

Ferromanganese nodules of the Kara Sea

Yu. A. Bogdanov, E. G. Gurvich, O. Yu. Bogdanova, G. V. Ivanov,
A. B. Isaeva, and K. G. Murav'ev

P. P. Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow

A. I. Gorshkov

Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow

G. I. Dubinina

Institute of Microbiology, Russian Academy of Sciences, Moscow

Abstract. The thinly laminated flat discoidal ferromanganese nodules of the Kara Sea are composed of alternating manganese- and iron-rich laminae. Birnesite (buserite 1) predominates in the manganese-rich laminae, and the iron-rich laminae are composed of bacterial-like protoferrihydrite particles. Mineralogical, crystallochemical, and chemical studies suggest that these shallow-water nodules are likely formed under conditions of periodically changing bottom waters dynamics which lead to alternating sedimentary matter accumulation and erosion by bottom currents.

Introduction

The investigation of ferromanganese nodules collected by trawls at station 4399 (coordinates 74°59.4'N, 79°48.0'E, depth of 41 m) during R/V *Dmitriy Mendeleev* cruise 49 in 1993 was aimed at two main tasks: first, to obtain a new representative information about the composition and properties of these authigenic mineral aggregates formed within a specific bottom environment; and second, to elucidate some characteristics of the sedimentary environment which could not be defined using the analyses of sediments themselves.

First reports about the occurrence of ferromanganese nodules in the Kara Sea appeared at the end of 19th century and at the beginning of 20th century (Figure 1) [Gorshkova, 1957, 1970; Kulikov, 1961; Manheim, 1965]. These publications contain information about the nodules distribution patterns, occurrence conditions, morphology, and bulk composition. Data on minor elements concentration in one of the Kara Sea nodules (unfortunately, a manganese-poor one that contains 15.99% Fe and 1% Mn) were published in the work by Strakhov *et al.* [1968]. In later publications, for example, by Volkov [1979] and others, data on the Kara Sea nodules are mainly considered in comparison with analogous nodules from other regions of the World Ocean.

About 200 kg of the ferromanganese nodules were collected by trawls at station 4399 (for the station location

see Figure 1). In this paper we present only preliminary results of laboratory studies of the nodules.

Morphology and Occurrence Conditions of the Ferromanganese Nodules

The ferromanganese nodules at station 4399 are discoidal in shape, 4–7 cm in diameter, and 0.5–1.5 cm thick (Figure 2). They are characterized by the thinly laminated inner structure. The nuclei occurring in some nodules are composed of well rounded crystalline rock fragments. The hydroxide coating is concentrically laminated. The character of lamination changes from the central parts to the nodule margins, reflecting a succession of the nodule growth. Dark brown laminae, 0.2–1.5 mm thick, alternate with thinner (0.05–0.2 mm) yellow laminae, often of discrete character. The marginal parts of nodules display a more frequent alternation of the laminae, as compared with that in the central parts. The laminated structure of the nodules is mainly formed by alternation of laminae with different proportions of the major iron and manganese minerals, and with various lithic components contents. An alternation of concentrically distributed thicker and thinner parts in the discoidal nodules corresponding to certain growth intervals indicates a cyclicity in the hydroxide precipitation.

Ferromanganese rims around stones of different size were also described in previous publications [Strakhov *et al.*, 1968]. Small spheroidal nodules, 1 to 8 mm in diameter, are common.

