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Distribution of Elements in Ferromanganese Nodules in Seas and Lakes

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Abstract—Based on original and literature data, the element composition of ferromanganese nodules from the bottom of lakes and intracontinental and Arctic seas is used for a comparison with nodules in the World Ocean. The main similarities and dissimilarities in the composition of nodules, as well as trends in the accumulation of chemical elements in them, are described. It is shown that high metal contents in the oceanic nodules are related to a relatively higher Mn content therein, which is also partially reflected in marine nodules. Coefficients of the correlation between elements in the entire sample set with diverse correlations are determined. High contents of some metals in the Arctic nodules are comparable with their average contents in the oceanic nodules, indicating local metal concentrations in ferromanganese formations in the East Arctic. Nodules are highly enriched in manganese and iron oxides (26.7 and 53.1%, respectively) relative to sedimentary rocks. At the same time, they are depleted in all other macroelements except P.

Keywords: ferromanganese nodules, basins of different types, geochemistry of trace elements
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INTRODUCTION

Ferromanganese nodules from the floor of present-day basins (including lakes, seas, and World Ocean) are traditional objects of the study by marine geologists, lithologists, and geochemists because of the abundance of mineral resources and perspectives of their extension. This idea was first expressed by Adolf Erik Nordenskiold, a graduate of the Russian Imperial Tartus University (later, Swedish academician), who discovered nodule fields on the Arctic basin floor during cruise of the wooden vessel *Vega* across the entire Northern Marine Pathway (Nordenskiold, 1881).

In Russia, the study of seas and mineral resources therein was initiated by academicians N.I. Andrusov (1890) and A.D. Arkhangel'skii (1927) and continued later after year 1917 by many researchers (Arkhangel'skii, 1927; Gorshkova, 1931; Samoilov and Gorshkova, 1924; Samoilov and Titov, 1922).

After World War II, issue of the study of seas and marine resources expanded significantly. Application of new methods yielded new information about marine sediments and associated ferromanganese nodules.

The aim of the present paper is to assess the present state of this issue based on the preceding and new data with the consideration of a wide range of analyzed chemical elements, making it possible to decipher similarities and dissimilarities in the composition of different ferromanganese nodules from the Russian and adjacent lakes and seas of different types.

MATERIALS AND METHOGS

We studied typical ferromanganese nodule samples taken by the author and colleagues at the Shirshov Institute of Oceanology and other research institutes from various lakes, several seas, and World Ocean in 1990–2000 (Fig. 1):

(1) Lake Krasnoe (Punnus Jarvi): averaged sample described in (Shterenberg et al., 1966);

(2) Lake Baikal: 8 samples (Amirzhanov et al., 1992; Baturin and Granina, 2009; Baturin et al., 2009a, 2009b, 2011; Granina et al., 1991; Leibovich-Granina, 1987);

(3) Black Sea: 8 samples of ferruginated phaseolina shells (Baturin, 1987, 2010; Baturin et al., 2002; Shnyukov, 1981, 1983; Shnyukov et al., 1985);

(4) Baltic Sea: 10 samples from Gulfs of Finland and Riga (Baturin, 2009; Baturin and Dubinchuk, 2009; Baturin et al., 1988; Gorshkova et al., 1993; Hartmann, 1964; Ingri, 1985; Ingri and Ponter, 1987; Manheim, 1965; Varentsov, 1973; Varentsov and Blazhchishin, 1976; Suess, 1979; Winterhalter, 1980).

(5) White Sea ("neck"): averaged sample (Gorshkova, 1931; Kalinenko and Pavlidis, 1982; Klinova, 1948; Shterenberg et al., 1985);

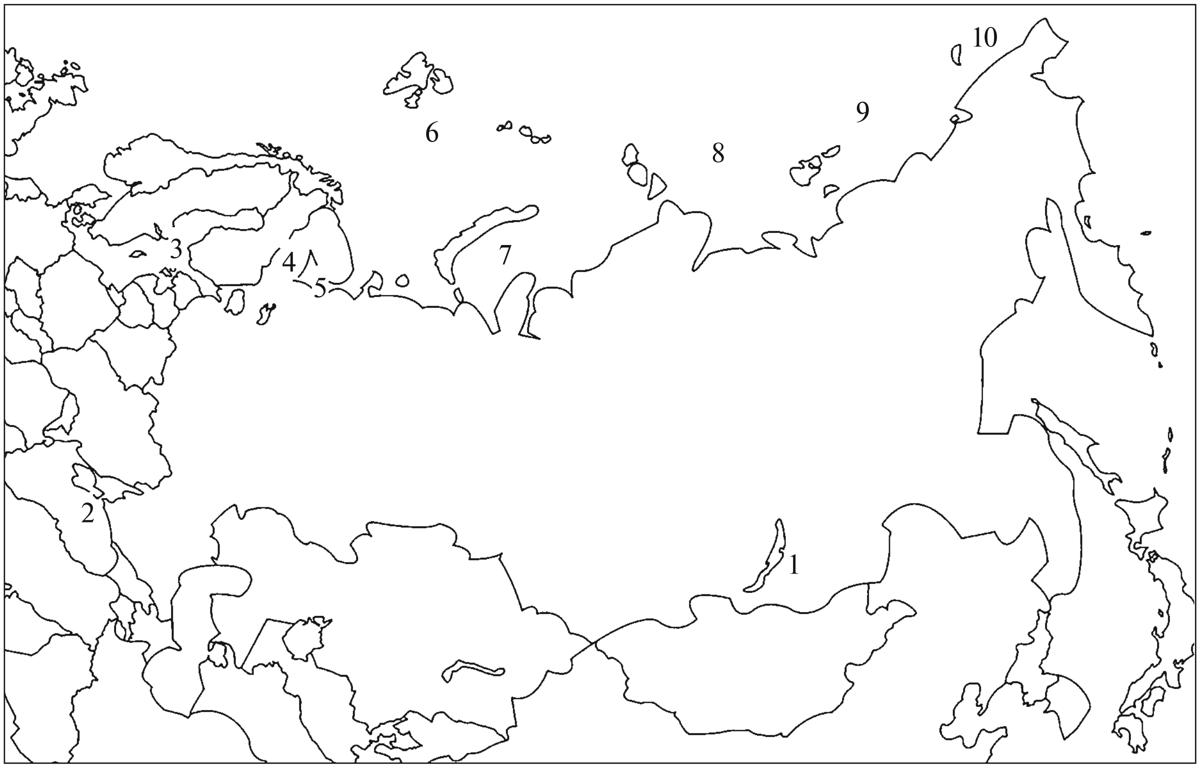

Fig. 1. Schematic location of basins, where ferromanganese nodules were sampled. (1) Lake Baikal; (2) Black Sea; (3) Baltic Sea; (4) Lake Krasnoe; (5) White Sea; (6) Barents Sea; (7) Kara Sea; (8) Laptev Sea; (9) East Siberian Sea; (10) Chukchi Sea.

