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MARINE GEOLOGY

Ferromanganese Nodules from the East Siberian Sea near Bennett Island

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Abstract—Ferromanganese nodules recovered from the bottom of the East Siberian Sea near Bennett Island are studied by coupled ultramicroscopic and ICP-MS methods. The majority of nodules are flattened dense formations 2.5 to 10 cm in cross section and circled by a thick rim, which is common in nodules from other Arctic basins. The major components of nodules are iron and manganese oxides in the form of ferruginous vernadite and magnetite, as well as accessory minerals, including apatite and titanomagnetite. The major and trace element compositions of nodules are comparable to Arctic nodules from other Arctic seas, but somewhat different compared to those from the Mendeleev Rise. A specific feature of these nodules is that they contain high amounts of mercury in all samples and a positive europium anomaly in one sample, along with gold; this may be related to the influence of endogenous gas-and-vapor exhalations.

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INTRODUCTION

Ferromanganese nodules were revealed for the first time by Nordernscold in the Arctic region in 1881 in the Kara Sea [26]; since then, they have been studied repeatedly studied by many other scientists, who described their structure and mineral and chemical compositions [3, 5, 8–10, 12, 15–21, 23, 24, 27, 28].

It has been found that Arctic nodules contain considerably smaller amounts of nonferrous metals compared to oceanic nodules from larger depths and that they form on the bottom predominantly owing to diffusion of chemical elements from the underlying sediments. Apart from this, ferromanganese nodules in oceans can also form owing to supply of metals with hydrothermal solutions from the Earth's interior in tectonically active zones [1, 2].

In recent years, because of expanded comprehensive studies in the Artic, it has been discovered that episodic powerful gas-and-vapor exhalation has been occurring in the northern East Siberian Sea near Bennett Island (Fig. 1) since 1973; it takes place in the form of streams which ascend, judging by satellite images, by up to 1000 km high [22–24, 30] (Fig. 2).

In 1983, comprehensive land and marine studies were carried out in this area by the Institute of Volcanology and Seismology, Far East Science Center of the Academy of Sciences of USSR, under the supervision of Yu.P. Masurenkov [22–25] to investigate the supposed location of regular gas exhalations which occurred here in February 1983 [30].

Marine works which included echo sounding and bottom dredging were carried out on board of the hydrographic R/V *Dmitrii Sterlegov* on September 16–17, 1983 [24].

Dredging on the eastern submarine slope of Bennett Island (carried out with the supervision and direct participation of A.A. Ovsyannikov) recovered a considerable amount of ferromanganese nodules. In terms of morphology, they are relatively dense oval and rounded units of up to 10 cm in cross section, with thickened rims.

After the expedition, about 40 samples of these nodules were studied by chemical, mineralogical, and spectral methods [23], and 13 whole samples underwent additional (however, incomplete) chemical analysis [24]. Based on the results of these studies, it was concluded that by some parameters, the analyzed nodules are comparable to hydrothermal oceanic nodules [23, 24].

In order to consider the problem in more detail, we continued to study ferromanganese nodules on the wider analytical basis.

Fig. 1. Eastern part of Russian Arctic Sector. Bennett Island (indicated with arrow) is north of New Siberia Island.

MATERIALS AND METHODS

For the present work, we selected four typical flattened samples with cross sections ranging from 5 to 8 cm from the entire available collection of nodules.

The microstructures of the nodules were analyzed with a scanning electronic microscope in the analytical laboratories of the Fedoronsky All-Russia Institute of Mineral Resources (ARIMS) and at the Shirshov Institute of Oceanology, Russian Academy of Sciences.

The mineral composition was determined with an ARIMS on a transilluminating electron microscope with a microdiffraction annex and a microprobe, which made it possible to see the morphology of microscopic particles and at the same time to determine their mineral and chemical compositions [7].

The total element composition was determined by ICP-MS at the Analytical Certified Testing Center of the Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences.

RESULTS

Structure and mineral composition. Examination on a scanning microscope showed that the studied samples are composed mainly of fine-grained and colloform material without any visible signs of holocrystalline aggregates.

For one of the samples, a microprobe revealed an oval magnetite particle up to 30 μm in size and finer apatite particles on the background of the general colloform mass (Fig. 3).

Nodules did not contain remains with clear biogenic origin, but one of the samples contained a particle less than 1 mm in size composed of iron and manganese hydroxides; it was similar to a corroded gastropod shell without carbonate (Fig. 4).

