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On the Main Aspects of Formation of Ferromanganese Ores in Recent Basins

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ABSTRACT

The distribution of Mn and Fe in water, sediments, hydroxide nodules and crusts of Eningi-Lampi ore-bearing lake is regular, and concordant from the source to the areas of accumulation of these components. Mn-Fe hydroxide nodules and crusts occur at the water-sediment interface, and more rarely in the upper (0.5 cm) film of brown watery mud. The leading role in the formation of Mn-Fe nodules and crusts is played by the chemisorption and auto-catalytic oxidation in the course of interaction of component-bearing solutions with active surfaces.

This is considered to be the basic process for the model of ferromanganese ore formation in recent basins.

Despite the differences in the physico-geographical and geochemical characteristics of lakes, mediterranean seas and oceans, the formation of ferromanganese hydroxide nodules and crusts in these basins may be explained by this model.

INTRODUCTION

MN-Fe HYDROXIDE NODULES AND CRUSTS in Karelian Lake Eningi-Lampi occurred at the water-sediment interface. More rarely they are found in the upper (0.5 cm) layer of brown watery mud. The important processes in the formation of Mn-Fe nodules and crusts are chemisorption and autocatalytic oxidation at the interface of the component-bearing solution with the active surfaces. Despite the differences of physico-geographical and geochemical characteristics of lakes, mediterranean seas and open oceans, the formation of ferromanganese hydroxide nodules and crusts in these basins may be explained by using the model discussed.

The purpose of the study was to construct a preliminary model for the formation of manganese and iron ores in recent basins. The Eningi-Lampi Lake in Central Karelia was chosen as the site for investigation of the ore-forming process. The mineral formation in the lake is evident, and the relationships between the source of the mineral-forming constituents and the areas of their accumulation are clear. It would be a naive over-simplification to suppose that the phenomena of mineral formation observed in this lake may be directly extrapolated to explain the details of Mn-Fe mineral formation in mediterranean seas and oceans. The preliminary model is not intended to cover all the particular features of each phenomenon, but to be used as an instrument in the study of the different processes of Mn-Fe mineral formation.

Eningi-Lampi Lake is a rather narrow (1.0-1.7 km) elongated (7 km) lake, up to 6 m deep. The tributaries of the lake drain areas of Lower Proterozoic metavolcanic basic rocks.

Authors' addresses are given at the back of this book.

Hydrochemical characteristics: The water of the lake is brownish, resulting from the dissolved humic content and suspended organic material. It is of relatively low mineral content (23.98-40.38 ppm) with predominant HCO_3^- ions (14.65-29.28 mg/l) among the anions, and Ca^{++} (1.80-3.60 mg/l) and Mg^{++} (1.70-3.89 mg/l) among the cations. The organic matter content reaches up to 32.86 ppm.

Mn and Fe in the lake water: The distribution of particulated and dissolved forms of Mn and Fe were studied where the samples were taken. The analysis of the filtrate (0.5μ filter) compared to the residue suggested that 72-92% of total Mn, and 30-48% of total Fe are dissolved rather than suspended.

The content of Mn in the waters of the lake (Fig. 1) decreases from Porusta River at the southern end, toward the north end of the lake. The concentration of Fe also decreases from south to north, but increases slightly again at the north end. The pH increases to the north.

Characteristics of sediments: A wide range of clastic sediments from boulder-pebbles to silt-clay sapropel-like muds has accumulated in the lake. Each type of sediment has a characteristic location and chemical composition (Fig. 2). In general, the sediments of the lake are the products of decomposition of Lower Proterozoic basic volcanic rocks.