(6) Barents Sea (central part): averaged sample (Dubinin, 2006; Ingri, 1985);

(7) Kara Sea: 15 samples (Baturin, 2011, 2013; Bogdanov et al., 2011; Gurevich and Yakovlev, 1993, 2005; Shyukov et al., 1985; Strekopytov and Dubinin, 2001);

(8–10) East Arctic seas (Laptev, East Siberian, and Chukchi): 16 samples (Baturin and Dubinchuk, 2011a, 2011b; Baturin et al., 2014; Masurenkov et al., 2012); and

(11) World Ocean: generalized data on hundreds of samples (Anikeeva and Kazakova, 2002; Baturin, 1986, 1988; Li, 1991; *Zhelezomargantsevye* ..., 1976).

Concentrations of elements in the oceanic nodule samples were determined mainly by the atomic absorption method (ICP-MS version for the remaining samples) with a high sensitivity at low aliquots and possibility to determine as much as 58 elements (Karandashev et al., 2016).

RESULTS AND DISCUSSION

Main composition of nodules

Lake Krasnoe. Nodules here, relative to sedimentary rocks, are enriched in oxides of Mn (26.7%) and Fe (53.1%), but depleted in all other macroelements except P.

Lake Baikal. Nodules of Lake Baikal, like the previous nodules, are enriched in oxides of Fe (55.3%) and Ti (0.32%), but depleted in oxides of Na (0.86%) and Ca (1.25%).

Baltic Sea (Gulfs of Finland and Riga). Nodules here are also marked by similarly high Fe concentration and composition, but samples from the Gulf of Finland are more enriched, relative to counterparts in the Gulf of Riga, in sodium and calcium oxides (1.75 and 2.15%, respectively) and total S (0.17%).

Black Sea. Nodules from this region differ from the Baltic variety by relatively lower contents of oxides of Fe (38.8%), Si (14.6%), Al (3.3%), Ti (0.10%), P (1.7%), and total S (1.7%), but higher contents of manganese oxide (14.1%) and calcium oxide (11.3%) composed of the undissolved remains of the carbonate fauna (shell and foraminiferal clasts).

White Sea. Nodules in the White Sea, relative to all remaining samples, are depleted in oxides of Fe (22.3%) and Mn (12.5%), but enriched in silica (43%).

Barents Sea. Nodules in the northern part of this sea are enriched in iron oxide (54.4%) and depleted in the remaining macroelements except total S (0.30%).

Kara Sea. Nodules here, relative to the previous Arctic samples, are depleted in Fe (14.3%) and total S (0.09%), but enriched in silica (34.7%), alumina (6.4%), as well as oxides of Ti, Na, and K.

Table 1. Average contents of the major components in ferromanganese nodules, %

Component	Clay*	Lakes		Gulfs		Seas							World Ocean
		Red	Baikal	Riga	Finland	Black	White	Barents	Kara	Laptev	East Siberian	Chukchi	
Fe_2O_3	6.7	53.1	55.3	52.8	52.9	38.8	22.3	54.4	16.2	25.4	23.4	24.4	17.9
MnO	0.12	26.7	2.1	9.2	11.5	14.1	12.5	0.13	14.6	17.4	17.5	12.2	24.0
SiO_2	50.3	8.6	17.7	–	16.0	14.6	43.0	13.5	34.7	24.6	22.8	23.4	16.5
Al_2O_3	16.6	0.53	5.9	6.3	4.1	3.3	4.6	4.0	6.4	3.8	3.7	4.5	5.10
TiO_2	0.50	0.13	0.32	0.16	0.11	0.10	0.28	0.22	0.28	0.14	0.18	0.21	1.12
Na_2O	1.38	0.07	0.86	0.69	1.75	1.20	1.7	0.68	2.4	2.1	2.1	2.2	2.7
K_2O	3.28	0.15	1.25	1.1	1.0	0.87	1.5	0.61	1.6	1.3	1.3	1.7	0.84
CaO	3.10	0.92	1.70	1.9	2.15	11.3	2.1	1.3	2.1	2.3	2.6	2.9	3.2
MgO	2.75	0.12	0.90	1.4	1.4	1.7	1.3	0.12	1.5	1.6	1.8	1.8	2.67
P_2O_5	0.18	2.3	2.9	3.0	3.7	1.7	1.6	1.4	1.9	5.7	4.2	6.3	0.57
S_{tot}	0.36	0.06	0.13	0.08	0.17	0.14	0.2	0.30	0.09	0.12	–	0.12	0.50
MnO/Fe_2O_3	0.02	0.50	0.04	0.17	0.22	0.36	0.56	0.002	0.90	0.68	0.74	0.57	1.34

(*) According to (Grigor'ev, 2003); (–) no data.

East Arctic Seas (Laptev, East Siberian, and Chukchi). Nodules in these seas have a monotonous composition: oxides of Fe (23.4–25.4%), Mn (12.2–17.5%), Si (22.8–24.6%), Al (3.7–4.5%), Na (2.1–2.4%), P (4.2–6.3%), K (1.3–1.7%), Ca (2.1–2.2%), and Mg (1.6–1.8%).

World Ocean. In general, oceanic nodules differ from the marine variety mainly by higher contents of oxides of Mn and Ti (24% and 1.12%, respectively) and total S (0.50%), but lower contents of oxides of Fe (17.9%), Si (16.5%), and P (0.57%).