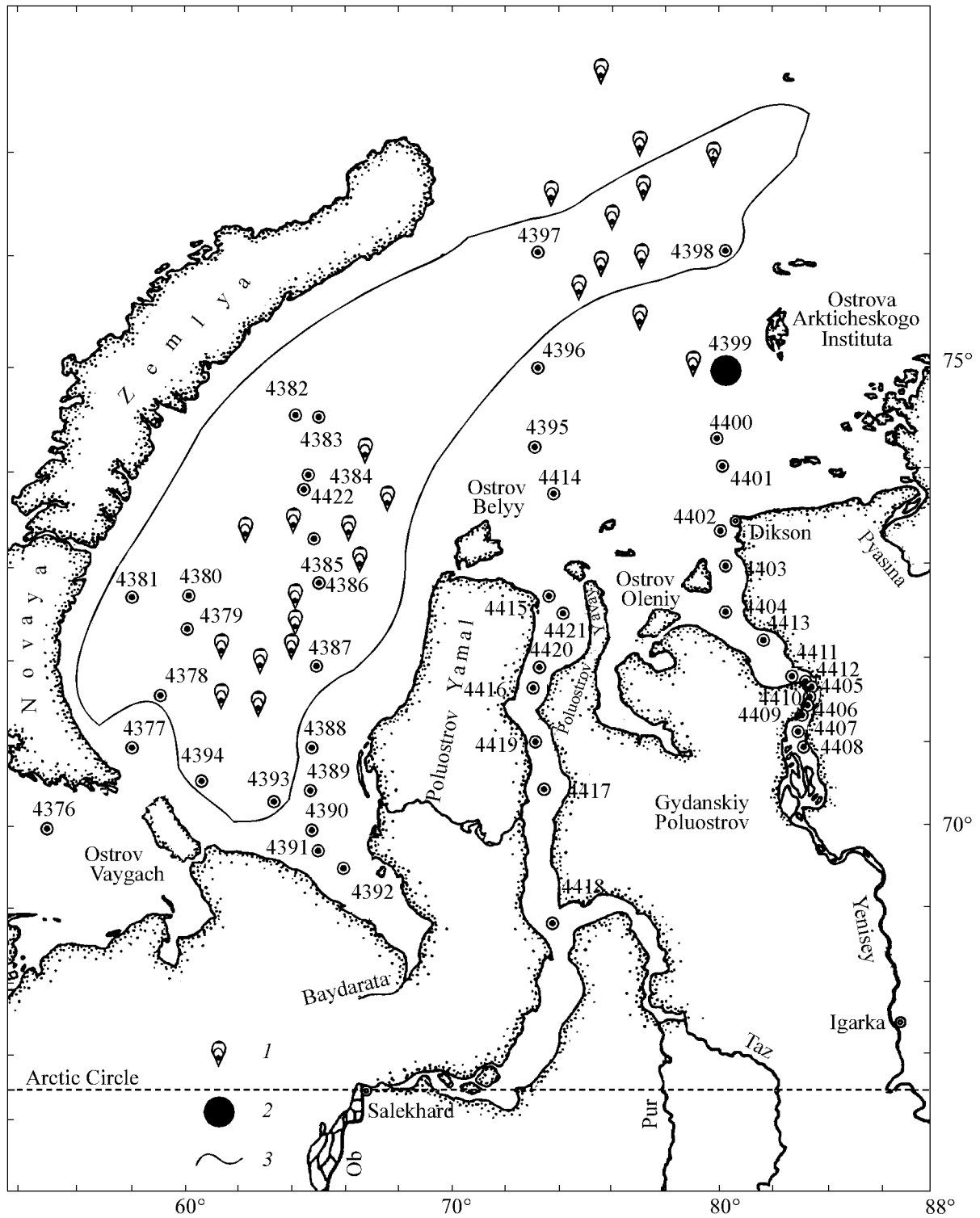


Figure 1. Distribution of ferromanganese nodules in the Kara Sea (from the work by *Gorshkova* [1970]: 1, location of stations where ferromanganese nodules were found; 2, location of station 4399 where nodule samples were collected for this study; and 3, boundary of the oxidized surface layer distribution.

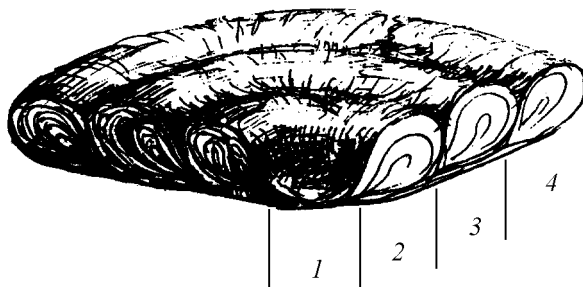


Figure 2. Typical nodule described in this paper: 1, 2, 3, and 4 denote sampling points for the investigation.

Ferromanganese nodules occur on the sediment surface at the water-bottom interface. The nodules are underlain by reduced terrigenous mud, locally with a thin, up to 10 cm thick, oxidized surface layer at the top. The nodules are commonly laying on this oxidized layer, although they also occur directly on the reduced mud surface (Figure 1), as did the nodules used for this study.

Mineralogy and Crystallochemistry of the Ferromanganese Nodules

For the mineralogical investigation we used a JFM 1000C transmission electron microscope equipped with a goniometer of $+60^\circ$ inclination and a Kevex 5100 energy dispersive spectrometer. The X ray diffraction method was also used to distinguish the so-called 10 Å buserite, possibly present in the specimens studied. The buserite is known to be transformed into a structure analogous to 7 Å birnessite under the electron microscope vacuum.

The electron microscopy showed that the dark brown laminae are mainly composed of the hexagonal birnessite [Gorshkov *et al.*, 1992c]. This mineral occurs largely as fine, flaky aggregates (Figure 3c), and the minor proportion is represented by aggregates of relatively large plates (Figure 3a). The electron diffraction patterns of the latter show basic $hk0$ reflexes, basal 001 reflexes, and often spatial $hk1$ reflexes (Figure 3b). Only basic $hk0$ reflexes and basal 001 reflexes are present on the electron diffraction patterns of the fine, flaky aggregates, which is characteristic for turbostratic structures. Trillings and elongated plates of the monoclinic birnessite also occur in minor amounts (Figures 3e and 3f). All these birnessite varieties are of the same composition (see energy dispersive spectra on Figures 3a, 3c, and 3e).

The X ray study revealed that the dark brown laminae are actually composed of dominant buserite 1 ($d_{001} = 9.87 \text{ \AA}$), and the birnessite is present in minor amounts. One can assume that initially the dark brown laminae were composed of buserite 1 only, while birnessite was formed later, as a product of partial buserite 1

transformation during the syneresis. However, more likely, both the coarser crystalline hexagonal birnessite, and the monoclinic birnessite comprising a minor proportion of the dark brown laminae composition, are primary phases, i.e., were formed directly during the early diagenesis as buserite 1. Unlike those, the fine, flaky birnessite with the turbostratic structure (as shown by the electron microdiffraction) was initially buserite 1 and was artificially transformed into birnessite in a vacuum during the electron microscope processing. It is interesting to note that flaky aggregates of the nonferrous vernadite were found in suspension specimens (Figures 4a and 4b), often in a fine intergrowth with birnessite (buserite) flakes.

Along with the minerals listed above, the dark brown laminae contain minor amounts of characteristic hydrogenetic minerals: Fe vernadite (Figures 4c and 4d) and Mn ferroxhyte (Figures 5a and 5b), both as fine, flaky aggregates. Rare finely dispersed goethite aggregates were also found.

The yellow laminae are composed of bacterial-like iron oxide particles (Figures 5c and 5d) morphologically similar to those found in the low-temperature hydrothermal deposits of the northern Lau Basin [Gorshkov *et al.*, 1992b] and of Franklin seamount [Gorshkov *et al.*, 1992a]. The microbiological investigation of the hydrothermal deposits by the optical phase-contrast microscopy showed that such particles represent relics of bacteria of genus *Gallionella*, replaced by metal oxides. It was also shown that those bacteria can adsorb silica, along with manganese. The opaline silica content in the bacterial-like particles can be high (up to 55%). Iron is represented in such particles by the extremely poor crystalline protoferrihydrite. This phase is called silica-bearing protoferrihydrite. Phosphorus (about 5%) was also detected in the bacterial particles from some low-temperature hydrothermal deposits, besides iron and silica.

The optical microscopy of the nodule specimens, after a partial removal of iron and manganese oxides by 1% oxalic acid, displayed distinct morphologic features of the microcolonies of unicellular sticky and coccoid ferrobacteria genus *Siderocapsa*. These bacterial structures highly predominate among the iron oxide phases within the ferruginous laminae. However, the same bacterial structures are also common in the predominantly manganiferous dark brown laminae. Rare intermittent spiral structures characteristic of the ferrobacteria genus *Gallionella* were found in the thin ochreous surface layer of the ferromanganese nodules.

