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Nodules in Sediments of an Artificial Reservoir in the Altai Territory

B. L. Shcherbov and V. D. Strakhovenko

United Institute of Geology, Geophysics, and Mineralogy, Siberian Division, Russian Academy of Sciences, pr. akademika Koptyuga 3, Novosibirsk, 630090 Russia
e-mail: strahova@uiggm.nsc.ru

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Abstract—Nodules of various compositions, including ferromanganese nodules, have been found in bottom sediments of an artificial reservoir in the central Altai Territory. The nodules were formed in the alkaline environment against the background of a high carbonate content and saturation with oxygen. The rate of nodule growth is no less than 1.7–1.8 mm/yr and the pH value of water varies from 8.0 to 9.7. Fe and Mn contents in soil and loam of the drainage area are lower than the global clarke value, whereas Ca, K, and Na contents are much higher. The main mass of bottom sediments in the reservoir is markedly enriched in Cd, Mg, Mn, Sr, Ni, Cr, Sb, V, and Pb, but they are depleted in Cu, Mo, Zn, and Li, relative to the soil and loam. Elements in ferromanganese nodules are arranged in the following way in terms of the decreasing concentration coefficient: Mn (27) > Ba (13.4) > Co (10.7) > Mo (9.2) > Cd (5.35) > Ni (3.88) > V (3.52) > Cu (3.3) > Fe (3.2) > Sb (2.17) > Sr (2.04) > Pb (1.5) > Zn (1.43) > Cr (1.1) > Li (0.78) > Mg (0.75) > Na (0.69) > K (0.67) > Ca (0.51). The microelemental composition of nodules in the reservoir qualitatively fits the composition of ferromanganese nodules in seas and oceans. However, the contents of major ore elements (Ni, Cu, Co, Zn, Pb, Mo, and V) in ferromanganese nodules from the World Ocean are much higher than in nodules from the examined reservoir.

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INTRODUCTION

More than two and half centuries elapsed from 1763 when I.G. Vallerius and M.V. Lomonosov described “stone intergrowths” and “formation of stones” on the bottom of water reservoirs. Hundreds of articles and dozens of monographs and collections of papers on this subject have been published over this period. The lion’s share of these works is devoted to ferromanganese nodules in oceans and seas. Lacustrine nodules have received a much less attention. Information on ferromanganese nodules formed in small artificial reservoirs is not available at all. We failed to find such information in the literature on lithology and geochemistry of Mn and Fe or in numerous references in textbooks, monographs, and articles. Seasonal dynamics of Fe distribution in a reservoir in Japan has been reported in a single publication (Yoshimura, 1936). However, the process did not reach the stage of nodule formation in this reservoir.

Among tens of lakes, oxbows, and reservoirs in the Altai Territory examined in the 1990s by Shcherbov *et al.* (2003), only the reservoir at the Porozhnee Settlement contains ferromanganese nodules in bottom sediments. Carbonate nodules were observed in many reservoirs of the Kulunda Basin and the Barabinsk Steppe. Such nodules in lakes of the Kulunda area were thoroughly studied by Vital (1950).

The objective of the present work was to study the chemical composition and formation conditions of ferromanganese and other nodules in an artificial reservoir built in the late 1930s.

GENERAL INFORMATION

The studied reservoir is a part of the system of artificial ponds near the Porozhnee Settlement in the central Altai Territory. The level of this reservoir dropped several times as a result of dam breach. No nodules were found in bottom sediments of two new reservoirs that were built upstream in the 1970s.

The area is located in the forest–steppe zone and characterized by the occurrence of numerous ravines (altitude 219–266 m). The reservoirs are surrounded by pastures and plough lands. The drainage system of the reservoirs covers approximately 10–15 km^2 and the water surface is no greater than 1500 m^2. Many small ravines with steep walls and subsoil water seeps are located nearby. The reservoirs are fed by a small intermittent creek and several seeps. One can also suppose the existence of underwater springs, because a creek (discharge no more than 2 l/s) permanently flows out of the reservoirs.

The soil cover near the Porozhnee Settlement is composed of steppe and meadow chernozem with a turf layer of variable thickness. Salt marshes occur in the

