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GEOCHEMISTRY

Phase Distribution of Elements in Ferromanganese Nodules of the Kara Sea

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Abstract—The relation of nonferrous metals and other elements to the main mineral phases in iron–manganese ore is a matter of interest in theoretical and practical terms and has long been discussed by experts. However, opinions on this issue diverge due to the vast variety of conditions of ore formation. This is particularly applicable to ferromanganese nodules of the Kara Sea. The results published here demonstrate that the ferromanganese nodules of the Arctic seas accumulate the same range of elements as pelagic ocean nodules, but in different concentrations and proportions: the contents of most ore elements is decreased by a significant influx of clastic material.

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The relationship between nonferrous metals and other elements and the main mineral phases of iron–manganese ores has attracted interest in both theoretical and practical ways. This problem has long been discussed by experts, but opinions diverge since these ores have formed in a wide range of conditions. This may be applied, in particular, to the ferromanganese nodules of the Kara Sea, which were first discovered by A.E. Nordenskiöld [1] and then studied by many researchers [2–13]. However, the first report regarding the full range of trace elements from several of the Kara Sea nodule samples appeared only recently [10]. The purpose of this work is to give more representative information on this subject.

Samples for the study were collected during several cruize of research vessels of the Shirshov Oceanology Institute, Russian Academy of Sciences, namely *Akademik Mstislav Keldysh* and *Professor Shtokman*. The location of the sampling stations is shown in Fig. 1. Most of the samples have been dragged from depths not exceeding 100 m. The nodules are predominantly of a pancake shape and were formed by the lateral (sideway) overgrowth of the solid core surface (gravel, rock fragment, or compacted sediment) by hydroxides of Fe and Mn. In the mouth of the Ob River, the deposits also contain ferruginated mud-eating worm tubes, similar to those known in sediments of the other northern seas, the Black Sea, and Lake Baikal. The microstructure and mineral composition of the samples have been studied by analytical electron microscopy techniques [15] at the Institute of Mineral Resources, Ministry of Geology (Moscow). Elemental analyses were performed by ICP-MS at the Institute of Microelectronics Technology and High-Purity Materials, Ministry of Geology, under the leadership of V.K. Karandashev. Examination of the ore material using transmission electron microscope revealed that a large proportion of the ore material occurred in an amorphous state as a shapeless mass of indistinctly shaped clots and spongy matter. However, in the compacted ferrous phase, hydrogoethite occurs and, in the manganese phase, the minerals asbolane and buserite occur (Fig. 2). Both minerals are weakly crystallized. In a relatively poorly mineralized worm tube, exotic mineral inclusions were found: a grain of koffinite (U mineral) 0.7 μm long and a grain of native Au 0.15 μm in size (Fig. 3).

For comparative examination of the main chemical composition of the nodules, representative analysis results of the material of the manganese and ferruginous phases, 8 samples of each, were selected (Table 1). Bulk samples were used for the analysis, along with some fragments of the nodules. The results of this comparison indicate that the manganese phase