When the same material was analyzed on a transilluminating electron microscope, it was found that the chief ore mineral was ferrugionous vernadite (Fig. 5), but idiomorphic crystalline forms of manganese minerals were not revealed, despite the predominance of

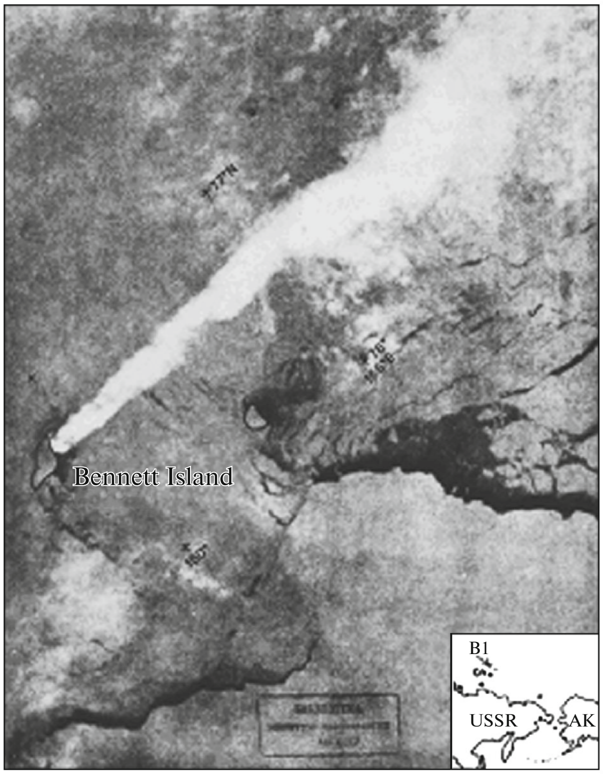


Fig. 2. Gas plume ascending into atmosphere during submarine eruption that began on February 18, 1983. Image 18943 by NOAA-6 [30].

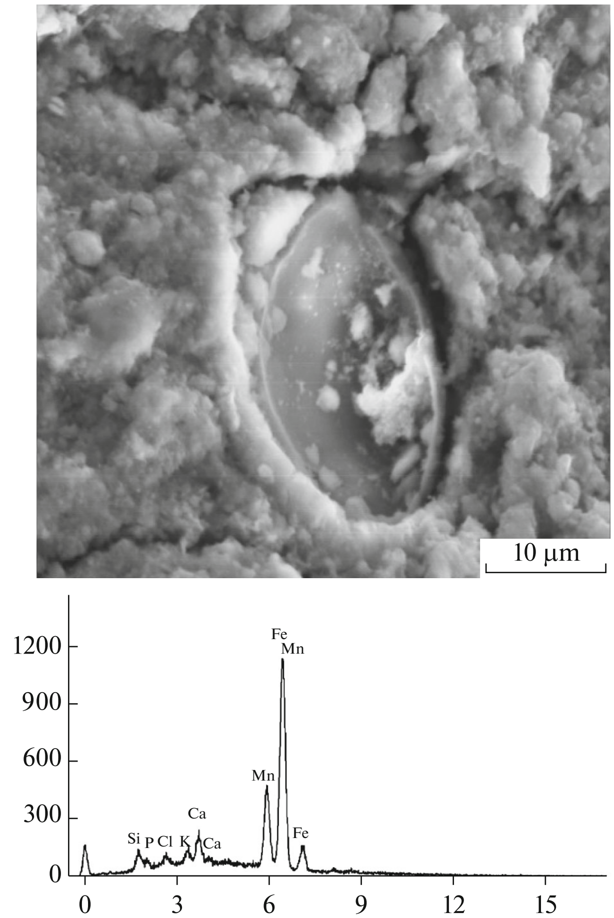


Fig. 3. Colloform structure of nodule groundmass containing inclusion of ellipsoidal magnetite particle on which microscopic apatite grains rest.

manganese over iron in many parts of the analyzed samples.

Apatite particles are quite frequently present in the colloform mass as elongated crystallites and their aggregates, and in one sample, we found a twin cerianite (rare-metal apatite) crystal (Fig. 6).

