

Ion Exchange Properties of Oceanic Ferromanganese Nodules and Enclosing Pelagic Sediments

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Abstract—Results of the experimental study of ion exchange properties of deep-sea pelagic sediments and related ferromanganese nodules (FMN) are considered. The exchange complex of sediments and nodules includes Na^+ , K^+ , Ca^{2+} , and Mg^{2+} cations. The FMNs also include Mn^{2+} cations. Series of reactivity of metal cations during exchange reactions in different types of pelagic clayey sediments and diagenetic–sedimentary FMN are compiled. Series of exchange capacity of the sediments and FMN for alkali and heavy metal cations are also presented. The exchange capacity of FMN is always higher than that of enclosing sediments. Sediments are characterized by reversible equivalent sorption of cations of both alkali and heavy metals. Irrespective of the mineral composition, the FMNs are characterized by the reversible equivalent sorption of alkali metal cations, whereas sorption of heavy metal cations is only partly reversible. Moreover, alkali metal cations do not replace heavy metal cations. The results obtained refine the role of ion exchange processes in the redistribution of heavy metal cations at the water–bottom sediment interface during the diagenetic–sedimentary formation of ferromanganese nodules.

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The water–bottom sediment interface represents a geochemical barrier between zones of sedimentogenesis and diagenesis. In the abyssal pelagic zone (below the carbonate compensation depth, CCD), under conditions of extremely slow sedimentation rate and oxidizing environment, this barrier zone includes both syngenetic and early diagenetic processes: decay of organic matter, dissolution of biogenic carbonates, formation of authigenic minerals, and formation of ferromanganese nodules and micronodules. In contrast to the near-continental zone of reductive diagenesis, the oxidative early diagenesis in pelagic sediments is usually confined to the centimeter-scale surface layer, where the labile portion of the precipitated organic matter is decomposed. This process serves as the driving force for early diagenesis (Strakhov et al., 1968; Volkov, 1980). Here, zones of sedimentation and early diagenesis converge. In eupelagic clays, these zones virtually overlap to make up a single barrier zone at the water–sediment interface (Emel'yanov, 1998; Murdmaa, 1991; Sval'nov, 1991). Nevertheless, we have retained in the present paper the widely used conventional terms “sedimentary” (or “hydrogenetic”) and “diagenetic” for the designation of two major types of ferromanganese nodules that differ in terms of morphology, internal structure, chemical and mineral compositions, and, consequently, genesis of their ore material. The majority of researchers believe that, like the compositionally similar ferromanganese crusts, the sedimentary FMNs grow as the result of extraction of ore components from the bottom water. In the diagenetic scenario, these com-

ponents are extracted from the interstitial water in the surface layer of sediments. Mechanisms of the formation of these two FMN types are scrutinized in numerous publications (*Zhelezomargantsevye...*, 1976, 1986; and others). Therefore, here we shall only emphasize the rigorous confinement of diagenetic nodules to abyssal pelagic facies of the carbonate-free siliceous–clayey (radiolarian and radiolarian–diatomaceous) sediments and miopelagic clays. In contrast, sedimentary FMN can form in diverse pelagic settings, including non-depositional environments.

Mechanisms of the concentration and occurrence mode of elements in pelagic sediments are crucial in the issue of the formation of oceanic authigenic minerals and nodular ores. The formation of the nucleus of mineral aggregate, its subsequent growth, and variations in chemical and mineral compositions depend on the input and concentration rate of reactive forms of elements in the reaction microzone. The chemical composition of newly formed minerals is related to various simultaneous and sequential physicochemical and biochemical processes, which are governed by reaction rates.

Ion exchange reactions have a significant influence on the formation of the chemical and mineral compositions of the solid phase, on the one hand, and the chemical composition of the bottom and interstitial water in the oceanic pelagic zone, on the other hand. The bottom and interstitial water, ferromanganese nodules, and diagenetically active surface layer of sediments make up a complex heterogeneous system, in which the solid

and liquid phases are located in metastable equilibrium. The equilibrium is maintained by the exchange complex of solid phases. The latter, in turn, is governed by the composition of liquid phase and, primarily, major cations of the ocean water (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}).

However, depending on chemical–mineralogical features of bottom sediments, the exchange complex can also include other metal cations.

It is well known that bottom sediments of oceans and seas can absorb many chemical elements. Nevertheless, their ion exchange properties are still insufficiently studied. Previous experimental investigations were carried out in two directions. Some works only concern the composition of exchange complex, the exchange capacity of sediment, and its pelite fraction (Bishoff et al., 1973; Gurskii and Levshenko, 1981; Skornyakova et al., 1975; Sverdrup et al., 1961; Tageva and Tikhomirova, 1962; Vitvitskaya et al., 1977; Zaitseva, 1957, 1959, 1966; *Zhelezomargantsevye...*, 1986; and others). In these works, the exchange capacity of sediment was determined for Ba^{2+} (to a lesser extent, Ca^{2+} and Mg^{2+}) cations or NH_4^+ ion. However, selective affinity of the sediment to a certain metal cation and the chemical nature of the sorbed cation were ignored. The second direction was focused on the study of sorption of heavy and rare metal cations by bottom sediments. Such works were related to the application of radioactive isotopes (tracers) (Gromov, 1975; Gromov and Spitsyn, 1975; Gromov et al., 1972; Shchebetkovskii and Kuznetsov, 1971; Tikhomirov, 1982, 1986; Tikhomirov and Lukashin, 1983; Tikhomirov et al., 1978, 1979). They ascertained that not only terrigenous and carbonate sediments, but also abyssal red clays absorb Mn, Co, Ni, Zn, Ce, Zr, and Nb isotopes. However, experimental settings in these works do not make it possible to determine the major ion exchange characteristics, such as capacity, composition of exchange complex, mechanism of metal cation sorption, and quantitative sorption parameters (coefficients of distribution and selectivity).

Occurrence of microcomponents and mechanisms of their concentration in manganese and ferruginous minerals of oceanic ferromanganese deposits (FMD) have been discussed since the beginning of the study of chemical and mineral compositions of deep-sea nodules. Application of various methods of mathematical statistics—pair correlation and major components of factor analysis—made it possible to recognize the following two groups of elements: Mn–Ni–Cu–Zn–Co–Mo–Ba and Fe–Co–Pb–Ti–V–Sr–Nb (Andreev, 1994; Anikeeva and Kazakova, 2002; Baturin, 1986, 1993; Cronan, 1980; *Zhelezomargantsevye...*, 1976, 1984, 1986; and others). These metals are primarily concentrated in the manganese and ferruginous components of the ore material of ferromanganese deposits. However, the reported data do not elucidate the occurrence mode of microcomponents in ore minerals and the geochemical behavior of metal ions in processes of sedimentary

and diagenetic ferromanganese mineralization. This statement is also valid for processes of the transformation of primary manganese minerals into other minerals during the whole life period of nodules and crusts.

As concerns mechanisms of the concentration of metal ions in the FMD, the majority of researchers believe that sorption is the most probable and achievable mechanism. This theoretical assumption has been formulated in many publications (Bogdanov et al., 1990; Burns, 1975, 1977; Cronan, 1980; Volkov, 1979; Goldberg, 1954; Halbach, 1986; Halbach et al., 1981; Skornyakova and Andrushchenko, 1970; Strakhov, 1976; Strakhov et al., 1968; *Zhelezomargantsevye...*, 1976, 1984, 1986; and others). However, no experimental evidence in favor of this hypothesis is reported in these works. At the same time, experimental data on the sorption of cations of heavy, rare, and other metals in natural ferromanganese nodules have been reported in a few publications (Balistreri and Murray, 1982, 1983; Krauskopf, 1957; Li, 1981; Nishoyame et al., 1984; Pronina and Varentsov, 1973; Pronina et al., 1973; *Zhelezomargantsevye...*, 1986). Investigations carried out in these works can be qualified as qualitative experiments. They have established the fact of sorptional concentration of cations of heavy metals (Cu, Pb, Zn, Co, and Ni) in samples of deep-sea nodules. However, the data obtained cannot be compared because of different experimental settings.

Results of the targeted study of ion exchange properties of the oceanic FMD of different mineral compositions are presented in works by one of the authors of this paper (Novikov, 1985, 1988, 1996; Novikov and Baturin, 1997; Novikov and Cherkashev, 2000; Novikov and Skornyakova, 1998; Novikov and Sval'nov, 1999; Novikov and Yashina, 1993; Novikov et al., 1995, 2006; and others). This aspect is also highlighted in (Chelishchev and Gribanova, 1983; Chelishchev et al., 1985, 1988, 1992). Data on exchange reactions in the FMD of different mineral and chemical compositions (primarily, Mn and Fe contents) and non-metallic components, as well as the chemical transformation of nodules and crusts indicate that the sorption complex of the FMD is mainly governed by manganese minerals (Novikov, 1988; Chelishchev et al., 1992). The authors interpreted the results obtained from the point of view of ion exchange properties of manganese minerals. They established the major ion exchange characteristics—equilibrium static and dynamic capacity, selective affinity to metal cations, kinetic and thermodynamic parameters, dependence of sorption on various physicochemical parameters and material dimension, and others. It is worth mentioning that the major ion exchange characteristics (except for selectivity) can only be determined at high concentrations of components in solutions, which significantly accelerate exchange reactions and decrease the time of equilibrium achievement in a heterogeneous system. At the same time, these experiments were characterized by the following drawback: they were mainly carried out with

bulk samples of nodules and crusts taken from different regions of the World Ocean. Therefore, authors of works cited above could not trace the relation of variations in ion exchange properties of manganese minerals to morphogenetic, chemical–mineralogical, and structural–textural features of nodules, as well as to the lithology of nodule-enclosing sediments.