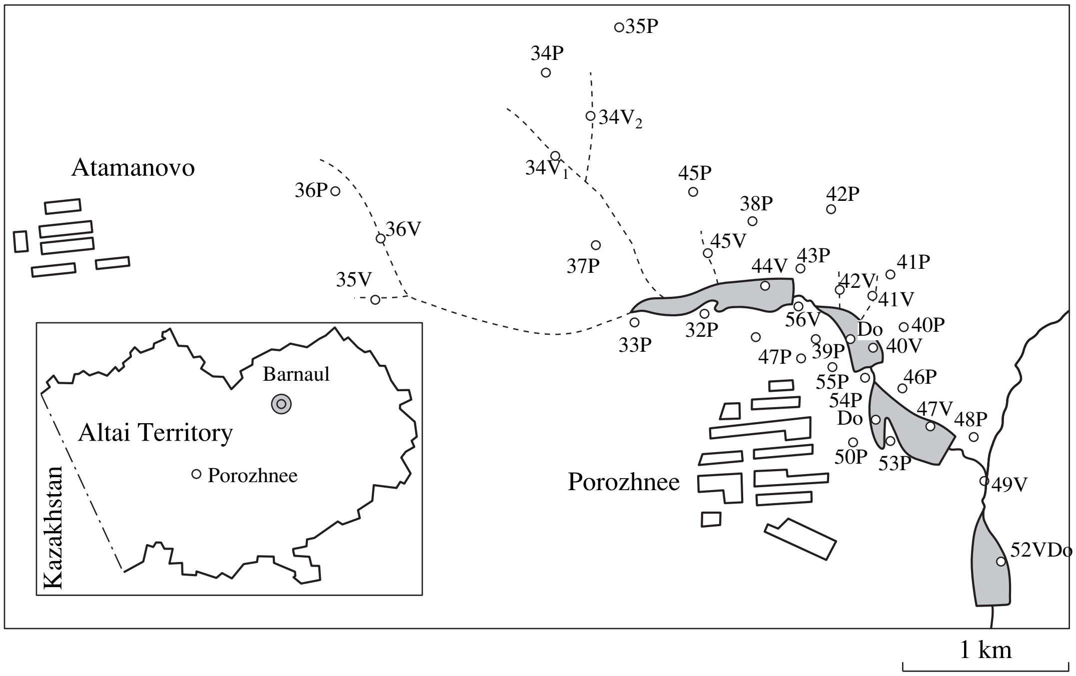

Fig. 1. Index map of soil, water, and bottom sediment samples taken in the Porozhnee Settlement area.

north. Gray and yellowish gray loesslike loams that effervesce upon reaction with 10% HCl solution serve as soil-forming rocks.

OBJECTS AND METHODS

As has been pointed out by A.P. Vinogradov, "ferromanganese nodules were found in all podzol soils extending from the Atlantic Ocean to Manchuria. They largely occur in the ortstein (spodic) unit. And further, "manganese nodules were found not only in the ortstein soil units, but also in the chernozem, brown forest, and other soils" (Vinogradov, 1957, pp. 138–139). We did not find such nodules in hundreds of soil sections examined in the Altai Territory and adjacent regions. They were not also revealed in the adjacent reservoirs under study. Films, lenses, and sinters of iron and manganese hydroxides frequently crop out under the soil on walls of gullies and ravines. However, they are missing in soil sections at a depth of 40–50 cm and even 1.5 m.

Down to a depth of 9 cm, bottom sediments of the reservoir consist of liquid carbonate–clayey mud without visible organic remains. The moisture content is 32%, and the density of air-dry material is 1.33 g/cm^3. Below a depth of 9 cm, the sediment has an agglomerate structure with spherical segregations of various compositions varying from 0.5–1.0 to 15–20 mm or more in diameter. These nodules are nonuniformly distributed along the profile of bottom sediments. The moisture content in this portion of the section is 26%, and the density of air-dry mass is 1.76 g/cm^3.

The agglomerate structure of bottom sediments is emphasized by the presence of irregular carbonate segregations that distinctly stand out against the gray background. Perfectly spherical nodules are also found. Relatively large carbonate segregations are often confined to fragments of bivalve shells.

Samples of soils, soil-forming loams, and water from intermittent creeks and seeps were taken in the drainage area. Bottom sediments in reservoir were sampled with cylindrical corer at each 3 cm. The soil was sampled down to a depth of 40 cm with a standard ring 50 mm in height and 42 mm in diameter.

All samples were examined by the AAS method for Fe, K, Na, Ca, Mg, Ba, Pb, Zn, Cu, Ni, Co, Cr, Sb, Cd, Mo, V, Sr, and Li. Radioactivity of ^{137}Cs was determined with gamma spectroscopy. The analyses were carried out in the Laboratory of geochemistry of rare elements and ecogeochemistry, Institute of Geology, Novosibirsk using the technique described in (Bobrov and Gofman, 1971; Simonova, 1986). The laboratory has been certified by the Association of analytical centers (ANALITIKA) and has the State Registry No. ROSS Ru 0101.510590. Results of the analysis of soils, loam, and bottom sediments were recalculated to the air-dry state of materials. Index map of the samples is given in Fig. 1.

RESULTS

Nodule growth rate. We studied the ^{137}Cs distribution in the vertical section of bottom sediments in the lower reservoir to estimate the nodule growth rate.

The cores were sampled in 1994 in order to assess the radioactive pollution of the Altai Territory. The soil and creeks near the Porozhnee Settlement were sampled later to provide insights into the nature of ferromanganese nodules.

In total, 58 radioactive clouds from the Semipalatinsk test site passed through the Altai Territory (Shoikhet *et al.*, 1996). Correlation of information presented by different authors (Gamayunov *et al.*, 1995; Loborev *et al.*, 1995; *Semipalatinskii*..., 1997) allows us to regard August 20, 1953—the time of the first nuclear explosion with a total energy release of 400 kt TNT equivalent—as the most reliable date of radioactive precipitation at the Porozhnee Settlement. The lowermost peak of ^{137}Cs at a depth of 21 cm in the sediment profile (Fig. 2) apparently corresponds to this date. The second peak at a depth of ~16 cm is related to precipitates from the explosion on August 7, 1962 with energy release of 10 kt TNT.