Range of macroelement concentrations. The average content of iron oxide in nodules varies from 16.2% in the Kara Sea and 17.9% in the World Ocean to 52–55.5% in nodules from the Gulf of Finland, Lake Baikal, and Barents Sea (Table 1). The average content of manganese oxide is minimal in nodules from the Barents Sea (0.13%) and Lake Baikal (2.1%) and maximal in nodules from the eastern Arctic (17.5%) and World Ocean (24.0%). At the same time, the ratio of oxides of Fe and Mn varies from 0.002 (Barents Sea) to 1.33 (World Ocean).

The content of lithogenic components shows a wide variation range: SiO_2 from 8.6% (Lake Krasnoe) to 43.0% (White Sea), TiO_2 from 0.10% (Black Sea) to 0.32% (Baikal), Na_2O from 0.007% (Lake Krasnoe) to 2.4% (Kara Sea), K_2O from 0.15% (Lake Krasnoe) to 1.7% (Chukchi Sea), CaO from 0.92% (Lake Krasnoe) to 11.3% (Black Sea), MgO from 0.12% (Lake Krasnoe and Barents Sea) to 1.8% (East Siberian and Chukchi seas), P_2O_5 from 1.4 and 1.9% (Black and Kara seas, respectively) to 4.2–6.3% (East Arctic seas), and S_{tot} from 0.006–0.17% (the majority of basins) to 0.20% and 0.30% (White and Barents seas, respectively) (Table 1).

Ratio of oxides of Mn and Fe in the studied nodules is an important property and varies from 0.002–0.04 (nodules from the Barents Sea and Lake Baikal) to 0.90–1.34 (Kara Sea and World Ocean). This ratio is 0.50–0.90 in the majority of Arctic nodules and 1.34 in the oceanic nodules.

Trace element composition of nodules

Lake Krasnoe. Relative to clayey rocks, nodules in lakes are enriched in Ba (3 times), Sr (1.5 times), as well as Mo, W, and As (2–3.5 times), but depleted in the remaining trace elements.

Baikal. Nodules in Lake Baikal, relative to marine nodules, are appreciably enriched in U (19 ppm), Th (15 ppm), Ta (1.1 ppm), Mo (27 ppm), W (38 ppm), Be (3.5 ppm), Sn (2 ppm), Cs (3.5 ppm), Nb (11 ppm), Cu (110 ppm), and Rb (86 ppm).

Baltic Sea (Gulfs of Riga and Finland). Nodules from both gulfs are slightly enriched in Bi (0.33–0.42 ppm), Y (40–48 ppm), and Ba (2334–2960 ppm). Samples from the Gulf of Finland are also enriched in Zn (415 ppm).

Black and White Seas. Nodules from both seas are enriched in Sb (5.1–7.2 ppm), Mo (3.1–11.2 ppm), W (4.1–19 ppm), Ni (84–465 ppm), As (220–2833 ppm), Co (109–160 ppm), and Zn (110–130 ppm). Samples from the Black Sea are also enriched in W (19 ppm), Ga (90 ppm), and Ba (2180 ppm).

Barents Sea. Nodules from the northern Black Sea are enriched in Fe (54.4%), Be (3.3 ppm), Hf (3.6 ppm), and Sc (23.6 ppm).

Kara Sea. Nodules from this sea are enriched in Fe. Among the subordinate Mn-bearing nodules, we examined the variety enriched in Sb (11.5 ppm), Sn (2 ppm), As (435 ppm), V (435 ppm), and Zr (83 ppm).

Laptev Sea. Nodules here are depleted in Bi (0.13 ppm), Ta (0.20 ppm), Tl (0.77 ppm), Sn (0.66 ppm), Nb (3.1 ppm), Cr (14 ppm), Cu (24 ppm), and Zr (48 ppm), but enriched in U (12 ppm), As (750 ppm), Pb (120 ppm), Co (340 ppm), and Sr (1070 ppm).

East Siberian Sea. Nodules in this region are depleted in several elements (Ag, Tl, Be, Sn, Hf, Nb, Th, Sc, Zr), but enriched in Cd (11.2 ppm), Sb (18.4 ppm), Tl (7.5 ppm), Mo (417 ppm), Li (95 ppm), and V (400 ppm). We also detected here signs of the exhalation of endogenic components (Hg and Au included) from the seafloor (Baturin et al., 2014; Baturin et al., 2016).

Chukchi Sea. Nodules from the Chukchi Sea are depleted in Hg (0.03 ppm), Tl (0.46 ppm), Sn (0.60 ppm), and Hf (0.95 ppm), but enriched in Bi (0.35 ppm), Sr (1335 ppm), and As (800 ppm).

World Ocean. Averages contents of the majority of trace elements in the oceanic nodules (22 samples among 34 studied) are higher than in the marine and lacustrine nodules (ppm): Bi (0.2–7), Cd (0.44–11), Sb (2.2–40), Tl (0.62–50), Ta (0.19–10), Mo (5.8–400), W (1.0–100), Th (2.9–30), Nb (3–50), Pb (10–900), Co (12.5–2700), Cu (11–4500), Ni (30–6600), and (Zn 90–1200) (Tables 2, 3).

The oceanic and marine nodules are marked by similar average contents of several trace elements (Se, Cd, Sb, Mo, As, Sr), concentrations of which are higher in nodules from the East Siberian and Chukchi seas. Hence, the Mn phase stimulates the accumulation of several nonferrous metals mainly in the oceanic nodules and less commonly in the marine nodules—an opinion expressed previously in (Mero, 1965; *Zhelezomargantsevyse* ..., 1976) but not always applied to marine nodules.

According to the generalized data, contents of elements vary in the following pattern (in accordance with increase of the atomic weight).

The Ag content varies from 0.02 to 0.05 ppm in nodules from the eastern Arctic, reaches the maximum (0.23 ppm) in nodules from the White Sea, and is 0.18 ppm in nodules from Lake Baikal and Gulf of Finland.

Based on scanty data, high Se content (4.1 ppm) is recorded in the Laptev Sea. Maximum Bi content (0.42 ppm), typical of nodules in the Gulf of Riga, corresponds to the average content in clayey rocks (0.42 ppm). The content is 7 ppm in oceanic nodules.

The Cd content in most nodules from the studied basins varies from 0.44 to 5.3 ppm. Maximum contents (10 and 11 ppm) were detected in nodules from the ocean and East Siberian Sea.

The Sb content in marine nodules is higher everywhere than in the clayey rocks and reaches 18.4 ppm in nodules from the East Siberian Sea and 40 ppm in the oceanic nodules.