In works related to the geochemistry of diagenetic ferromanganese nodules and enclosing sediments, special attention was focused on the study of interrelation between their chemical compositions. Based on the Me^{n+}/Mn ratio (Me^{n+} designates the heavy metal cation) in nodules and sediments recalculated to the bulk content and reactive forms, Volkov (1979) concluded that the chemical composition of the ore component in nodules is governed by the reactive forms of enclosing sediments, whereas its variations are primarily related to differences in the reactive forms. In general, one can agree with this conclusion. However, we should probably speak about not only compositional differences in the reactive forms of elements, but also about their quality. For example, based on comparison of original data on the Me^{n+}/Mn ratio in diagenetic (Site 2483) and sedimentary (sites 2474 and 2520) nodules with the data by Volkov (1979) on nodules of the Trans-Pacific profile, Baturin (1986) suggested that different methods of the statistic processing of analytical data yield various conclusions concerning the presence or absence of genetic relation between nodules and enclosing sediments. According to Kretov et al. (1988), the type of nodule-enclosing sediment governs the morphology, structure, and distribution of ore deposits. Mel'nikov (1992) indicated that variations in the mineral composition of nodules depend on the enclosing sediment type. Thus, the chemistry and lithology of sediments control the structure and composition of ferromanganese nodules. However, experimental data on modeling of the concentration of heavy metal cations in nodules from the interstitial waters of sediments are virtually absent.

The aim of the present paper is to compare ion exchange characteristics of ferromanganese nodules and enclosing pelagic sediments from different regions of the Pacific. We analyzed the following parameters: exchange capacity, composition of exchange complex, reactivity of metal cations, selectivity of manganese minerals of nodules for heavy metal cations (based on their sorption from model solutions of ocean water), and nodule capacity versus sediment type relationship. Based on similarities and distinctions during the sorption of metal cations by minerals in nodules and sediments, we discuss the role of ion exchange reactions during the redistribution of heavy metal cations at the ocean water–sediment interface.

EXPERIMENTAL

Characteristics of the initial material. We studied diagenetic and sedimentary (hydrogenetic) ferroman-

ganese nodules and enclosing surface (0–5 cm) sediments from the Pacific abyssal pelagic zone: Clarion–Clipperton ore province (sites 666, 2474, 2483, and 3833), Central Basin (Site 2520), Guatemala Basin (stations 3852, 3854, 3857, 3874, and 3875), and South Basin (Site 6298). Experiments were carried out with FMN and sediment samples sufficiently well described in literature (Andreev, 1994; Anikeeva et al., 2002; Skornyakova and Zaikin, 1988; Skornyakova and Uspenskaya, 1989, 1990; Sval'nov and Novikova, 1995; Uspenskaya et al., 1995; *Zhelezomargantsevye...*, 1976, 1984, 1986). Therefore, we used in this paper only data on the geochemistry and mineralogy of sediments that are essential for the discussion of results obtained.

The *mineral composition* of diagenetic and sedimentary FMN is characterized by the characteristic paragenetic association of manganese minerals for each nodule type. Diagenetic nodules from the Guatemala Basin are mainly composed of buserite I, birnessite (stations 3852/2, 3854, 3857, 3874, and 3875), todorokite, and asbolane-buserite (Site 3852/1). In the Clarion–Clipperton ore province, buserite I and asbolane-buserite are the major minerals (stations of sites 666, 2483, and 3833). Birnessite, buserite II, todorokite, and Fe-free vernadite occur as admixtures. Sedimentary nodules from the Clarion–Clipperton ore province (Site 2474), Central basin (Site 2520), and South Basin (Site 6298) are mainly composed of Fe-vernadite and Mn-feroxyhyte. In nodules from stations 2483-25 and 2520-25/2, the above minerals are supplemented with approximately equal amounts of asbolane-buserite. Nodules from stations 666-5, 2483-19, 2474-20, 2520-8, 2520-24, and 6298-9, 6298-19, and 6298-28 contain a small amount of the X-ray amorphous ferromanganese phase. Mineral composition of the studied nodules is identical to that of FMN previously studied in the Pacific (Andrushchenko, 1976; Chudaev, 1986; Uspenskaya and Skornyakova, 1991; Uspenskaya et al., 1987, 1995).

The surface layer of nodule-hosting sediments is composed of Pleistocene carbonate-free siliceous–clayey sediments (clayey radiolarian ooze and radiolarian clay with diatoms at some stations), Pliocene–Pleistocene miopelagic clay (with radiolarians at some stations), and eupelagic clays with phillipsite (Sval'nov and Novikova, 1995; *Zhelezomargantsevye...*, 1976, 1986). The sediments are dominated by pelite and fine silt fractions, which make up >85% of the total material.

Diagenetic nodules of the Clarion–Clipperton ore province (sites 666, 2483, and 3833) and Guatemala Basin (stations 3852, 3854, 3857, 3874, and 3875) occur in the surface layer of the clayey radiolarian ooze and miopelagic radiolarian clay. Sedimentary nodules of the Clarion–Clipperton ore province (Site 2474), Central Basin (Site 2520), and South Basin (Site 6298) occur on the radiolarian clay, clayey radiolarian ooze, and eupelagic clay, respectively.

Radiolarian clays and clayey oozes are mainly composed of clay minerals and the biogenic amorphous silica

(opal-A). Clay minerals consist of smectite and hydromica, subordinate chlorite, and rare kaolinite. Quartz and feldspars occur as admixtures. Eupelagic clay from the South Basin (Site 6298) consists of smectite and mixed-layer illite-smectite with a variable amount of phillipsite. Palagonite, bone debris, and quartz are subordinate components. The quantity of manganese micronodules as admixture shows a wide variation range.

The *chemical composition* of the nodules is presented in Table 1. Diagenetic nodules from the Clarion–Clipperton ore province are characterized by relatively stable contents of elements. As compared to them, nodules from the Guatemala Basin are enriched in Mn and depleted in Fe. Contents of Mg, Na, and Zn are relatively higher, whereas contents of Cu, Ni, Co, Pb, and Cd are lower. In sedimentary nodules, contents of ore and lithogenic elements differ by approximately 1.5 times, while contents of heavy metals differ by 1.65 (Co) to 4.4 (Ni) times. At the same time, the Cu and Ni contents are higher in the FMN from the Clarion–Clipperton ore province, while the Co and Pb contents are higher in nodules from the South Basin. Thus, taking into consideration data on the Guatemala FMN, diagenetic nodules are enriched in Mo, Mn, Ni, and Cu (relative to sedimentary nodules), while sedimentary nodules are enriched in Fe, Pb, and Co (Table 1). In the nodule-enclosing surface sediments, contents of lithogenic elements are naturally appreciably higher, while contents of heavy metals are one to three orders of magnitude lower (Table 2). Among all samples studied, sediments of the Guatemala Basin are marked by high contents of Mn and Ca. Contents of Fe in them are almost three times higher than in nodules from the same basin. In general, we can affirm that the Fe content in sediments is approximately equal or slightly higher than that in diagenetic nodules. The content of organic carbon is low (0.26–0.36%) in the surface layer of sediments.

METHODS

Prior to the determination of chemical compositions and experiments with sorption, the sediments were obligatorily washed in distilled water to remove the marine salt left in the sediments after their drying in air. Otherwise, contents of cations of alkaline and alkaline earth metals, which play the major role in the determination of ion exchange characteristics, will be significantly overestimated, resulting in the incorrect calculation of sorptional parameters. The treatment of sediments with distilled water does not affect the content of heavy metals. This was checked by the analysis of aqueous extract by the atomic sorption method. Ferromanganese nodules were prepared for the analysis in accordance with results reported in (Novikov, 2005). Fraction 0.25–0.10 mm was used in the experiments.

Ion exchange characteristics of the manganese minerals in nodules and clay minerals in surface sediments were determined in aqueous solutions of metal salts (1.0–0.01 g-equiv/l) in the static regime at room tem-

perature. The solution with the liquid (L): solid (S) ratio equal to 100 was intensely stirred. Experiments with the microscopic sorption of heavy metal cations on manganese minerals of the FMN from model solutions of different types of ocean water were also performed in the static regime at room temperature and L : S ratio equal to 1000. Experiments with desorption of the sorbed metal cations from nodules were carried out in both static and dynamic sorption regimes. In order to displace the sorbed metal cations we used distilled water, 0.45 N NaCl, natural ocean water with salinity $S = 35\%$, and model solutions of natural and interstitial waters. Preliminary kinetic experiments showed that ion exchange equilibrium in the sediment–solution system is achieved in 4 days. However, we increased the run duration to 1 week in order to obtain certainly equilibrium phases. Analogous experiments for ferromanganese nodules were conducted based on regularities established in (Novikov, 1998; Chelishchev et al., 1992). The pH value of solutions was measured with an Ionomer EV-74 device before and after runs.

Phases were separated on the “blue band” filter after the runs. The solid phase was washed with distilled water and dried in air at room temperature up to constant weight. Then the sample was decomposed in respective reagents depending on the mineral composition. In equilibrium solutions, we successively determined pH values and concentrations of metal cations transferred from samples.

Acidic decomposition of aluminosilicate sediments was carried out according to the method proposed in (Ponomarev, 1963). The ferromanganese component in nodules was dissolved in the concentrated ($\text{HCl} + \text{H}_2\text{O}_2$) solution in the course of boiling for 3–5 min. Concentrations of metal ions were determined in the respective solutions by the flame atomic sorption method with a Perkin-Elmer 503 device (chemical analyses were carried out by N.N. Zavadskaya, L.A. Fedorova, and N.P. Tolmacheva in the Analytical Laboratory of the Shirshov Institute of Oceanology, Moscow). We used the following standard samples: SDO-1, SDO-2, SDO-8, and SDO-9 for sediments; SDO-4, SDO-5, and SDO-6 for FMN.