Thus, 22 cm of sediments were deposited over 40 yr from 1953 to 1994. Taking into account the compaction of upper units of bottom sediments, the thickness should be not more than 20 cm. Hence, the sedimentation rate was approximately 5 mm/yr. This estimate appreciably exceeds the rate of sedimentary material deposition in plain lakes of the Altai Territory estimated at 4.3 mm/yr (Mikhailov, 1993). Calculation of sedimentation rates between the first and second explosions (5 cm over 9 yr) yields a slightly higher value of 5.5 mm/yr. This discrepancy is undoubtedly caused by the construction of two upper reservoirs in the 1970s, which began to serve as filters (settling tanks) on the way of mineral materials of loam and soil to bottom sediments of the third reservoir. This issue requires additional investigations. Nevertheless, the value of 5.5 mm/yr should be accepted as a minimum sedimentation rate in the third reservoir. Judging from the estimated rate, approximately 14 years were required for the deposition of sediments up to the upper nodule-bearing horizon (~7 cm with the consideration of compaction of the first three sampling intervals). Assuming that sedimentation and nodule growth are contemporaneous processes like in oceanic nodules (Volkov, 1979), the growth rate of nodules with the maximum size of 20–25 mm may be estimated at 1.7–1.8 mm/yr. However, the growth rate may be higher. This suggestion is supported by the fact that coastal deposits include nodules and manganese compounds that have replaced tree leaves, which cannot exist in water for a long time (Fig. 3). Furthermore, manganese coatings are observed on the constantly collapsing margins of the newly formed ravines at the outlets of some subsoil seepages.

Very high nodule growth rates have been reported in the literature. For example, many objects drowned in lakes of Karelian in the war period of 1939–1940 turned out to be coated with a 5-cm-thick ferruginous crust during 8–9 yr. Under laboratory conditions, ferrobacteria build up micronodules over a few weeks

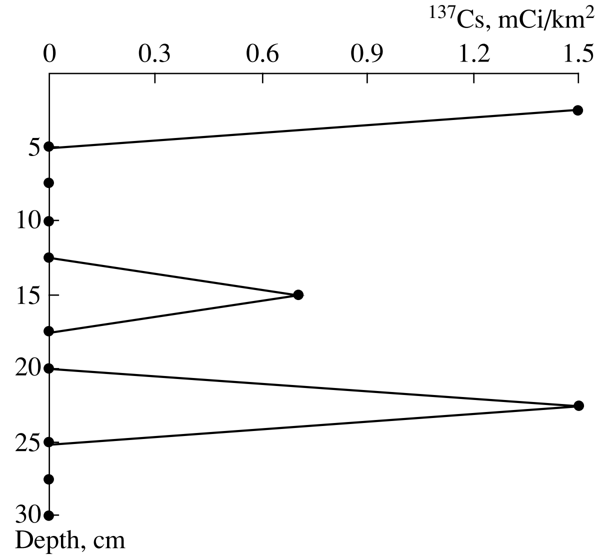

Fig. 2. Vertical distribution of ^{137}Cs in bottom sediments.

(Kalinenko, 1949). The rate of ferromanganese crust formation on shell fragments reaches 10 cm/100 yr (Mero, 1965).

The rate of ferromanganese nodule growth in our calculations is an order of magnitude higher that the typical growth rate of recent ferromanganese crusts in lakes, bays, fjords, and inner and marginal seas estimated at *n* cm/ka (Volkov, 1979).

Soil and loam. Table 1 shows that the soil cover of the study area is markedly enriched in Na, K, Ca, and Mg relative to the global clarke values for soils (Vinogradov, 1957). The content of trace elements are below the background value established for the soil cover of the forest–steppe zone of western Siberia (*Eko-geokhimiya*..., 1996), and only Co contents are somewhat above this level.

The soil-forming loam is also depleted in microelements in comparison with the loam from western Siberia (Il'in, 1991). In terms of contents of major and minor elements, this loam is similar to the loess from Kansas (United States) and the mean composition of the Earth's crust (Taylor *et al.*, 1983; Taylor and McLennan, 1981).

It should be noted that the Fe and Mn contents in soil and loam are lower than the global clarke values for soils, while Ca, K, and Na contents are higher than this level (Table 1).

Waters of the district. The reservoir-feeding groundwaters have alkaline properties with pH = 8.0–9.7 (Table 2). Seeps from clayey and loamy sediments in the ravine between the first and second reservoirs located at a depth of 4–5 m from the surface are characterized by a lower pH value of 8.0–8.2 (samples 56V and $56V_1$). Their discharge rate does not exceed 1–2 l/h.

