocks — up to 40%. The coarse-clastic varieties are, as a rule, considerably enriched in fragments of rocks, whereas fine-grained sediments — in mineral components: quartz, feldspars, dark-coloured minerals.

TABLE 2

*Content of iron and manganese in water of the Lake Eningi-Lampi, Central Karelia**)

№	Station №	Sample №	Index on the scheme**)	pH	Eh (mv)	Depth (m)	Content (ppm)		Mn/Fe (n·10²)	Notes
							Mn	Fe		
1.	—	101[a]	I	5,90	+490	0,0	871	420	206,88	
2.	—	101	I[a]	5,90	+490	0,0	110	400	27,25	
3.	2[a]	122	II	7,25	+510	0,0	68	300	22,66	
4.	2[a]	124	II	6,75	+440	2,70	80	300	26,66	Bottom water
5.	2[g]	139	III	7,10	—	0,0	48	200	24,00	
6.	2[e]	142	IV	7,40	+540	0,0	39	150	26,00	
7.	2[e]	143	IV	7,20	+440	2,40	51	200	25,50	
8.	1[d]	111	V	7,45	+510	0,0	35	200	17,50	
9.	2[b]	131	—	6,76	+510	2,70	70	300	23,33	Middle of the mouth, Porusta River (bottom water)
10.	2[s]	147	—	6,80	+405	3,80	51	250	20,40	Centre of Southern part of the lake (bottom water)
11.	—	105	—	4,45	+440	—	95	7000	1,36	Trickling out of ground waters
12.	—	106	—	6,90	+582	0,0	99	900	11,00	Shuavan-Degi River, 200 m upstream the mouth

*) *Analyst:* M. I. STEPANETS, Geol. Inst. Ac. Sci. USSR, the samples were collected 29 July to August 1, 1967 Determinations of Mn, Fe were performed by colorimetric methods.
**) *See fig. 2.*

Boulder-pebbly, gravelly deposits, coarse- and middle-grained sands are accumulated predominantly in the channel of the Porusta river as a narrow (50—100 m) band that is framing the shores of the lake *(fig. 3)*. Their composition reflects mineralogy, petrography of the basic metavolcanites composing the drainage areas. If to exclude iron-manganese nodules and crusts developed in these areas, the amounts of the concerned components in coarse- and middle grained sands are as following (weight %, in brackets — mean): Fe: 1,91—11.49 (5.79); Mn: 0.03—1.41 (0.44); P: 0.004—0.22 (0.058); CO_2: nil — 0.08 (0.06); C_{org}: 0.64—2.16 (1.40).

Fine-grained sands — coarse-grained silts are an intermediate type of a sediment developed between the areas of more coarse-grained varieties and prevailing in the lake of silt-clayey, sapropel-like muds. They are stretching as a relatively narrow (20—100 m) band that separates these sediments *(fig. 3.)*. They are characterized by the following contents of the components concerned: Fe: 3.25—6.66 (4.95); Mn: 0.07—0.16 (0.11); P: 0.06—0.10 (0.08); CO_2: 0.08—0.36 (0.21); C_{org}: 5.50—6.24 (5.84).

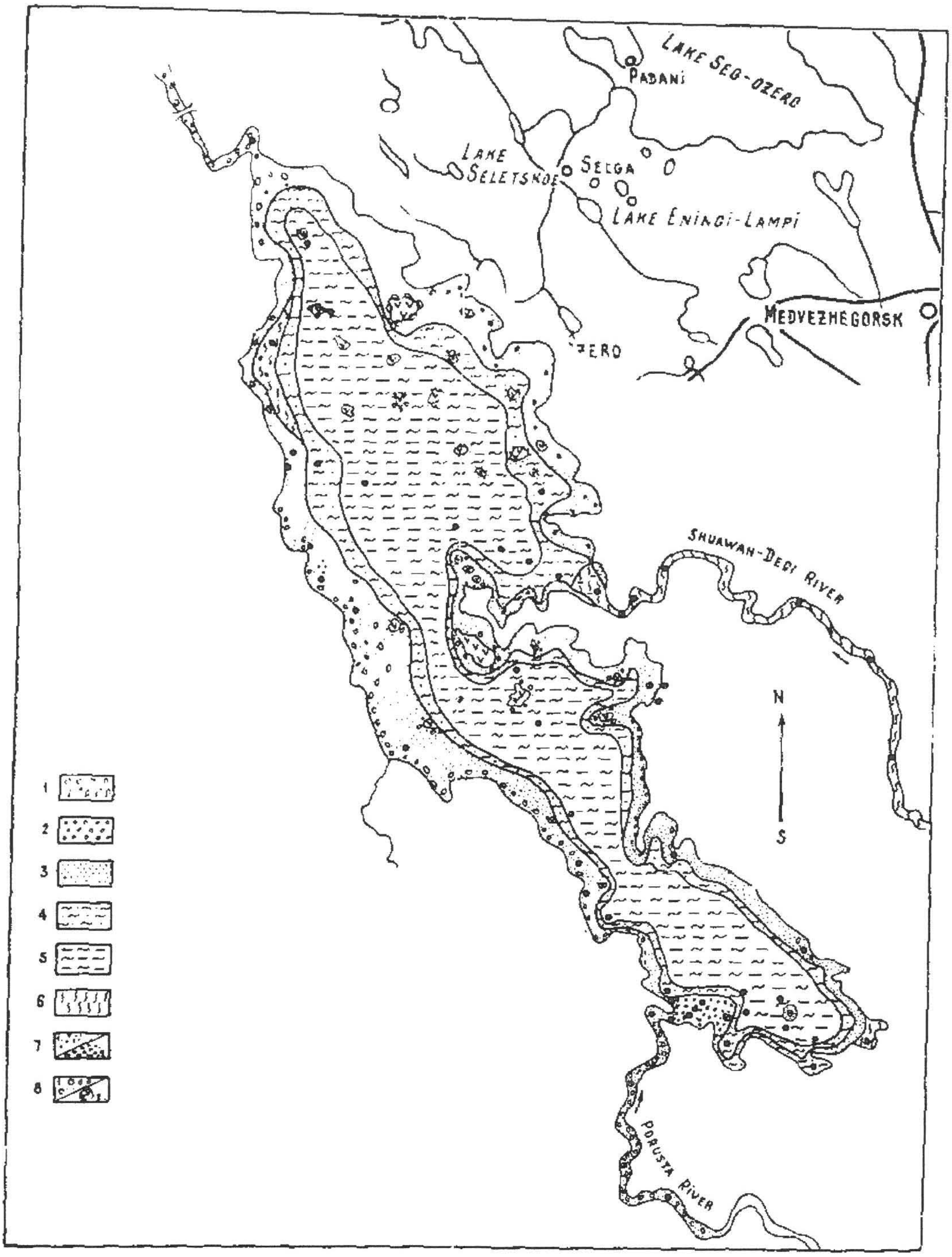


Fig. 3. Schematic map of sediments (Depth: 0,0—10 cm), the Lake Eningi-Lampi. Sediments: *1.* Boulders-pebbles, predominance of basic palaeovolcanites, quarzites, gneisses, granulites, altered arkoses. *2.* Gravel (see the composition above) greywackes. *3.* Greywacke sands coarse-medium-grained. *4.* Greywacke fine-grained sands coarse-grained silts. *5.* Fine-grained silty-clayey muds with considerable admixture of fine plant detritus, sapropel-like organic matter (the muds greenish-grey, dark, often with reddish-brown watery muds). *6.* Peat-like sediments, presented by plant detritus accumulations. *7.* 1) The nodules of Mn, Fe hydroxides. 2) Crust-like agregates of the nodules of Mn, Fe hydroxides. *8.* Coatings, crusts of Mn, Fe hydroxides 1) around sandy-pebbly fragments; 2) around blocks, boulders, outcrops of country rocks near the water level of the lake. Note: the circle with point — the stations where collected the samples of sediments, water, measured pH, Eh.