Major element composition. The data on the studied nodules (Table 1) indicates the quite homogeneous main composition of the samples in terms of contents of such elements as aluminum (7.0–9.3%), titanium (0.61–0.65%), sodium (2.7–2.9%), potassium (1.6–1.8%), calcium (2.0–2.7%), and magnesium (1.6–1.7%). The more noticeable (however, by a factor of no more than 2) are variations in contents of oxides of iron (16.1–22.9%), manganese (16.1–22.9%), phosphorus (1.0–1.8%), and sulfur (0.09–0.16%).

The mean iron content in the studied samples (9.9%) is 2–2.5 times lower than the respective mean contents in nodules from other Arctic seas and World Ocean (Table 1). Additionally, we should note that the mean content of manganese, potassium, calcium, and magnesium in the considered samples almost coincides with that in nodules from the Laptev Sea, whereas the mean contents of aluminum, titanium, sodium, and phosphorus are similar to those in nodules from the Mendeleev Rise.

Trace element composition. Investigation of the trace element composition of the studied samples (Table 2) also revealed certain patterns.

A common feature of the studied samples is their depletion in arsenic, cobalt, selenium, tellurium, and strontium compared to nodules from other seas; they are characterized by low uranium contents as well, but this is also characteristic of oceanic nodules.

In terms of Ba, Cu, Ga, Mo, Ni, Pb, Sb, and W contents, the studied samples are close to nodules from the East Siberian Sea, while in the contents of such elements as Ba, Be, Bi, Cd, Cs, Rb, Sc, Te, Va, Y, and Zn, they are close to nodules from the Laptev Sea.

The studied samples are similar to nodules from the Mendeleev Rise only in lithium, strontium, and tantalum contents, whereas similarity to deep oceanic nodules is reflected only in the contents of such elements as As, Cr, Mo, Sn, and U.

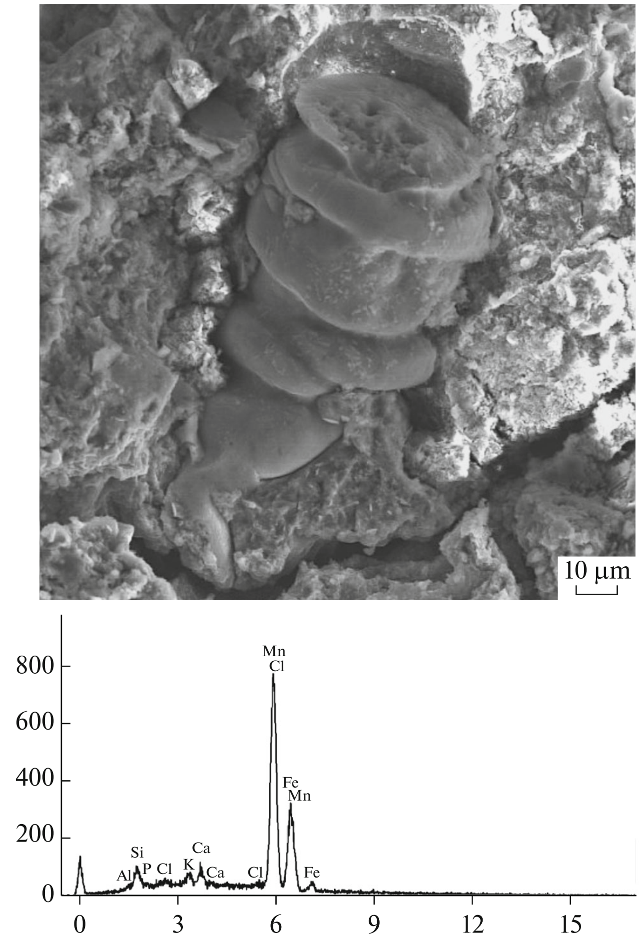


Fig. 4. Compacted ferromanganese inclusion in colloform groundmass of nodule.

A unique feature of the studied nodules is anomalous enrichment of all samples in mercury, with a peak concentration of 11.6 g/t, which generally exceeds the respective mean value in sedimentary rocks by one to two orders of magnitude (0.089 g/t) [15] and in marine and oceanic ferromanganese nodules [1, 2].

Another peculiarity of these samples is that ICP-MS analysis revealed gold in one sample (30 mg/t), while microprobe analysis revealed traces of palladium in another sample; we had observed this earlier in samples from the Mendeleev Rise [13].