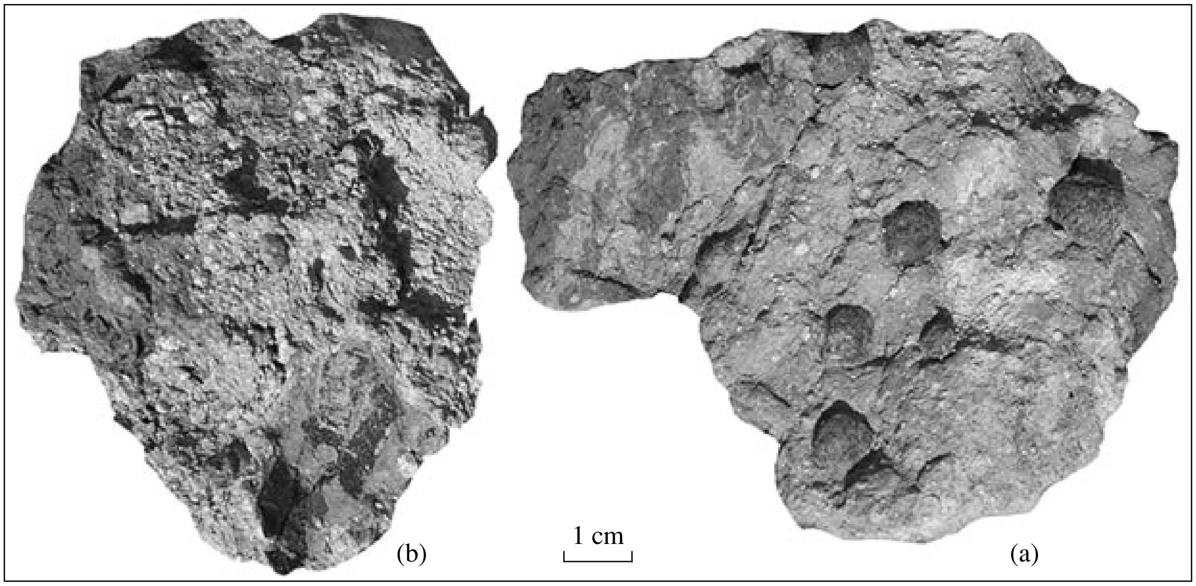

Fig. 3. (a) Fe–Mn nodules taken from the water line of reservoir and (b) replacement of tree leaves with manganese hydroxides.

The pH value of water from wells in the Porozhnee Settlement (depth 5–7 m) is 7.8–8.0.

Moderate pH values are also established in two seeps at headwaters of the ravine 2 km north of the Porozhnee Settlement (samples $34V_1$ and $34V_2$). These and other pairs of creeks located at a distance of 200–300 m from each other have virtually the same pH values, but they are sharply distinct in contents of some chemical elements (Table 2).

High pH values (8.8–9.7) are recorded in waters of reservoirs, intermittent creeks, and seeps with extended water flows (samples 35V, 36V, 44V, 45V, and others). Concentrations of some elements in these samples are two or three times higher than the average value (Co in sample 35V, Zn in sample 45V, As in sample 49V, and so on). In general, waters in the study area are depleted in Fe, Pb, Zn, Cu, and Ni in comparison with average contents in the groundwater of western Siberia (*Ekogeokhimiya…*, 1996), but they are enriched in Mg, Mn, Ba, Co, Cr, Sb, and Mo.

Bottom sediments and nodules. As was mentioned above, water level in the reservoir repeatedly dropped as a result of dam breach. The upper portion of bottom sediments was apparently formed after the building of two upper reservoirs in the 1970s and the stabilization of water level in the third reservoir.

The section of bottom sediments was sampled in the stagnant part of the reservoir, where the chemical processes were probably more active than in the running water area. Quartz, mica, chlorite, plagioclase, potassium feldspar, and iron oxides are identified in sediments by the XRD analysis. The diffraction pattern is weak, indicating that a considerable amount of the X-ray amorphous phase (most likely, iron and manganese hydroxides) is present in the samples. The organic component is probably negligible, because the L.O.I. value is below 10 wt %. The XRD pattern shows lines with $d = 2.40$ Å (vernadite) and $d = 2.95$ Å (ankerite). Vernadite was found in various places of the Indian Ocean as the major ore-bearing component along with psilomelane (Bezrukov and Andryushchenko, 1972).

The structure and mineral composition of bottom sediments suggest their formation as a result of the input of materials in both solid and liquid states. Numerous gullies and ravines deliver a great amount of clastic material of loam and soil during the thawing of snow and rainy seasons. In the dry seasons, seeps and creeks mainly transport the dissolved chemical components that form carbonates and hydroxides of Fe and Mn. In order to estimate the share of carbonate material, the sediments were treated with 10% HCl solution and washed out with distilled water. In the upper section of bottom sediments, the carbonate fraction readily dissolved in HCl (calcite) amounts to 16–17%. In agglomeratic sediments, the content is 20% within the intervals enriched in ferromanganese nodules and 23–24% in the depleted intervals. The chemogenic fraction of sediments should undoubtedly increase substantially due to the presence of vernadite, ankerite, and ferromanganese hydroxides in nodules and groundmass. Unfortunately, we failed to estimate quantitative proportions of ankerite, vernadite, and other authigenic minerals, which are insoluble in HCl, relative to the remaining mineral phases.