Like other metals, the bivalent Mn was determined by the atomic sorption method after its extraction from a separate nodule sample using the 1%- H_2SO_4 solution according to (Bazilevskaya, 1976).

RESULTS AND DISCUSSION

Before the consideration of experimental results, let us define the notions and characteristics discussed in the present paper.

Ion exchange is a property of the solid phase (ionite) to exchange metal ions with liquid electrolytes without its destruction.

Exchange capacity of ionite (in our case, nodules and sediments) is a quantitative measure of its capacity to absorb ions from solutions. The value of this param-

Table 1. Average chemical composition of ferromanganese nodules in the Pacific (wt %)

Site no.	Sam- pling area	Depth, m	Fe	Mn _{tot}	Mn ²⁺	Ni	Co	Cu	Zn	Pb	Mo	Cd	Ca	Mg	Na	K	$\frac{Mn}{Fe}$
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
666-1	Clarion-Clipperton ore province	4105	5.45	26.40	1.73	1.20	0.18	1.06	0.17	0.040	0.060	5.4	1.20	2.02	1.48	0.65	4.85
-3		4125	6.17	25.80	1.41	1.36	0.16	1.10	0.20	0.036	0.062	6.3	1.87	1.97	2.21	0.57	4.18
-5		4083	6.85	28.25	1.56	1.30	0.18	1.10	0.16	0.035	0.066	7.0	1.34	2.06	1.50	0.72	4.12
-8		4133	4.78	29.24	1.80	1.18	0.13	0.92	0.16	0.038	0.057	8.1	1.58	1.98	2.28	0.66	6.12
-11		4086	5.78	25.46	1.43	1.43	0.15	1.13	0.18	0.036	0.060	7.4	2.28	1.80	1.96	0.52	4.40
-14		4075	7.86	23.38	1.17	1.24	0.24	0.96	0.14	0.054	0.052	5.7	2.43	1.72	1.91	0.48	2.97
-17		4114	5.71	26.18	1.65	1.30	0.17	1.05	0.20	0.033	0.066	8.8	2.32	1.70	2.24	0.68	4.58
-21		4105	6.11	24.88	1.24	1.46	0.18	1.12	0.18	0.035	0.042	7.1	2.40	1.67	1.88	0.74	4.07
2483-6		5141	5.30	28.90	1.58	1.38	0.16	1.24	0.18	0.044	0.041	6.0	1.50	1.80	1.78	0.80	5.45
-7		5163	4.86	25.25	1.43	1.37	0.23	1.27	0.24	0.039	0.043	5.6	1.43	1.86	1.22	0.54	5.20
-12	Guatemala Basin	5074	5.52	26.16	1.47	1.24	0.20	1.06	0.12	0.035	0.037	6.8	1.36	1.88	1.47	0.74	4.74
-18		5250	6.39	27.22	1.52	1.28	0.18	0.94	0.13	0.040	0.043	6.6	1.38	1.38	1.51	0.58	4.26
-19		5154	4.46	24.18	1.16	1.10	0.17	1.05	0.14	0.044	0.034	6.4	1.50	1.44	1.55	0.83	5.08
-20		5187	5.60	25.90	1.33	1.30	0.17	1.13	0.13	0.048	0.030	6.3	1.54	1.72	1.33	0.80	4.62
-24		5002	7.15	23.31	1.06	1.08	0.25	0.96	0.10	0.056	0.031	6.8	1.40	1.48	2.25	0.48	3.26
-38		5188	6.33	24.43	1.24	1.05	0.20	1.00	0.12	0.051	0.036	7.4	1.63	1.92	1.94	0.70	3.86
-39		5136	5.36	24.76	1.38	1.07	0.17	0.96	0.11	0.051	0.047	7.5	1.77	1.94	2.06	0.68	4.62
3833-7		4700	5.88	26.32	1.36	1.41	0.26	1.17	0.13	0.033	0.040	4.8	1.92	1.85	1.53	0.50	4.47
-18		4750	4.84	31.67	1.48	1.47	0.28	1.22	0.15	0.052	0.054	5.4	1.88	1.97	1.72	0.55	6.54
-27		4860	5.23	28.90	1.53	1.20	0.24	1.08	0.20	0.043	0.044	6.0	1.65	1.92	1.10	0.063	5.53
3852-1 ¹	Guatemala Basin	3580	4.26	37.60	1.26	0.80	0.024	0.47	0.24	0.0057	0.021	2.4	1.88	2.23	2.38	0.86	8.83
3852-2 ²		"	0.72	41.50	1.78	0.48	0.013	0.20	0.12	0.0042	0.023	2.2	1.46	1.67	2.35	0.57	57.6
3854		3650	2.24	46.45	2.04	0.62	0.012	0.33	0.15	0.023	0.032	2.5	2.13	1.84	1.76	0.68	20.7
3857		3710	1.36	40.86	1.86	0.67	0.16	0.40	0.25	0.013	0.040	2.8	1.06	2.44	2.10	0.55	30.3
3874		3600	2.04	34.90	1.47	0.58	0.09	0.40	0.12	0.0020	0.031	2.6	2.06	1.82	1.58	0.54	17.1
3875-1		3610	1.67	39.40	1.92	0.72	0.016	0.28	0.24	0.047	0.028	2.8	1.57	1.78	1.83	0.73	23.6
3875-2		"	0.78	45.27	1.98	0.16	0.006	0.14	0.08	0.0012	0.022	2.3	1.34	1.64	2.07	0.58	48.7

Table 1. (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
2474-3	Clarion-Clipperton ore province	5266	11.26	18.70	0.38	0.68	0.29	0.55	0.071	0.074	0.030	6.0	1.52	1.36	1.18	0.75	1.66
-20		5016	10.65	20.44	0.45	0.70	0.30	0.54	0.091	0.076	0.034	6.0	1.38	1.58	1.94	0.70	1.92
-25		5322	10.16	19.48	0.42	0.68	0.26	0.52	0.080	0.063	0.038	7.2	1.45	1.36	1.70	0.67	1.91
-39		5317	13.20	21.12	0.57	0.65	0.30	0.42	0.070	0.051	0.030	4.1	1.63	1.41	1.44	0.46	1.60
2483-25		4980	10.62	21.36	0.52	1.24	0.31	1.19	0.20	0.031	0.033	7.0	1.46	1.95	1.05	0.46	2.00
2520-2	Central Basin	5215	9.85	17.66	0.37	0.67	0.24	0.54	0.082	0.053	0.022	8.3	1.55	1.66	1.59	0.66	1.79
-4		5333	12.46	14.15	0.30	0.34	0.32	0.37	0.076	0.072	0.020	8.0	1.48	1.16	1.74	0.78	1.14
-8		5540	11.80	18.54	0.42	0.56	0.30	0.43	0.064	0.068	0.026	7.0	1.60	1.10	1.66	0.52	1.16
-17		5450	9.30	17.96	0.41	0.65	0.28	0.47	0.065	0.057	0.028	4.4	1.32	1.26	1.85	0.71	1.93
-24		5220	11.44	19.78	0.44	0.68	0.30	0.56	0.060	0.064	0.030	4.3	1.48	1.37	1.69	0.64	1.73
-25/2 ³		5415	6.63	21.90	0.87	0.98	0.10	0.66	0.041	0.054	0.042	5.8	0.97	1.50	1.21	0.35	3.30
6298-7	South Basin	4850	10.34	11.96	0.132	0.43	0.29	0.39	0.32	0.072	0.001	3.4	1.08	1.14	1.13	0.30	1.16
-9		3180	18.68	17.57	0.50	0.32	0.48	0.18	0.070	0.21	0.005	4.0	1.77	1.28	1.26	0.32	0.94
-12		3050	18.94	13.26	0.33	0.35	0.40	0.12	0.064	0.17	0.007	3.6	1.92	1.35	1.44	0.36	0.70
-19		4840	20.32	10.56	0.25	0.26	0.37	0.18	0.055	0.24	0.011	4.2	2.06	1.24	1.27	0.52	0.52
-28		3470	18.22	14.77	0.38	0.41	0.35	0.25	0.062	0.18	0.008	4.4	1.87	1.53	1.56	0.58	0.81
-35		4900	14.50	15.26	0.43	0.45	0.38	0.22	0.038	0.12	0.012	3.8	2.04	1.56	1.48	0.35	1.05
-47		4640	17.67	12.90	0.32	0.24	0.43	0.16	0.050	0.14	0.007	3.0	1.80	1.30	1.36	0.62	0.73
-51		4760	16.25	14.12	0.38	0.22	0.37	0.13	0.045	0.16	0.010	3.3	1.95	1.44	1.50	0.84	0.87
-56		4250-4350	15.34	15.61	0.48	0.28	0.48	0.44	0.15	0.078	0.010	5.0	0.94	1.27	1.56	0.33	1.02

Note: The Cd content is given in ppm; indexes "1" and "2" designate middle and lower portions, respectively, of the nodules; index "3", sedimentary-diagenetic nodules from Site 2520-25/2.