The Tl content varies from 1.2 to 4.3 ppm in most nodules. The content is higher in the East Arctic nodules (7.5 ppm) and oceanic nodules (150 ppm).

As for other elements in the oceanic nodules, average contents of 11 elements among them (Ta, W, Be, Sn, U, Cs, Th, Nb, Cu, Cr, Rb) are higher than average values in all marine nodules.

MnO/Fe_2O_3 ratio in nodules. This ratio is a factor determining the composition of ferromanganese nodules. In our case, it illustrates the trace element composition of nodules against the background of the ratio of hydroxides of Mn and Fe (Tables 1–3).

The results show that, relative to the average composition of clayey rocks, nodules are depleted in 11 elements (Ta, Sn, Hf, Cs, Th, Nb, Hf, Sc, Cr, Rb, Zr). In addition, contents of several elements (Ag, Bi, Be, Y, Li) fit or approximate their average contents in the clayey rocks. Contents of the remaining 17 elements (except Cu) in nodules from the studied basins are higher than their contents in the clayey sediments.

Minimum MnO/Fe_2O_3 values (0.002 and 0.04) are recorded in nodules from the Barents Sea and Lake Baikal, with the average contents of manganese oxide at 0.13 and 2.1%, respectively. The Mn-rich nodules from the East Arctic seas are marked by the following average contents: MnO 15% and Fe_2O_3 22%.

Minimum value of this parameter (0.002 in nodules from the Barents Sea) matches the maximal contents of Be, Hf, and Sc (3.3, 3.6, and 23.6 ppm, respectively). The second low value (0.04, Lake Baikal) matches maximum contents of 11 elements (ppm): Ta (1.1), W (38), Be (3.5), Sn (2.0), U (19), Cs (3.5), Th (15), Nb (11), Cu (110), Cr (70), and Rb (86). The majority of these elements (except Cu and U) are usually associated with the terrigenous components.

Nodules from the Gulf of Finland are enriched in Zn (415 ppm) and Zr (83 ppm); nodules from the Black Sea, in Zn (465 ppm); nodules from the Barents Sea, in Hg (0.31 ppm), Be (3.3 ppm), Hf (3.6 ppm), and Sc (23.6 ppm); nodules from the Kara Sea, in Zr (83 ppm); nodules from the Laptev Sea, in Pb (120 ppm) and Co (340 ppm); nodules from the East Siberian Sea, in Cd (24 ppm), Sb (18.4 ppm), Mo (417 ppm), Li (95 ppm), and V (400 ppm); and nodules from the Chukchi Sea, in As (800 ppm) and Sr (1335 ppm).

Comparison of these data shows that concentrations of some trace elements in marine nodules formed

Table 2. Average contents of trace elements in ferromanganese nodules, ppm

Element	Clayey rocks	Lakes		Gulfs		Seas							World Ocean*
		Red	Baikal	Riga	Finland	Black	White	Barents	Kara	Laptev	East Siberian	Chukchi	
Hg	0.089	–	–	–	–	–	–	**0.31**	–	0.15	0.07	0.03	**0.32**
Ag	0.2	<0.05	0.18	0.13	0.18	0.08	**0.23**	0.06	0.13	0.05	0.02	0.05	0.9
Se	0.36	–	1.3	–	–	–	–	<1.5	2	**4.1**	2.7	3.4	0.6
Bi	0.38	<0.3	0.2	**0.42**	0.33	0.20	0.18	0.08	0.16	0.13	0.24	0.35	**7**
Cd	1.0	0.4	3.1	1.7	5.3	2.7	1.0	0.44	1.4	2.4	**11.2**	1.3	**10**
Sb	1.0	0.13	2.5	2.2	4.0	7.2	5.1	2.5	11.5	14.3	**18.4**	15.8	**40**
Tl	1.3	0.5	2.3	2.8	4.1	1.2	4.3	0.62	2.1	0.77	**7.5**	0.46	**150**
Ta	1.4	0.04	**1.1**	0.28	0.44	0.19	0.6	0.23	0.52	0.20	0.20	0.24	**10**
Mo	1.6	6.0	27	5.8	6.7	31	112	43	153	190	**417**	90	**400**
W	2.6	5.0	**38**	3.0	7.7	19	4.1	1.0	10	8.5	5.5	5.0	**100**
Be	2.8	0.7	**3.5**	1.2	1.9	1.25	0.6	**3.3**	0.9	1.1	0.7	1.2	**2.5**
Sn	3.5	0.26	**2.0**	0.74	1.1	0.72	0.65	0.8	**2.0**	0.66	0.43	0.60	**2**
U	4.5	0.6	**19**	4.8	14	3.1	2.7	3.1	5.3	12	9.3	9.2	5
Hf	5	0.15	2.1	1.7	2.0	1.2	3.5	**3.6**	2.0	1.1	0.8	0.95	**8**
As	9.3	32	200	265	137	283	220	265	435	750	527	**800**	140
Cs	10	0.2	**3.5**	1.2	1.5	1.7	0.9	1.2	2.1	2.3	1.8	2.4	1
Th	10	0.9	**15**	5.7	6.3	2.9	6.8	3.4	4.4	3.4	3.2	4.1	**30**
Nb	11	1.0	**11**	5.8	6.7	3.0	6.0	3.2	5.0	3.1	3.1	4.0	**50**
Pb	14	4.0	28	50	36	26.2	14	10	23	**120**	48	73	**900**
Sc	15	1.1	10	5.8	6.3	6.7	7.2	**23.6**	8.0	5.4	4.2	5.3	10
Ga	16	**177**	23	75	170	90	8.0	5.7	53	15	42	28	10
Co	19	15	107	154	145	160	109	–	12.5	**340**	314	250	**2700**
Y	31	14	32	**48**	40	26.4	24	40	37	30	38	41	**150**
Cu	36	40	**110**	46	35	42	11	33	48	24	37	23	**4500**
Li	46	0.8	22	10.6	14	15	49	18	60	34	**95**	16	80
Ni	47	13	320	120	194	**465**	84	30	125	127	226	95	**6600**
Zn	52	114	146	278	**415**	130	110	90	130	190	320	170	**1200**
Cr	76	8.0	**70**	14	26	16	60	34	48	14	26	38	35
V	120	<2	195	66	69	218	225	290	365	173	**400**	305	**500**
Rb	130	4	**86**	34	48	26	28	20	40	33	31	39	17
Zr	190	15	65	78	**83**	58	70	58	**83**	42	37	44	**560**
Sr	240	320	326	545	655	930	570	190	500	1070	970	**1335**	830
Ba	460	**12043**	2970	2334	2960	2180	650	560	525	1020	900	1060	2300
MnO/Fe_2O_3	0.02	**0.50**	0.04	0.17	0.22	0.36	0.56	0.002	0.90	0.68	0.74	0.57	1.33

Maximal contents are given in the bold type; (–) no data; (*) according to (Baturin, 1986).

mainly in the Arctic seas are similar to those in the oceanic nodules and vary within the same range.