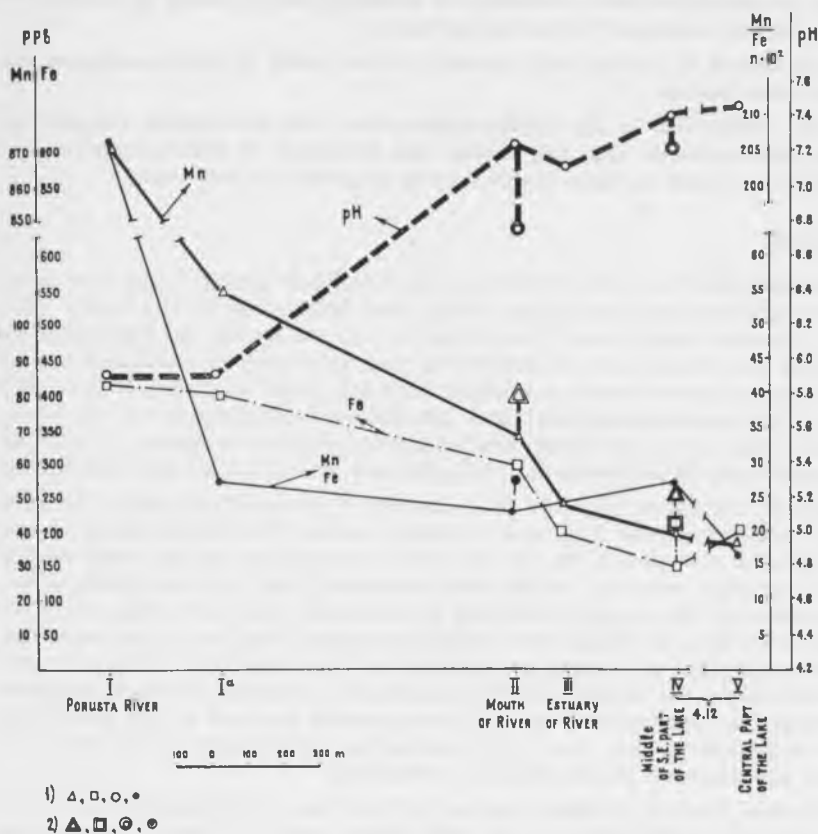


FIGURE 1 — Distribution of Mn, Fe (ppm), $\frac{\text{Mn}}{\text{Fe}}$ (n. 100), pH in waters of Eningi-Lampi Lake, Central Karelia.

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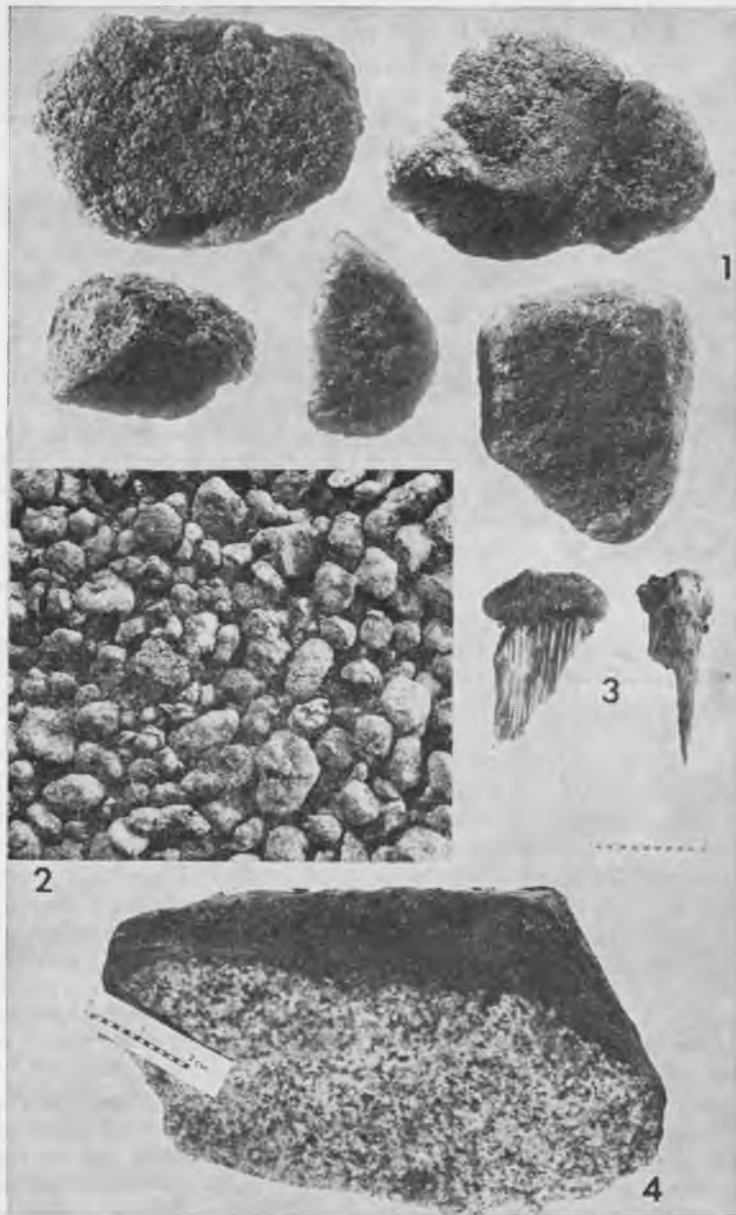