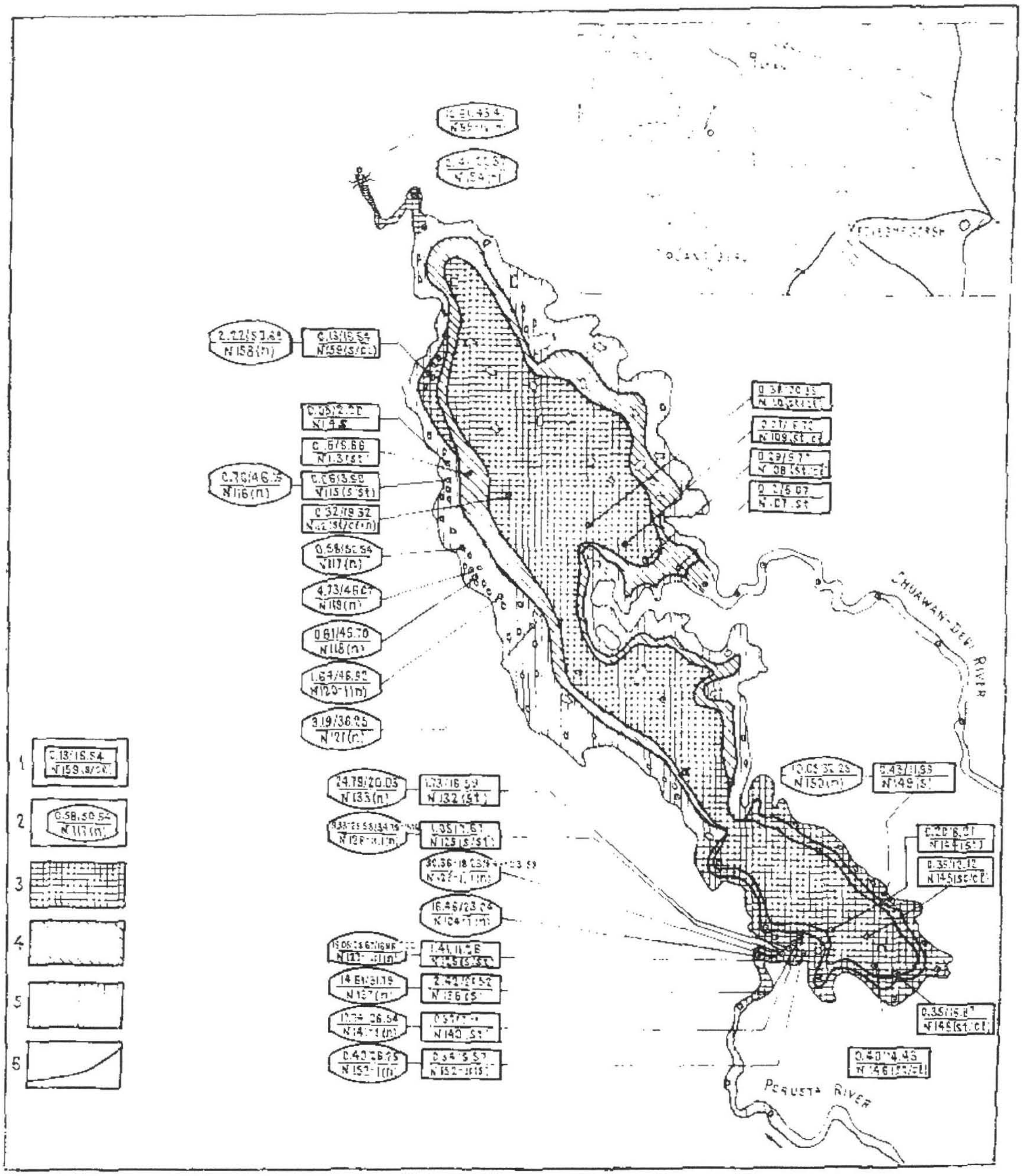


Fig. 4. Schematic map of Fe (wt.%) distribution in sediments (Depth 0.0—10,0 cm), Lake Eningi-Lampi. *1.* Stations where samples of sediments recovered. *2.* Stations where samples of nodules and crusts of Mn, Fe hydroxides recovered. Above the line, numerator — Mn content, denominator — Fe content (wt.%). Under the line — the number of sample, type of sediment: *S* — sand, *St* — silt; *s/cl* — silty clay, *n* — nodule crust of Mn, Fe hydroxides. *3.* Sediments of Fe content 10.00—20.00% (including ore accumulations). *4.* Sediments of Fe content 5.00—10.00%. *5.* Sediments of Fe content less 5.00%. *6.* Borders of sediment distribution with the given gradation of Fe content.

Silt-clayey muds are the preponderant sediments developed on a greater part of the lake. These are dark-green, greyish-green, seldom black muds enriched in a fine-dispersed sapropel-like organic matter. Above they are, as a rule, covered by reddish-brown watery mud (0.5—5 cm) in the composition of which there prevail suspended particles of ferric hydroxides; down the column, green-grey muds (about 25—50 cm) are replaced by black varieties. The total thickness of muds in the central part of the lake is over 3 m. The clay components of these sediments are presented by extremely degraded minerals from the group of *montmorillonite*, *chlorite*, *biotite-vermiculite* and their mixed-layered intergrowths. In other words, the composition of clastic and clayey components of these muds indicate a certain composition of initial rocks the products of which were subjected to intense leaching and decomposition.