Chemical Composition of the Ferromanganese Nodules

After drying in a ventilated desiccator at a temperature of 105°C , the chemical composition of the ferromanganese nodules was analyzed using different methods. Concentrations of Fe, Mn, Ti, Ni, Co, Cr, V, Zn,

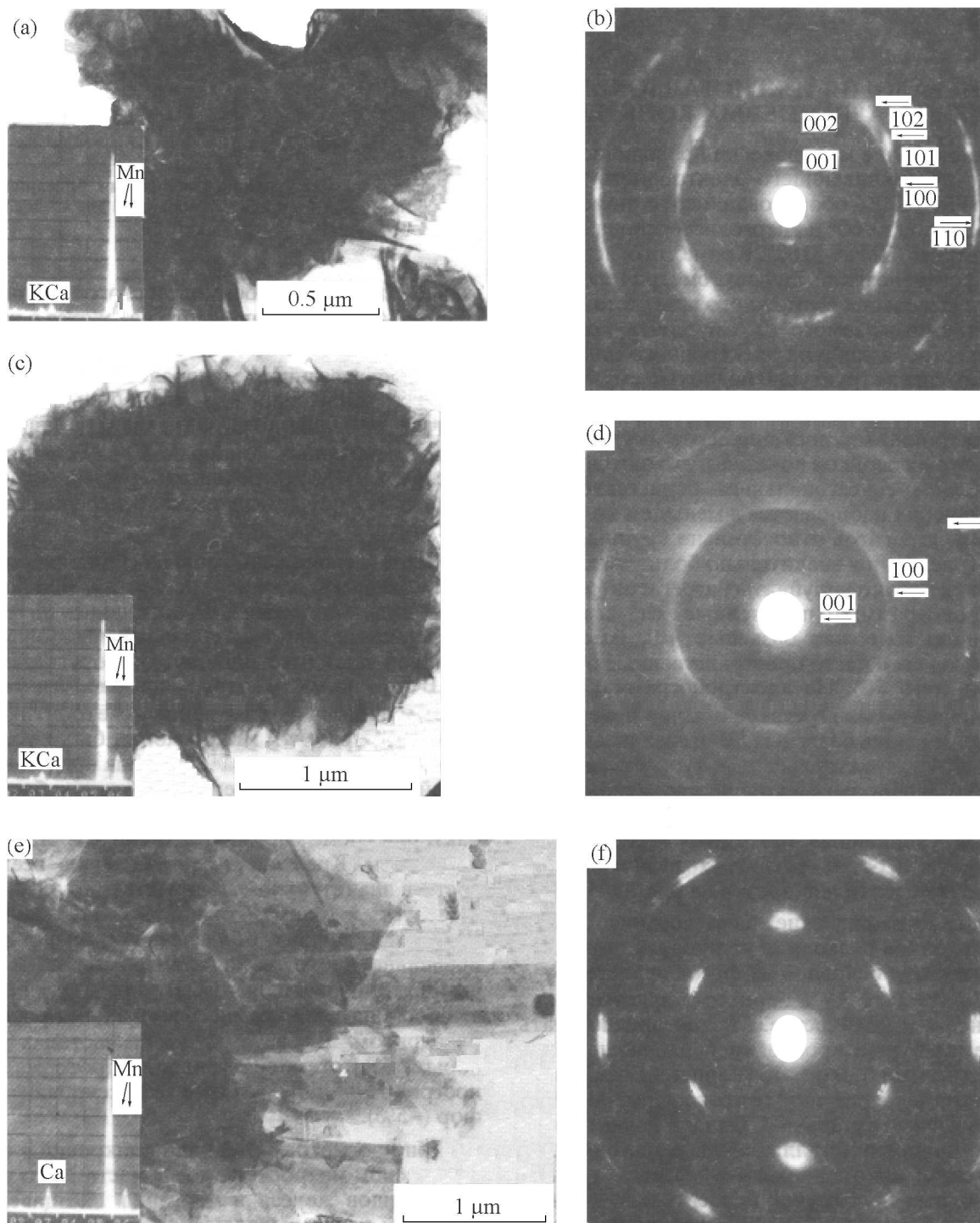


Figure 3. Electron microscope images, electron diffraction patterns, and energy dispersion spectra of manganese minerals: (a, b) platy aggregates of hexagonal birnessite with ordered structure; (c, d) fine, flaky aggregates of birnessite with turbostatic structure; and (e, f) plates of monoclinic birnessite.