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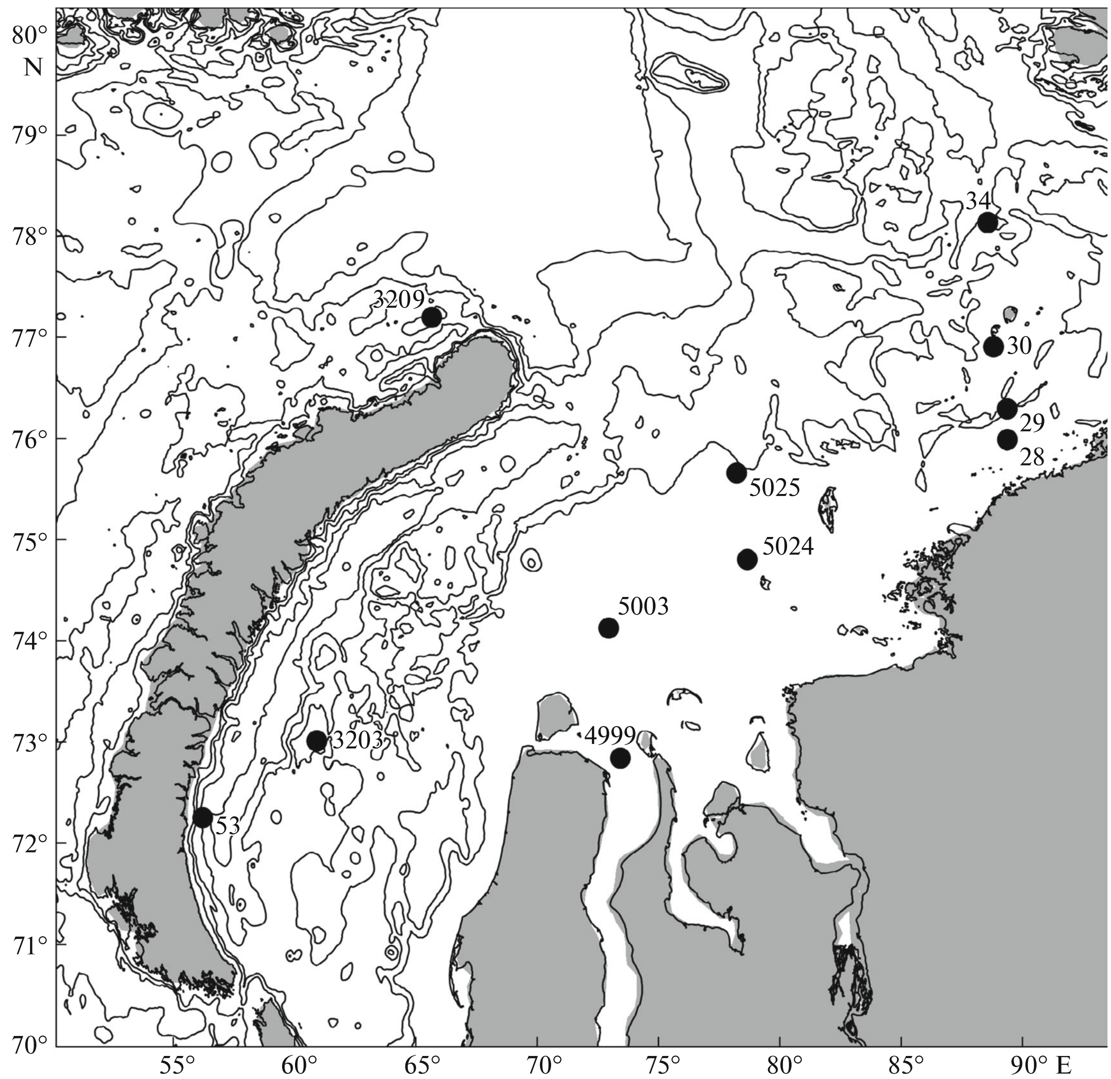