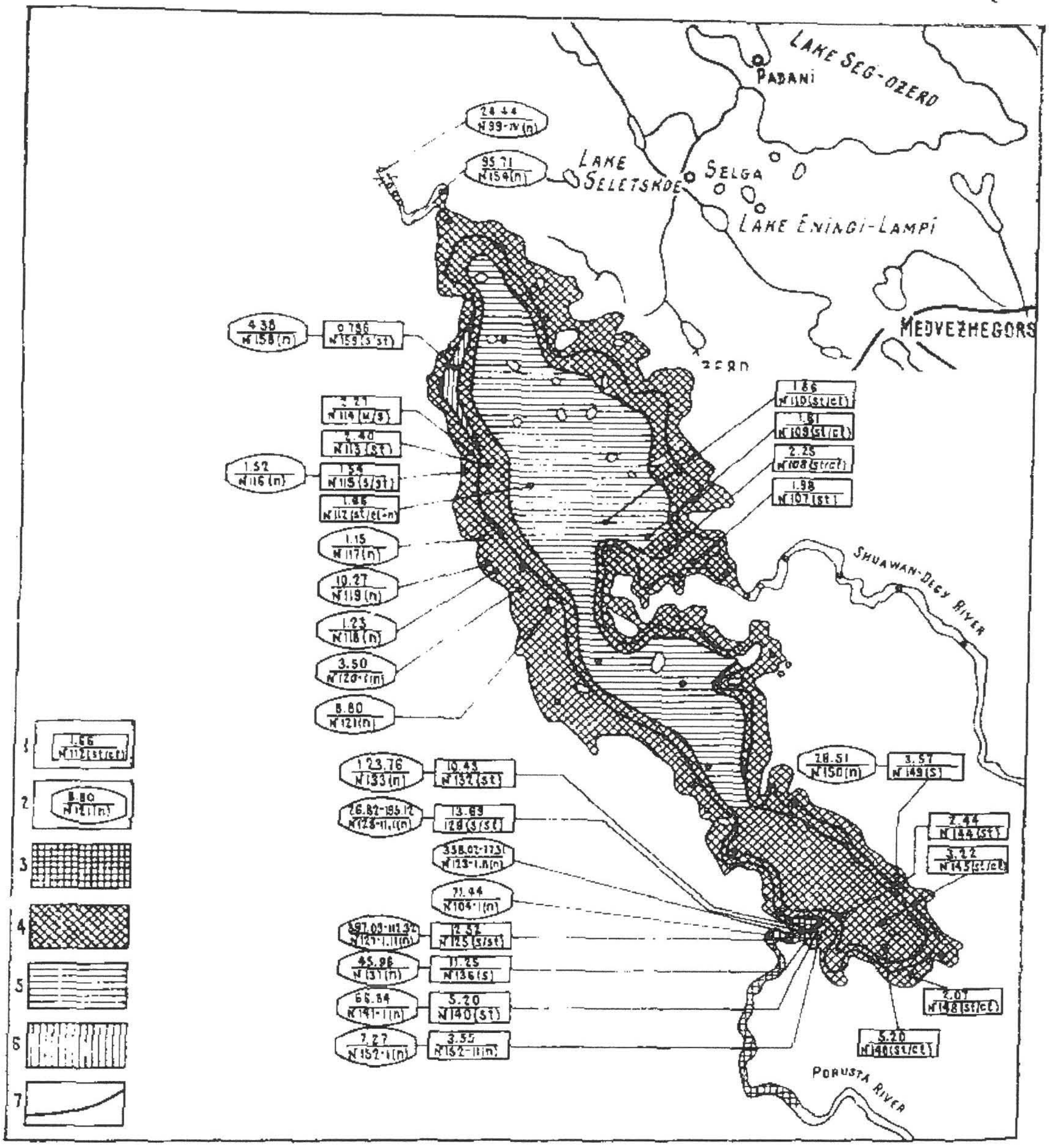


Fig. 5. Schematic map of ratio $\frac{Mn}{Fe}$ (n×100) distribution in sediments, Eningi-Lampi Lake. *1.* Stations where samples of sediments recovered. *2.* Stations where samples of nodules and crusts of Mn, Fe hydroxides recovered. The numerator — value of ratio $\frac{Mn}{Fe}$ (n×100); the denominator — *number of sample, in brackets* — sediment type: *S* — sand, *st* — silt, *s/cl* — silty clay, *n* — nodule, crust of Mn, Fe hydroxides. Gradational values of ration $\frac{Mn}{Fe}$ (n×100) in sediments. *3.* $\frac{Mn}{Fe}$ (n×100) over 10.000. *4.* $\frac{Mn}{Fe}$ (n×100):2.00—10.00. *5.* $\frac{Mn}{Fe}$ (n×100) 1.00—2.00. *6.* $\frac{Mn}{Fe}$ (n×100) lesser 1.00.

7. Borders of sediment distribution with the given gradation of ratio $\frac{Mn}{Fe}$ (n×100).

In the Northern (North. dep.) and Southern depressions (South. dep) of the lake these muds considerably differ in their chemical composition (weight percentage. in brackets — the mean, *m:* mean for these sediments of the lake).

Fe: South dep. 12.12—16.87 (14.37); North dep. 6.07—20.35 (14.46); *m:* 14.45.

Mn: South dep. 0.35—0.40 (0.38); North dep. 0.12—0.38 (0.26); *m:* 0.31.

P: South dep. 0.10—0.31 (0.23); North dep. 0.18—0.32 (0.22); *m:* 0.22.

CO_2: South dep. nil-0.54 (0.33); North dep. 0.24—0.84 (0.54); *m:* 0.46.

C_{org}: South dep. 10.03—12.93 (11.98); North dep. 4.74—20.68 (12.41) *m:* 12.24.

$\frac{Mn}{Fe}$ $(n \times 10^2)$; *m:* South dep. 2.64; North. dep. 1.79.

The data cited show that variations of Mn and Fe contents in the lake sediments *(fig. 4,5)* are subjected to a relatively well-pronounced tendency: with the moving from the Porusta river, the main source of ore components, via the southern depression towards the northern one of the lake, Mn concentrations considerably decrease, whereas Fe concentrations, on the contrary, increase. This can be rather clearly seen in $\frac{Mn}{Fe}$ ratio $(n \times 10^2)$ for silt-clayey sapropel-like muds: southern (2.64) and northern (1.79) depressions *(fig. 5, 6, 7, 8).*

In sandy-silt deposits and silt-clayey sapropel-like muds of the lake the amounts of trace elements $(n \times 10^{-4}\%)$ have been determined by a spectral method (I. Yu. Lubchenko, A. I. Gusareva, GIN of the USSR Academy of Sciences): V 8—33; Cr 5—42; Ni 5—21; Co 5—31; Cu 5—10; Pb 2—12; Ge < 1—10; Mo 1.0—10.0; Ga 3—14 (Table 3). The relationships of some of these elements and the main components of a sediment are not always subjected to well-pronounced regularities. The following associations can be established concerning the character of the positive correlation of these elements: Fe — C_{org} — CO_2 — P ------------- Mn; V — Cr — C_{org}; Mn — Ni — Co — C_{org} ------------- Fe (the dashed line denoted a weak correlation). Such elements as Cu, Pb, Mo fall to form any pronounced association.

IRON-MANGANESE NODULES, CRUSTS

The Eningi-Lampi lake is characterized by a wide development of Fe—Mn accumulations presented by nodules, crust-shaped hydroxide formation of these metals. Despite comparatively small extensions of this basin there can be observed a clear diversity of nodular types, crusts differing in mode of occurrence, morphology, structure, composition and areal localization.

Mode of occurrence. Fe—Mn nodules and crusts are found, as a rule, in the areas of sedimentation of coarse-clastic deposits of gravelly—pebbly sands—coarse silts *(fig. 3,4)*. Almost always do they laying on the ground-water interface. Less frequently they can be observed in a thin (1—5 cm) watery layer of the reddish-brown mud covering greenish-grey, dark silty-clayey muds with rather high amount C_{org} (up to 13.00%) *(fig. 8.)*. In these muds, as well as in sapropel-like varieties almost no nodules were found. Only in the marginal parts of the zone of silt-clayey sapropel-like muds, in the uppermost 5—7 cm of a sediment were observed sporadic (roughly 0.1% from the volume of a sediment) microconcretions (1—3 mm) of iron hydroxides. These microconcretions are relics that were temporarily preserved when a sediment was passing to more reducing conditions, as such muds rich in organic matter were being accumulated.