Nodules in the bottom sediments can be divided into two contrast types. The first type is mainly composed of carbonates, while the second type consists of Fe–Mn or Mn–Fe compounds. Carbonate segregations have irregular shape (Fig. 4, photographs 10, 11). They are composed of calcite with an admixture of quartz, mica, pla-

Table 1. Average contents of elements in loam and soil, mg/kg

Element	Loam	Soil	Worldwide estimate for soils*	Soils of forest-steppe zone of western Siberia**	Loam of western Siberia***
Fe	2.54 (2.1–2.95)	2.4 (1.75–2.75)	3.8	–	–
K	1.64 (1.39–2.1)	1.76 (1.28–2.03)	1.36	–	–
Na	1.54 (1.15–1.98)	1.24 (1.09–1.36)	0.63	–	–
Ca	3.05 (0.4–5.93)	1.76 (0.9–7.5)	1.37	–	–
Mg	0.89 (0.67–1.23)	0.87 (0.5–3.26)	0.63	–	–
Mn	570 (464–819)	656 (518–938)	850	773	598
Ba	610 (421–877)	458 (180–857)	500	420	–
Pb	13.4 (9–17)	16.4 (13–32)	10	19.1	13.3
Zn	56.8 (46–63)	64.4 (52–76)	50	78.4	72
Cu	20.8 (17–38)	23.4 (21–27)	20	25.5	36
Ni	31.2 (19–42)	33.2 (25–46)	90	35.7	43
Co	12.5 (9–15)	12.2 (8–16)	8	9.2	14.4
Cr	57.5 (46–93)	57.5 (37–71)	200	92.3	73
Sb	0.75 (0.45–1.2)	0.66 (0.2–1.1)	–	–	–
Cd	0.1 (0.08–0.11)	0.16 (0.11–0.21)	0.5	0.18	0.043
Mo	3.6 (1.4–5.0)	3.4 (2.0–5.0)	2.0	–	1.45
V	64.7 (47–76)	63.4 (49–88)	100	68.2	76
Sr	261 (139–417)	267 (118–1875)	300	185	139
Li	24.0 (17–27)	21.5 (18–26)	30	26.5	–
Mn/Fe	0.022 (0.017–0.03)	0.027 (0.022–0.044)	–	–	–

Note: Fe, K, Na, Ca, and Mg contents are given in %; *based on (Vinogradov, 1957); **based on *Ekogeokhimiya*…, 1996); ***based on (Il'in, 1991); (–) not analyzed. The range is given in parentheses.

gioclase, potassium feldspar, and chlorite. Ferromanganese nodules with an almost perfect spherical shape and zonal structure (Fig. 4, photographs 1–6) largely consist of vernadite and hematite in various proportions. Irregular ferruginous nodules (Fig. 4, photographs 7–9) usually represent intergrowths of several segregations up to 25 mm in size. The XRD results indicate that the trace element composition is similar in both iron and carbonate nodules. All these features show that the nodules captured terrigenous minerals of the loess-type loam and soil in the drainage area.

The chemical composition of bottom sediments substantially differs from the composition of soil and loam (Tables 1, 3). The groundmass of sediments is depleted in K and Na, but it is appreciably enriched in Co, Mg, Mn, Sr, Ni, Cr, Sb, and V. Contents of some elements, such as Cu, Mo, Zn, and Li, are virtually the same or less as in loam.

Contents of all elements, except K, Na, and Li, in nodules are higher than those in the soil and loam. Contents of Fe, Pb, Zn, Cu, Co, Cr, Sb, and V are 1.5–4 times higher, while contents of Ba, Ni, Cd, Mo, and Sr are 5–12 times higher (Tables 1, 3). For the majority of elements, this trend is retained in the case of comparison of nodules and groundmass of bottom sediments. During sedimentation, Cu, Mg, and Li are largely concentrated in the groundmass, while Fe, Mn, and other microelements enter the nodules.

DISCUSSION

Complex geochemical processes in the soil-forming rocks–soil–groundwater–bottom sediments system near the Porozhnee Settlement produced sediments with various nodules in the artificial reservoir. The nodules are mainly represented by the carbonate and ferruginous varieties. Another variety of nodules is represented by Fe–Mn or Mn–Fe concretions. Based on the Mn/Fe module, Skornyakova (1976) classified the Pacific concretions into the following types: iron nodules (Mn/Fe < 0.25), Mn–Fe nodules (0.25–1.0), Fe–Mn nodules (1–4) and manganese nodules (>4). Table 3 shows that the nodules from intervals of 9–12 cm (PR-3) and 18–21 cm (PR-8) match the Mn–Fe type, while the nodules from 15–18 cm (PR-7) and 21–24 cm (PR-10) match the Fe–Mn type. The average Mn/Fe value increases along the path of element migration from soil-forming rocks of the catchment area to nodules in the following sequence: loam (Mn/Fe 0.02) ⟶ soil (0.03) ⟶ groundwater (0.16) ⟶ groundmass of

