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SHORT COMMUNICATIONS

Conditions of Formation of Ferromanganese Nodules in the Bottom Sediments of Lakes in the Baltic Shield

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The water basins in the bottom sediments (BS) of which ferromanganese nodules (FMN) are formed have long drawn close attention of researchers, mostly as sources of iron ore for the mining industry. Such ore occurrences are relatively widespread in various regions of the ocean [1] and continental freshwater basins, including Lake Baikal [2], Lake Onega [3], and many small lakes in northwestern Russia [4–7]. Thematic studies by the Institute of Geography, Academy of Sciences of the USSR [6] showed that ferromanganese mineralization in lacustrine BS is common in the Baltic shield, both in Karelia and in the Kola Peninsula. In the latter case, the mineralization is mainly confined to deep lakes, and the largest ore occurrences occur in the upper mud levels of deep-water areas.

Fedorova [6] evaluated limnological conditions in the lakes of the Kola Peninsula where FMN were found and distinguished the following indicators of such basins: (a) near-neutral pH values of water; (b) high content of dissolved oxygen throughout the entire water column down to the bottom; (c) high redox potential of water, which is related to the previous condition; (d) low oxidizing capacity of water; and (e) low iron content in water. Most authors assigned the accumulation of considerable amounts of Fe and Mn in BS to early diagenetic processes [5, 8, 9]. Some types and phases of ferromanganese mineralization can be related to physicochemical processes, whereas others are probably connected with the activity of microorganisms, for instance, iron bacteria [5, 9, 10]. Most likely, these two groups of processes occur simultaneously and are closely coupled with each other.

The first findings of FMN in the BS of Lake Imandra (largest lake of Murmansk oblast) were described in one of the earliest studies of the lake [11]. The investigations of the late 1920s (i.e., in the period before the beginning of the development of mining and metallurgical production on the coast of the lake in the 1930s) revealed widespread occurrence of iron oxides in mud as small smearing segregations, thin iron-rich films, or compact dark brown crusts composed of larger hard grains. Consequently, the recent findings of FMN in the BS of polluted and conditionally pure areas of the lake, as well as their description in the preindustrial period of the development of the catchment area, support the suggestion that FMN formation is primarily controlled by natural early diagenetic processes rather than the anthropogenic contamination of the lake with industrial sewage. The latter factor also influences the process of FMN formation, for instance, owing to the development of eutrophication and acidification resulting in an oxygen deficit, an increase in the concentration of hydrogen ions, and, correspondingly, formation of reducing environments and acid conditions in bottom water layers and upper BS levels, which hampers the formation of FMN.

During the investigation of Lake Imandra [12], FMN were found both in the northern pool known as Bol'shaya Imandra (middle part of the Monche Guba) at a depth of 14.5 m in the area contaminated by the industrial sewage of the Severonikel' Plant (high contents of heavy metals and flotation reagents) and in the conditionally uncontaminated area of the western pool (Babinskaya Imandra in the middle part of the Pasma Guba) at a depth of 13.5 m. Brown ferromanganese crusts, up to 10 mm thick, were found 0–4 mm from the surface of BS (gray or black mud). The concentrations of Fe and Mn in them are significantly higher than the average crustal contents (4.65 wt % Fe and 0.1 wt % Mn [13]): 304.5 ± 37.1 mg/g Fe (30.45%) ($n = 3$) and 81.7 ± 7.64 mg/g Mn (8.17%) ($n = 3$). These results also suggest that the intense natural processes of early diagenesis that produced FMN are similar to anthropogenic processes (for instance, anthropogenic pollution) in that they can cause extremely low species diversity and low invertebrate population density in zoobenthic communities, i.e., FMN restrict the development of bottom organisms owing to the formation of a solid barrier impermeable for hydrobionts [12].

The geochemistry of Mn and Fe in the water column and BS deserves special attention because these metals play a key role in the geochemical cycles of other elements [14]. The insoluble forms of Fe and Mn are usually characterized by high oxidation states, whereas lower oxidation states are common in soluble and other forms with relatively low affinity for complexation. For instance, ferrous hydroxide is four orders of magnitude more soluble than ferric hydroxide. The solubility of iron hydroxides depends also on the concentration of hydrogen ions; for instance, the solubility of ferric hydroxide also increases by four orders of magnitude when pH decreases from 8 to 6 [15]. Therefore, under the conditions of eutrophication and acidification, FMN do not form in the BS of lakes, and the concentrations of Mn in lacustrine sediments are very low and may be several ppm, which is comparable with the concentrations of such heavy metals as Ni and Cu, while the Fe content is more than an order of magnitude lower than the clarke value [16]. Consequently, Mn and Fe ions are mobile, and their concentration profiles reflect the character of transportation of these elements. A number of studies addressed the distribution of Fe and Mn in the profile of a water body and BS [17–20] and mathematical modeling of the behavior of these elements [14, 21–23]. On the other hand, with a few exceptions [24–26], all these studies considered mainly marine systems. There is only limited evidence on the distribution of these elements in the water columnes of lakes [27].