TABLE 3

Fe, Mn, CO_2, C_{org}, V, Cr, Ni, Co, Cu, Pb, Ge, Mo, Ga
*content in the sediments, the Lake Eningi-Lampi**)

№	Sample №	CONTENT												
		(wt) %				p.p.m								
		Fe	Mn	CO_2	C_{org}	V	Cr	Ni	Co	Cu	Pb	Ge	Mo	Ga
1	107	6,07	0,12	0,24	8,69	30	42	21	31	5	6	2,0	1,1	12
2	108	9,77	0,22	0,34	20,68	24	34	11	12	5	2	<2,0	1,0	6
3	109	16,72	0,27	0,58	17,79	17	24	10	11	5	2	<1,0	1,0	3
4	110	20,35	0,38	0,84	4,74	32	25	10	20	5	3	<1,0	2,4	4
5	113	6,66	0,16	0,36	5,50	14	16	6	8	5	4	<1,0	1,2	4
6	114	2,20	0,05	nil	1,15	15	18	5	5	9	4	<1,0	1,0	5
7	126	4,00	0,40	0,26	5,86	33	42	14	12	10	4	<1,0	2,1	14
8	130	3,25	0,07	0,08	6,24	26	23	9	8	5	4	<1,0	1,8	11
9	146	14,43	0,40	0,54	12,93	31	41	16	26	5	3	<1,0	2,0	9
10	148	16,87	0,35	0,44	12,96	44	41	16	19	5	3	<1,0	2,5	8
11	149	11,99	0,43	nil	1,09	16	8	5	11	5	6	<1,0	5,8	11
12	159a	16,54	0,13	—	—	8	5	5	8	5	12	10,0	10,0	3

1. The mud dark green, brownish, sandy fine-grained *with plant detritus. Sample No. 107*, Shuavan-Degi River, 200 m, upstream from the mouth.

2. The mud dark green with thin (10 mm) cover of brown watery mud, silty-clayey, with *considerable content of sapropel-like material.* Sample No. 108, Open part of Shuavan-Degi River estuary.

3. The mud greenish-brown, silty-clayey with considerable content of sapropel-like material. Sample No. *109*, see *fig. 4,5.*

4. The mud dark-green with brown-olive tint, sandy-clayey, covered by characteristic brown watery mud. *Sample No. 110. Middle part of* Northern depression of the lake; see *fig. 4,5.*

5. The mud greenish-brown, sandy with pro*minent content of sapropel-like material.* Sample No. 113, see *fig. 4,5.*

6. The mud greenish-brown, sandy with small *nodules of* Mn, Fe hydroxides, oftenly growing around the clastic grains. Sample No. 114, see *fig. 4,5.*

7. The mud dark-olive, clayey with abundant *plant remnants, Sample No. 126, Porusta* River, 200 m upstream from the mouth, see *fig. 4,5.*

8. The mud dark green, sandy, silty with plant detritus. Sample No. 130, mouth of Porusta-River, *the middle part, see fig. 4,5.*

9. The mud dark green silty-clayey with prominent amounts of sapropel-like material. Sample No. 146, *see fig. 4,5.*

10. The mud dark, silty-clayey covered by characteristic thin (to 1 cm) layer of brown watery mud, and containing substantial amount of sapropel-like material. Sample No. 148, see *fig. 4,5.*

11. The sand greenish-gray, gravely with nodules of Fe—Mn hydroxides. Sample No. 149, see *fig. 4,5.*

12. The relatively dense peat-like mass, composed by grass vegetations, contains penny-*like* nodules of Fe, Mn hydroxides. Sample No. 159a, see *fig. 4,5.*

*) Determinations were done by using the spectral analysis, I. YUR. LUBCHENKO, A. I. GUSAREVA, Mn, Fe, CO_3, C_{org} were determined by R. M. MICHAILOVA, V. P. SIMONOVA; Geol. Inst. Ac. Sci. USSR.