All this gives us grounds to suggest that the found anomalies are related to some mercury-containing exhalations of unclear general composition, and according to satellite images these exhalations are repeatedly activated in the area of Bennett Island to reach the altitudes of many kilometers. Probably, mercury extracts gold from the host rocks on its way up from the interiors. As is known, this property of mercury is widely used in recovery of gold.

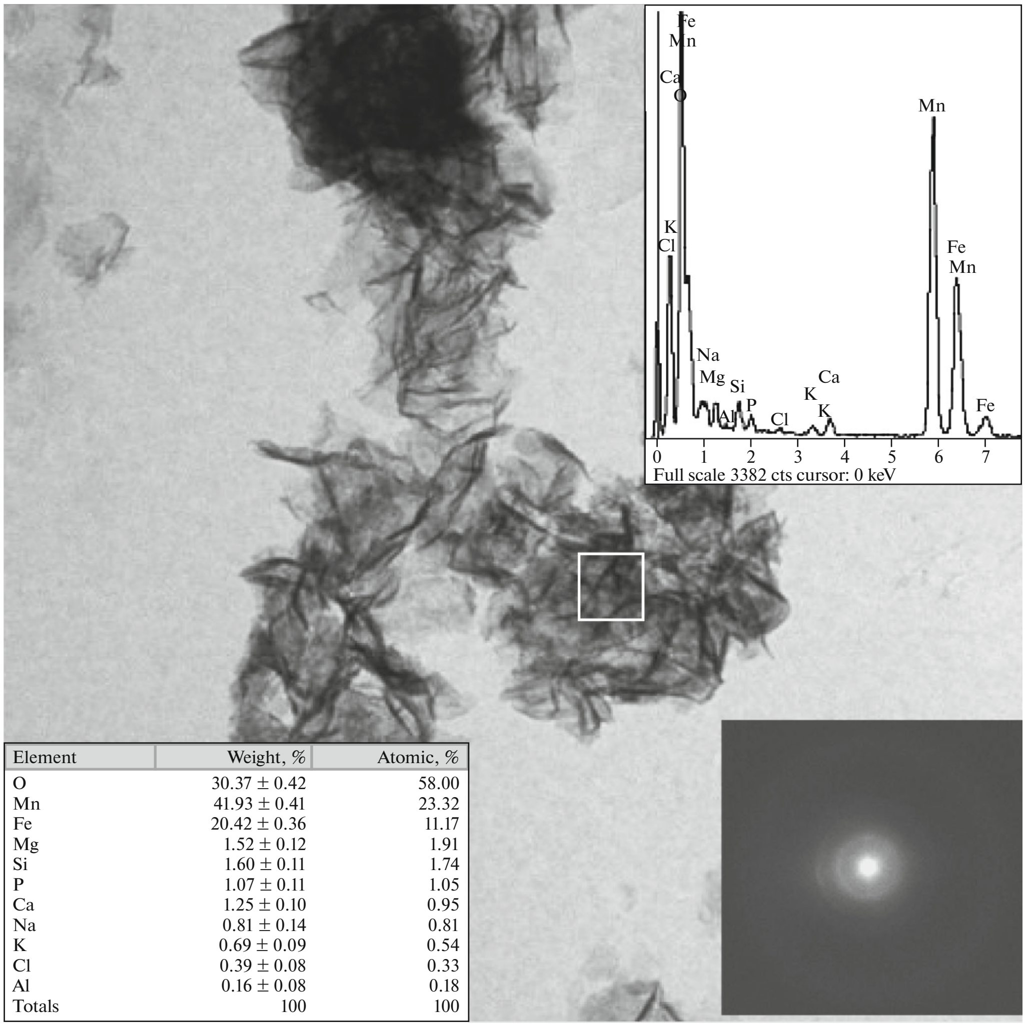
Rare-earth elements. The total contents of 14 rare-earth elements (REE) in the studied samples range from 124 to 156 g/t (Table 3), which is insignificantly lower than their mean contents in clay sedimentary rocks (175 g/t, after [15]). In ferromanganese nodules from the Mendeleev Rise, the total content of these elements is higher by more than an order of magnitude (about 2000 g/t) and is close to the respective content in oceanic ferromanganese nodules and crusts [1, 2].

A key characteristic of the REE composition is the values of Ce and Eu anomalies, which are calculated from the ratios of the schist-normalized contents of cerium and europium to the half-totals of two adjacent elements: (a) lanthanum–praseodymium and (b) samarium–gadolinium, respectively [17].