Moiseenko et al. [28] considered the behavior of Mn and Fe under reduced and oxidized conditions in the water column and BS of a subarctic water basin by the example of Lake Imandra. It was found that the water body is stratified with respect to O_2 saturation in the winter and spring periods owing to the oxidation of organic matter accumulated at the bottom. The subarctic region is characterized by the occurrence of small forest and swampy lakes with high humus contents. Therefore, O_2 deficit may develop in the bottom environments of lakes both under the influence of anthropogenic pollution and in natural swampy basins. It was shown that the lacustrine redox cycle of Mn and Fe is the main mechanism of oxidation and reduction of these elements, Fe^{3+}–Fe^{2+} and Mn^{4+}–Mn^{2+}. The redox systems of Mn and Fe are well known in the scientific literature [14].

(1) Under anoxic conditions, Fe and Mn reduction is catalyzed by microorganisms:

$$CH_2O + 2MnO_2 + 3H^+ \rightleftharpoons 2Mn^{2+} + HCO_3^- + 2H_2O$$

and

$$CH_2O + 4FeOOH + 7H^+ \rightleftharpoons 4Fe^{2+} + HCO_3^- + 6H_2O.$$

The reduction of Mn^{4+} oxides to dissolved Mn^{2+} species occurs at a higher redox-potential (i.e., higher concentration of dissolved O_2) than the reduction of Fe^{3+} to Fe^{2+}.

(2) The oxidation of Fe and Mn under oxic conditions can be described by the following reactions:

$$4Fe^{2+} + O_2 + 10H_2O \rightleftharpoons 4Fe(OH)_3 + 8H^+$$

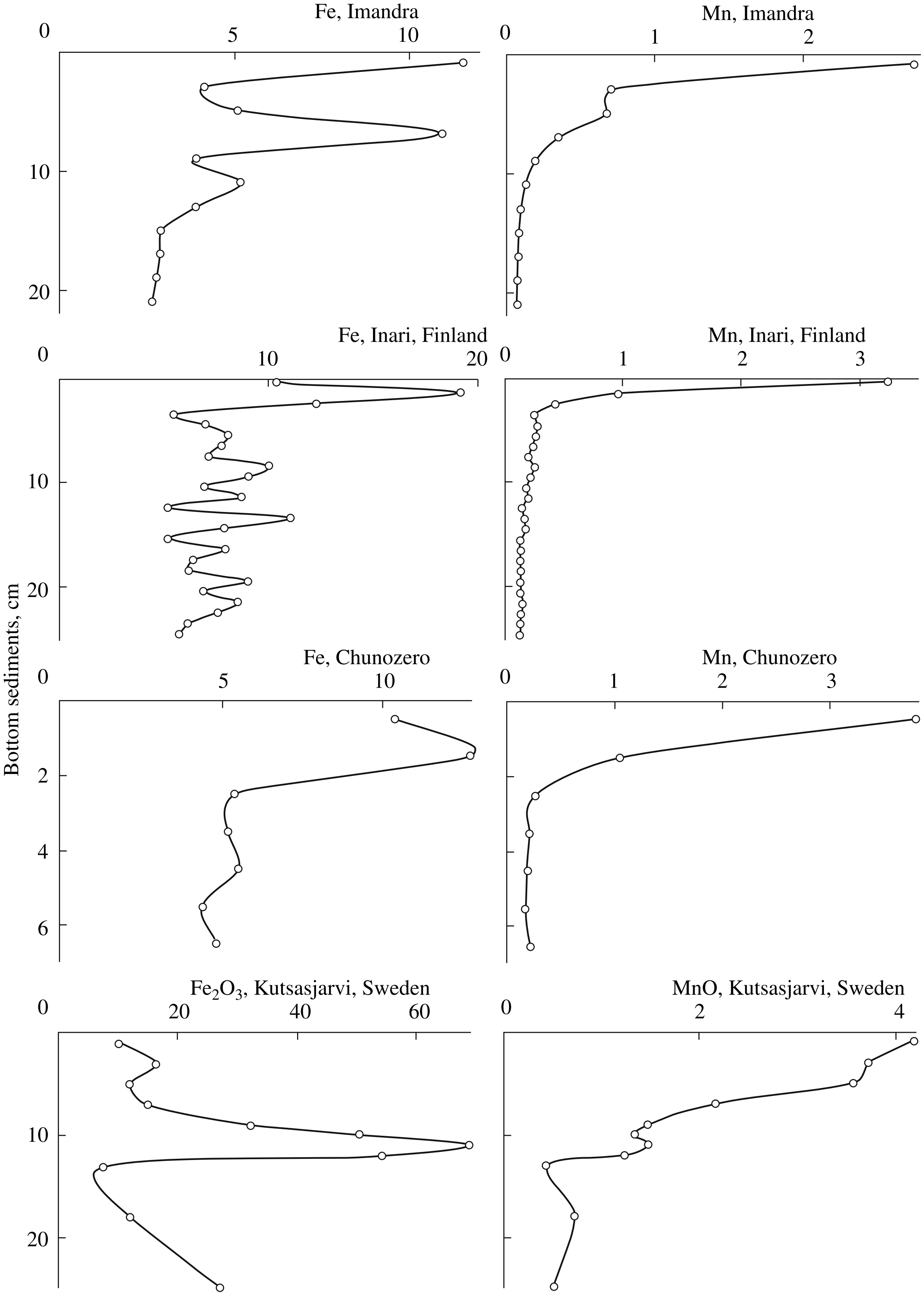
and

$$2Mn^{2+} + O_2 + 2H_2O \rightleftharpoons 2MnO_2 + 4H^+.$$

The oxidation of dissolved Fe^{2+} to suspended Fe^{3+} oxides occurs more rapidly than Mn^{2+} oxidation to Mn^{4+} oxides. Manganese oxidation occurs rather slowly under typical pH conditions of surface waters. Therefore, when Fe^{2+} and Mn^{2+} enter water basins, Fe is oxidized and precipitates before Mn. On the other hand, the reduction of oxidized Mn compounds in the BS of water basins occurs more readily than the reduction of oxidized Fe compounds [29].

At the boundary between oxic and anoxic conditions (i.e., oxidizing and reducing environments), the degrees of Fe and Mn oxidation change. The cycling of these elements occurs via the following mechanism [30]. The Fe (III) and Mn (IV) oxides that are formed under oxygen-saturated conditions precipitate mechanically in a water medium. When they reach the anoxic layer of water and BS, the reduction of Fe (III) and Mn (IV) occurring in oxides begins and these oxides are gradually dissolved. The dissolved Fe (II) and Mn (II) species diffuse upward along the resulting gradient of Fe and Mn in the water column or in the pore water of BS. In the oxygen-rich environment, Fe (II) and Mn (II) are oxidized and precipitate as Fe (III) and Mn (IV) compounds. The latter settle mechanically reaching anoxic conditions, after which the cycle is repeated.

The figure shows the vertical distribution of Fe and Mn concentrations in the BS of lakes of Murmansk oblast and of the northern regions of Finland and Sweden. An increase in the concentrations of Fe and Mn in the near-surface layers of BS is characteristic of both large (Imandra [31] and Inari [32], the largest lakes of Murmansk oblast and Finnish Lapland, respectively) and small lakes (Lake Chuna in the Imandra catchment [31] and Lake Kutsasjarvi in northern Sweden [33]). The maximum contents of Mn (10–50 times clarke and background contents) were detected in the uppermost one-centimeter-thick layer of BS of the aforementioned lakes. The reason is probably that a change from oxidizing to reducing conditions takes place in this upper layer and, as was noted above, the reduction of Mn^{4+} oxides to dissolved Mn^{2+} species occurs at a higher redox potential (i.e., higher concentrations of dissolved O_2) than the reduction of Fe^{3+} to Fe^{2+}. Consequently, the maximum Fe contents (up to 10 times clarke and background contents) can be found in BS at greater depths also, i.e., under lower Eh conditions (at low concentrations of dissolved O_2). Thus, it can be concluded that the better the oxygen supply to the bottom water and surface BS layers, the greater is the depth where low-soluble Fe^{3+} oxides are deposited in BS and FMN are formed. In the end of winter (May 2003), there was no oxygen deficit beneath ice in Lake Kutsasjarvi, northern Sweden, and the boundary between oxidizing and reducing conditions lay below the water–BS interface [33]. This resulted in a considerable increase in Fe_2O_3 content up to 70% at a depth of 11 cm (figure). On the



Vertical distribution of Fe and Mn concentrations (%) in the bottom sediments of lakes of Murmansk oblast and the northern regions of Finland and Sweden.

other hand, the Mn concentration began to increase at a depth of 12 cm, and the maximum MnO content of 4.2% was detected in the upper centimeter of sediment. This provides additional evidence for the suggestion that dissolved Fe^{2+} is oxidized to low-soluble Fe^{3+} oxides faster than Mn^{2+} is oxidized to Mn^{4+} oxides. An increase in Fe concentration in the subsurface layers of BS (figure) is related to the processes of molecular diffusion of dissolved ferrous species from the underlying BS, which are characterized by anaerobic conditions and elevated reducing potential, towards the contact with the oxidized zone of the water body, where they are oxidized, immobilized, and accumulated in the surface oxidized layer [34]. Furthermore, Malinovskii et al. [33] showed that the precipitation of Fe^{3+} generated under oxidizing conditions results in the formation of oxides enriched in heavy isotopes (primarily, ^{56}Fe).

Thus, FMN can be formed in the BS of lakes of the Baltic shield if the following three major conditions are fulfilled: (1) near neutral pH values of water, and no processes of lake acidification; (2) high content of dissolved oxygen throughout the entire water column to the bottom and the absence of eutrophication processes; and (3) sufficient depth of lakes, about 15 m or deeper. The highest Mn concentrations in these lakes are usually observed in the upper centimeter of BS, whereas the highest Fe contents are confined to deeper BS layers at the boundary between oxidized and reducing environment. This is related to the geochemical properties of these metals: the oxidation of dissolved Fe^{2+} to insoluble Fe^{3+} oxides occurs faster (at lower values of redox potential and lower concentrations of dissolved O_2) than Mn^{2+} oxidation to Mn^{4+} oxides.

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