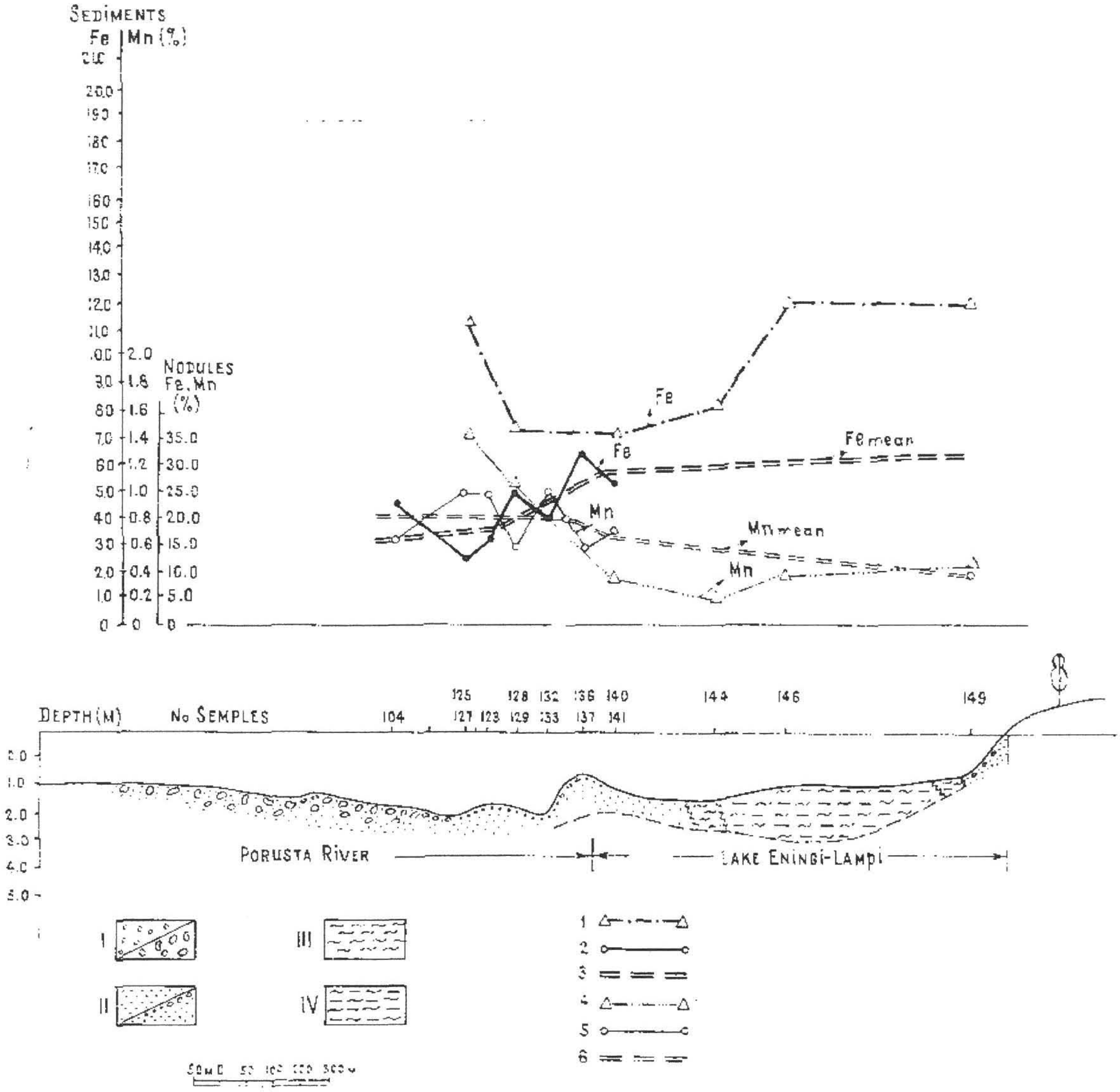


Fig. 6. Distribution of Fe, Mn concentrations in sediments, nodules and crusts from Porusta River across the Southern basin of the Lake Eningi-Lampi. I. a) Gravel-pebbly sediments with boulders, the fragments of volcanic metabasites predominated. b) The same as "a" but with coatings and crusts of Fe, Mn hydroxides. II. a) Coarse-medium-grained greywacke sands;, b) The same as "a" but with nodules and crusts of Fe, Mn hydroxides. III. Greywacke sands fine-grained — silts coarse-medium-grained. IV. Fine-grained silty, clayey sapropel-like muds, dark, greenish-gray. Content (wt.%): 1) Fe in sediments; 2) Fe in nodules, 3) Fe in nodules, mean values, 4) Mn in sediments, 5) Mn in nodules, 6) Mn in nodules, mean values.

Morphology. Nodules and crusts of Fe and Mn hydroxides can be regarded as different morphologically but uniform relative to their genetic essence of formation. They are presented by growths of Fe and Mn hydroxides on active surfaces. Detrital particles playing the role of a nucleus around which a gradual growth of Fe and Mn hydroxides is proceeding, may serve as such surfaces for the nodules.

Crusts and crust-shaped formations are coatings of Fe and Mn hydroxides on relatively large surfaces of boulder fragments, the rock walls etc.

The following morphological types of nodules and crusts can be distinguished in the basin concerned:

1. Irregular rounded nodules sized 1—3 to 70, average 15—30 mm. Frequently such nodules remind small book shots and beans.

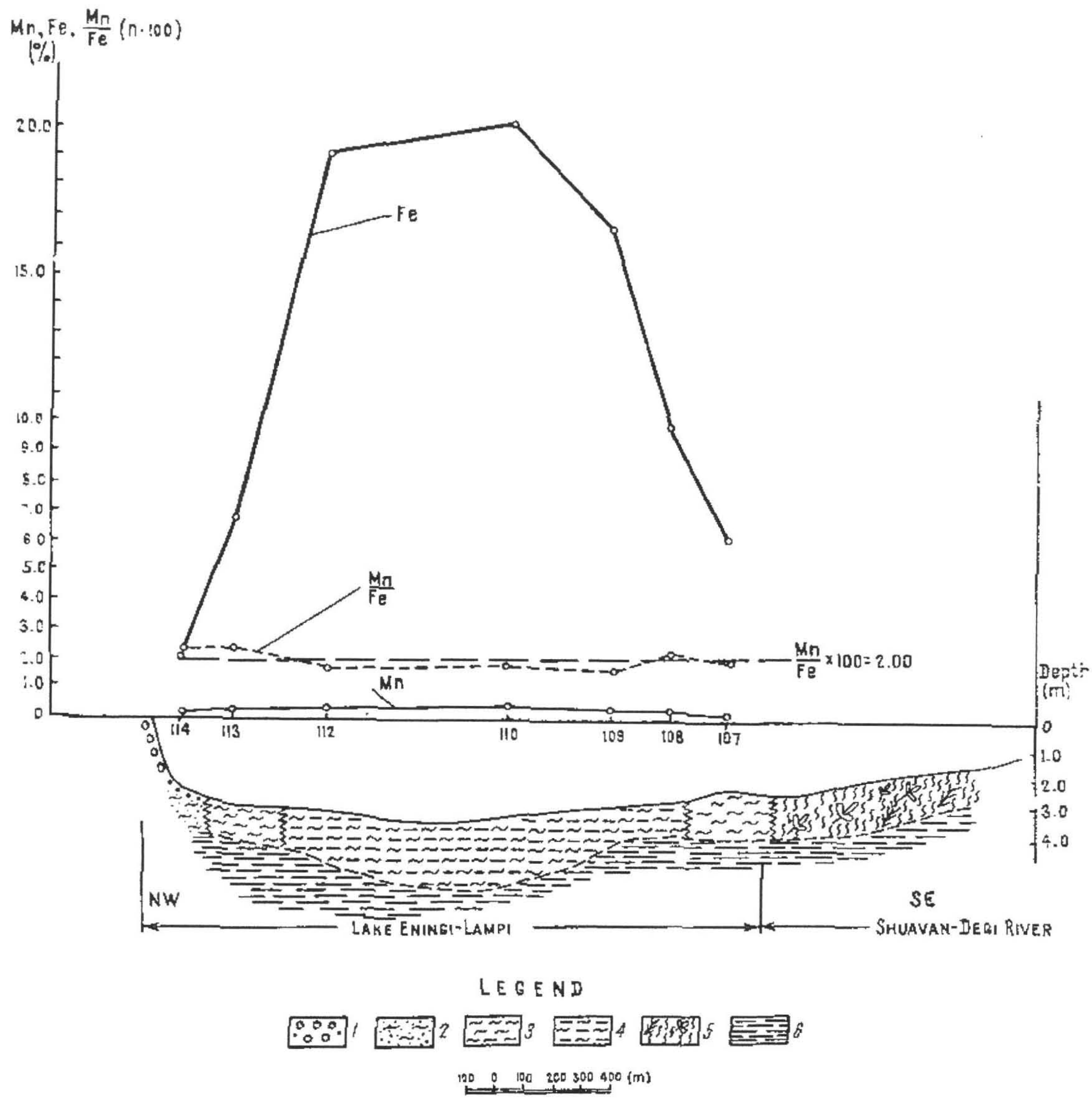


Fig. 7. Distribution of Fe, Mn (wt.%) and ratios $\frac{Mn}{Fe}$ (n×100) in sediments across the Northern basin of the Lake Eningi-Lampi from Shuavan-Degi River. *1.* Gravel-pebbly sediments with boulders, the fragments mainly of volkanic metabasites. *2.* Greywacke silty sands. *3.* Greywacke silts. *4.* Fine-grained silty-clayey sapropel-like muds. *5.* Sandy-silty peat-like accumulations, essentially enriched by plant detritus. *6.* Country rocks- glacial pale-gray clays.

2. Accretions of bean nodules forming aggregates and crusts up to 15—50 mm thick and sized 30—70 cm. Such accretions can be found in the areas of intense development of nodules (mouth-estuary of the Porusta river).

3. Penny-shaped and discoidal nodules that are elongated in the plane concentric overgrowths of clastic particles. Sizes: 3×25×25 up to 10×60×80 mm.

4. Overgrowths with Mn and Fe hydroxides in the shape of thin coatings, crusts on rock fragments, boulders, prominences of shore outcrops near the water line. Their thickness is from a quota (pigmentation of the surface-) to 30—50 mm.