Table 2. Chemical composition of different types of surface sediments in the Pacific pelagic zone

Site no.	Sampling area	Depth, m	Sediment type	Horizon, cm	Si	Al	Fe	Mn	Cu	Ni	Zn	Co	Pb	Mo	Cd	Ca	Mg	Na	K	C _{org}
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
666-1	Clarion-Clipper-ton ore province	4105	Clayey radiolarian ooze	0-1	27.8	8.07	9.45	1.32	0.052	0.040	0.018	100	120	7.2	2.0	1.07	2.68	4.08	1.78	0.33
-9		4145		0-1	27.6	7.88	5.05	1.22	0.048	0.034	0.016	52	26	7.4	0.7	1.56	2.46	3.94	2.12	0.35
2483-7		5163		0-1	26.1	6.36	3.92	0.55	0.043	0.020	0.013	52	41	7.0	1.4	1.45	2.33	3.76	1.94	0.34
-20		5187		0-2	26.9	7.16	4.24	0.55	0.044	0.018	0.013	48	14	3.6	1.2	1.80	2.55	4.12	2.48	0.34
3833-6		4880		0-2	26.7	7.60	4.55	0.66	0.033	0.016	0.013	45	18	7.4	2.0	0.92	2.24	3.63	2.60	0.36
2474-3	Radiolarian clay	5266	Radiolarian clay	0-2	25.7	6.68	4.52	0.40	0.035	0.015	0.014	60	16	6.4	1.2	1.52	2.21	3.85	1.90	0.32
-20		5016		0-5	25.6	6.36	4.58	0.56	0.030	0.015	0.012	66	20	4.4	1.0	1.97	2.60	4.06	1.9	0.36
-25		5322		0-2	25.8	7.04	4.58	0.51	0.035	0.016	0.012	68	16	7.4	2.7	1.62	2.38	3.76	2.27	0.26
-39		5317		0-5	26.3	6.26	4.74	0.45	0.034	0.013	0.014	40	20	6.4	1.2	1.08	2.24	3.94	1.94	0.33
2483-39		5136		0-5	26.5	6.63	4.48	0.38	0.041	0.014	0.015	60	15	6.3	2.2	1.16	2.13	3.86	2.04	0.32
2520-2	Central Basin	5215	Clayey radiolarian	0-2	26.4	7.22	4.64	0.50	0.034	0.016	0.013	78	22	4.2	1.3	0.90	2.18	3.75	2.06	0.27
-4		5333		0-2	26.7	7.00	5.04	0.40	0.031	0.014	0.011	76	20	5.2	1.0	0.84	2.50	3.66	2.14	0.35
-8		5540		0-2	27.3	6.87	4.86	0.44	0.037	0.015	0.014	71	18	4.8	1.2	1.06	2.34	3.57	1.94	0.31
-17		5450		0-3	27.1	7.36	4.70	0.42	0.033	0.014	0.012	75	24	4.6	1.3	1.24	2.25	3.61	2.18	0.30
-24		5220		0-2	25.7	6.44	4.50	0.53	0.042	0.015	0.017	66	25	5.0	1.0	1.18	2.14	3.50	2.00	0.31
3855	Guatemala Basin	3740	Miopelagic radiolarian clay	0-2	26.8	5.00	3.86	2.32	0.040	0.046	0.027	41	12	7.2	1.0	7.64	2.64	4.30	1.46	
6298-6	South Basin	4850	Eupelagic clay with phillipsite	0-5	28.6	8.64	8.04	1.80	0.023	0.025	0.015	245	54	3.2	4.1	2.30	1.96	3.17	3.00	
-55		4250		0-5	29.3	8.98	7.71	1.80	0.033	0.037	0.016	220	26	4.4	4.8	2.94	2.30	3.64	2.41	

Note: Contents of Co, Pb, Mo, and Cd are given in ppm; other elements, in wt %.

eter is determined as the quantity of exchange ions per 1 g of the air-dry ion and expressed in mg-equiv/g. Therefore, these measurement units are used for values of the exchange capacity of nodules and sediments for metal cations in the present paper.

Ionite capacity, one of the major characteristics, is a variable value that depends on physicochemical and crystallochemical properties of ionite, as well as conditions of the sorption procedure. In the present paper, we report data on the equilibrium static exchange capacity of nodules and sediments (hereafter, exchange capacity or just capacity).

Reactive forms of elements in nodules and sediments designate such forms that are transferred into the solution as the result of ion exchange reactions. We estimated reactivity of metal cations based on the degree of their extraction into solution using the following formula: $[(c_o - c_k) : c_o] \times 100\%$, where c_o and c_k are contents of a metal cation in the solid phase before and after the sorption.

The ion exchange composition of FMD is governed by the composition of metal cations transferred to the solution, whereas the quantitative extraction (in mg-equiv/g) of each cation corresponds to its share in the total capacity of nodules or sediments.

Selectivity is the property of ionite for the preferential sorption of a certain ion (relative to other ions) from a multicomponent solution.

Experimental conditions of ion exchange reactions were identical for nodules and enclosing sediments. Therefore, the data obtained could be interpreted from a single point of view, although the samples were characterized by different mineral compositions. Interpretation of the results obtained is based on the following assumption: exchange reactions primarily take place in the major minerals of each specific sample, and their ion exchange properties are governed by crystallochemical and physicochemical properties of the solid phase, as well as by chemical properties of the sorbed metal ion.

Ferromanganese Nodules

Exchange reactions with the participation of alkali metal cations are characterized by their virtually complete transfer into the solution (during the interaction of FMN with alkali metal solutions), irrespective of the mineral composition of nodules. The degree (average value) of Na^+ and K^+ extraction accounts for 94.3–96.6 and 83.6–87.8%, respectively, of the bulk content in samples. These values correspond to 0.62–0.88 and 0.12–0.18 mg-equiv/g, respectively (Table 3). The amount of alkali metal cations transferred from nodules into solution is virtually a constant value. As will be shown below, this value is independent of the nature of the sorbed metal cation. At the same time, the wide range of extraction of these cations, particularly Na^+ (in mg-equiv/g), depends on their contents in nodules. Moreover, the content of K^+ cations is always lower

than that of Na^+ cations (Table 1). Cations of alkali metals in solutions partly exchange with Ca^{2+} , Mg^{2+} , and Mn^{2+} cations. Their extraction is as high as 3.43–17.8, 0.77–4.65, and 0.26–10.6%, respectively, i.e., 0.05–0.12, 0.01–0.05, and 0.01–0.02 mg-equiv/g, respectively (Table 3). At the same time, alkali metal cations in solutions virtually do not replace heavy metal cations (Cu, Ni, Co, Pb, and others) from manganese minerals of nodules. The total degree of heavy metal extraction does not exceed 3–4% (0.02 mg-equiv/g). The maximal degree of extraction (4.30% or 0.021 mg-equiv/g) is only recorded for Ni^{2+} cations from the buserite I and asbolane-buserite association from stations 3833-7 and 3833-18. Thus, based on exchange reactions with the participation of alkali metal cations in solutions, we can propose the following sequence (series) of increase in the reactivity of metal cations in manganese minerals of nodules, irrespective of their mineral composition: $(\text{Pb}, \text{Co} < \text{Mo}, \text{Cu}, \text{Zn}, \text{Cd} < \text{Ni}) \ll (\text{Mg} < \text{Mn}^{2+} < \text{Ca}) < (\text{K} < \text{Na})$.

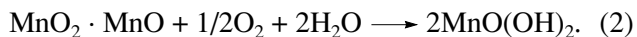
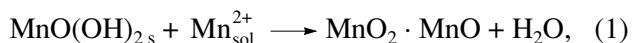
Interaction of solutions of heavy metal salts with manganese minerals of nodules leads to the retention of high reactivity of Na^+ and K^+ cations mentioned above, on the one hand, to the significant increase in the reactivity of Ca^{2+} , Mg^{2+} , and Mn^{2+} cations, on the other hand (Table 3). Extraction of Ca^{2+} cations accounts for 64.7–90.6% (0.36–0.66 mg-equiv/g) of their total content in samples. At the same time, their reactivity expressed in both measurement units not only approaches the reactivity of Na^+ cations, but also surpasses (particularly, in mg-equiv/g) the reactivity of K^+ cations. Moreover, like Na^+ and K^+ cations, Ca^{2+} cations are forced out into the solution, irrespective of the sorbed cation of heavy metal.

Reactivity of Mg^{2+} cations in diagenetic nodules (composed of 10 Å manganese minerals with different structures) and sedimentary nodules (composed of Fe-vernadite and Mn-feroxyhyte) increases 7–8 and 13–14 times, respectively, relative to exchange reactions with alkali metal cations (Table 3). Irrespective of the mineral composition of nodules, the extraction of Mg^{2+} cations is no less than three to four times higher during the sorption of Mn^{2+} , Cu^{2+} , Co^{2+} , and Pb^{2+} cations, relative to Zn^{2+} , Ni^{2+} , and Cd^{2+} cations. Comparison of the two most widespread mineral associations in nodules—(buserite I + asbolane-buserite) and (Fe-vernadite + Mn-feroxyhyte)—shows that the extraction of Mg^{2+} cations from the second association is several times higher than that from the first association. The extraction of Mg^{2+} cations from the nodules is minimal in the sample from Station 3852-1 mainly composed of todorokite (Table 3).

Manganese occupies a special place among all ore metals of nodules. This metal can occur in various degrees of oxidation (IV, II, and probably III). The hydrated manganese dioxide ($\text{MnO}_2 \cdot n\text{H}_2\text{O}$) is characterized by different phase compositions and extremely low solubility in water; i.e., this mineral is a chemically

stable solid phase. This phase can only dissolve (reduction of Mn^{4+} into Mn^{2+}) as the result of the following reductive process: $\text{MnO}_2 \xrightarrow{\text{OM}} \text{Mn(II)}$. Consequently, the hydrated manganese dioxide does not participate in exchange reactions.