Table 2. Chemical composition of water in the Porozhnee Settlement area, ppm

Sample no.	pH	Fe	Na + K	Ca	Mg	Mn	Ba	Pb	Zn	Cu	Ni	Co	Cr	Sb	Mo	Mn/Fe
$34V_1$	8.1	0.8	459	114	67	110	89	1	6	3	3	1	2.5	19	3	0.14
$34V_2$	8.1	0.11	186	68	35	50	39	1	4	2	2	5	2.5	31	5	0.45
35V	8.8	0.88	290	82	126	114	110	3.6	15	4	8	16	5.4	26	9	0.13
36V	8.9	0.71	296	85	131	105	100	18	52	3	12	6	6.7	25	9	0.15
40V	9.3	0.55	312	62	100	69	50	3	23	4	5	1	4.6	18	3	0.13
41V	8.8	0.32	405	62	93	22	40	20	50	5	9	6	6.2	11	3	0.07
42V	8.7	0.68	524	82	82	84	60	1	14	3	10	1	5	24	2	0.12
44V	9.5	0.40	391	62	116	69	50	1	10	2	6	1	3.3	3	5	0.17
45V	9.7	1.02	418	59	88	128	50	1	160	5	7	6	5.4	12	4	0.12
47V	9.4	0.36	240	47	67	51	50	1	23	5	4	1	2.9	4	5	0.14
49V	8.6	0.09	159	59	54	29	40	1	9	1	1	1	3	5	2	0.32
51V	9.5	0.04	65	35	19	5	5	1	2	2	1	1	3	3	2	0.12
52V	9.2	0.28	176	56	61	23	50	2.5	29	2	2	1	3.3	37	3	0.08
56V	8.0	0.04	229	35	61	5	6	1	2	2	2	1	3	3	2	0.12
$56V_1$	8.2	0.04	40	103	13	5	9	1	2	2	1	1	3	3	2	0.12
Average	7.9	0.38	279	69	74	58	50	0.5	17	3	5	3	15	15	4	0.08
*		0.58	261	65	54	37	23	4.3	52	10	8	0.9	1.9	1.9	1	0.06

Note: *Groundwater of dry steppe in western Siberia (*Ekogeokhimiya*…, 1996). Cd, Be, and Hg contents are below the detection limit; Fe, (Na + K), Ca, and Mg contents are given in mg/l. Sample locations: ($34V_1$) left seep at the ravine head 3 km north of the Porozhnee Settlement; ($34V_2$) right seep; (35V) seep on the right wall of creek; (36V) intermittent creek between the Artamonovo and Porozhnee settlements; (40V) left part of the second reservoir; (41V) seep at the left coast of the second reservoir; (42V) the same; (44V) first reservoir near the dam; (45B) intermittent creek falling into the reservoir from the left side; (47V) middle part of the third reservoir; (49V) Zagonikha River near the bridge; (51V) reservoir at headwaters of the Zagonikha River; (52V) central part of the lower reservoir; (56V) seep from blue-green clays between the second and the third reservoirs; ($56V_1$) seep from a rusty loam.

bottom sediments (0.12) ⟶ nodules (0.93). Within each sampling group, the module values vary in a wide range and they occasionally overlap the adjacent intervals.

Uniqueness of the nodule-containing reservoir is related to geochemical and hydrochemical settings of the area. The alkaline property of ground and surface waters in the reservoir (pH 8.1–9.7) provided an active migration of Ca, Mn, Mg, Ba, Co, Sb, and Mo. Even Cr commonly regarded as an inert component (Ovchinnikov, 1970; Voitkevich and Zakrutkin, 1970) is concentrated in this area (especially, in seeps). At the same time, contents of mobile elements, such as Cu, Pb, and Zn, are decreased relative to groundwaters of steppes in western Siberia. This is probably related to low contents of the respective elements in loam and soil. However, the assumption of low Cu, Pb, and Zn solubility in the presence of carbonates (Kabata-Pendias and Pendias, 1989) also seems to be valid.

Pathways of the migration of Mn and Fe diverge in the natural systems with reducing and alkaline environments. The mobility of Fe is limited ($Fe(OH_2)$ precipitates at pH = 5.5), whereas Mn readily migrates ($Mn(OH)_2$ precipitates at pH = 8.5). They precipitate together in the process of carbonate formation (Tugarinov, 1973). Nodules formed under such conditions are commonly depleted in Fe (Perel'man, 1989). This is observed in ferromanganese nodules of the studied reservoir. The Fe content in these nodules is much lower than in nodules from the freshwater Lake Baikal with the Fe content of 33% (Strakhov *et al.*, 1954) and in marine and oceanic nodules with the Fe content of 42% (Baturin, 1986). This statement is also valid for Mn. The highest Mn content in nodules from the reservoir is 11.8%, whereas the average Mn content in Pacific ferromanganese nodules is 17.9% (maximum 42.3%). For the Indian and Atlantic oceans, these values are 14.7 (37.0) and 14.9 (36.0)%, respectively (Volkov, 1979).

Despite this difference, the main microelemental composition of the nodules studied qualitatively fits the composition of spherical ferromanganese nodules from seas and oceans. In both cases, Ni, Cu, Co, Zn, Pb, Mo, and V are concentrated. However, their concentration is significantly higher in nodules of the World Ocean than in counterparts from the reservoir (%): Ni 0.66, Cu 0.45, Co 0.27, Zn 0.16, and Pb 0.83 (Baturin, 1986).