Structure and composition. It has been said above that nodules and crusts are overgrowth of Fe and Mn hydroxides on the active surfaces. It follows from the field observations and microscopic study of thin sections that such coatings usually occur on an altered, corroded surface that plays the role of an activized basis. The

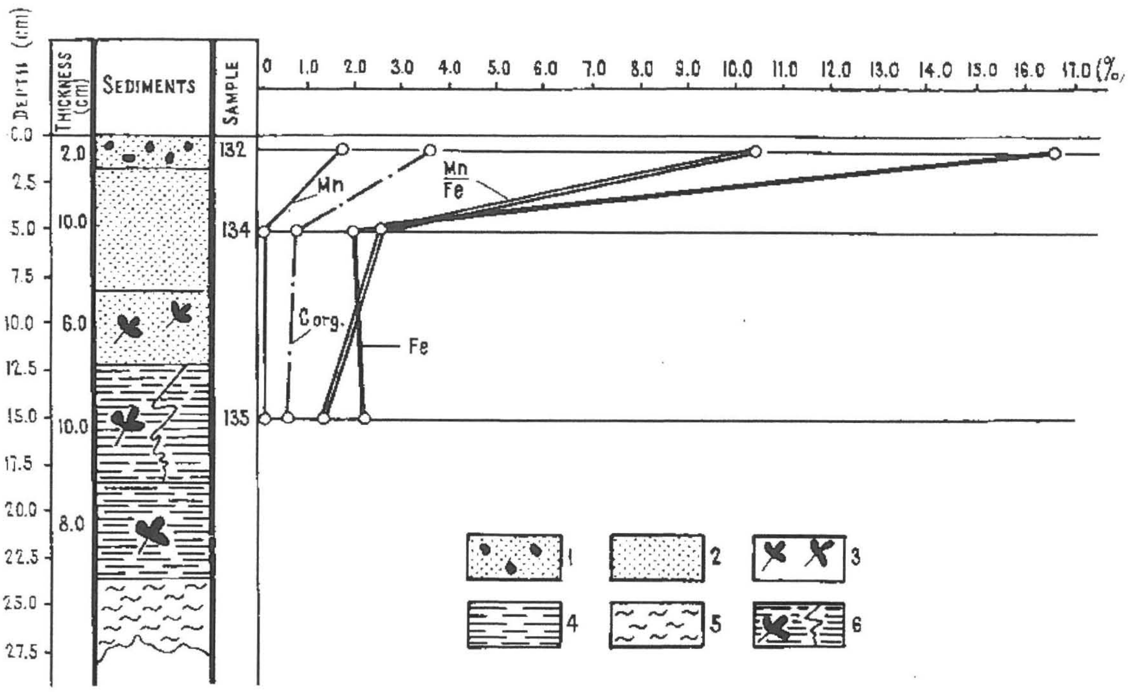


Fig. 8. Distribution of Mn, Fe, C_{org} (wt.%) and $\frac{Mn}{Fe}$ (n×100) in the column of sediments (cm) (station 2b, mouth part of estuary of Porusta-River). *1.* Sand greenish-olive coarse-grained with gravel particles covered by brown watery mud. Upper 2 cm of the sand are essentially enriched in nodules of Mn, Fe hydroxides. *2.* Sand greenish-olive coarse-grained with coalified detritus. *3.* Coalified plant detritus. *4.* Mud dark, almost black, sapropellike enriched by coalified plant detritus. *5.* Gray silt. *6.* Lateral substitution of black mud by greenish-gray varieties.

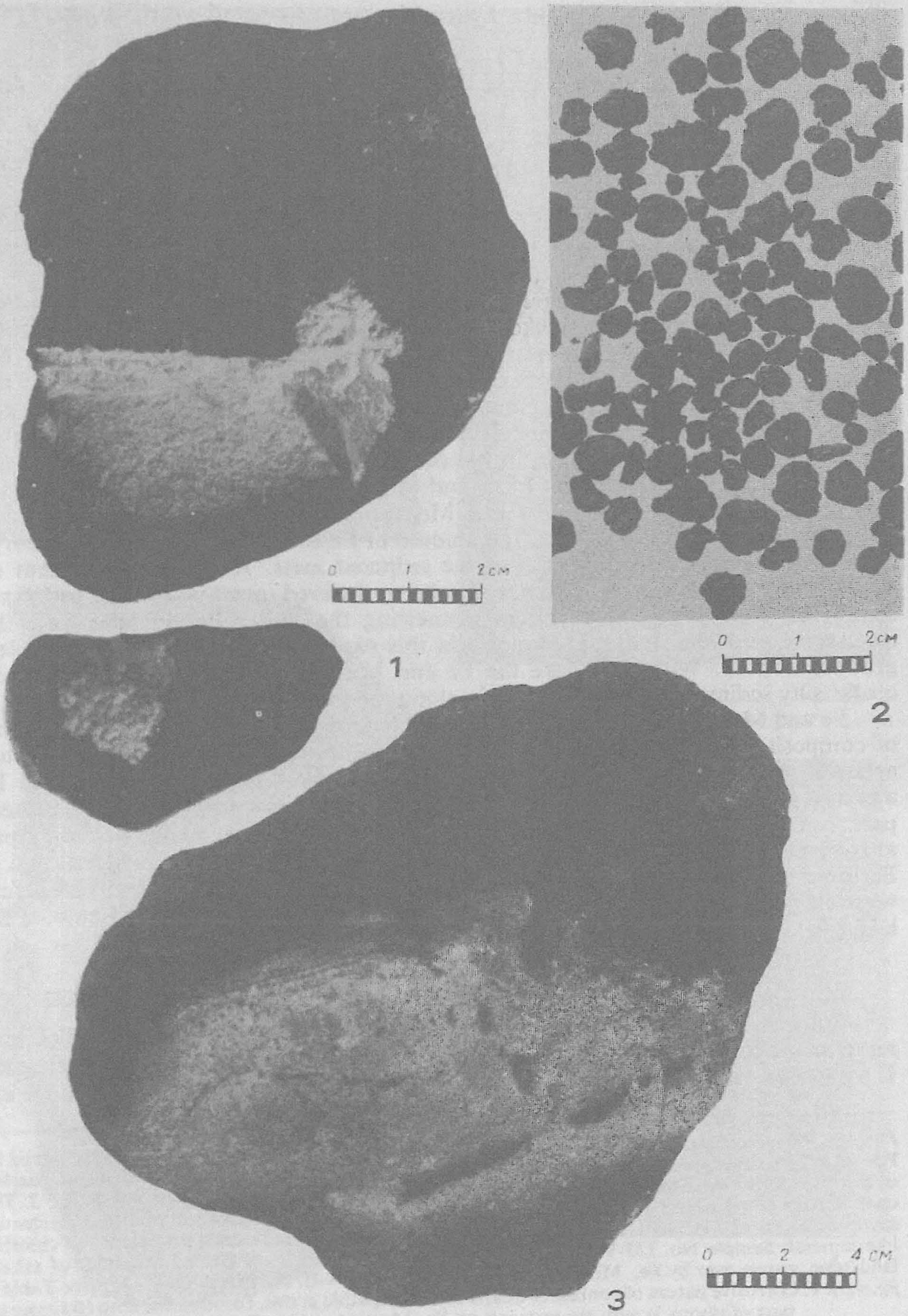
latter in the most cases is overgrown with the thinnest (0.01—0.5 mm) coating of Fe hydroxides. Then, this hydroxidic ferrugineous coating, depending on the composition of interacting solutions, pH, Eh values, can be overgrown with Mn or Fe hydroxides, or their complex mixture *(fig. 9)*.