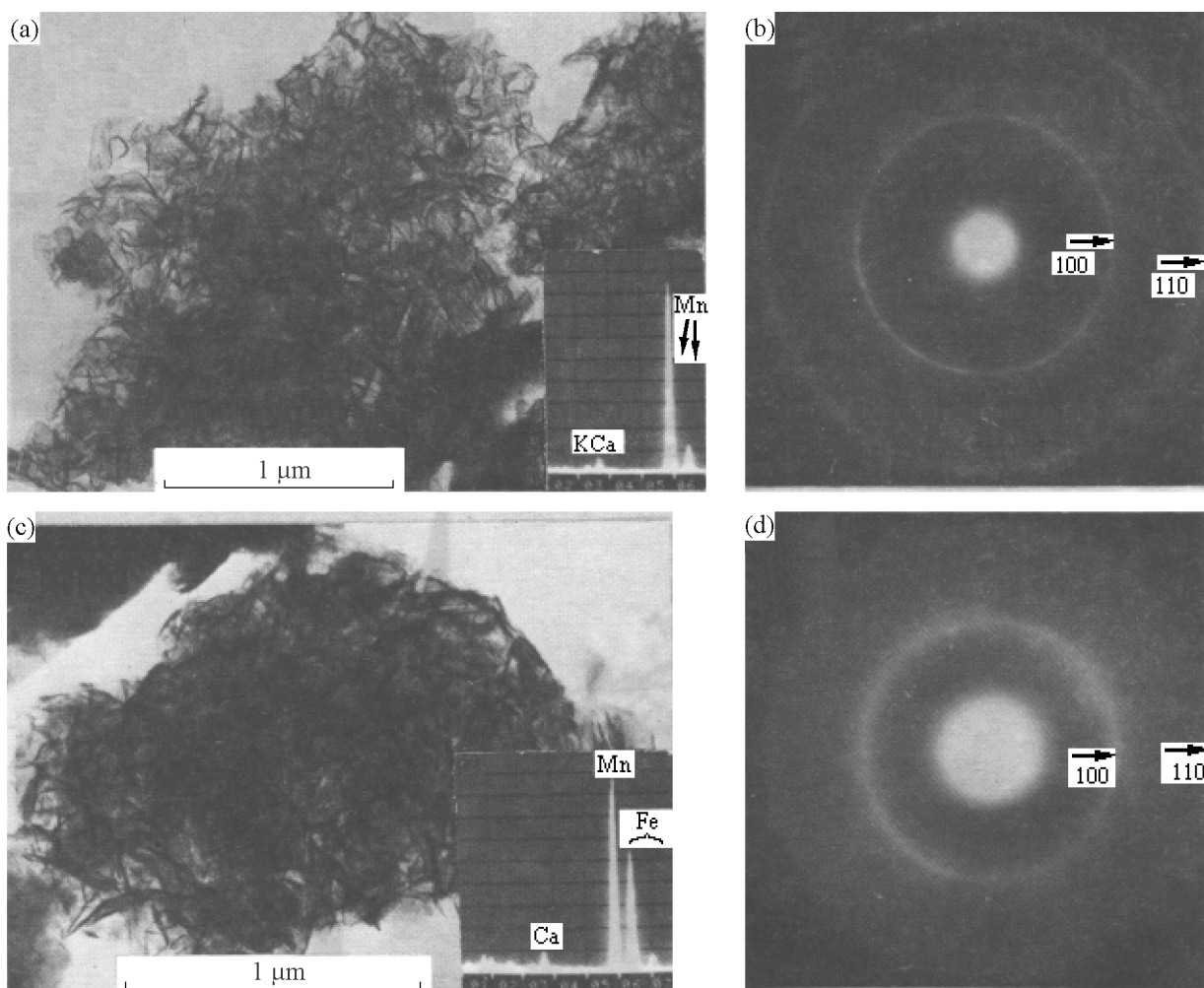


Figure 4. Electron microscope images, electron diffraction patterns, and energy dispersion spectra of manganese minerals: (a, b) fine, flaky aggregates of nonferruginous vernadite and of (c, d) ferruginous vernadite.

Ba, and Sr were determined by the automatic X ray fluorescence spectrometer SPARK 1, run by a DZ 28 computer. Wet chemical analyses with the ending on KFK 3 photocolimeter were used for the determination of Si, Al, and P. Organic carbon (C_{org}) was determined by the gas method with automatic titration on the AN 7529 carbon express analyzer.

The Kara Sea ferromanganese nodules are composed of two major components: a metal phase represented by iron and manganese oxyhydroxides and a nonmetallic phase that is indicated by silica and aluminum contents (Table 1). The sum of two major metals (Fe and Mn) ranges from 24.7 to 35%, with an averaging of 30.9%. The silicon content in the nodules is 9.8–19.3% (average 13.3%), and the aluminum content is 2.1–3.2% (average 2.5%). Therefore the ferromanganese nodules studied are just as high in their metal content as the “richest” nodules from the inner seas, or from the open ocean (Table 2). The Kara Sea nodules are close to the sedi-

mentogenetic (hydrogenetic) oceanic nodules and crusts in their manganese content and Mn/Fe ratio, i.e., manganese module (0.8–1.9), but are lower in these parameters as compared with the typical oceanic diagenetic nodules. However, as was mentioned above, there are alternating laminae within the nodules, composed mainly either of manganese oxide minerals or of iron oxyhydroxides. Hence the manganese module cannot characterize the genetic nature of the nodules.

The minor elements are captured by iron and manganese oxide minerals and do not form individual mineral phases. The nickel content in the nodules studied is close to that in the shallow-water marine nodules, and is much lower than that in the deep-sea pelagic nodules and in the seamounts ferromanganese crusts (Table 2, Figure 6). The concentrations of Co, Zn, Cu, and V in the Kara Sea nodules are intermediate between those in the shallow-water marine nodules and those in the deep-sea pelagic nodules. However, interrelations be-