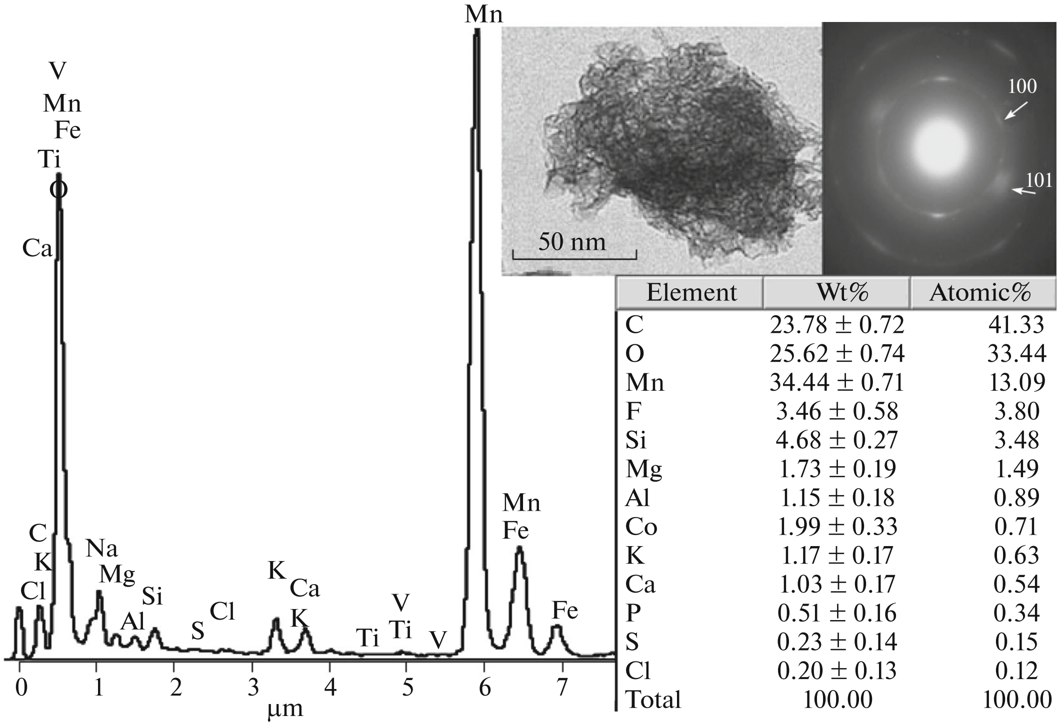
Fig. 1. Scheme of nodules sampling stations.

is enriched with Mn compared to ferruginous phase by five times (30 and 5.7% MnO) and depleted in Fe by 2.5 times. Moreover, the manganese phase is enriched relative to the ferruginous phase with Na by 1.5 times (2.9 and 1.8%) but is depleted in P by two times (1.3 and 2.7% P_2O_5). But the concentrations of the other main components in both phases are similar.

A similar comparison of the trace elements is given in Table 2. The total content of trace elements concentrated in the manganese and ferruginous phases is substantially equal, but in its "attractive" force, the Mn phase is more efficient. By the contents of Li and Mo, the manganese phase exceeds the ferruginous one by 8–10 times, in the concentrations of Cd and Ni by 3 times, and in that of Ag, Ba, Bi, Ga, Hg, Sb, Sn, Ta, and W, by 1.4–2 times. As for the ferruginous phase, it is superior to the manganese phase by the content of As (3 times), and by the content of certain metals (including Co, Pb, Zn, V, and Y) and inactive elements (Be, Hf, Nb, Rb, and Zr) by not more than 1.3–1.5 times.

Earlier comparison of the compositions of the nodules and sediments had shown that, of the number of rock forming elements accumulated in the nodules, only P occurs along with Fe and Mn [14]. Regarding trace elements, in this case the nodules are enriched relative to the sediments with the group of nonferrous metals (Cu, Ni, and Mo), which does not include Pb and Zn, unlike the ocean nodules for which such an imbalance is not typical [14]. Among other elements, the nodules area enriched relative to the sediments first of all with As and Zn (on average by 8 times) and to a lesser extent (2–3 times) with Ba, Sr, Sb, U, V, Ta, and Y.

The question of the mechanism of concentration of the trace elements in the nodules remains debatable.



Element	Wt%	Atomic%
C	23.78 ± 0.72	41.33
O	25.62 ± 0.74	33.44
Mn	34.44 ± 0.71	13.09
F	3.46 ± 0.58	3.80
Si	4.68 ± 0.27	3.48
Mg	1.73 ± 0.19	1.49
Al	1.15 ± 0.18	0.89
Co	1.99 ± 0.33	0.71
K	1.17 ± 0.17	0.63
Ca	1.03 ± 0.17	0.54
P	0.51 ± 0.16	0.34
S	0.23 ± 0.14	0.15
Cl	0.20 ± 0.13	0.12
Total	100.00	100.00

Fig. 2. The morphology, composition, and microdiffraction patterns of asbolane and buserite.