The bivalent manganese plays a different geochemical role. Precisely this modification bears two (oxidative and ion exchange) characteristic functions. The oxidative function is responsible for the formation of the hydrated manganese dioxide in two stages:



Reaction (1) is fast, whereas reaction (2) is slow.

The ion exchange function controls the residence of $\text{Mn}_{\text{sorp}}^{2+}$ in the newly formed solid phase. Moreover, the sorbed Mn in the solid phase is more rapidly oxidized than Mn^{2+} in the solution (Morozov, 1995).

Naturally, the study of ion exchange reactions in manganese minerals was primarily focused on the behavior of $\text{Mn}_{\text{sorp}}^{2+}$ cations. Their content in diagenetic and sedimentary nodules was 1.24–1.98 and 0.30–0.52 wt %, respectively (Table 1). The results obtained are consistent with data reported in (Skornyakova et al., 1975). According to these data, the Mn^{2+} content is higher in more crystallized manganese minerals of nodules.

Reactivity of Mn^{2+} cations depends on the mineral composition of nodules. Table 3 shows that the extraction of Mn^{2+} cations is higher during the following evolution of the mineral composition of nodules: todorokite, asbolane-buserite < buserite I, asbolane-buserite < buserite I, birnessite < Fe-vernadite, Mn-feroxyhyte. Comparison of data on the Mn^{2+} extraction expressed in percentages and mg-equiv/g yields at first glance apparently contradictory results. However, the contradiction is related to the following fact: the Mn^{2+} content in sedimentary nodules is always lower than that in diagenetic ones (Table 1). Consequently, the degree of extraction expressed in mg-equiv/g is also lower.

Reactivity of Mn^{2+} also depends on the sorbed heavy metal cations that can be divided into two groups with respect to the degree of Mn^{2+} extraction from nodule samples. Group 1 includes Co^{2+} , Cu^{2+} , and Pb^{2+} cations, while group 2 includes Ni^{2+} , Zn^{2+} , and Cd^{2+} cations. Cations of group 1 can extract one and a half to three times or more Mn^{2+} cations than cations of group 2, irrespective of the mineral composition of nodules. The sorption of Co^{2+} cations promotes the maximal extraction of Mn^{2+} cations (85–100%). In the case of the sorption of Cu^{2+} and Pb^{2+} cations, the extraction of Mn^{2+} cations from manganese minerals of diagenetic nodules varies from ~18.0% (FMN with the prevalence of todorokite) to 85.0% (FMN with the prevalence of buserite I). The extraction of Mn^{2+} cations from sedi-

mentary nodules of the vernadite composition is 85–93%. In the case of the sorption of Ni^{2+} , Zn^{2+} , and Cd^{2+} cations, the extraction of Mn^{2+} cations from manganese minerals of the diagenetic and sedimentary nodules does not exceed 40 and 65%, respectively. These results testify to a high reactivity of the bivalent Mn in solutions of heavy metal salts. In the case of manganese minerals in diagenetic nodules, the reactivity turns out to be similar to that of Mg^{2+} cations.

Reactivity of heavy metal cations of various manganese minerals in nodules is higher than the intensity of exchange reactions of alkali metal cations, but remains sufficiently low. The total extraction of manganese minerals does not account for more than 8–10% (0.03–0.04 mg-equiv/g) of their content in samples. Among the heavy metal cations, Ni^{2+} shows the maximum reactivity. During the sorption of Cu^{2+} , Pb^{2+} , and Co^{2+} cations, the extraction of Ni^{2+} cations is as much as 17–20% (0.03–0.05 mg-equiv/g). Moreover, their extraction from layered minerals (buserite I, asbolane-buserite, Fe-free vernadite, and Fe-vernadite) is higher than from tunnel (todorokite) minerals. This trend is also typical of other cations of heavy metals. In some samples (stations 2483-7, 2483-25, 3833-27, 3857), reactivity of Cu^{2+} and Ni^{2+} cations is slightly higher (0.13–0.18 mg-equiv/g) during the interaction of nodules with solutions of cobalt and lead salts. The minimal reactivity is recorded for Pb^{2+} . The degree of its extraction from any mineral type of nodules is independent of the sorbed heavy metal cations and does not exceed 1% (<0.01 mg-equiv/g).

Thus, results of the interaction of nodules with solutions of heavy metal salts make it possible to draw the following series of increase in reactivity (in %) of metal cations in manganese minerals: (Pb , Co < Mo , Cu , Zn < Cd < Ni) << (Mg < Mn^{2+}) < (K < Ca < Na).

Like in the case of exchange reactions with the participation of alkali metal cations, one can divide the above metals into three groups in terms of their degree of extraction from the manganese minerals of nodules. However, we should mention the following exception: Mn^{2+} is located in the group of K^+ , Ca^{2+} , and Na^+ cations in sedimentary nodules, because the degree of Mn^{2+} extraction from such nodules is higher than that from diagenetic nodules.

Thus, the exchange complex of manganese minerals in diagenetic and sedimentary nodules comprises cations of alkali, alkali earth, and some heavy metals. However, the number of metal cations located in the ion exchange state is variable. The content of sorbed forms of Na^+ , K^+ , Ca^{2+} , and Mn^{2+} cations in the manganese minerals listed above accounts for 83.6–100% of their total content in the samples. The content of Mg^{2+} and Ni^{2+} cations accounts for 50 and 20%, respectively. The share of sorbed forms of bivalent Cu , Zn , Co , and Pb varies from <1 to 10%. The remaining part of these cations (including Ni and Mg) is located in other crystal-

Table 3. Sorption–desorption characteristics of bottom sediments in the Pacific pelagic zone

Predominant minerals in nodules	Number of samples	Solution concentration, N	Exchange capacity ¹ , mg-equiv/g						
			Mn ²⁺	Ni	Co	Cu	Zn	Cd	Pb
1	2	3	4	5	6	7	8	9	10
Ferromanganese nodules									
Bs I, B	10	1.0	$\frac{2.48-2.78}{2.67}$	$\frac{1.91-2.15}{2.02}$	$\frac{3.08-3.43}{3.25}$	$\frac{2.90-3.41}{3.17}$	$\frac{2.03-2.28}{2.13}$	$\frac{1.95-2.20}{2.11}$	$\frac{2.67-3.20}{3.01}$
	10	0.1	2.50	1.81	3.14	3.08	2.00	2.05	2.93
	10	0.01	$\frac{2.18-2.38}{2.26}$	$\frac{1.46-1.76}{1.57}$	$\frac{2.62-2.85}{2.77}$	$\frac{2.68-2.85}{2.81}$	$\frac{1.52-1.64}{1.61}$	$\frac{1.48-1.63}{1.55}$	$\frac{2.52-2.66}{2.60}$
Bs I, A-bs	50	1.0	$\frac{1.73-1.95}{1.84}$	$\frac{1.40-1.63}{1.50}$	$\frac{1.96-2.42}{2.13}$	$\frac{2.01-2.30}{2.15}$	$\frac{1.65-1.90}{1.80}$	$\frac{1.66-1.88}{1.76}$	$\frac{1.98-2.43}{2.22}$
	50	0.1	1.76	1.38	2.02	2.10	1.70	1.70	2.13
	50	0.01	$\frac{1.28-1.56}{1.43}$	$\frac{1.38-1.58}{1.45}$	$\frac{1.78-2.22}{1.90}$	$\frac{1.80-2.18}{2.00}$	$\frac{1.30-1.47}{1.40}$	$\frac{1.20-1.33}{1.30}$	$\frac{1.71-2.18}{1.87}$
T, A-bs	3	1.0	$\frac{1.71-1.84}{1.80}$	$\frac{0.77-0.88}{0.84}$	$\frac{1.20-1.34}{1.30}$	$\frac{1.57-1.68}{1.66}$	$\frac{0.64-0.73}{0.68}$	$\frac{0.61-0.67}{0.63}$	$\frac{1.25-1.38}{1.32}$
Fe-V, Mn-F, A-bs	7	1.0	$\frac{1.33-1.95}{1.92}$	$\frac{1.38-1.50}{1.46}$	$\frac{2.00-2.13}{2.05}$	$\frac{2.12-2.20}{2.16}$	$\frac{1.60-1.76}{1.70}$	$\frac{1.62-1.70}{1.67}$	$\frac{2.00-2.10}{2.07}$
Fe-V, Mn-F	56	1.0	$\frac{1.33-1.95}{1.74}$	$\frac{1.11-1.83}{1.52}$	$\frac{1.71-2.27}{2.03}$	$\frac{1.87-2.33}{2.26}$	$\frac{1.23-1.88}{1.62}$	$\frac{1.17-1.90}{1.61}$	$\frac{1.82-2.41}{2.14}$
	56	0.1	$\frac{1.26-1.92}{1.61}$	$\frac{1.06-1.74}{1.39}$	$\frac{1.55-2.12}{1.87}$	$\frac{1.81-2.32}{2.00}$	$\frac{1.14-1.75}{1.48}$	$\frac{1.07-1.80}{1.44}$	$\frac{1.77-2.30}{1.99}$
	56	0.01	$\frac{1.05-1.77}{1.52}$	$\frac{0.82-1.56}{1.24}$	$\frac{1.34-1.98}{1.71}$	$\frac{1.64-2.08}{1.90}$	$\frac{0.93-1.54}{1.27}$	$\frac{0.88-1.38}{1.29}$	$\frac{1.54-1.93}{1.77}$
Pelagic sediments									
Sediment type									
Clayey radiolarian ooze	1.0		$\frac{0.36-0.48}{0.44}$	$\frac{0.44-0.49}{0.47}$	$\frac{0.39-0.46}{0.42}$	$\frac{0.56-0.74}{0.68}$	$\frac{0.46-0.56}{0.51}$	$\frac{0.40-0.47}{0.44}$	$\frac{0.70-0.82}{0.76}$
	0.01		$\frac{0.19-0.27}{0.22}$	$\frac{0.25-0.32}{0.28}$	$\frac{0.20-0.28}{0.26}$	$\frac{0.39-0.53}{0.46}$	$\frac{0.31-0.36}{0.34}$	$\frac{0.22-0.28}{0.25}$	$\frac{0.48-0.56}{0.51}$
Radiolarian clay	1.0		$\frac{0.40-0.53}{0.46}$	$\frac{0.48-0.56}{0.50}$	$\frac{0.40-0.46}{0.43}$	$\frac{0.58-0.80}{0.71}$	$\frac{0.50-0.61}{0.54}$	$\frac{0.36-0.46}{0.42}$	$\frac{0.75-0.84}{0.79}$
	0.01		$\frac{0.28-0.36}{0.31}$	$\frac{0.31-0.38}{0.33}$	$\frac{0.23-0.31}{0.27}$	$\frac{0.42-0.68}{0.53}$	$\frac{0.33-0.42}{0.37}$	$\frac{0.24-0.28}{0.25}$	$\frac{0.52-0.71}{0.61}$
Miopelagic radiolarian clay	1.0		0.55	0.81	0.68	1.58	0.86	0.52	1.47
	0.1		0.48	0.74	0.56	1.47	0.78	0.44	1.30
	0.01		0.36	0.62	0.47	1.27	0.67	0.33	1.08
Eupelagic clay with phillipsite	1.0		0.76	0.48	0.54	0.90	0.75	1.00	1.40
	0.01		0.58	0.32	0.37	0.66	0.53	0.80	1.06