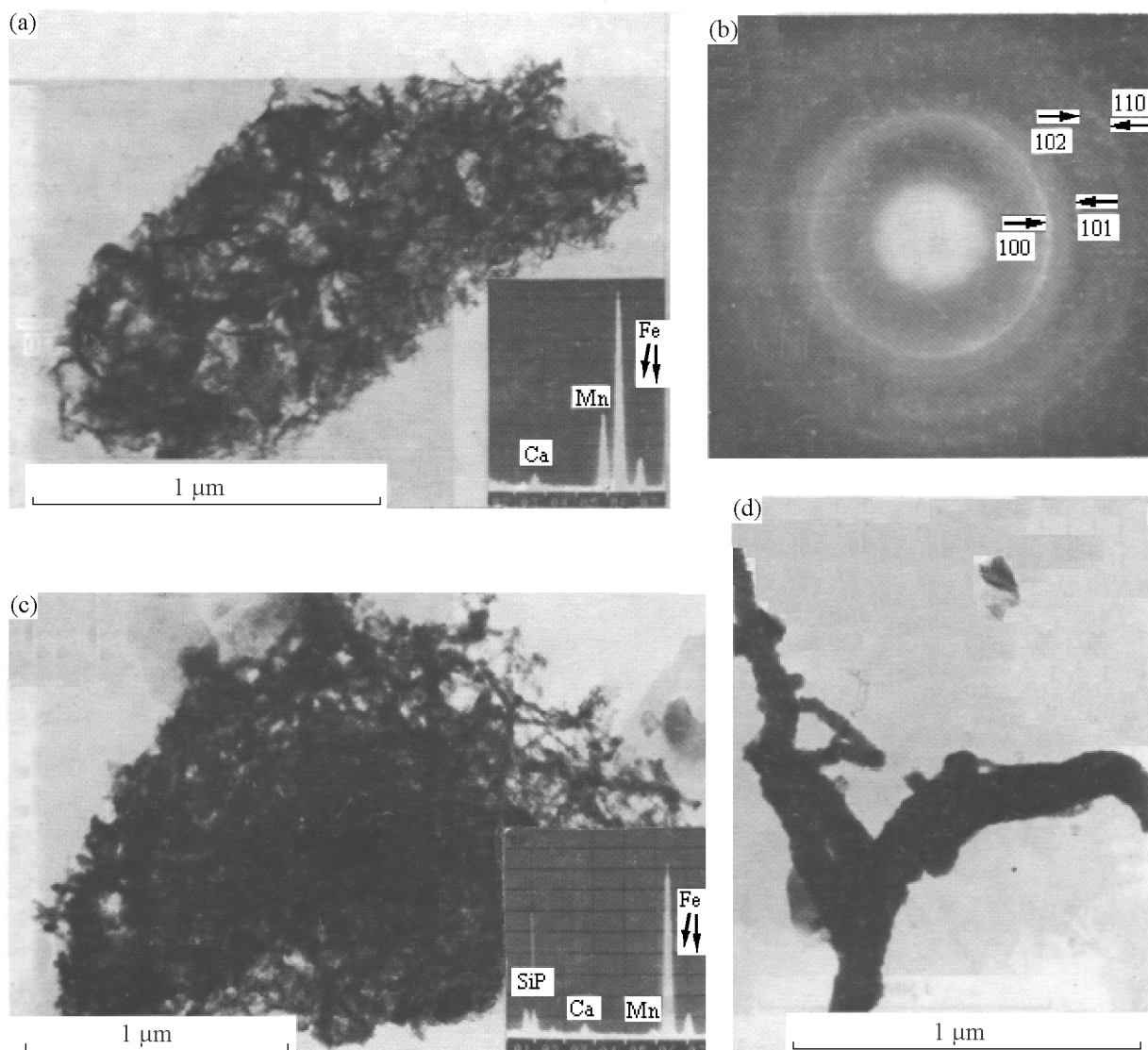


Figure 5. Electron microscope images, electron diffraction patterns, and energy dispersive spectra of iron minerals: (a, b) fine, flaky aggregate of Mn ferroxigite and (c, d) bacteriallike forms of extremely disordered iron hydroxide: protoferrihydrite.

tween the minor elements in the Kara Sea nodules are more similar to those in the shallow-water marine nodules than to those in the deep-sea pelagic nodules, as shown by the elements distribution diagrams (Figure 6). Undoubtedly, attempting to explain the latter, we have to consider not so much the differences in composition and in properties of the iron and manganese minerals serving as sorbents, as the environmental conditions of transferring of the dissolved minor elements into a solid state.

The ratio of indicator elements of the nonmetallic (aluminosilicate) phase of the ferromanganese nodules, Si/Al averages at 5.3. The ratio value in the most nodules of the World Ocean is close to that in bottom sediments, thus reflecting a capture of lithic components

of the sediments by growing nodules. The average Si/Al value in the surface layer of the pelagic sediments is 3.67 and that in the whole sediment cover of the ocean is 3.61, according to data by *Lisitsyn* [1978]. Similar values were obtained in the nodule-bearing Kara Sea sediments: the average for oxidized sediments is 3.4 and that for reduced sediments is 3.6. The lithic component of the Kara Sea nodules is likely enriched in quartz, widespread in the Kara Sea sediments. The quartz content in the ferromanganese nodules estimated by the module method using equation $Q = \text{SiO}_2 - 2.55 \cdot \text{Al}_2\text{O}_3$ by *Gurvich et al.* [1994], ranges within 9.3–20.2% (average 16.3%).

Titanium content in the Kara Sea nodules is close to that in other shallow-water marine nodules where tita-

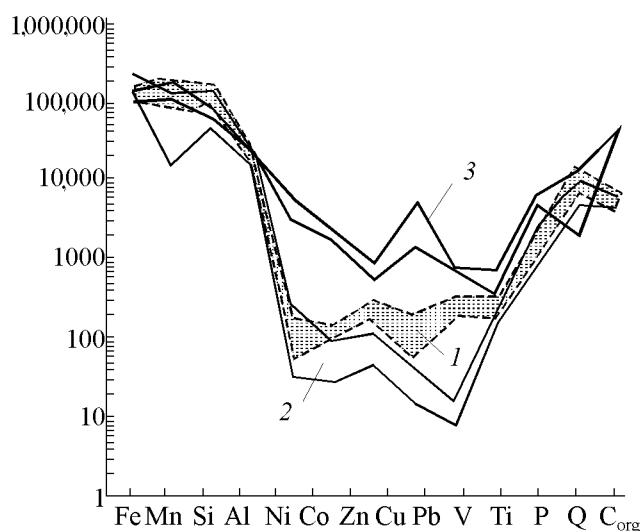


Figure 6. Comparison diagram of chemical element concentrations in ferromanganese nodules from different environments ($10^{-4}\%$): 1, Kara Sea; 2, shallow-water marine (Table 2) and deep-sea pelagic (Table 2).

niium is commonly associated with lithic components, with an average of 0.16%. The value is low as compared with the deep-sea pelagic nodules where titanium is precipitated together with iron (Table 2).

The oceanic ferromanganese oxide deposits occurring within the oxygen minimum zone of the water column are in many cases enriched in phosphorus because of the formation of almost insoluble phosphates [Bogdanov *et*

al., 1990]. The Kara Sea ferromanganese nodules are strongly enriched in phosphorus, as are most shallow-water marine nodules: the phosphorus content is much higher as compared with that in deep-sea pelagic ferromanganese nodules. The organic carbon content in the shallow-water nodules is much higher than that in pelagic nodules.

As we already mentioned above, describing the nodule morphology, most of them are discoidal in shape and display morphological features of growth in a horizontal direction from center to periphery. To study the age related changes in the nodule composition and properties, we sampled the nodules by the scheme shown on Figure 2. The chemical analyses of samples taken by the scheme showed an absence of any direction changing trends in the element concentrations within individual nodules. Only in rare cases did we observe some decrease in lithic constituents (silicon, aluminum, and titanium) and in iron, and an increase in phosphorus from the central parts to the nodule margins. However, the manganese concentration does not show distinct changing trends in these cases. It is important to note that a distinct correlation between the variations in minor elements and in the indicator elements of their “host” components (iron and manganese) is absent.