Rare earth elements

The content of total rare earth elements (Table 4) is minimal in nodules from the Black, White, and Barents seas (73–101 ppm). The content increases in East Arctic seas (136–205 ppm) and reaches 304–324 ppm in Lake Baikal and Gulfs of Finland and Riga. The average total REE content is maximal (1668 ppm) in oceanic nodules.

Comparison with the average total REE content (172 ppm) in sedimentary rocks (Balashov, 1976)

Table 3. High contents of trace elements in ferromanganese nodules in different basins, ppm

Elements	Clayey rocks	Basin		
		Lake Baikal	seas and gulfs (maximal content)	World Ocean
Ag	0.2	0.18	0.23 (White Sea)	**0.9**
Se	0.36	1.3	**4.1** (Laptev Sea)	0.6
Bi	0.38	0.2	0.42 (Gulf of Riga)	**7**
Cd	1	3.1	**11.2** (East Siberian Sea)	**10**
Sb	1	2.5	**184** (East Siberian Sea)	40
Tl	1. 3	2.3	75 (East Siberian Sea)	**150**
Ta	1.4	1.1	0.6 (White Sea)	10
Mo	1.6	27	**417** (East Siberian Sea)	**400**
W	2.6	38	19 (Black Sea)	**100**
Be	2.8	**3.5**	3.3 (Barents Sea)	2.5
Sn	**3.5**	2.0	2.0 (Kara Sea)	2.0
U	4.5	**19**	14 (Gulf of Finland)	5
Hf	5	2.1	3.6 (Barents Sea)	**8**
As	9.3	200	**800** (Chukchi Sea)	140
Cs	10	**3.5**	2.4 (Chukchi Sea)	1.0
Th	10	15	10.6 (Baltic Sea)	30
Nb	11	11	8.4 (Baltic Sea)	**50**
Pb	14	28	120 (Laptev Sea)	**900**
Sc	15	10	**23** (Barents Sea)	10
Ga	16	23	**70** (Gulf of Finland)	10
Co	19	107	340 (Laptev Sea)	**2700**
Y	31	32	48 (Gulf of Riga)	**150**
Cu	36	110	48 (Kara Sea)	**4500**
Li	46	22	**95** (East Siberian Sea)	80
Ni	47	320	465 (Black Sea)	**6000**
Zn	52	146	700 (Baltic Sea)	**1200**
Cr	76	70	60 (White Sea)	35
V	120	195	400 (East Siberian Sea)	**500**
Rb	130	**86**	60 (Baltic Sea)	17
Zr	190	65	96 (The same)	**560**
Sr	240	320	**1335** (Chukchi Sea)	830
Ba	460	**2970**	**2960** (Gulf of Finland)	2300

Maximal contents are shown in the bold type.

shows that the decreased total REE content (up to 100 ppm) is typical of nodules from the Black, White, and Barents seas; the moderate content (123–205 ppm) is observed in Lake Krasnoe and East Arctic seas; and high contents (more than 300 ppm) recorded in nodules from Lake Baikal and Gulfs of Riga and Finland are 5.5 times lesser than in oceanic nodules.

The Ce anomaly calculated according to the standard method (Balashov, 1976; Dubinin, 2006) is maximal in nodules from Lake Baikal, and World Ocean (1.30–1.36), and Gulf of Finland (1.16).

The Eu anomaly is 1.2 in nodules from Lake Baikal, 0.86–1.02 in other samples, and 0.83 in oceanic nodules, testifying to a monotonous behavior of REE during marine sedimentation. However, positive Eu anomaly in nodules from Baikal can support the influence of endogenic factor on sedimentary process.

ELEMENT ASSOCIATIONS IN NODULES

Macroelements. Comparison of the composition of nodules from different basins shows that lacustrine nodules, relative to clayey sediments, are enriched in Fe more than Mn, but contents of several terrigenous components (Si, Al, Ti, P) are moderate or decreased. The maximum SiO_2 content (43%) is observed in nodules from the White Sea. The oceanic nodules contain, in addition to SiO_2, Al_2O_3 (5.1%), Na_2O (2.7%), CaO (3.2%), MgO (2.67%), and S_{tot} (0.50%), providing an insight into the general composition of terrigenous components in nodules.

Trace elements. As is evident from Table 2, high (relative to clayey rocks) contents of some trace elements can be observed in nodules from all studied basins.

Table 4. Contents of rare earth elements in ferromanganese nodules (average content in the basin), ppm