Note: Abbreviations used in this paper: (A-bs) asbolane-buserite; (B) birnessite; (Bs I) buserite I; (T) todorokite; (Fe-V) Fe-vernadite; (Mn-F) Mn-feroxyhyte. ¹Range of values and average values of capacity are given in the numerator and denominator, respectively; for Bs I and Bs I + A-bs, at 0.1 N concentration of solutions; for miopelagic and eupelagic clays, average values of capacity; degree of metal cation extraction from nodules: numerator shows average values at the sorption of alkali metal cations; denominator shows average values at the sorption of heavy metal cations (average capacity values of alkali and heavy metal cations are the same for sediments).

Exchange capacity ¹ , mg-equiv/g				Average degree of metal cation extraction from initial materials									
				%					mg-equiv/g				
Mo	K ₁	K ₂	Na	Na	K	Ca	Mg	Mn ²⁺	Na	K	Ca	Mg	Mn ²⁺
11	12	13	14	15	16	17	18	19	20	21	22	23	24
Ferromanganese nodules													
<u>3.32–3.53</u>	<u>1.10–1.20</u>	<u>1.12–1.24</u>	<u>1.08–1.22</u>	<u>94.5</u>	<u>83.6</u>	<u>8.48</u>	<u>4.65</u>	<u>3.00</u>	<u>0.84</u>	<u>0.10</u>	<u>0.08</u>	<u>0.03</u>	<u>0.02</u>
3.41	1.14	1.20	1.16	96.6	86.7	89.5	32.4	51.5	0.90	0.12	0.66	0.48	0.38
0.83	1.02	1.02	1.06										
<u>0.42–0.51</u>	<u>0.80–0.88</u>	<u>0.88–0.91</u>	<u>0.89–0.97</u>										
0.45	0.86	0.90	0.94										
<u>2.38–2.73</u>	<u>0.86–1.12</u>	<u>0.83–1.05</u>	<u>0.87–1.10</u>	<u>96.6</u>	<u>85.4</u>	<u>17.8</u>	<u>3.17</u>	<u>4.20</u>	<u>0.65</u>	<u>0.15</u>	<u>0.12</u>	<u>0.05</u>	<u>0.02</u>
2.56	0.96	0.94	0.97	96.8	87.6	90.6	25.1	42.7	0.67	0.16	0.55	0.40	0.25
0.66	0.90	0.90	0.92										
<u>0.40–0.64</u>	<u>0.74–0.91</u>	<u>0.73–0.90</u>	<u>0.74–0.94</u>										
0.47	0.81	0.80	0.83										
<u>1.20–1.32</u>	<u>0.81–0.86</u>	<u>0.83–0.90</u>	<u>0.17–0.30</u>	<u>94.3</u>	<u>86.6</u>	<u>3.43</u>	<u>0.77</u>	<u>0.26</u>	<u>0.88</u>	<u>0.18</u>	<u>0.05</u>	<u>0.01</u>	<u>0.01</u>
1.26	0.84	0.87	0.26	97.0	88.7	64.7	5.84	15.5	0.93	0.20	0.36	0.10	0.08
<u>3.18–3.27</u>	<u>0.80–0.90</u>	<u>0.80–0.92</u>	<u>0.80–0.95</u>	<u>95.2</u>	<u>84.8</u>	<u>10.6</u>	<u>2.08</u>	<u>8.75</u>	<u>0.62</u>	<u>0.12</u>	<u>0.09</u>	<u>0.03</u>	<u>0.01</u>
3.23	0.84	0.87	0.86	96.3	85.5	87.8	28.7	76.6	0.64	0.13	0.58	0.32	0.14
<u>2.68–4.26</u>	<u>0.73–0.94</u>	<u>0.73–0.93</u>	<u>0.73–0.95</u>	<u>95.6</u>	<u>87.8</u>	<u>12.0</u>	<u>2.34</u>	<u>10.6</u>	<u>0.63</u>	<u>0.14</u>	<u>0.10</u>	<u>0.03</u>	<u>0.02</u>
3.60	0.86	0.85	0.86	96.6	88.4	90.6	30.7	80.4	0.64	0.14	0.62	0.37	0.15
<u>0.70–1.02</u>	<u>0.70–0.89</u>	<u>0.70–0.90</u>	<u>0.68–0.90</u>										
0.81	0.78	0.78	0.77										
<u>0.37–0.56</u>	<u>0.66–0.87</u>	<u>0.65–0.87</u>	<u>0.65–0.90</u>										
0.53	0.74	0.77	0.78										
Pelagic sediments													
<u>0.03–0.09</u>	<u>0.16–0.36</u>	<u>0.15–0.32</u>	<u>0.19–0.36</u>	<u>34.6</u>	<u>13.5</u>	<u>29.0</u>	<u>3.95</u>	<u>8.00</u>	<u>0.21</u>	<u>0.05</u>	<u>0.15</u>	<u>0.07</u>	<u>0.03</u>
0.06	0.26	0.25	0.28										
<u>0.01–0.04</u>	<u>0.10–0.24</u>	<u>0.11–0.22</u>	<u>0.13–0.24</u>										
0.03	0.19	0.18	0.19										
<u>0.04–0.10</u>	<u>0.23–0.30</u>	<u>0.22–0.30</u>	<u>0.24–0.33</u>	<u>36.8</u>	<u>14.8</u>	<u>26.7</u>	<u>5.14</u>	<u>8.46</u>	<u>0.19</u>	<u>0.06</u>	<u>0.18</u>	<u>0.04</u>	<u>0.04</u>
0.08	0.25	0.25	0.27										
<u>0.02–0.05</u>	<u>0.18–0.22</u>	<u>0.17–0.22</u>	<u>0.17–0.21</u>										
0.03	0.20	0.18	0.18										
0.28	0.34	0.30	0.37	40.5	14.9	37.7	6.23	14.8	0.29	0.08	0.25	0.12	0.11
0.19	0.32	0.27	0.33										
0.10	0.28	0.25	0.27										
0.09	0.64	0.66	0.64	43.4	16.2	21.0	9.18	12.6	0.25	0.16	0.24	0.10	0.08
0.02	0.47	0.48	0.48										

lochemical positions, where the cations are more rigidly bonded with the main elements of the structure of manganese minerals. Therefore, they do not participate in ion exchange reactions under the specified experimental conditions.

Irrespective of the genetic affiliation, exchange capacity of manganese minerals in nodules increases from the alkali to heavy metals (Table 3). The capacity of manganese minerals shows a narrow variation range (0.65–1.18 mg-equiv/g) for alkali metals and a wide variation range (0.62–4.25 mg-equiv/g at solution concentration equal to 1.0–0.1 N) for heavy metals. The capacity of nodules is virtually constant within the concentration range of 1.0–0.1 N and decreases by 0.25–0.45 mg-equiv/g at the concentration of 0.01 N. The rate of decrease depends on the sorbed metal cation and remains sufficiently high for natural ion exchangers. The exception is represented by Mo absorbed from the solution as MoO_4^{2-} anion, which corresponds to its occurrence mode in ocean water (Bruland, 1983). The high exchange capacity of minerals for Mo is recorded only when its concentration in the solution is high. At lower concentrations (0.1–0.01 N), the capacity drastically decreases and becomes even lower than the value for Na^+ and K^+ . At the same time, the manganese minerals absorb simultaneously both molybdate ion and K^+ cation (Table 3). Sorption of metals as both cations and anions by different manganese minerals in nodules indicate that they can be referred to as natural ampholyte. The potassic capacity of manganese minerals during the sorption of this element from KCl and K_2MoO_4 solutions is virtually similar (Table 3, K_1 and K_2).