PLATE 1 — (Photo 1-3, common linear scale). Photo 1, Mn, Fe hydroxides growing over the surface of pebbles (cherts, altered basalts), thickness of coating to 30 mm. Photo 2. Mn, Fe, hydroxide nodules, their cores - clastic grains. Photo 3. fragments of wood, their upper part, rising above the water-sediment interface are coated by cap-like Mn and Fe hydroxides. Photo 4. the pebbles of igneous rocks, their surfaces rising above water-sediment interface, are coated by Mn-Fe hydroxides.

Fe-Mn NODULES AND CRUSTS

The nodules and crusts are morphologically different, but genetically very similar products. Some of the morphological varieties of nodules and crust-like coatings are shown in Plate I. Especially noteworthy is photo 3, showing that the upper part of wood fragments is covered by a cap-like growth of Mn-Fe hydroxides. During sampling from undisturbed sediments, one can observe these cap-like Mn and Fe coatings rising above the sediment-water interface. The part of a diorite pebble (photo 4) rising above the sediment surface is covered by black Mn-Fe hydroxide, but the lower part, which was buried in sediment, has a clean unstained surface. The water-sediment interface is well shown by the distinct border of Mn-Fe hydroxides growth.

The composition of nodules and crusts is as follows:

1. Manganese nodules: predominantly Mn hydroxide (birnessite), Mn up to 33%, Fe up to 8-10%.
2. Iron nodules: predominantly ferric hydroxide (goethite, hydrogoethite, amorphous hydroxides of Fe), Fe up to 51%, Mn up to 2%.
3. Nodules and crusts of intermediate composition: represented chiefly by mixtures of the above-mentioned hydroxide minerals of Mn and Fe. This type is predominant.

The compositions of inner and external parts of the nodules are of particular interest.

1. Inner parts of nodules are mainly composed of Mn hydroxides and to a lesser extent of Fe hydroxides. The external crust is mainly composed of Fe hydroxides with admixture of Mn hydroxides.
2. There is an evident association of Mn hydroxides with: Co (120-180). $10^{-4}\%$, Zn (104-402). $10^{-4}\%$ and BaO (1.27-2.15%); Fe hydroxides are associated with: C_{org} (0.85-1.80%), Co (1.44-3.46%), Ni (5-40). $10^{-4}\%$, Cu (3-13). $10^{-4}\%$.
3. The SiO_2 and Al_2O_3 components of the nodules are very low; also such elements as V and Cr, which occurs in amounts of less than 0.0034%. None of these form distinct associations with the Mn and Fe.

Mode of occurrence: Mn-Fe nodules and crusts are found mostly in the zone of deposition of sands and coarse silts (Fig. 2). As a rule, the nodules and crusts occur on the surface of sediments. More rarely, they are in the upper thin layer (5 cm) of brown watery mud; below this mud there is greenish-gray silty mud, enriched by organic material without any Mn-Fe hydroxide nodules. In the zone of accumulation of dark green, often dark gray, silty, clayey, sapropel-like muds, the nodules are not found.