In some cases (the mouth, estuary of the Porusta river) in thin sections of the nodules there can be observed patches and/or concentric layers of chlorite-like substance that is isotropic to a considerable degree, but clearly crystallized into aggregates of needle-shaped and tabular crystalls (up to 0.01 mm) on the contact of Fe and Mn hydroxides. Rather sporadic are patches of ferrugineous carbonates in hydrogoethitic parts of the nodules. These authigenic newly-formed minerals are considered as the later relative to hydroxidic phases of nodules.

Table 4 and 5 present the composition of the nodules and crusts concerned *(fig. 10)*. The study carried out enable to distinguish the following types:

1. Properly manganese that are predominantly composed of birnessite with an admixture of Fe hydroxides. The Mn content is up to 33%, that of Fe up to 8—10%;

Fig. 9a. 1. The quarzite pebble coated by Fe—Mn hydroxides, thickness to 1—3 mm. Similar pebbles, boulders, coated by Fe—Mn hydroxides occur on the bottom of the channel, connected the Lakes Eningi-Lampi and Seletskoe Ozero (see *figs. 4,5*), sample No. 99. *2.* Shot-like nodules of Mn, Fe hydroxides (see Table 4, *figs. 4,5*), sample No. 133. Mouth of Porusta-River. *3.* The pebble of altered basic volcanite coated by Fe, Mn hydroxides. Bottom view. The upper part of the pebble, rising above the water-sediment interface is covered by black Fe—Mn hydroxides, thickness to 25—40 mm. The lower part of the pebble is free of Fe—Mn hydroxide coatings. Sample No. 156, North-western part of the lake.


0 1 2 см
1
0 1 2 см
2
0 2 4 см
3

$\frac{Mn}{Fe}$ (n. 100)=330−413. The Mn hydroxides are associated with Co, n. 10^{-4}% (120−180), Zn (104−402); Ba 0(1.27—2.15%).

2. Properly ferrugineous presented by X-amorphous Fe hydroxides, hydrogoethite, goethite, lepidocrocite, Fe up to 51%, Mn−2%, $\frac{Mn}{Fe}$(n · 100)=3.92. Fe hydroxides are associated with (n · 10^{-4}%); Ni (5−40); Cu (3−13); C_{org} 0.85−1.80%, CO_2 1.44− 3.46%.

3. Nodules and crusts of an intermediate, Fe—Mn composition mostly wide-developed. Worth attention is that the terrigenous components of oies are associated with V (nil−34) and Cr (nil−4), (n · 10^{-1}%) *(fig. 10,11)*.

Localization and lateral changes. Sufficient accumulations of Fe and Mn nodules and crusts in the Eningi-Lampi lake are formed in the areas where the rates of their formations considerably exceed those of terrigenous sedimentation. These phenomena are most clearly seen in the places of a rather intense water currents, and, on the contrary, can not be observed in the areas where, in accordance with hydrodynamic conditions, there takes place an increase of accumulation of fine-grained sediments enriched in organic matter. Thus, in the course of the Perusta river, in its estuary and delta an intense development of Fe and Mn nodules and crusts can be observed. The sediments associated with Fe and Mn formations are presented by gravelly and pebbly sands *(figs. 3, 5, 6, 7)*. The amount of Fe and Mn nodules in the estuary-delta of the river reaches 50—80% of the sediment mass. A wide development of crusts, and to a lesser extent nodules, has been observed in a shallow (up to 2.5 m) stream of a relatively rapid current connecting the Eningi-Lampi lake with the Seletskoe Ozero one. Bottom sediments in this case are also presented by pebbles, gravel and sand. Within the lake the Fe and Mn nodules develop among sandy coarse-silty sediments framing this basin along the periphery *(figs. 3, 4, 5)*.

Fe and Mn nodules of the lake are characterized by a regularly lateral changing of composition, from the source of ore components to the relatively far remoted areas of their accumulation. When following the lateral alteration of Mn and Fe amounts (see *figs. 7, 8, 9)* in nodules and crusts through its estuary and the Southern part, towards its North-Eastern shore and then the Northern basin, one may pay attention that the Mn-content in this direction decreases significantly, whereas that of Fe increases. Approximately the same pattern of distribution was observed before when reviewing the behaviour of these elements in the waters and sediments of the lake *(figs. 4, 5, 6, 7)*.

…TION OF Fe AND Mn ORES IN THE ENINGI-LAMPI LAKE

Both all the above observations, and the data of experimental studies may serve as a basis for considerations on the formation processes of Fe and Mn ores. It should be emphasized that the nodules and crusts of Fe and Mn hydroxides are

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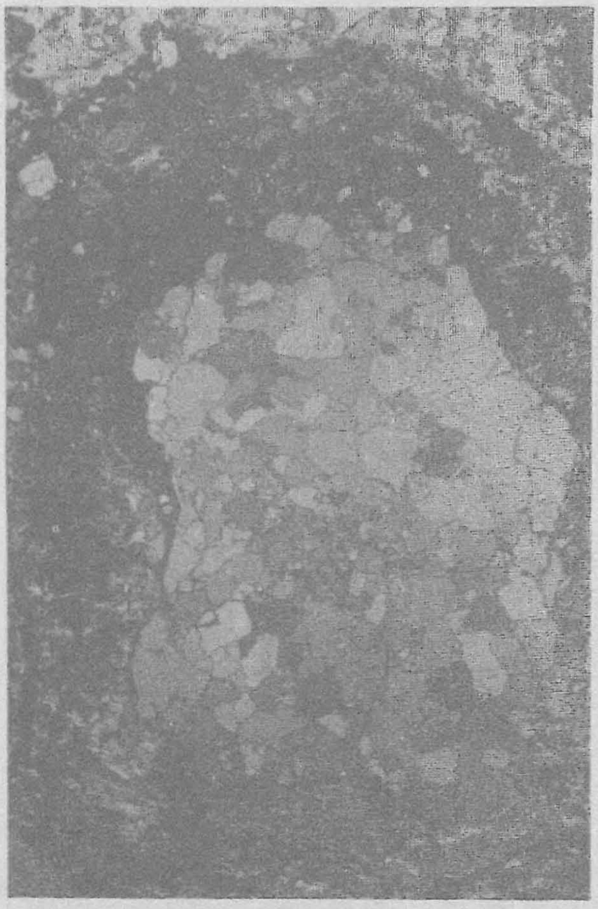
Fig. 9b. Photomicrographs. *1.* The core of the nodule — the gravel fragment of quarzite, covered by Fe—Mn hydroxides, around which is developed the mixture of Fe—Mn hydroxides and patches of chlorite-like mineral. Sample No. 133-IV. Polarized light, x14 (see Table 4, *figs. 4,5,* 9a/2). *2.* The core of the nodule — the gravel fragment of quarzite, around which grown alternating concentric sayers of Fe, Mn hydroxides (black) and the mixture of Fe, Mn hydroxides with patches of chlorite-like mineral. Sample No. 133-V. Polarized light, x10 (see photo 1). *3.* Gravel fragment of arkose landstone, grown over by Fe, Mn hydroxides. Sample No. 104-II. Polarized light, x15, (see Table 5, *fig. 4,5*). *4.* Corrosive nature of contact of quartz and feldspathic grains, forming the core (fragmented part of photo 3) with the growing on Fe, Mn hydroxides. Plane light, x 100.