Concentrations of elements are different in the ferromanganese nodules. In terms of the concentration coefficient ($C_{nodule}/C_{groundmass}$), the chemical elements of ferromanganese nodules make up the following series:

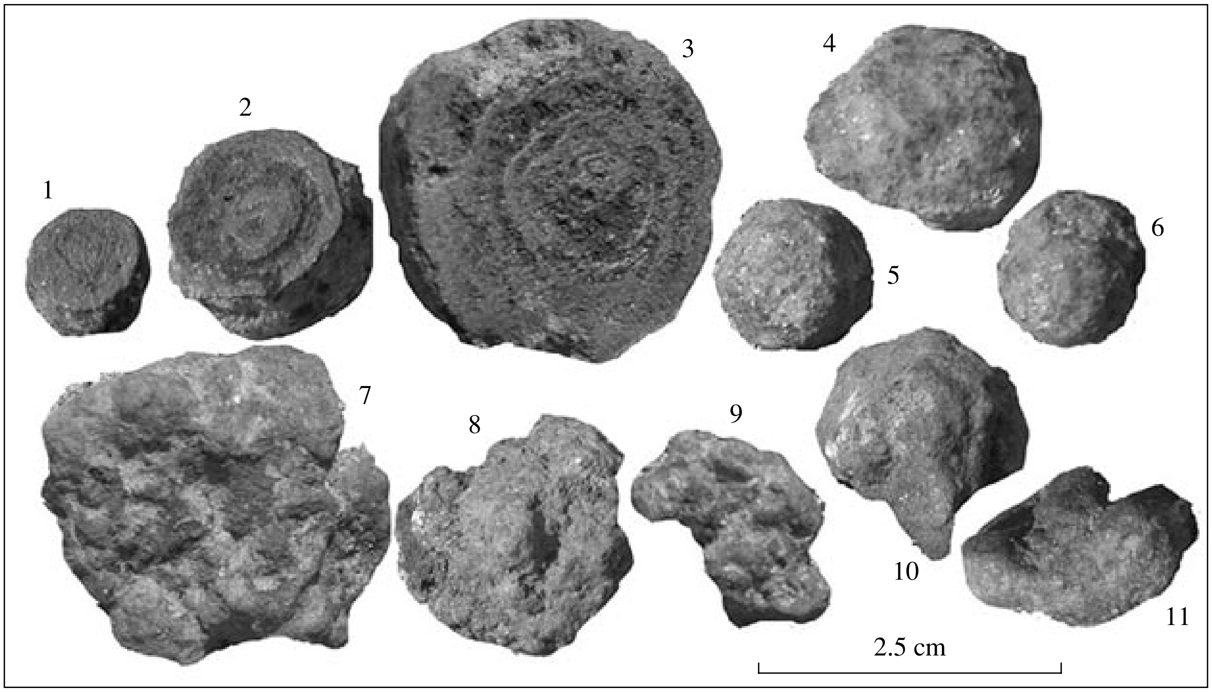

Fig. 4. Morphology of nodules: (1–6) ferromanganese, (7–9) mainly ferruginous, and (10, 11) carbonate.

Mn (27) > Ba (13.4) > Co (10.7) > Mo (9.2) > Cd (5.35) > Ni (3.5) > V (3.5) > Cu (3.3) > Fe (3.2) > Sb (2.17) > Sr (2.04) > Pb (1.5) > Zn (1.43) > Cr (1.1). As can be seen from this series, the major metals of oceanic nodules (Ni, V, Cu, Zn, Pb, and Cr) behave in our case as moderately or even weakly concentrating elements, whereas Ba, Co, Mo, and Cd are intensely concentrated.

The geochemical correlation of chemical elements with Fe, Mn, and Ca—the major constituents of nodules—undergo substantial changes on the pathway from soil and loam to bottom sediments. Interestingly, Mn lacks significant correlation with any element in both loams and soils. In water, Mn is correlated with Cu, Cr, Zn, Mo, Fe, and Sb. In sediments, Mn is correlated with Cu, Cd, Ni, Sb, Fe, and Ca.

In loams, Fe is correlated with V, Pb, Zn, and Li. In the soil cover, only Li retains correlation with Fe, whereas other elements mentioned above are replaced by Cr. In water, Mn is correlated with Fe, although the migration style of these elements in the alkaline environment is different (see above). Additionally, Cu, Zn, Ni, Sb, Mo, and the low-mobile Cr are closely associated with Fe. In bottom sediments, correlation between Fe and Mn is prominent. Barium demonstrates a siderophile trend in the bottom sediments, although this element is only correlated with Ca in water. This property of Ba becomes more distinct in nodules. This fact contradicts the suggestion that Ba is usually concentrated in manganese nodules (Kabata-Pendias and Pendias, 1989). In the bottom sediments, almost all elements with a high concentration coefficient (Mn, Ba, Co, V, Cd, and Ni) are significantly correlated with Fe. The exceptional Mo is not correlated with any element, although the Mo content in nodules is more than nine times higher relative to the groundmass.

Calcium is also a major element in nodules. This element is correlated with Li, Zn, V, Sr, and Mg in loams; with Mg and Sr, in soils; and only with Ba, in waters. In the bottom sediments, Ca has a strong correlation with K, Na, Mg, Mn, Cu, Ni, and Cd.