Areal distribution of Mn-Fe concentration in the nodules: The content of Mn in the nodules and crusts decreases from the Porusta River mouth across the southern part of the lake and remains low along the northeastern bank. The concentration of Fe in the nodules increases in this direction (Fig. 3).

Discussion

The accumulation of Mn-Fe hydroxides is actively taking place on the surfaces of coarse clastic particles, walls of outcrops exposed at the edge of water, and even on fragments of wood (Plate I, 3).

The morphological variety of nodules and crusts depends on the environment at the exposed surfaces. In most cases, surfaces are in contact with bottom waters; more rarely, they are in contact with interstitial solutions of muds.



FIGURE 2
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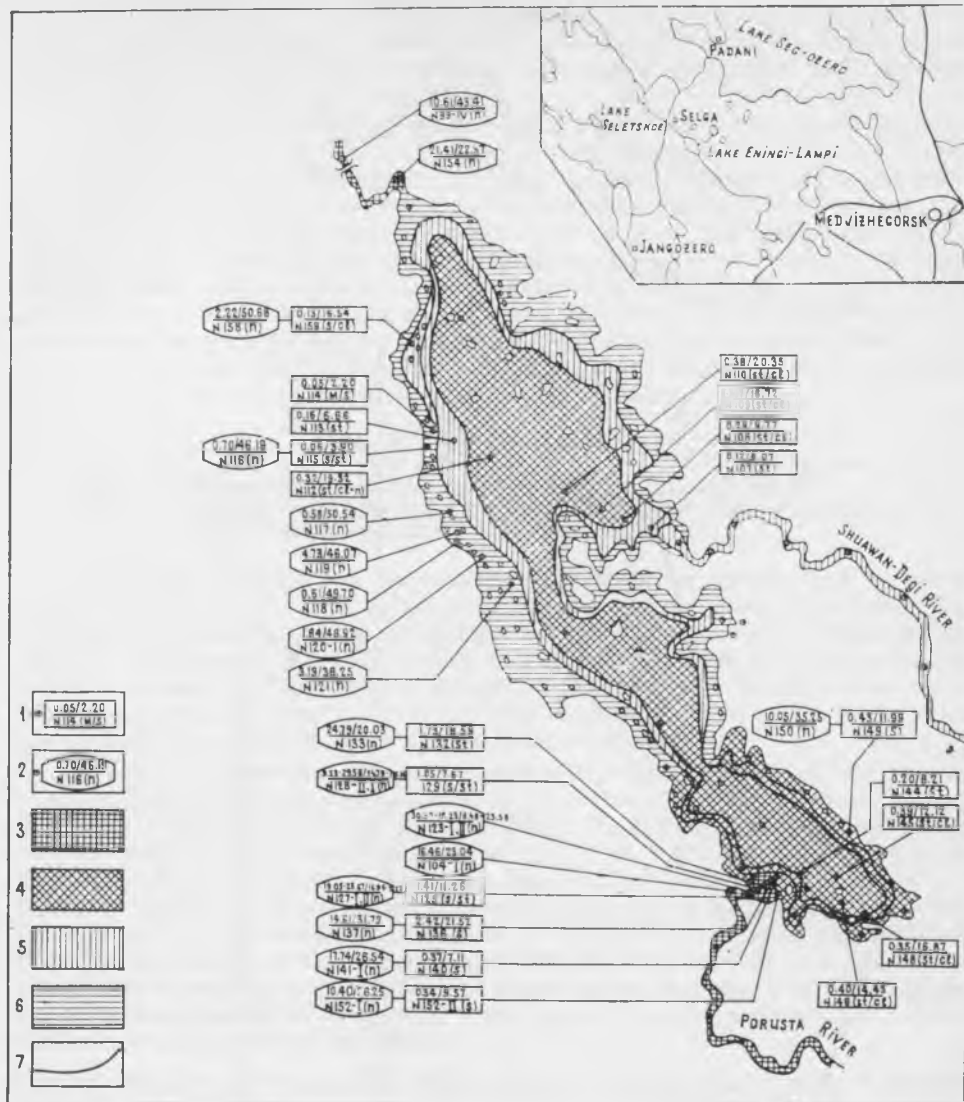


FIGURE 2 —Distribution of Mn in sediments (interval 0.0-10.0 cm), Eningi-Lampi Lake.