Element	Clays	Lakes		Gulfs		Seas							World Ocean**
		Red	Baikal	Riga	Finland	Black	White	Barents	Kara	Laptev	East Siberian	Chukchi	
La	32	27.9	58.	62.5	60.7	14.8	16.8	22.4	44	25.6	29	26.7	130
Ce	73	43.8	80	137	157	21	31.8	41.9	65.9	46.6	61	41.4	412
Pr	7.9	5.2	8.0	15.1	14.5	2.7	4.02	4.4	9.2	5.5	6.6	5.4	33
Nd	33	21.1	15	52.2	47.8	14	15.6	17.9	40.6	23.5	26	24	129
Sm	5.7	<4	7.0	12.0	9.9	2.3	3.07	3.5	10	5.0	5.6	5.6	37
Eu	1.24	<2	2.5	<3	<2	0.7	0.61	0.74	2.3	1.2	1.3	1.3	6.9
Gd	5.2	4.21	10	12.5	12.7	3.8	2.56	3.8	10.4	5.9	5.8	6.7	36
Tb	0.85	0.49	1.1	1.5	1.6	0.6	0.35	0.58	1.4	0.83	0.86	1.0	5.7
Dy	5.2	2.9	4.5	8.3	8.8	3.7	2.00	3.4	8.8	4.9	4.9	5.8	34
Ho	1.04	9.45	1.3	1.9	1.56	0.9	0.42	0.75	1.6	1.0	0.92	1.2	4.2
Er	3.4	1.5	3.9	4.1	4.4	2.7	1.11	2.1	4.8	2.8	2.7	3.5	17.4
Tm	0.5	0.30	0.4	0.60	0.51	0.3	0.14	0.29	0.63	0.39	0.36	0.48	2.7
Yb	3.1	2.1	3.6	4.0	3.9	2.9	0.89	2.0	3.6	2.4	2.30	3.0	14.2
Lu	0.48	0.45	0.5	0.58	0.59	0.5	0.17	0.30	0.48	0.38	0.35	0.48	2.25
∑REE	172	123	304	315	324	73	81.3	101	205	136	145	158	1668
Ce*	1.00	0.78	1.3	0.95	1.16	0.8	0.91	0.90	0.70	0.85	0.96	0.79	1.36
Eu*	1.00	–	1.2	–	–	1.0	0.86	0.89	0.99	0.98	1.02	0.93	0.83

(–) No data; (*) Ce and Eu anomalies; (**) according to (Baturin, 1986).

In Lake Baikal, nodules are most enriched in seven elements (Ta, U, Be, Cs, Cr, Rb, Ba). In the Arctic seas (mainly eastern sectors), nodules are enriched (relative to the western sectors) in Se, Cd, Sb, Mo, As, Sc, Ga, Li, Sr, and Ba. The oceanic nodules are most enriched in Bi, Cd, Tl, Mo, Hf, Nb, Pb, Co, Y, Cu, Ni, Zn, V, Zr, Ba, and REE.

Nodules in the freshwater lakes are enriched (relative to sedimentary rocks) in some elements. Marine nodules are enriched in 10 elements, whereas oceanic nodules are enriched in 30 elements (except Hg, Au) and platinum group elements that can be included into this group, according to some determinations reported in (Anikeeva and Kazakova, 2002).

Discrepancies in the degree of metal accumulation in the marine and oceanic nodules suggest the influence of the following factors: composition of sediments underlying the nodules, composition of the marine and interstitial waters, and sedimentation rate and ratio of Mn–Fe oxides in nodules. The last, likely most probable, factor is supported by the combination of increased contents of nonferrous metals and high contents of Mn (Baturin, 1986).

CORRELATION BETWEEN ELEMENTS IN NODULES

As is evident from Table 5, correlation between the major elements (Fe, Mn) is virtually absent. As concerns other elements, Fe shows a weak correlation only with Be and Ga, while Mn is correlated with the majority of ore elements (Mo, Pb, Co, Cu, Ni) and some rare elements (Bi, Sb, Tl, Ta, Ba).

Examination of correlation between trace elements (except Fe and Mn) revealed correlation groups of elements with varying compositions. Table 6 presents the composition of such ten groups identified based on the number of chosen ore and associated trace elements (Ag, Bi, Co, Cu, Mo, Ni, Pb, Sb, Sn, Zn). The largest groups associated with Sb and Ag include 16 and 17 elements, respectively. The smaller groups are associated with Sn and Mo (11 and 12 elements, respectively).

Tables 5 and 6 show that, among 17 elements listed above, only 6 elements (Pb, Bi, Cu, Co, Zn, Zr) are present in all ten groups.

The second (in terms of abundance) elements are Ag, Sb, Tl, Ni, and Zn (they occur in 7 or 8 groups).

Several other elements occur in the studied groups not more than 5 or 6 times (Cd, Mo, Sn, W, Th, Ta).