Many researchers believe that some of the trace elements (Li, Ba, Zn, and Cd) are constituents of manganese minerals [14], but this is not applicable to most other elements that are accumulated in nodules. During study of the composition of ferromanganese concretions with an electron microscope, it has been revealed that the colloformic material contains a higher proportion of nonferrous metals than the crystalline phases. This demonstrates the prevalence of sorption accumulation of metals in the nodules at the initial stages of their formation, rather than during crystallization, which removes impurities from the minerals.

Table 1. Average concentration of the main components in the manganese and iron phases (%)

Components	Manganese phase		Iron phase	
	range	average	range	average
MnO	21.1–34.2	30.0	2.5–10.0	5.75
Fe_2O_3	5.8–16.0	11.5	20.5–36.3	28.5
Al_2O_3	4.8–6.8	5.7	5.2–9.5	7.0
TiO_2	0.21–0.30	0.25	0.20–0.44	0.30
Na_2O	2.5–3.0	2.9	1.6–2.1	1.85
K_2O	1.3–1.8	1.5	1.0–1.8	1.45
CaO	1.9–2.3	2.1	1.5–2.2	1.8
MgO	1.6–2.2	2.0	1.2–2.5	1.65
S_{tot}	0.11–0.15	0.12	0.08–0.12	0.10
P_2O_5	0.4–1.7	1.3	1.0–3.6	2.7