Exchange capacity of manganese minerals in diagenetic nodules depends on various factors, among which the relationship of manganese minerals in sample, their crystallochemical perfection, and the content of tetravalent Mn are probably the major ones. In general, capacity of manganese minerals for each element within the respective mineral type of nodules and their geographic position in the ocean is sufficiently stable and varies within a narrow interval range. Among nodules of the specified genetic type, nodules mainly composed of buserite I with an insignificant admixture of birnessite (stations 3852-2, 3854, 3857, 3874, 3875) have the maximum exchange capacity (Table 3). For example, the capacity of K and Mo is 1.12 and 3.44 mg-equiv/g, respectively (hereafter, the capacity value is given for nodules after their interaction with 1 N solutions of metal solutions). The nodules contain not only buserite I, but also asbolane-buserite (stations of sites 666, 2483, and 3833). Therefore, they are characterized by lower values of capacity (mg-equiv/g): K 0.86, Mo 2.73. Exchange capacity of these associations of manganese minerals demonstrate a complex relationship with the Mn (IV) content: increase in the MnO_2 content is accompanied by not linear but stepwise increase in the exchange capacity with prominent maximums and minimums at certain points (Figs. 1a, 1b).

Such results were also obtained for other samples of diagenetic nodules of the analogous mineral composition (Novikov and Baturin, 1987; Novikov and Skornyakova, 1988). Relative to two mineral associations of diagenetic nodules considered above, nodules primarily composed of todorokite with an admixture of asbolane-buserite (Station 3852-1) are characterized by an appreciably lesser capacity for all cations of heavy metals, particularly Mo (mg-equiv/g): Cd 0.61, Mn 1.80. At the same time, todorokite (>90% of the sample) from the Charko Redondo (Cuba) has a capacity of 2.25, 1.57, 0.54, and 0.59 mg-equiv/g for Mn^{2+} , Cu^{2+} , Ni^{2+} , and Co^{2+} cations (Novikov et al., 1993b). Hence, we can draw the following conclusions. First, todorokite has a higher affinity to Mn, which is expressed in its maximum capacity relative to other heavy metal cations. Second, the presence of asbolane-buserite in todorokite nodules drastically enhances their sorption capacity relative to Ni and Co cations.

Sedimentary nodules primarily composed of Fe-vernadite and Mn-feroxyhyte also demonstrate the trend typical of diagenetic nodules. Their capacity increases from alkali metals to heavy metals (mg-equiv/g): K and Na 0.65, Mo 4.25 (Table 3). At the same time, one can see a virtually linear correlation between the capacity for heavy metals and the content of tetravalent Mn (MnO_2) in the case history of nodules from the South Basin (Fig. 1b). We also recorded similar relationship in previous works (Novikov, 1996; Novikov and Skornyakova, 1998; Novikov and Yashina, 1993). On the other hand, relative to nodules from the Clarion–Clipperton ore province (Site 2474) and Central Basin (Site 2520), nodules from the South Basin (Site 6298) are marked by the minimum capacity for all metals except Mo. This is explained by the low Mn^{4+} content in the nodules (Table 1). At the same time, the presence of asbolane-buserite, in addition to Fe-vernadite and Mn-feroxyhyte, in sedimentary nodules (stations 2483-25, 2520-25/2) enhances the Mn capacity, on the one hand, and decreases the Mo capacity, relative to other samples of sedimentary nodules, on the other hand. For other metals, the average capacity of nodules remains virtually unaltered (Table 3). In this case, the situation is similar to that in nodules mainly composed of todorokite and asbolane-buserite (Station 3852-1). The manganese phases mentioned above are likely characterized by a higher affinity with Mn and lower affinity with Mo.

Despite compositional differences of nodules in the oceanic pelagic realm with corresponding different values of exchange capacity for the studied spectrum of elements, the capacity growth sequence is generally similar:

$(\text{Na}, \text{K}) < (\text{Ni} < \text{Cd} < \text{Zn} < \text{Mn}) < (\text{Co} < \text{Cu} < \text{Pb} < \text{Mo})$.

Thus, based on values of exchange capacity of manganese minerals, the sorbed metal cations are divided into three groups. In some samples, metal cations of groups 1 and 3 can trade places because of close values of exchange capacity. However, this situation does not influence the mode of exchange reactions.

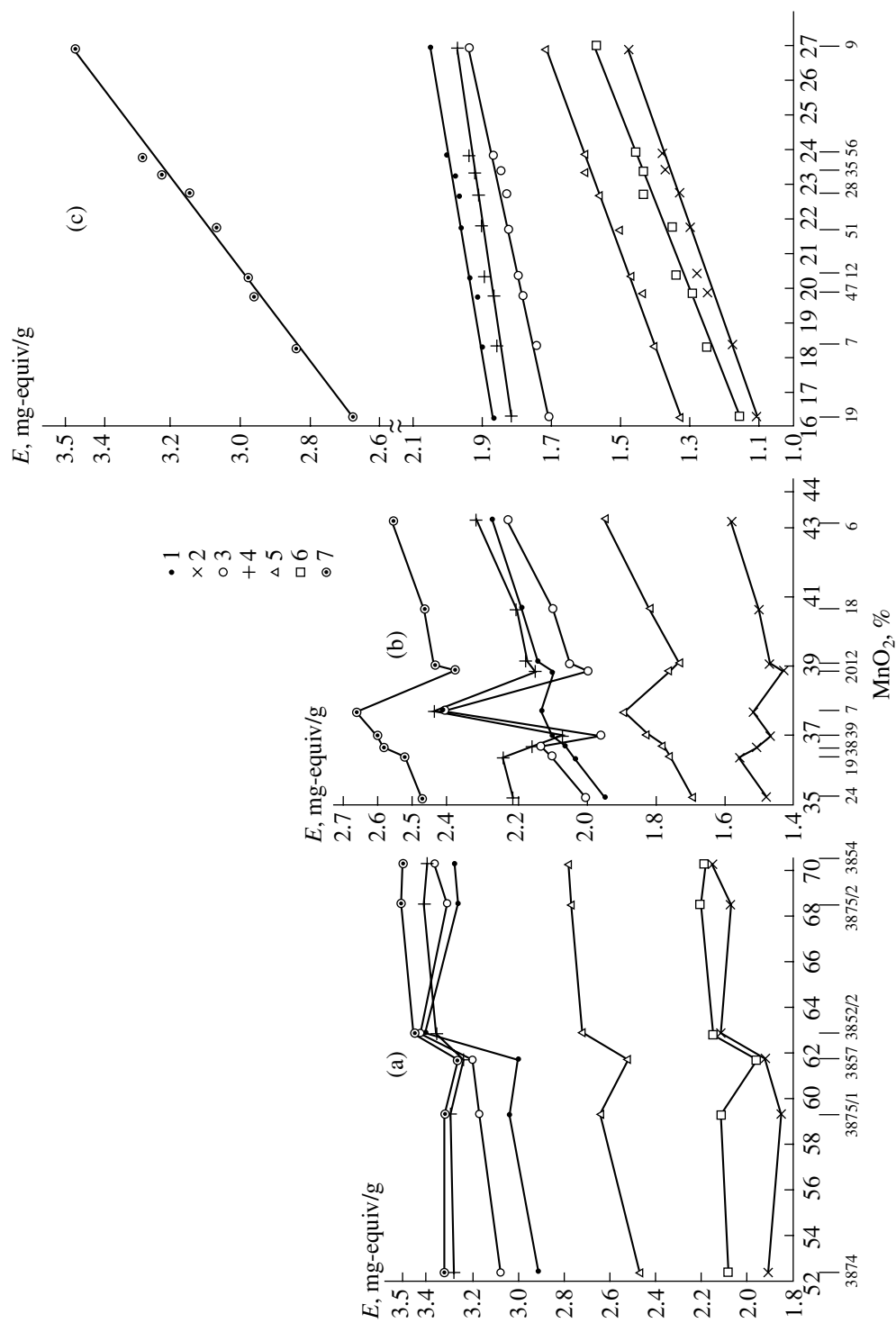


Fig. 1. Exchange capacity of manganese minerals in (a, b) diagenetic and (c) sedimentary nodules for heavy metal cations vs. MnO_2 content in them. (a) Guatemala Basin; (b) Clarion-Clipperton ore province, Site 2483; (c) South Basin, Site 6298. Metals: (1) Cu, (2) Ni, (3) Co, (4) Pb, (5) Mn, (6) Cd, (7) Mo. Numerals near the X-axis designate sample numbers.