The zoning of ferromanganese nodules in sediments of the reservoir is undoubtedly related to seasonal fluctuations of the hydrochemical environment as a result of the increase of temperature in summer, the saturation with oxygen in spring, the drop of these factors in winter, and the consequent variation of pH. These processes are accompanied by the irregular precipitation of Mn, Fe, and Ca from solutions as nodules and a component of the groundmass of bottom sediments.

Transfer and precipitation of Mn and Fe are assumed to take place in the colloidal form (Perel'man, 1975) or in true solutions (Verigina, 1950). In our case, probably, both mechanisms are possible, as was demonstrated for some nodules with Liesegang rings in Lake Ladoga (Semenovich, 1966). At the same time, ferromanganese nodules in sediments of the studied reservoir could also be formed owing to the activity of bacteria that played a crucial role in the formation of lacustrine nodules (Dubinina and Deryugina, 1969). The greenish color of water in the reservoir testifies to the presence of microflora.

Table 3. Chemical composition of bottom sediments and nodules in the reservoir, mg/kg

Element	PR-1	PR-2	PR-4	PR-5	PR-9	X	PR-6	PR-3	PR-7	PR-8	PR-10	X*
	Groundmass						Nodule					
Fe, %	2.16	1.96	1.8	3.56	2.96	2.5	6.67	8.57	8.57	9.14	7.29	8.0
K, %	1.54	1.38	1.38	1.43	1.38	1.4	0.82	1.18	0.92	0.92	0.86	0.94
Na, %	1.13	0.9	1.22	0.99	0.99	1.05	0.63	0.87	0.69	0.72	0.69	0.72
Ca, %	6.57	10.9	4.67	5.62	6.29	6.8	14.9	2.19	3.33	4.67	3.71	3.47
Mg, %	1.03	1.06	1.64	1.19	1.44	1.27	1.14	0.97	0.94	1.06	0.89	0.96
Mn, %	0.12	0.15	0.104	0.65	0.67	0.34	1.41	7.96	11.84	8.47	8.67	9.2
Ba, %	0.035	0.027	0.037	0.077	0.077	0.051	0.109	0.564	0.696	0.748	0.704	0.678
Pb	21	19	11	21	32	20.8	17	37	21	39	28	31.3
Zn	68	58	61	71	81	67.8	95	68	125	108	88	96.8
Cu	22	17	15	22	22	19.6	239	54	128	30	46	64.5
Ni	41	48	36	49	50	44.8	83	197	204	153	14	173.8
Co	10	7.4	7.6	38	31	18.8	57	179	226	214	188	202
Cr	134	78	128	149	137	125	149	134	146	125	122	135
Sb	0.5	1.0	1.7	1.4	1.5	1.2	1.5	2.3	2.8	3.3	2.0	2.6
Cd	0.18	0.14	0.15	0.22	0.18	0.17	0.19	0.7	1.0	1.0	0.95	0.91
Mo	3.0	4.0	2	4	6	3.8	12	41	43	32	24	35
V	75	69	69	100	70	76.6	112	344	262	258	218	270
Sr	585	539	692	508	681	601	785	1039	1460	1194	1206	1225
Li	20	26	18	24	23	22.2	16	23	16	17	15	17.4
Mn/Fe	0.06	0.08	0.06	0.18	0.23	0.12	0.21	0.93	1.38	0.93	1.19	1.11

Note: *Without the consideration of PR-6; (PR-1) bottom sediments (depth 3–6 cm); (PR-2) bottom sediments enriched in carbonates (3–6 cm); (PR-3) Fe–Mn nodules (9–12 cm); (PR-4) groundmass (9–12 cm); (PR-5) groundmass (15–18 cm); (PR-6) Ca–Fe nodule (15–18 cm); (PR-7) Fe–Mn nodules (15–18 cm); (PR-8) Fe–Mn nodules (18–21 cm); (PR-9) groundmass (21–24 cm); (PR-10) Fe–Mn nodules (21–24 cm).

CONCLUSIONS

Sediments of the reservoir at the Porozhnee Settlement were accumulated under conditions of high carbonate and iron concentrations in the water. Therefore, the groundmass was enriched in carbonate and carbonate–ferruginous nodules. The formation of ferromanganese nodules was likely controlled by fluctuations of water level in the reservoir due to the repeated dam breaches. This is indicated by the nonuniform distribution of nodules in the section of bottom sediments. The absence of nodules in the two upper reservoirs, where the dams were not destroyed, serves as indirect evidence in favor of such suggestion. The nodules are also absent in the upper units of sediments that were deposited after stabilization of the dam in the third reservoir. The occurrence of nodules near the shore line of the reservoir is an additional argument in favor of the proposed interpretation. In other words, Fe–Mn hydroxides were transformed into nodules in an oxic environment, as was pointed out for lacustrine nodules (Krotov, 1950).

Formation conditions of ferromanganese nodules in marine and fresh-water basins are substantially different, but their microelemental compositions are qualitatively similar. However, oceanic nodules are much more enriched in the major ore elements relative to their counterparts in the artificial reservoir. The cause of this discrepancy is obviously related to the sources of ore matter.

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