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| 1, Mn/Fe content (%) in sediments. | 5, 0.1 to 0.2% Mn. |
| 2, Mn/Fe content (%) in nodules. | 6, Less than 0.1% Mn. |
| 3, More than 1% Mn. | 7, Boundary of sediment type distribution. |
| 4, 0.2 to 1.0% Mn. | |

Patterns used in legend are as follows: 3, Fine-grained sands, coarse silts with admixture of clay and organic matter. 4, Silt-clay sapropel-like muds, dark grey to black. 5, Fluvial deposits: pebbles, boulders and coarse sands coated with Mn-Fe hydroxide crusts. 6, Near shore sands, gravels and pebbles.

N —number of sample
 n —nodule of Mn-Fe hydroxide
 S —sand
 St —silt
 Cl —clay
 S/cl —sandy clay
 St/cl —silty clay

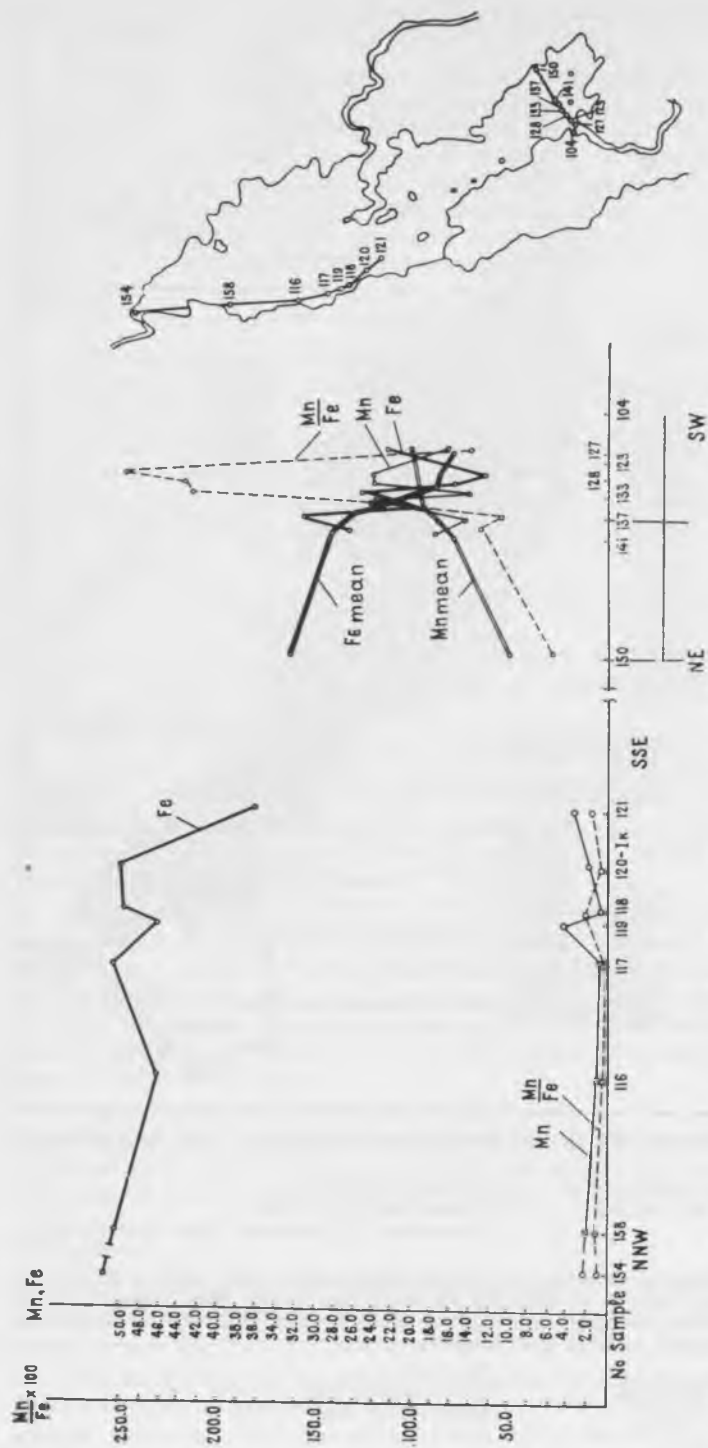


FIGURE 3 — Distribution of Mn, Fe, $\frac{Mn}{Fe}$ in nodules, Eningi-Lampi Lake.

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Mn and Fe dissolved in the lake waters are present mainly as organic complexes (humic and others); probably bicarbonate compounds of Mn play a certain role. Most of the material in suspension is organic particles and plant detritus, with minor non-organic particles.

In the course of interaction of Mn and Fe solutions with exposed surfaces, the oxide phases of these metals are formed. Our field observations, and the results of our experiments, as well as the work of others, allows us to conclude that the leading role in these phenomena is played by chemisorption interactions, followed by autocatalytic oxidation (Morgan and Stumm, 1964; Michard, 1969). The phase of Mn and Fe hydroxide forming on the active surface can, in turn, react as a very active sorbent, which promotes new acts of chemisorption of Mn and Fe; these elements are fixed as the oxide phases. The interaction of the multivalent components may be accompanied by destruction or oxidation of their organic complexes. For the approximate estimation of kinetics of these processes the following simplified equation may be used (Michard, 1969): —

$$\frac{d(\text{Me})}{dt} = K (\text{Me}^{++})$$

Me — number of moles of metal, fixed by the weight unit (g) of solid;
 (Me⁺⁺) — concentration of metal of lower state of oxidation in solution (ppb);
 K — kinetic constant, dependant on the nature of sorbent;