The correlation analysis subdivided all chemical elements studied into several groups (Table 3). Manganese, the main nodule-forming component that “dilutes” the lithic components (Si, Al, quartz) and iron, displays significant positive correlation coefficients with nickel and cobalt. Note that in the deep-sea pelagic nodules nickel also correlates with manganese, whereas cobalt belongs to the iron group. However, in the typi-

Table 1. Chemical composition of Kara Sea nodules

Studied nodule and sample No	%				$10^{-4}\%$							%			
	Fe	Mn	Si	Al	Ni	Co	Zn	Cu	Pb	V	Ti	P	C _{org}	Quartz	
1	1-1	12.0	18.6	12.8	2.51	180	150	210	160	280	310	0.19	0.76	0.48	15.3
	1-2	12.5	17.1	13.7	2.45	150	120	240	190	270	340	0.16	0.79	2.44	17.5
	1-3	12.3	19.3	12.4	2.45	160	110	260	150	270	280	0.18	0.92	0.64	14.7
	1-4	13.7	18.0	11.5	2.32	90	110	210	<110	250	260	0.13	1.19	0.66	13.4
2	2-1	11.6	15.5	13.3	2.34	130	120	210	<110	200	280	0.21	0.85	0.42	17.2
	2-2	11.7	17.7	14.2	2.59	130	130	190	<110	220	280	0.16	0.91	0.51	17.9
	2-3	13.4	18.9	12.4	2.42	110	120	320	160	240	280	0.13	1.13	0.52	14.9
	2-4	15.0	18.1	10.3	2.12	110	110	230	150	320	250	0.14	1.24	0.65	11.8
3	3-1	14.1	18.9	11.3	2.29	110	140	250	<110	360	290	0.14	1.08	0.77	13.2
	3-2	13.9	10.8	19.3	3.22	80	90	230	<110	360	330	0.12	1.01	0.57	25.2
	3-3	15.0	15.0	14.9	2.72	140	130	220	<110	290	270	0.18	1.14	0.59	18.8
	3-4	12.2	22.8	9.8	2.42	130	110	230	<110	310	280	0.16	1.09	0.60	9.3
4	4-1	11.9	18.2	14.7	2.86	110	130	290	230	290	310	0.19	1.85	0.48	17.7
	4-2	11.9	18.8	13.4	2.59	110	120	190	150	270	330	0.17	1.01	0.53	16.2
	4-3	17.5	14.5	15.5	2.70	60	100	220	160	350	240	0.15	1.49	0.76	20.2
	4-4	15.8	17.0	14.0	2.70	110	140	260	150	300	210	0.14	1.39	0.77	17.0

cal hydrogenetic ferromanganese crusts and nodules from seamounts cobalt is genetically associated with manganese oxyhydroxides. Iron, the other nodule-forming metal, correlates positively with lead and organic carbon. Among other elements studied, zinc shows a positive correlation coefficient with phosphorus and copper; vanadium shows a weak positive correlation with nickel, and negative correlations with iron, phosphorus, and organic carbon; titanium correlates positively with nickel and cobalt, and negatively with iron, lead, and organic carbon.

The factor analysis with varimax matrix rotation was carried out on the chemical results obtained to reveal causes controlling the composition of the ferromanganese nodules (Figure 7).

Four factors were identified as responsible for a major proportion of the variations in nodule composition as follows.

Factor 1 involves 37.6% of the total dispersion. It bears significant positive factor loads (above 0.25) for Al and quartz and negative loads for Mn and Ni. The factor can be interpreted as dilution by manganese of all major constituents of ferromanganese nodules, and especially of lithic components. The presence of nickel in the same group with manganese reflects the genetic relations between these elements: capture of nickel by manganese oxyhydroxides.

Factor 2 involves 24.7% of the total dispersion. It controls the distribution of Ni, Co, and Ti (significant positive loads), and of Fe, Pb, P, and C_{org} (negative loads). The first group of elements, except for titanium, is captured by their host, i.e., by manganese oxyhydroxides. An absence of titanium in the group is likely evidence for a control over the intensity of elements transition from liquid to solid phase by variations in capture conditions, rather than by the sorbent concentration in nodules. A second group of elements likely characterizes the intensity of the diagenetic transformations of sediments. This factor reflects the authigenic mineral formation intensity, depending on transformations of the unstable components of the organic matter. It is important to note that the processes of enrichment of the ferromanganese nodules in the major nodule forming elements, iron and manganese, are separated from each other.

Factor 3 involves 15.3% of the total dispersion. It bears positive factor loads for Fe, P, and C_{org} and negative loads for Al, V, and Ti. The first group coincides with the factor 2 group with negative loads (except for Pb), and likely indicates the intensity of diagenetic transformations of sediments. Thus we see that iron, one of the major metals of the ferromanganese nodules, falls into the same group with P and C_{org} .

Factor 4 is responsible for 8.55% of the total dispersion and influences the geochemical behavior of Zn, Cu, and P. It is difficult to interpret this factor because of its small contribution into the dispersion. Possibly, it represents a residual dispersion.

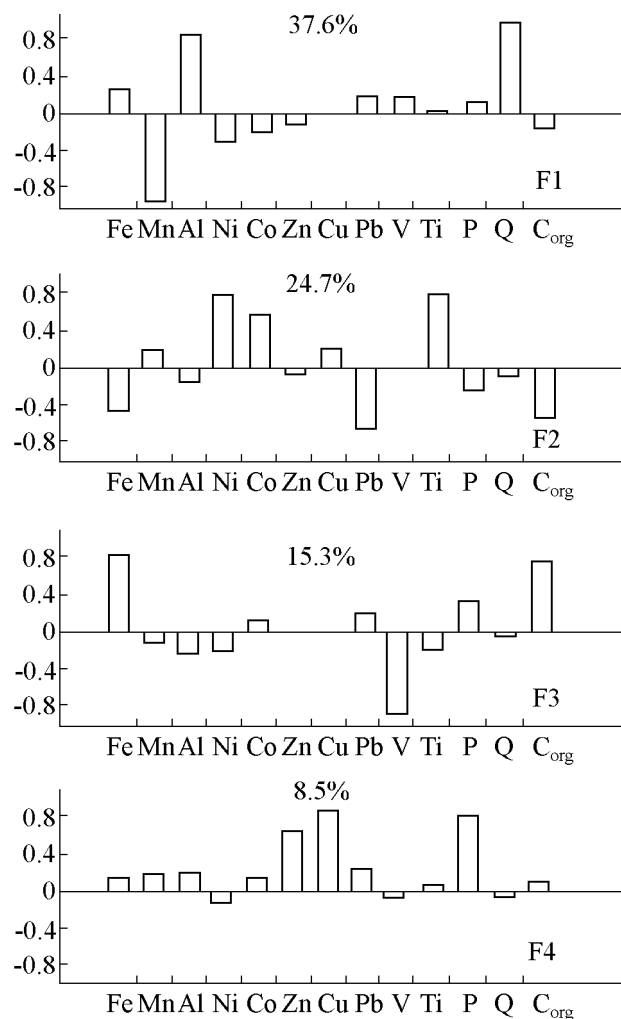


Figure 7. Results of factor analysis of the Kara Sea ferromanganese nodules chemistry.