1



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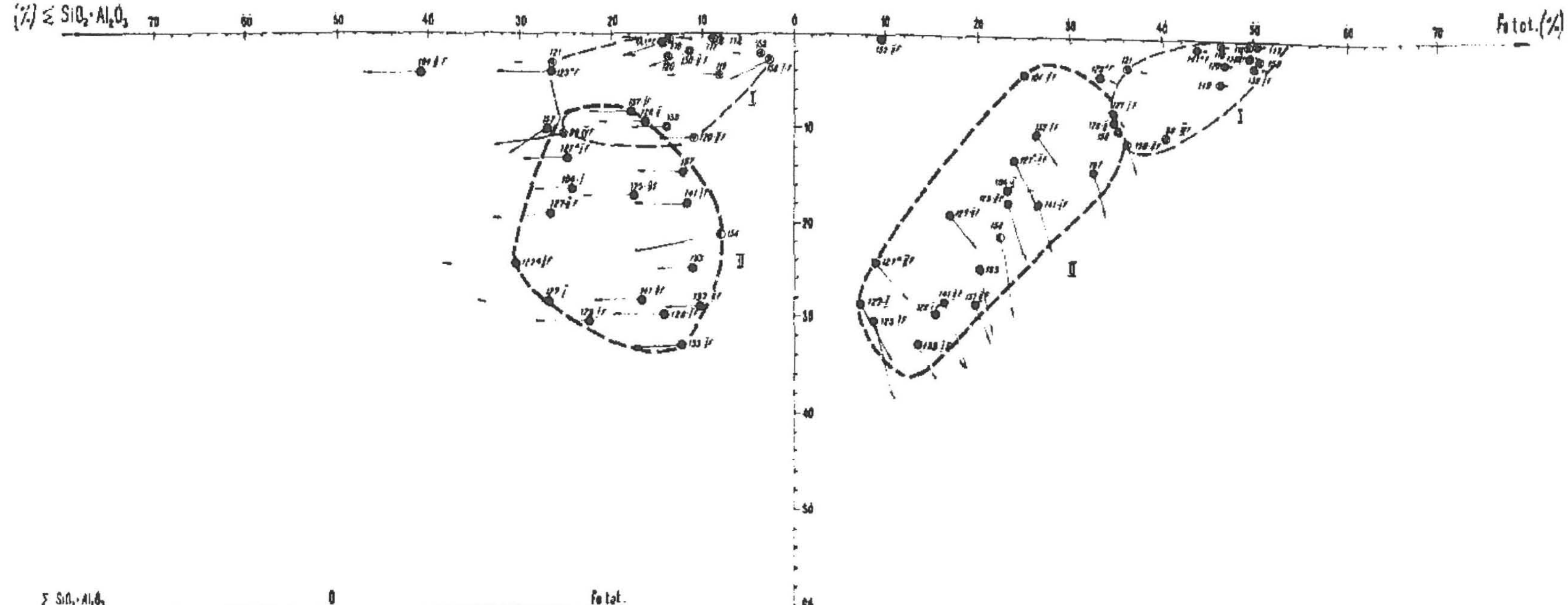

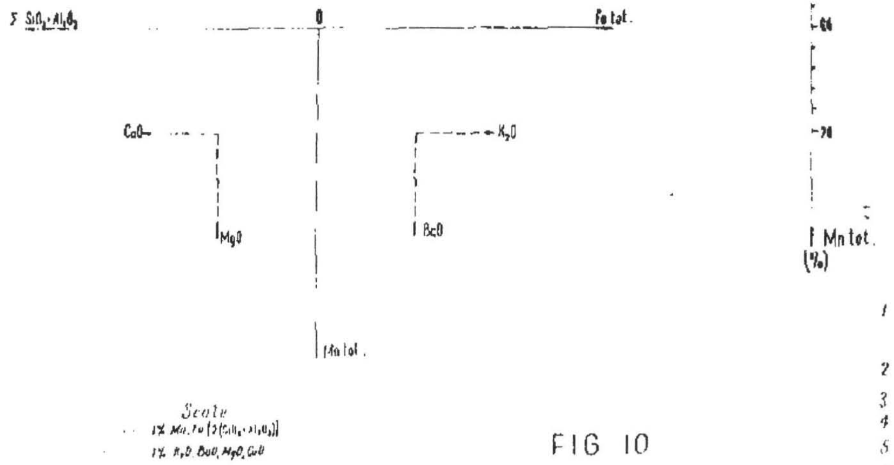

FIG 10

Fig. 10. The diagram of chemical composition of Fe—Mn hydroxide nodules, crusts, their fragments, the Lake Eningi-Lampi. In the left lower corner the scheme of design and the linear scale are shown. The multicomponent petrochemical diagram of A. N. ZAVARITSKI is taken as basis for the given one. *1.* Iron, manganese-iron nodules, crusts (Fe: 35—52%, Mn: 0—12%) mainly Northern Central, lesser — Southern depressions of the lake. *2.* Ba-bearing manganese, iron-manganese nodules and crusts (Mn: 5—50%, Fe: 5—35%), mainly Porusta River (stream-channel, mouth, estuary). F - fragment taken from nodules and crusts. Location of sampling: *3.* Porusta River, estuary and adjacent areas. *4.* Southern depression of the lake. *5.* Northern and Central lake's depressions. *6.* The channel connected the Lakes Eningi-Lampi and Seletskoe Ozero.

TABLE 4

№	Sample №	(p.p.m) V	Cr	Zn	Cu	Ni	Co	C_{org}	BaO	Sum	Fe_{tot}	Mn_{tot}	$\frac{Mn}{Fe}(n \cdot 10^2)$
1	133	nil	3	127	3	8	60	.12	1,70	100,84	20,03	24,79	123,76
2	133—I	nil	nil	154	4	8	120	.54	0,90	100,81	13,38	32,86	245,59
3	137—I	II	4	104	5	10	120	.80	0,20	100,75	34,88	8,46	24,25
4	137—II	TR	4	131	2	7	180	.62	0,95	100,76	19,62	28,64	145,97
5	141—I	nil	nil	146	3	5	130	.66	1,27	100,36	26,54	17,74	66,84
6	141—II	9	nil	208	2	1	150	.60	1,70	100,61	16,06	28,28	176,09
7	150	nil	4	175	4	20	60	.39	0,39	100,58	35,25	10,05	28,51
8	154	34	4	402	13	41	60	.85	2,15	100,75	22,37	21,41	95,71

1. Bean-like nodules, the interior part is composed by of manganese (birnessite), the external crust — by iron hydroxides. Sample No. 133, see *fig. 10,11.*

2. The material composing the interior part of bea main phase — birnessite, X-ray amorphous iron h No. 133-I, see *fig. 10,11.*

3. The brown hydroxides composing the external cr The main phase — goethite, minor one — birnessite, tic quarz and feldspars. Sample No. 137-I, see *fig. 1*

s, irregularly rounded (2—20 mm), crust-like coat- r bottom part composed by iron hydroxides, the nanganese hydroxides. In the sample predominate e — birnessite. Sample No. 150, see *fig. 10,11.*

hydroxides coating as thin crust pebbles, boulders, untry rocks near the water edge. The main phase nor one — X-ray amorphous iron hydroxides. *fig. 10,11.*

*) V, Cr, Cu, Ni, Co determined by colorimet preliminary chromatographic separation. The tot RIGINA, M. G. SEMENOVA in the chemical laborat Acad. Sci. USSR