 t — time.

From this equation one may make the general conclusion that, at given values of pH and Eh, with increasing concentration of metal in solution the amount of hydroxides of this metal fixed on the active surface will also be increased. The intensity of such fixation depends on the surface properties of the solids — altered silicates, hydroxides of Mn and Fe, etc. The experiments of Morgan and Stumm (1964) show that with increasing pH of solution, the rates of autocatalytic oxidation of Mn and Fe sharply increase.

The data suggest that the major part of the Mn and some of the Fe was liberated from solution and accumulated as hydroxide compounds (nodules, crusts, sediments) within the Porusta River estuary. The northern part of the lake is supplied with relatively small amounts of Mn (Fig. 1-3). Meanwhile, the main quantities of Fe (in particulate forms) accumulated in fine-grained muds, enriched by organic matter. In this environment the decay of Fe-bearing compounds takes place, and Fe moves into solution. This element is able to diffuse from interstitial solutions toward the bottom waters. In areas of very slow sedimentation the autocatalytic accumulation of Fe on active surfaces then takes place. Probably the relative enrichment of waters with Fe in the northern part of the lake may be explained by this model.

General Features of Formation of Mn and Fe Nodules and Crusts in Recent Basins

The problems of formation of Mn and Fe hydroxide nodules and crusts in Recent basins (lakes, seas, oceans) have been discussed in some comprehensive works (Goldberg and Arrhenius, 1958; Semenovitch, 1958; Manheim, 1965; Mero, 1960; Price, 1967; Vinogradov, 1967; Strakhov *et al.*, 1968; Cronan and Tooms, 1969; Skonyakova and Andrushenko, 1970). The main features of formation processes in differing physico-geographical environments may be summarized as follows:

1. Nodules and crusts of Mn and Fe hydroxides occur in lakes, mediterranean seas and oceans, mostly at the water-sediment interface, as crust-like coatings growing on rock, boulders and on many kinds of surfaces. More rarely, Mn-Fe nodules are found in the upper part of the oxidized zone of sediments.