Discussion

The formation of ferromanganese nodules is the result of redistribution of chemical elements delivered to the sea bottom with sedimentary matter. Since the nodules studied lie directly on the reduced sediments, the main diagenetic transformations take place only at the water-sediment geochemical barrier. The primary sedimentary matter participating in these transformations is represented either by suspended matter, or by a thin surface layer of semiliquid mud, lost during sampling. One can assume that the composition of this mud should be intermediate between the suspended matter composition and the composition of oxidized sediments.

Following are the concentration coefficients of chemical elements obtained from dividing their concentrati-

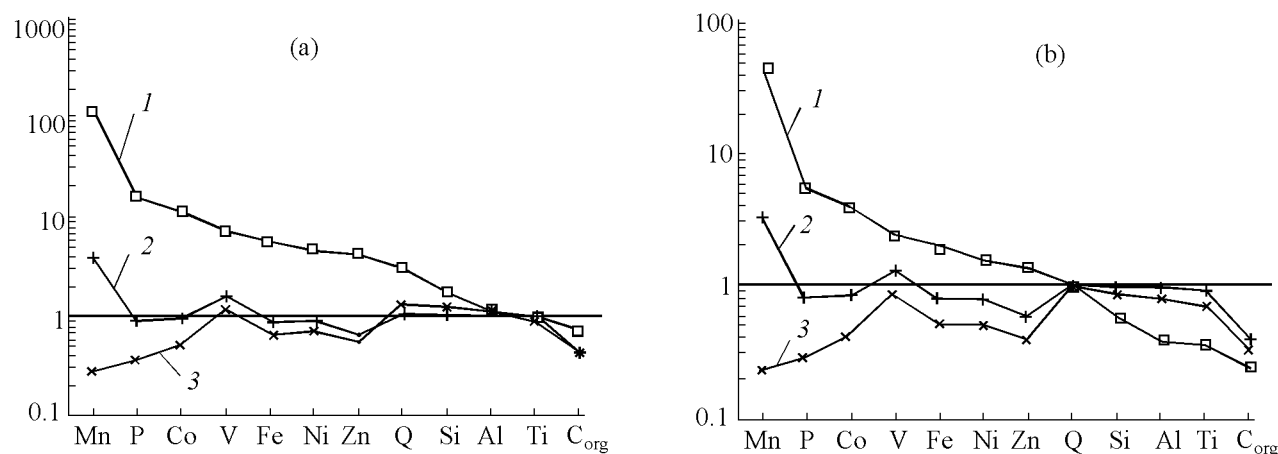


Figure 8. Concentration successions of chemical elements in ferromanganese nodules (1) in suboxidized (2) and in reduced (3) sediments of the Kara Sea, relative to the "lithogenic matrix." The points plotted on the diagrams were obtained as follows: (a) $(El/Al)/(El_{sus}/Al_{sus})$

ons in the ferromanganese nodules by the concentrations in suspended matter:

$Mn > P > Co > V > Fe > Ni > Zn > Q > Si > Al > Ti > C_{org}$
44.7 5.6 4.0 2.5 1.9 1.5 1.4 1.0 0.6 0.4 0.3 0.2

and in the oxidized surface layer of sediments:

$Mn > P > Co > Fe > Zn > Ni > V > Q > C_{org} = Si > Al = Ti$
11.7 6.2 4.2 2.2 2.2 1.7 1.6 0.9 0.5 0.5 0.3 0.3

The data on concentrations of chemical elements in the suspended matter and in the sediments are from the work by *Gurvich et al.* [1994].

The figures indicate a distinct differentiation of the chemical composition of sedimentary matter during nodule formation in good agreement with the geochemical mobility of elements. The nodules are lower in lithic elements (Si, Al, and Ti) as compared with both the suspended matter and the surface layer of sediments, and are almost equal in quartz content. Possibly, this indicates a partial destruction of the aluminosilicate minerals, less stable compared to quartz, during the nodule formation. Such partial destruction of aluminosilicates likely explains the high Si/Al ratio values of the nodules as compared with those of underlying sediments.

Among the ore elements, the highest concentration coefficient is that of manganese. The concentration coefficients of minor elements of the manganese group (Cu and Ni) are substantially lower than those of manganese, although the manganese minerals serve as their hosts. The concentration degree of iron is much less than that of manganese. Among other elements, the geochemical behavior of C_{org} and P can be interpreted. Transformations of the unstable compounds of organic carbon are largely responsible for the redistribution of the reactive forms of chemical elements, especially of

metals. The organic carbon content in the nodules is substantially lower as compared with that of sediments, and especially with that of suspended matter. To the contrary, the nodules are strongly enriched with phosphorus as compared with both sediments and suspended matter, which is likely due to the formation of authigenic phosphates in the nodules.

In order to reveal the mechanisms of the chemical element concentration in nodules, let us return to the results of mineralogical and chemical studies. Undoubtedly, two spatially separated mineral associations (predominantly ferruginous and manganiferous), observed in the nodules, are evidence for strong changes in the precipitation conditions of metallic components during the nodule growth. Buserite 1 and birnessite, the main components of the dark brown laminae, are certainly formed as a result of the diagenetic redistribution of manganese, the most geochemically mobile chemical element in the redox processes [*Chukhrov et al.*, 1989]. An extensive redistribution of chemical elements in the Kara Sea sediments is confirmed by differences in concentrations of their reactive forms in reduced sediments and in the oxidized surface layer [*Gurvich et al.*, 1994]. Manganese is highest in its geochemical mobility, while all other metals studied are much lower.

The nonferruginous vernadite found in the nodules in a fine intergrowth with birnessite (buserite) can be interpreted as a product of biogenic replacement of birnessite [*Chukhrov et al.*, 1989].

The substantially ferruginous laminae within the nodules indicate a sharp disturbance of the metal concentration conditions. Such a separation of iron and manganese is possibly related to different redox potentials of the elements. Oxidation and hydration of iron anticipate those of manganese.