Table 5. Correlation of elements in ferromanganese nodules

	Fe_2O_3	MnO	Ag	Bi	Cd	Sb	Tl	Ta	Mo	W	Be	Sn	U	Hf	As	Cs	Th	Nb	Pb	Sc	Ga	Co	Y	Cu	Li	Ni	Zn	Cr	V	Rb	Zr	Sr	Ba
Fe_2O_3		–45	–32	–35	–38	–70	–37	–38	–72	–28	43	–48	17	–35	–39	–55	–39	–36	–40	11	52	–40	–34	–36	–78	–35	–23	–54	–55	–31	–38	–62	39
MnO	–45		31	43	39	46	44	42	45	32	–56	21	–38	15	–22	–4	36	38	44	–52	32	43	28	43	39	41	34	–23	–11	–15	39	40	58
Ag	–32	31		96	50	75	96	97	49	93	36	66	–6	89	–36	–26	98	98	94	14	–26	94	93	96	43	96	93	27	48	–20	97	2	–8
Bi	–35	43	96		58	84	100	100	59	94	33	61	–13	85	–29	–19	98	99	99	13	–24	99	97	100	46	100	94	11	49	–25	99	15	1
Cd	–38	39	50	58		72	61	57	83	54	3	29	16	40	–5	11	57	58	59	–11	–9	64	61	58	75	59	71	–3	48	10	57	37	–16
Sb	–70	46	75	84	72		85	84	85	80	11	57	4	66	18	26	82	83	88	1	–46	89	85	84	72	85	81	20	71	1	83	52	–26
Tl	–37	44	96	100	61	85		100	62	94	32	62	–13	87	–30	–18	98	99	99	14	–26	99	97	100	51	100	94	14	51	–24	99	15	–1
Ta	–38	42	97	100	57	84	100		60	94	33	65	–14	88	–30	–17	99	100	99	16	–27	98	97	100	49	99	93	17	51	–22	99	14	–3
Mo	–72	45	49	59	83	85	62	60		52	–9	37	1	46	21	25	57	58	63	–2	–47	65	60	60	93	59	59	21	69	1	57	43	–29
W	–28	32	93	94	54	80	94	94	52		43	55	8	74	–22	–24	90	94	94	5	–25	95	89	95	37	97	92	8	59	–35	92	5	–4
Be	43	–56	36	33	3	11	32	33	–9	43		16	34	41	–12	–27	31	35	32	65	–25	32	40	34	–22	36	39	2	37	–30	33	–44	–25
Sn	–48	21	66	61	29	57	62	65	37	55	16		–18	70	–20	23	68	66	61	30	–16	56	67	62	48	61	55	41	41	30	70	6	–26
U	17	–38	–6	–13	16	4	–13	–14	1	8	34	–18		–30	50	15	–12	–10	–8	–27	–7	–4	–6	–14	–13	–9	15	–8	23	17	–16	0	–35
Hf	–35	15	89	85	40	66	87	88	46	74	41	70	–30		–39	–15	91	89	84	51	–41	82	87	86	48	84	75	43	46	–9	90	0	–23
As	–39	–22	–36	–29	–5	18	–30	–30	21	–22	–12	–20	50	–39		72	–30	–30	–19	–15	–51	–18	–20	–29	9	–28	–25	7	33	34	–32	54	–54
Cs	–55	–4	–26	–19	11	26	–18	–17	25	–24	–27	23	15	–15	72		–14	–17	–10	3	–29	–12	–6	–19	27	–19	–18	12	18	77	–14	75	–57
Th	–39	36	98	98	57	82	98	99	57	90	31	68	–12	91	–30	–14		99	97	17	–29	96	97	98	50	97	93	24	48	–10	99	16	–11
Nb	–36	38	98	99	58	83	99	100	58	94	35	66	–10	89	–30	–17	99		98	16	–27	98	97	99	48	99	95	19	51	–18	100	13	–6
Pb	–40	44	94	99	59	88	99	99	63	94	32	61	–8	84	–19	–10	97	98		12	–30	100	97	99	48	99	94	9	51	–20	98	22	–4
Sc	11	–52	14	13	–11	1	14	16	–2	5	65	30	–27	51	–15	3	17	16	12		–44	8	24	15	5	13	2	32	27	–2	20	–29	–39
Ga	52	32	–26	–24	–9	–46	–26	–27	–47	–25	–25	–16	–7	–41	–51	–29	–29	–27	–30	–44		–30	–32	–26	–45	–26	–15	–53	–71	1	–26	–18	75
Co	–40	43	94	99	64	89	99	98	65	95	32	56	–4	82	–18	–12	96	98	100	8	–30		96	99	50	99	95	9	54	–22	97	23	–6
Y	–34	28	93	97	61	85	97	97	60	89	40	67	–6	87	–20	–6	97	97	97	24	–32	96		97	49	96	94	15	54	–9	98	18	–16
Cu	–36	43	96	100	58	84	100	100	60	95	34	62	–14	86	–29	–19	98	99	99	15	–26	99	97		47	100	94	12	51	–26	99	13	0
Li	–78	39	43	46	75	72	51	49	93	37	–22	48	–13	48	9	27	50	48	48	5	–45	50	49	47		47	45	42	64	17	49	34	–37
Ni	–35	41	96	100	59	85	100	99	59	97	36	61	–9	84	–28	–19	97	99	99	13	–26	99	96	100	47		95	11	53	–27	98	14	–2
Zn	–23	34	93	94	71	81	94	93	59	92	39	55	15	75	–25	–18	93	95	94	2	–15	95	94	94	45	95		3	48	–14	93	13	–5
Cr	–54	–23	27	11	–3	20	14	17	21	8	2	41	–8	43	7	12	24	19	9	32	–53	9	15	12	42	11	3		50	25	19	–3	–54
V	–55	–11	48	49	48	71	51	51	69	59	37	41	23	46	33	18	48	51	51	27	–71	54	54	51	64	53	48	50		–11	49	12	–59
Rb	–31	–15	–20	–25	10	1	–24	–22	1	–35	–30	–30	17	–9	34	77	–10	–18	–20	–2	1	–22	–9	–26	17	–27	–14	25	–11		–15	52	–51
Zr	–38	39	97	99	57	83	99	99	57	92	33	70	–16	90	–32	–14	99	100	98	20	–26	97	98	99	49	98	93	19	49	–15		14	–7
Sr	–62	40	2	15	37	52	15	14	43	5	–44	6	0	0	54	75	16	13	22	–29	–18	23	18	13	34	14	13	–3	12	52	14		–24
Ba	39	58	–8	1	–16	–26	–1	–3	–29	–4	–25	–26	–35	–23	–54	–57	–11	–6	–4	–39	75	–6	–16	0	–37	–2	–5	–54	–59	–51	–7	–24	

Table 6. Correlation associations of elements in ferromanganese nodules

Group	Composition of correlating element groups
1	Ag, **Bi,** Cd, **Co, Cu**, Mo, Hf, Ni, **Pb**, Sb, Sn, Th, Ta, Tl, W, **Zn**, **Zr**
2	**Bi**, Ag, Cd, **Co, Cu,** Hf, Nb, Ni, **Pb**, Sb, Th, Ta, Tl, W, **Zn**, **Zr**
3	**Co,** Ag, **Bi,** Cd, **Cu**, Mo, Hf, Nb, Ni, **Pb**, Sb, Ta, Tl, W, **Zn**, **Zr**
4	**Cu,** Ag, **Bi, Co**, Hf, Mo, Nb, Ni, **Pb**, Sn, Ta, Th, Tl, **Zn**, **Zr**
5	Mo, **Bi,** Cd, **Co, Cu**, Li, Ni, **Pb,** Sb, V, Y, **Zn**, **Zr**
6	Ni, Ag, **Bi, Co, Cu**, Hf, Nb, **Pb** Sb, Sn, Ta, Th, Tl, W, **Zn**, **Zr**
7	**Pb,** Ag, **Bi, Co, Cu**, Hf, Mo, Nb, Sb, Sn, W, Y, **Zn**, **Zr**
8	Sb, Ag, **Bi,** Cd, **Co, Cu**, Hf, Li, Mo, Nb, Ni, **Pb**, Ta, Th, Y, **Zn**, **Zr**
9	Sn, **Bi, Co, Cu**, Hf, Nb, **Pb,** Ta, Tl, Th, Y, **Zr**
10	Zn, Ag, **Bi**, Cd, **Co, Cu,** Hf, Nb, Ni, **Pb**, Sb, Ta, Th, Tl, Y, **Zr**

The bold type designates elements (**Bi**, **Co**, **Cu**, **Pb**, **Zn**, **Zr**) participating virtually in all groups.