2. Intensive formation of Mn-Fe nodules occurs where their rate of growth is considerably higher than the rate of sedimentation. For example, in the Baltic Sea, Mn-Fe nodules and crusts are most common on the slopes, summits of submarine elevations, and areas of submarine erosion of the floor country rocks (Varentsov and Blazhchishin, 1970). In oceans, the nodules occur widely on the abyssal floor, where the rates of sedimentation are relatively slow ($0.2-3.0 \times 10^{-3}$ mm/year) (Bezrukov and Romankevitch, 1970).

In those rarer cases where Mn-Fe nodules are found in the upper oxidized part of sediments, their formation is controlled by a complex set of conditions: the rates of their growth versus that of the accumulation of sediments, the content of organic matter in the sediments, and Eh condition of the bottom waters. Different values for these variables lead to different results: burial of oxide nodules, their dissolution, transformation of oxides of Mn and Fe and some other transitional metals into silicate, carbonate, and sulphide compounds, and the upward migration of the nodule-bearing interval of mud in accordance with sedimentation. The available information suggests that in areas where sediments have a low content of active organic matter (for example, the Pacific abyssal red clays), the burial of ferromanganese oxide nodules takes place. The composition of these buried nodules is practically the same as those lying on the surface of sediments (Cronan and Tooms, 1969).

3. Recent work (Manheim, 1965; Price, 1967; Cronan and Tooms, 1969) has shown that in both their mineralogical composition and the association of trace elements with major ones, nodules distinctly reflect the depth of their formation. The data suggest that at relatively shallow depths (to 3000 m) birnessite-rich nodules associated with Co, Cu, Pb, V and Ba predominate. In deeper waters, todorokite enriched by Ni and Cu predominates. Some authors (Mero, 1965; Manheim, 1965) stated that Fe-nodules accumulate mainly in shallow waters and are not typical of abyssal environments.

The physical reason for the relationship between depth and the composition of nodules is not clear. In some cases, the problem may be complicated by the difficulty in identifying the sources of the elements. For example, in such vast basins as the Pacific Ocean (Cronan and Tooms, 1969), there might be a local endogenous supply.

4. The role of constituent supply is an important factor in those lake and sea basins (Baltic, Black and Arctic Seas) where features of run-off distribution essentially control the general pattern of sedimentation. In open oceans and in some seas there are combinations of exogenous and endogenous sources of ore-forming components. The role of endogenous and volcanic processes is rather evident in the formation of Mn-Fe nodules in the central and southern parts of the Pacific Ocean (Mero, 1965; Cronan and Tooms, 1969; Skornyakova and Andrushenko, 1970). The latter are associated with volcanic materials (basalts and hyaloclastites). The prominent part in the balance of these elements belongs, probably, to processes of submarine leaching of basic volcanites (Varentsov, 1970) and biogenic transformations. In 1932, Vernadskiy (1960) pointed out that these elements were present in the waters of open oceans as organic compounds — by-products of the activity of plankton. Johnston (1964) found that maximum concentration of some transitional elements occurred in the areas of plankton development — zones of divergence. In many cases, the parts of the ocean where the water masses contain high concentrations of these elements could be correlated with intensive development of nodules on the floor (Schutz and Turekian, 1965).

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CONCLUSIONS

1. The distribution of Mn and Fe in waters, sediments and nodules of Enings-Lampi Lake, Central Karelia, shows regular and consistent patterns related to source and accumulation areas.
2. Mn-Fe hydroxide nodules and crusts occur at the water-sediment interface. More rarely, they are found in the upper oxidized part of sediments. The dominant process in their formation is selective chemisorption, fixation of Mn and Fe and some other transitional elements, followed by autocatalytic oxidation.
3. In this brief review of the main features of Mn-Fe nodule formation in recent lakes, seas and oceans, it is assumed that in spite of the substantial physiogeographical and geochemical differences of these basins, the model of Mn-Fe nodule formation may be based on chemisorption autocatalytic interaction of active surfaces with component-bearing solutions.

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