We can assume that the manganiferous laminae were formed under calm dynamic conditions in bottom wa-

Table 2. Comparison of chemical compositions of ferromanganese nodules from the Kara Sea and other regions of the World Ocean

Regions, nodule types	%				10 ⁻⁴ , %						%		
	Fe	Mn	Si	Al	Ni	Co	Zn	Cu	Pb	V	Ti	P	C _{org}
Kara Sea (our results)	13.4	17.5	13.3	2.5	119	121	235	< 110–230	286	284	0.16	1.12	0.60*
Seas**													
Baltic Sea													
Main sea area	16.6	10.8	16.5	2.88	71	100	132	42	16	128	0.31	0.91	0.47
Gulf of Finland	19.0	15.8	8.14	1.66	35	96	113	9	9	40	0.29	1.20	0.97
Gulf of Riga	22.8	10.2	11.4	1.84	47	64	135	17	25	98	0.29	0.72	1.06
White Sea	16.9	14.2	–	–	35	30	51	16	8	224	0.19	0.54	–
Black Sea	26.6	6.79	5.56	1.69	283	83	–	37	16	186	0.10	1.10	0.68
Atlantic Ocean***	15.7	12.8	7.06	3.04	3500	2700	560	1500	820	740	0.53	0.30	–
Indian Ocean***	14.2	16.4	8.99	2.63	3900	2000	700	1700	770	370	0.61	1.34	–
Pacific Ocean***	11.0	21.1	7.22	2.72	8000	2700	960	5900	700	450	0.72	0.20	0.15
Pacific Ocean****													
Hydrogenetic nodules	7.1	17.6	–	–	6500	2500	650	4500	–	–	–	–	–
Hydrogenetic-digenetic nodules	6.0	27.4	–	–	14800	–	1200	11200	–	–	–	–	–
Digenetic nodules	5.75	28.4	–	–	11000	1600	1300	10300	–	–	–	–	–
Pacific Ocean*****, Ita Maitai Guyot													
Hydrogenetic nodules of seamounts	13.5	18.9	3.7	0.92	4600	4100	830	1000	–	–	0.83	–	–

* Anomalous high C_{org} concentration in Sample 1–2 is excluded;

** Volkov [1979];

*** Skornyakova [1989];

**** Skornyakova [1984];

***** Bogdanov et al. [1990].

ters when reduced sediments were coated by an ephemeral film of semiliquid mud that acted as an oxidized surface layer. An acceleration of the bottom water dynamics led to washing away of the film, so exposing the reduced sediments at the bottom surface. Only iron was oxidated and precipitated as oxide minerals at the sediment-water geochemical barrier in such a situation. Manganese migrated from bottom sediments back into the water and was removed from the area of nodule formation by bottom currents. A periodic repetition of these two modes of sediment surface conditions in a shallow marine environment can explain the formation of typical digenetic manganiferous and ferruginous laminae within the ferromanganese nodules.

As was shown above, unlike manganese, the iron accumulation in the ferruginous laminae is related to bacterial activity. A sharp acceleration of the latter is further evidence for dramatic changes of the sediment surface conditions. We assume that the water dynamics acceleration periods, with corresponding disturbance of the sediment surface by stirring up the mud, are fixed in the nodules by formation of the ferruginous laminae. The whole water column is extensively mixed during

these periods, and the bottom temperature increases. Today, in relatively calm conditions, the bottom temperature is below zero degrees almost throughout the study region, thus limiting the bacterial activity.

The changing fixation conditions of chemical elements in the ferromanganese nodules result in considerable variations in relations between the major nodule-forming metals and captured minor elements.

Element to aluminum (El/Al) and element to quartz (El/Q) ratios in the ferromanganese nodules, in the reduced sediments, and in the oxidized sediments of the Kara Sea, normalized by the suspended matter composition, are shown on Figure 8. In other words, concentration successions of the chemical elements are shown relative to a "lithogenic matrix." A second diagram is more informative because the quartz content in all objects compared is almost equal. However, the quartz content, determined by the module method, is less reliable. The diagrams allow us to conclude that an element is concentrated in the ferromanganese nodules, relative to the initial sedimentary matter (i.e., suspended matter), the more, the higher the element concentration in the oxidized sediments relative to the re-

Table 3. Correlation matrix of chemical elements in Kara Sea ferromanganese nodules (station DM 4399)

Chemical elements	Fe	Mn	Si	Al	Ni	Co	Zn	Cu	Pb	V	Ti	P	Quartz	C _{org}
Fe	1.00	-.41	.19	.12	-.59	-.21	.09	.01	.60	-.65	-.52	.45	.20	.77
Mn	-.41	1.00	-.86	-.63	.41	.34	.17	.15	-.22	-.05	.16	-.03	-.90	-.01
Si	.19	-.86	1.00	.90	-.32	-.25	-.06	.02	.20	.25	-.06	.11	.98	-.13
Al	.12	-.63	.90	1.00	-.29	-.20	.04	.05	.31	.25	-.07	.27	.83	-.11
Ni	-.59	.41	-.32	-.29	1.00	.55	-.05	.10	-.42	.28	.61	-.58	-.31	-.43
Co	-.21	.34	-.25	-.20	.55	1.00	.06	.15	-.23	-.04	.38	-.06	-.25	-.10
Zn	.09	.17	-.06	.04	-.05	.06	1.00	.47	.10	-.08	-.20	.43	-.09	.09
Cu	.01	.15	.02	.05	.10	.15	.47	1.00	.02	.12	.16	.38	.01	-.05
Pb	.60	-.22	.20	.31	-.42	-.23	-.10	.02	1.00	-.05	-.46	.35	.15	.64
V	-.65	-.05	.25	.25	.28	-.04	-.08	.12	-.05	1.00	.21	-.40	.24	-.62
Ti	-.52	.16	-.06	-.07	.61	.38	-.20	.16	-.46	.21	1.00	-.14	-.05	-.57
P	.45	-.03	.11	.27	-.58	-.06	.43	.38	.35	-.40	-.14	1.00	.05	.31
Quartz	.20	-.90	.98	.83	-.31	-.25	-.09	.01	.15	.24	-.05	.05	1.00	-.13
C _{org}	.77	-.01	-.13	-.11	-.43	-.10	.09	-.05	.64	-.62	-.57	.31	-.13	1.00

duced sediments. Therefore the enrichment of nodules in any element reflects, to a certain extent, the mobility of elements in diagenesis. We have to note also that a part of the chemical elements showing lower concentrations in the sediment surface layer, as compared with the initial sedimentary matter (P, Co, Fe, Ni, and Zn), was included into the ferromanganese nodules during sedimentation of the suspended matter. The substantial decrease of the "lithogenic" element (Al, Ti) content in nodules relative to quartz, as compared with that in bottom sediments, is certainly evidence for a destruction of aluminosilicates within the nodules.

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