Thus, we can suggest that the nodules demonstrate a specific distribution pattern of elements characterized by a joint accumulation in Fe–Mn hydroxides despite diverse marine settings in different basins. At the same time, in addition to ore metals, Zr is present in all studied groups. Some groups also include Nb, Hf, and less common Li (low-mobile elements) that were entrapped by Fe–Mn hydroxides from the host sediments.

On the whole, contents of trace elements in various nodules from different basins is unstable, but a notable enrichment (relative to the average composition of clays) is typical of several trace elements in all multicomponent nodules (particularly, nodules from Lake Baikal). Nodules from seas and gulfs are marked by sporadic high contents of 17 trace elements (Se, Bi, Cd, Sb, Tl, Mo, U, As, Pb, Sc, Co, Li, Ni, Zn, V, Sr, Ba), suggesting that the nodules were formed and deposited under similar conditions.

In oceanic nodules, the highest average contents are typical of 17 trace elements (Ag, Bi, Tl, Mo, W, Hf, As, Th, Nb, Pb, Co, Y, Cu, Ni, Zn, V, Zr) and 14 rare earth elements. This observation is consistent with the composition of the nodule-hosting pelagic sediments. At the same time, marine nodules are always enriched in Fe and Mn. Sometimes, they are also enriched in other elements (Se, Cd, Sb, Tl, Mo, W, U, Co, Pb).

ELEMENT COMPOSITION OF FERROMANGANESE NODULES

Examination of the composition of nodules revealed that the maximum Mn–Fe oxide ratio (1.34) is recorded in oceanic nodules. This value is consistent with the maximum concentrations of the main ore metals (Co, Cu, Ni, Zn, Pb) and some other metals (Bi, Mo, Cd, Sn, Se, V) recorded therein (Tables 1, 2).

For example, nodules in the Barents Sea are extremely depleted in Mn. At the same time, they are distinguished from other nodules by the minimal content of most metals under consideration. Hence, the long-term rewashing of nodules by bottom currents and the diffusion of metals from the underlying sediments promote the accumulation of metals in nodules during their prolonged exposure on the seafloor. The main reason, however, is enrichment of nodules in Mn, which is accumulated in lacustrine nodules despite the decrease of Mn in lake waters and sediments.

Irrespective of the basin type, dissimilarities in the composition of marine and oceanic nodules are related to some reasons, such as higher concentration of metals in sediments and waters, sedimentation rate, composition of interstitial waters of sediments, activity of diagenetic processes, and sorptional properties of nodules.

Mn/Fe relationship in nodules

The possible influence of Mn and Fe on processes of metal accumulation in ferromanganese nodules was assumed and discussed several times based on typical examples (Mero, 1965; *Zhelezomargantsevyse* ..., 1976). In our case, such influence can be analyzed on the basis of several different basins.

Since oceanic nodules contain different amounts of manganese and iron oxides (24% and 16.9%, respectively), the predominance of Mn exerts a significant influence on the accumulation of most trace elements in nodules in the eastern Arctic (Table 1). At the same time, Mn entraps the associated elements (Bi, Cd, Sb, Tl, Mo, As, Pb, Co, Ni, Zn, V), contents of which in the pelagic manganese nodules are much higher than in the marine Fe-rich nodules.

The MnO/Fe_2O_3 ratio in nodules from the eastern Arctic seas is dissimilar: 0.57 in the Chukchi Sea and as much as 0.9 in the Kara Sea. In the western Arctic, the ratio increases from 0.002 in the Barents Sea to 0.56 in the White Sea.

Sources of elements in nodules

Researchers have proposed different versions of sources for elements in the oceanic ferromanganese nodules (bottom sediments, seawater, and interstitial water included), as well as volcanic exhalations (Baturin, 1986). This hypothesis is also supported to a certain extent by the recent data including the hydrothermal factor (Bogdanov et al., 2006).

Marine nodules occur usually in the terrigenous sediments relatively close to continents. They are mainly composed of the terrigenous material, testifying contrarily to the hypothesis of the possible high concentration of nonferrous metals in nodules in usual marine settings.

The compositional similarity of all nodules and sedimentary rocks described above is suggested by the comparable contents of many inert and low-mobile elements in both nodules and host sediments.

According to the known hypotheses, metals in oceanic nodules can be sourced from episodic hydrothermal solutions, abyssal fluids, and plumes. Although unknown so far, they are assumed in the polar seas (Baturin, 1986).

CONCLUSIONS

Analysis of the modern literature and original data made it possible to: compare the major and trace element compositions of ferromanganese nodules from the bottom of two lakes, three internal seas in East Europe and five Arctic seas with the average composition of nodules in the World Ocean; determine average contents of elements and variations of their concentrations in nodules from each basin; and decipher similarities and dissimilarities in their trace element composition; establish enrichment of nodules from the eastern Arctic (relative to other samples) in several elements, such as Se, Cd, Sb, Mo, Pb, Co, Li, V, and Sr.

The nodule composition is irregular and varies in different basins. In terms of some elements, nodules from the eastern Arctic are similar to the oceanic varieties. Maximal concentrations of nonferrous metals in them are accompanied by high contents of manganese oxides, stimulating the extraction of metals that are soluble in sea water. Hence, this factor plays an important role in the metal potential of nodules (Baturin and Dubinchuk, 2011b).

According to the data presented above, the MnO/Fe_2O_3 ratio in the studied samples serves as an indicator of the concentration rate of nonferrous metals closely associated with Mn. In the studied nodules, this ratio varies from 0.002 (nodules in the Barents Sea) to 1.33 (average value in oceanic nodules). Thus, the content of Fe–Mn oxides in these samples can reach three orders of magnitude variation range.

At the same time, the high share of terrigenous material in the studied marine nodules suggests that they can be assigned to the transitional (rather than ore) type, while the economic-grade oceanic nodules can be qualified as commercial ores that are currently infeasible only because of the economic and technological reasons. Enrichment of the marine and oceanic nodules with metals is related to the input of elements from the underlying sediments, sea water, and, probably, endogenic sources functioning in all oceans and, possibly, in some seas. The general relative depletion of the Arctic nodules in ore elements is correlated with increased concentrations of trace elements in nodules from separate sectors of the Arctic seas, probably, owing to endogenic factors. Assessment of perspectives of the exploitation of nodules in the eastern Arctic requires a comprehensive detailed study, including prospecting for the assumed ore fields and hydrothermal manifestations.

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