In this case, the values of cerium anomaly in the studied samples are slightly lower than the equilibrium ones (0.94–0.99). The values of europium anomaly in two samples are also insignificantly below the equilib-

Table 1. Main composition of nodules (%)

Component	Bennett Island area					Kara Sea [3]	Laptev Sea [9]	Mendeleev Rise [5]	Ocean [1]
	sample 1	sample 2	sample 3	sample 4	mean				
Fe_2O_3	13.6	10.0	7.6	8.7	9.9	23.4	25.4	25.1	17.9
MnO	22.0	17.7	16.1	22.9	19.9	10.9	17.3	12.0	24.0
Al_2O_3	7.0	8.0	8.8	9.3	8.5	5.3	3.8	8.1	5.1
TiO_2	0.62	0.61	0.64	0.65	0.63	0.24	0.14	0.54	1.12
Na_2O	2.7	2.8	2.9	2.8	2.6	2.0	2.1	2.5	2.7
K_2O	1.6	1.6	1.8	1.7	1.7	1.3	1.3	0.8	1.04
CaO	2.0	2.1	2.2	2.7	2.5	2.0	2.3	4.1	5.4
MgO	1.6	1.7	1.6	1.6	1.62	1.7	1.6	3.5	2.63
P_2O_5	1.8	1.1	1.0	1.6	1.45	2.6	5.6	1.1	2.4
S_{total}	0.10	0.09	0.16	0.15	0.11	–	0.12	0.48	0.5



Element	Weight, %	Atomic, %
O	30.37 ± 0.42	58.00
Mn	41.93 ± 0.41	23.32
Fe	20.42 ± 0.36	11.17
Mg	1.52 ± 0.12	1.91
Si	1.60 ± 0.11	1.74
P	1.07 ± 0.11	1.05
Ca	1.25 ± 0.10	0.95
Na	0.81 ± 0.14	0.81
K	0.69 ± 0.09	0.54
Cl	0.39 ± 0.08	0.33
Al	0.16 ± 0.08	0.18
Totals	100	100

Fig. 5. Morphology and composition of ferruginous vernadite (magnification ×100000). Bottom right corner, microdiffraction image of vernadite.

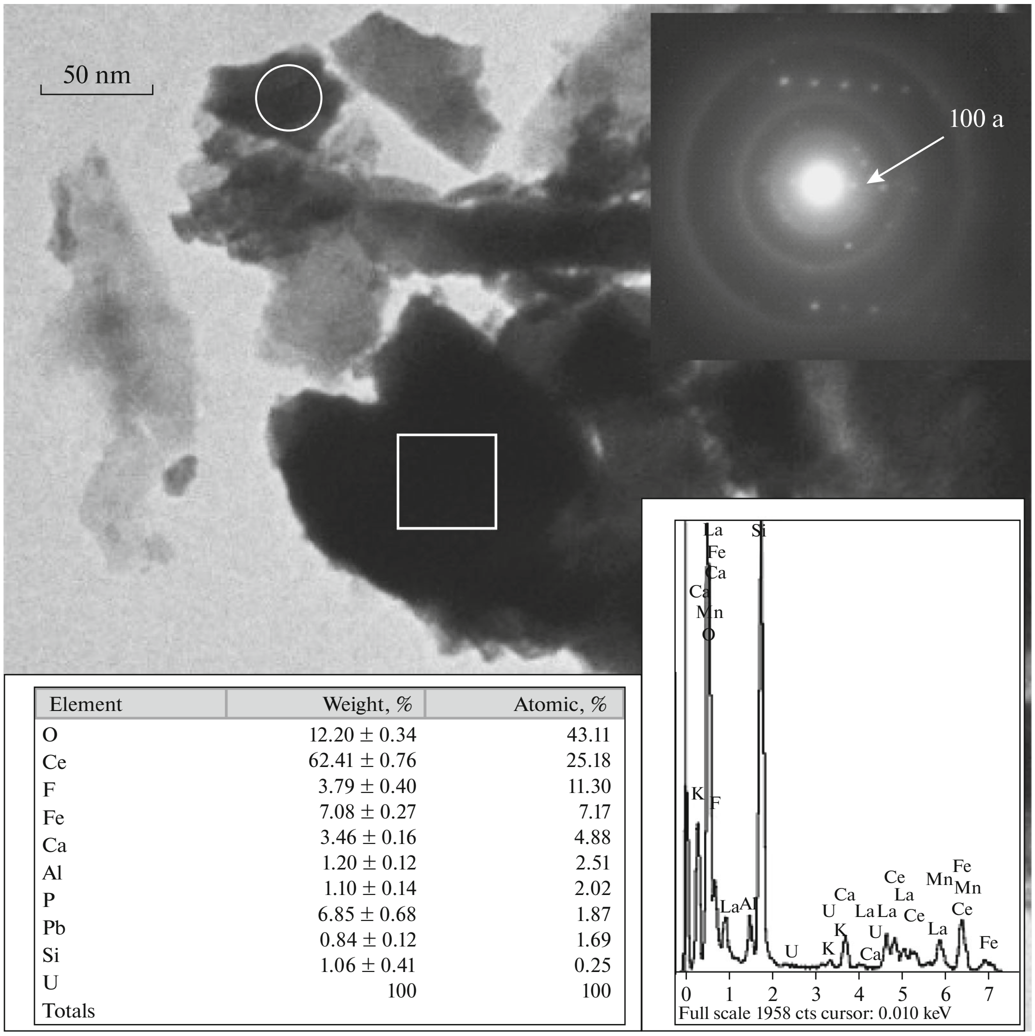
rium value (0.95 and 0.97), whereas in the third and fourth samples, they are insignificantly higher (1.03) and high (Eu* = 1.11), respectively, which is typical of oceanic hydrothermal deposits and some volcanic rocks [4, 6, 11–14, 29].