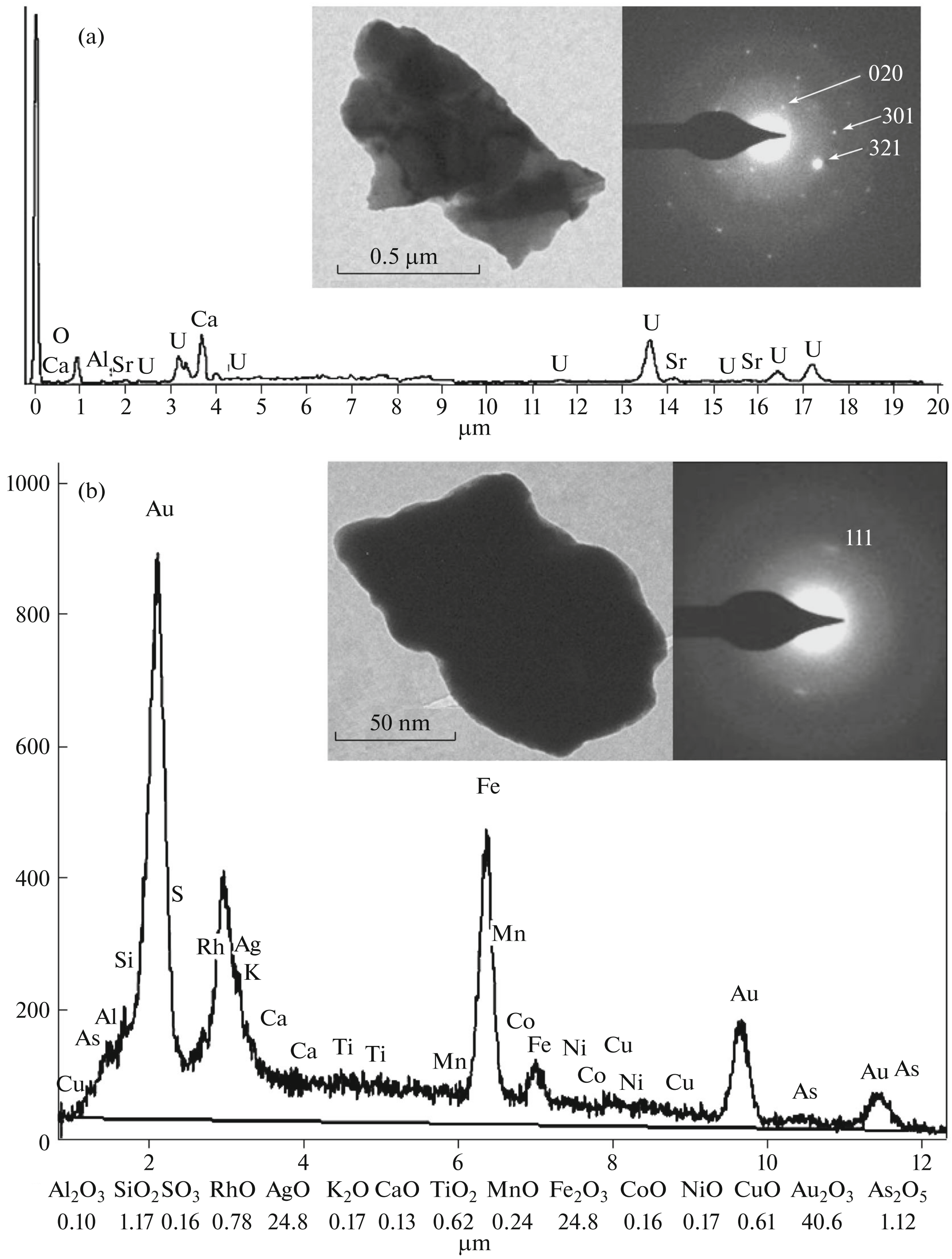


Fig. 3. The morphology, composition, and microdiffraction patterns coffinite particles (a) and native Au (b).

The present results demonstrate that ferromanganese nodules of the Arctic seas accumulate the same spectrum of elements as the pelagic ocean nodules, but in different concentrations and proportions, with a reduced concentration of the majority of ore elements as a result of active clastic sedimentation. Therefore, the shallow sea nodules do not correspond to ore conditions, but may serve as indicators of ore occurrences in the adjacent on-shore areas, as was evidenced by the above-described finding in the estuary zone of the Ob River.

Table 2. Average concentration of trace elements in the manganese and iron phases (ppm)

Element	Manganese phase		Iron phase		Sediment
	range	average	range	average	
Ag	0.11–5.7	1.0	0.20–5.8	1.5	<0.3
As	254–1283	954	140–467	306	50
Ba	443–890	573	530–1800	800	425
Be	0.23–2.1	1.2	0.67–0.89	0.80	1.4
Bi	0.07–0.23	0.18	0.10–0.25	0.13	0.27
Cd	0.08–1.6	0.5	0.5–6.0	2.4	0.20
Co	36–227	140	83–143	98	22
Cr	27–85	38	30–100	44	71
Cs	1.3–3.6	2.2	1.9–3.9	2.0	4.7
Cu	11–65	50	45–182	92	27
Ga	7–12	10	20–23	22	16
Hf	1.1–3.3	2.0	0.7–2.4	1.2	2.8
Hg	–	0.016	–	1.03	–
Li	19–65	34	71–380	280	32
Mo	44–178	60	473–868	578	10
Nb	2.9–19.5	6.0	2.9–6.5	3.7	9
Ni	73–198	122	188–480	270	45
Pb	17–57	31	11–46	20	20
Rb	35–60	42	34–72	37	82
Sb	5.9–15.9	13	13–75	29	1.6
Sc	5.9–21	7.5	4.9–7.0	6.2	13
Se	1.6–2.3	2.0	–	–	–
Sn	0.5–2.4	0.9	0.4–6.3	1.4	1.8
Sr	340–737	588	494–1150	570	180
Ta	0.27–0.42	0.35	0.23–0.53	0.40	0.80
Te	–	–	–	0.31	<0.3
Th	3–4	6.2	2.6–8.1	3.6	8.3
Tl	0.34–8.8	3.1	2.8–15.4	5.3	0.51
U	2.6–10.7	7.0	3.4–10.7	5.8	1.9
V	278–846	536	215–318	286	135
W	2.5–8.3	5.0	4.8–15	7.4	4.3
Y	26–54	44	21–59	29	17
Zn	56–206	125	62–180	97	84
Zr	43–150	70	34–92	43	102

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