DISCUSSION

The results indicate that ferromanganese nodules from Arctic seas are generally characteristic of a certain homogeneity and relative depletion in nonferrous metals, manifested when comparing the compositions of the studied samples from the northern East Siberian Sea and mean composition of nodules from other Arctic seas and oceans. Oceanic nodules are especially enriched in Ag, Ba, Bi, Co, Cu, Ti, Ni, Y, Zn, and Zr compared to nodules from the sea bottom. However, nodules from the Mendeleev Rise are intermediate in this sense, because among the Arctic nodules they are the most enriched in Be, Bi, Co, Hf, Nb, Ni, Sb, Se, Te, Tl, and Y.

The most significant are three geochemical peculiarities revealed in the compositions of the studied nodules, namely, higher contents of mercury, gold, and europium.

When interpreting these data, it should be taken into account that some gas-and-vapor exhalations have been repeatedly reported in the study area. In this respect, it is natural to think that endogenous mercury is present in their composition and extracts gold from bedrocks during the ascent of the gas-and-vapor mixture from the interior towards the Earth's surface and further into the atmosphere. However, when the gas-and-vapor mixture reaches the water–bottom interface, certain components of this mass are extracted



Element	Weight, %	Atomic, %
O	12.20 ± 0.34	43.11
Ce	62.41 ± 0.76	25.18
F	3.79 ± 0.40	11.30
Fe	7.08 ± 0.27	7.17
Ca	3.46 ± 0.16	4.88
Al	1.20 ± 0.12	2.51
P	1.10 ± 0.14	2.02
Pb	6.85 ± 0.68	1.87
Si	0.84 ± 0.12	1.69
U	1.06 ± 0.41	0.25
Totals	100	100

Fig. 6. Twin cerianite crystal in colloform groundmass of vernadite (magnification ×100000-fold). Top right corner, microdiffraction image of apatite.

(absorbed) by marine sediments, including nodules. Thus, gold in nodules is likely coupled with mercury.

Regarding the anomalously high europium content, this phenomenon is typical of many volcanic rocks and hydrothermals and has been regularly observed in tectonic activity zones, where europium appears to be the most mobile element compared to the other REEs.

In the first work dedicated to the samples described above, it was supposed that the low contents of nonferrous metals is related to their hydrothermal origin [24]. However, the depletion of marine ferromanganese nodules in metals compared to oceanic ones is typical of all Arctic nodules from the White and Barents seas to the East Siberian Sea (see [1, 3, 5, 8, 9, 15], etc.), and no visible hydrothermal activity has been reported the areas where these nodules were found. In basic composition, the studied nodules correspond to other Arctic nodules, whereas the presence of exotic components in them may be related to gas exhalations.

CONCLUSIONS

Ferromanganese nodules collected from the bottom in the northern East Siberian Sea near Bennett Island are close to nodules from other Arctic in morphology and mineralogy; however, they differ in specific geochemical anomalies, namely, an unordinarily high mercury content in all the studied samples and higher contents of gold and europium in one of the samples. These are arguments for the earlier supposed endogenous origin of gas-and-vapor exhalations, which have been visually observed in this area for several years but whose direct investigation had been impossible. Our study shows that these

Table 2. Trace element composition of nodules (g/t)

Element	Nodules near Bennett Island					Kara Sea [3]	Laptev Sea [9]	Mendeleev Rise [5]	Ocean [1]
	sample 1	sample 2	sample 3*	sample 4	mean				
Ag	0.083	0.034	0.064	0.094	0.07	<0.03	0.048	0.35	0.9
As	259	160	134	142	170	527	750	550	140
Ba	912	923	737	747	840	900	1020	425	2300
Be	1.2	1.2	1.3	1.2	1.2	0.73	1.1	5.5	2.5
Bi	0.25	0.13	0.13	0.15	0.16	0.24	0.13	9	7
Cd	2.3	5.6	1.9	1.9	2.9	11.2	2.4	5.5	10
Co	266	184	200	217	215	314	340	4590	2700
Cr	42	43	55	36	45	26	14	25	35
Cs	2.3	1.9	2.2	2.4	2.2	1.8	2.3	1.6	1
Cu	43	41	39	41	40	37	24	542	4500
Ga	49	43	11	20	30	42	15	7	10
Hf	2.2	3.0	2.3	1.9	2.3	0.8	1.1	**9**	8
Hg	2.4	1.2	11.6	2.4	4.5	0.076	0.15	0.003	0.02
Li	40	104	24	21	47	95	34	45	80
Mo	480	400	344	377	400	417	190	265	400
Nb	8.5	12.2	11.1	9.2	10	3.1	3.1	42	50
Ni	179	141	173	183	167	127	226	2490	6600
Pb	33.8	27.3	33.1	30.0	31	48	19	530	900
Rb	45	44	57	52	50	31	33	27	17
Sb	16.7	19.0	13.2	14.6	16	18	14	54	40
Sc	6.0	6.5	6.8	6.2	6.2	4.2	5.4	37	10
Se	2.2.	2.0	<1.3	<1.2	1.2	2.7	4.1	12	0.6
Sn	0.8	1.0	1.5	1.5	1.2	0.43	0.66	4	2
Sr	610	523	492	504	530	970	1070	737	1030
Ta	0.49	0.70	0.68	0.58	0.61	0.20	0.20	1	10
Te	<0.15	<0.2	<0.06	0.18	0.1	0.52	0.14	26	10
Th	4.6	5.4	4.1	4.7	4.7	3.2	3.4	100	30
Tl	1.8	3.0	1.5	1.3	1.9	7.5	0.77	140	150
U	5.2	4.3	4.2	5.5	5.0	9.3	12	11	5
V	205	156	159	188	176	400	173	890	500
W	6.2	4.6	4.2	7.5	5.6	5.5	8.5	55	100
Y	32	28	27	27	27	38	30	240	150
Zn	159	154	150	160	158	320	190	400	1200
Zr	91	126	104	83	100	37	42	280	560

* Sample 3 contained 0.03 g/t of gold.

Table 3. REE contents in nodules (g/t)

Element	Sample 1	Sample 2	Sample 3	Sample 4	Mendeleev Rise [5]
La	29.8	31.8	26.0	29.2	210
Ce	60.1	67.7	55.0	60.8	1226
Pr	6.6	7.3	6.0	6.6	55.7
Nd	26.7	28.6	24.4	25.5	221
Sm	5.9	5.9	5.1	5.5	54.4
Eu	1.4	1.3	1.3	1.3	16.2
Gd	6.7	6.2	5.2	5.6	62.3
Tb	0.99	0.91	0.76	0.8	10.2
Dy	5.6	4.9	4.3	4.6	58.1
Ho	1.1	1.0	0.86	0.93	11.3
Er	3.2	2.8	2.4	2.7	32.5
Tm	0.42	0.37	0.33	0.35	4.7
Yb	2.8	2.4	2.1	2.1	29.6
Lu	0.42	0.35	0.30	0.33	4.3
Sum	151	161.5	124.1	156.3	1991
Ce*	0.94	0.97	0.99	0.94	2.22
Eu*	0.97	0.95	1.11	1.03	0.98

periodically activated exhalations actually exist in the Arctic region and is supported by the considered geochemical markers.

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