Table 4. Average pH values of solutions before and after the sorption of metal cations from the Pacific pelagic bottom sediments

Metal salt solution	pH of initial solution at concentration, N		Average pH values of equilibrium solutions at concentration, N															
			1.0	0.01	1.0	0.01	1.0	0.01	1.0	0.01	1.0	0.01	1.0	0.01	1.0	0.01	1.0	0.01
			predominant minerals of the FMN								Sediment type							
			Bs I		Bs I + A-bs		T + A-bs		Fe-V + Mn-F		CR		RC		MC		ECZ	
NaCl	7.30	7.65	7.40	7.65	7.35	7.70	7.35	7.65	7.30	7.65	7.30	7.70	7.35	7.65	7.30	7.65	7.45	7.70
KCl	7.55	7.70	7.60	7.70	7.60	7.70	7.55	7.75	7.65	7.75	7.60	7.70	7.60	7.70	7.50	7.75	7.60	7.80
MnCl ₂	4.80	6.30	4.50	6.20	4.60	6.35	4.70	6.20	4.65	6.30	4.90	6.35	4.85	6.30	5.00	6.45	4.80	6.35
NiCl ₂	3.60	6.30	3.90	6.45	3.95	6.45	3.70	6.40	3.85	6.40	3.70	6.35	3.70	6.30	3.70	6.40	4.00	6.50
CoCl ₂	3.30	6.60	3.90	6.75	3.65	6.70	3.30	6.50	3.80	6.85	3.50	6.70	3.45	6.70	3.55	6.75	3.60	6.70
CuCl ₂	3.20	4.90	3.00	4.75	3.00	4.75	3.15	4.90	2.90	4.70	3.05	4.80	3.10	4.90	3.10	4.85	3.20	5.00
ZnSO ₄	4.15	6.00	4.15	6.05	4.30	6.20	4.30	5.90	4.35	6.20	4.20	6.10	4.15	6.05	4.15	6.05	4.20	6.10
Cd(NO ₃) ₂	5.20	6.10	5.30	6.25	5.35	6.30	5.40	6.20	5.40	6.30	5.30	6.15	5.25	6.15	5.40	6.25	5.10	6.00
Pb(NO ₃) ₂	3.65	5.40	3.00	5.15	3.30	5.25	3.50	5.30	3.25	5.20	3.50	5.30	3.50	5.35	3.40	5.35	3.40	5.30
K ₂ MoO ₄	8.40	8.75	8.50	8.80	8.50	8.75	8.45	8.80	8.45	8.70	8.40	8.70	8.40	8.70	8.45	8.80	8.50	8.75

Note: (CR) Clayey radiolarian ooze; (RC) Radiolarian clay; (MC) miopelagic clay; (ECZ) eupelagic clay with zeolite (phillipsite). Other designations are as in Table 3.

The presence of two groups of heavy metals in the capacity growth sequence reflects the difference in their sorptional behavior. The capacity of manganese minerals for Ni²⁺, Zn²⁺, and Cd²⁺ cations is lower than the sum total of exchange cations (including Mn²⁺) transferred into the solution. In this case, the exchange remains equivalent owing to the sorption of H⁺ protons, in addition to heavy metal cations, leading to increase in the pH value of the equivalent solution relative to the pH value of the initial solution, i.e., the shift of pH values toward the alkaline group (Table 4). Manganese minerals have a higher capacity for Cu²⁺, Co²⁺, Pb²⁺, and Mn²⁺ cations. In the case of virtually monomineral buserite nodules (e.g., FMN from the Guatemala Basin), the capacity is considerably higher than the sum total of exchange cations of minerals transferred into the solution. In the latter scenario, the pH value of equilibrium solutions is lower than that of initial solutions (Table 4), but the exchange remains equivalent owing to the transition of H⁺ protons, in addition to exchange cations, into the solution. Although the H⁺ protons participate in exchange reactions, their contribution to the capacity of manganese minerals is likely insignificant.

Variation in the exchange capacity of manganese minerals in nodules for the whole spectrum of elements shows the following sequence (Fig. 2): todorokite < asbolane-buserite < Fe-vernadite, Mn-feroxyhyte, asbolane-buserite < Fe-vernadite, Mn-feroxyhyte < buserite I, asbolane-buserite < buserite I, birnessite, i.e., from minerals with an ordered tunnel structure (todorokite) to minerals with disordered layered structure. Analysis of values of the exchange capacity in various associations of manganese minerals indicate that buserite I and Fe-vernadite associated with asbolane-buse-

rite have the highest contribution to the capacity of respective nodules. Values of the capacity of buserite I + asbolane-buserite and vernadite + asbolane-buserite associations are similar. The contribution of asbolane-buserite to the capacity of these associations is likely minimal. At the same time, as was mentioned above, the presence of asbolane-buserite in the todorokite nodules enhances their sorption capacity for Ni²⁺ and Co²⁺.

Depending on the geographic position, the studied regions are arranged in the following sequence in terms of the exchange capacity of manganese minerals in nodules for metals: South Basin < Central Basin ~ Clarion-Clipperton ore province < Guatemala Basin. Relative to nodules in other studied regions of the ocean, sedimentary nodules in the South Basin have the lowest capacity for heavy metal cations, while diagenetic nodules in the Guatemala Basin have the highest capacity.

Data presented above unambiguously testify to the intense sorption of metal ions by various manganese minerals in nodules. However, retention strength of the sorbed cations in manganese minerals is no less important issue. Results of the interaction between the respective cations of manganese minerals and aqueous solutions of electrolytes indicate the following regularity: the displacement of alkali metal cations from Na- and K-bearing phases does not depend on their residence time in manganese minerals of FMN, while the displacement of heavy metal cations is appreciably lower.

The absence of gegenions in the distilled water (pH 6.75) is responsible for the insignificant extraction of heavy metal cations both from fresh cationic forms of FMN, e.g., 0.14% Pb (Station 666-1) and 6.53% Mn (Station 2483-25), and from cations with a residence time of 1 yr, e.g., 0.02% Pb (Station 666-1) and 0.97%

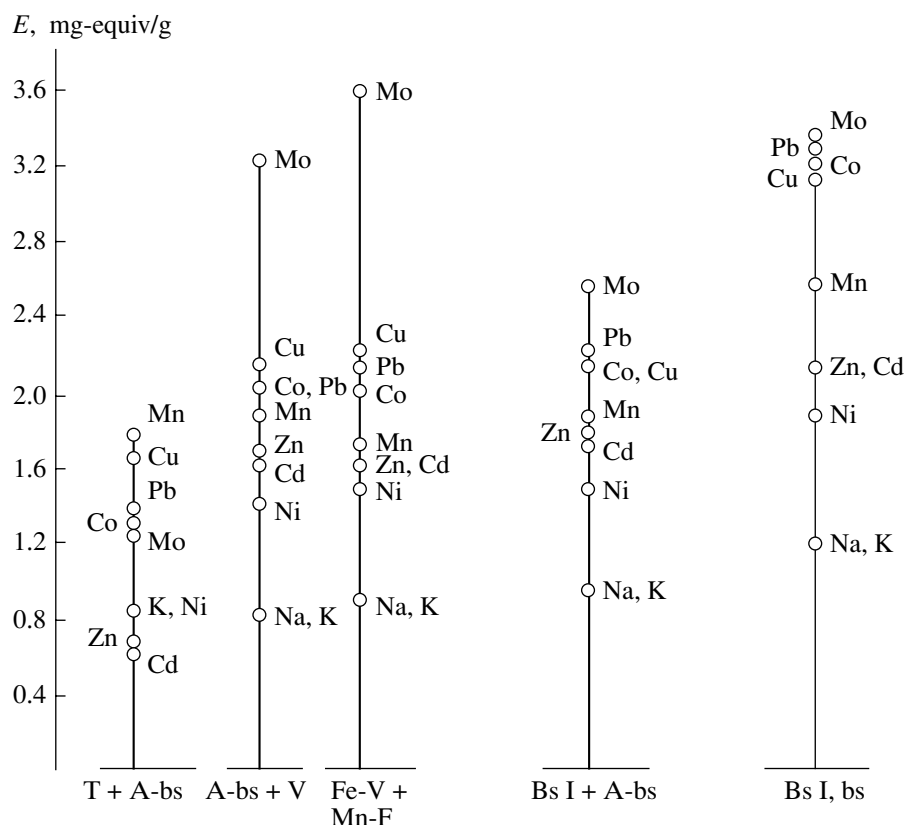


Fig. 2. Exchange capacity of different associations of manganese minerals in nodules. (A-bs) Asbolane-buserite, (Bs I) buserite I, (V) vernadite, (Fe-V) Fe-vernadite; (Mn-F) Mn-feroxyhyte; (T) todorokite.

Mn (Station 2483-39). The extraction of K^+ cations from manganese minerals varies from 2.98 (Station 666-1) to 6.27% (Station 6298-56).

In contrast to the distilled water, the ocean water includes gegenions, such as Na^+ (0.45 N NaCl solution), Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . Therefore, the ocean water is characterized by a significant extraction of sorbed metal cations from the respective FMN forms (Fig. 3). At the same time, a greater amount of metal cations is transferred into the ocean water than into the NaCl solution due to the additional substitution of the sorbed metal cations by K^+ , Ca^{2+} , and Mg^{2+} cations. K^+ cations are completely replaced by Na^+ cations irrespective of the existence duration of K-bearing phases of FMN, testifying to the equivalent ion exchange mechanism of the sorption of these metals. Among the heavy metals, the maximum reactivity is recorded for Mn^{2+} and Ni^{2+} cations in both fresh (unaltered) and 1-yr-old forms. The minimum reactivity is recorded for Pb^{2+} cations, irrespective of the age of Pb-bearing phases in the nodules. In this case, exchange reactions in the diagenetic and sedimentary nodules are accompanied by the partial equivalent substitution of sorbed heavy metal cations for Na^+ or the cation group of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} .

Thus, results of the study of exchange reactions (sorption and desorption) of metal cations in homogeneous (in terms of structure and texture) nodule layers with a specific association of manganese minerals testify to the differential influence of physicochemical and mineralogical features of nodules on the exchange capacity of manganese minerals. The sorption capacity of sedimentary (vernadite) nodules for heavy metals shows a positive linear correlation with the content of Mn^{4+} (MnO_2). The capacity of diagenetic nodules depends not only on the latter factor, but also on mineralogical characteristics. For both nodule types, the alkaline, alkaline earth, or heavy nature of the sorbed metal has an important significance. The compositional stability of the exchange complex is another essential ion exchange parameter of minerals in nodules. This property indicates similar formation settings of nodules over vast areas of ocean basins.

Data on the main ion exchange characteristics of manganese minerals presented above were obtained at high concentrations of metal cations in aqueous solutions of metal salts. Of course, such high concentrations do not exist in the ocean. Therefore, it is impossible to assess completely the sorption capacity of natural bodies. However, selectivity, an essential parameter of ion exchanger, can most correctly be determined in diluted

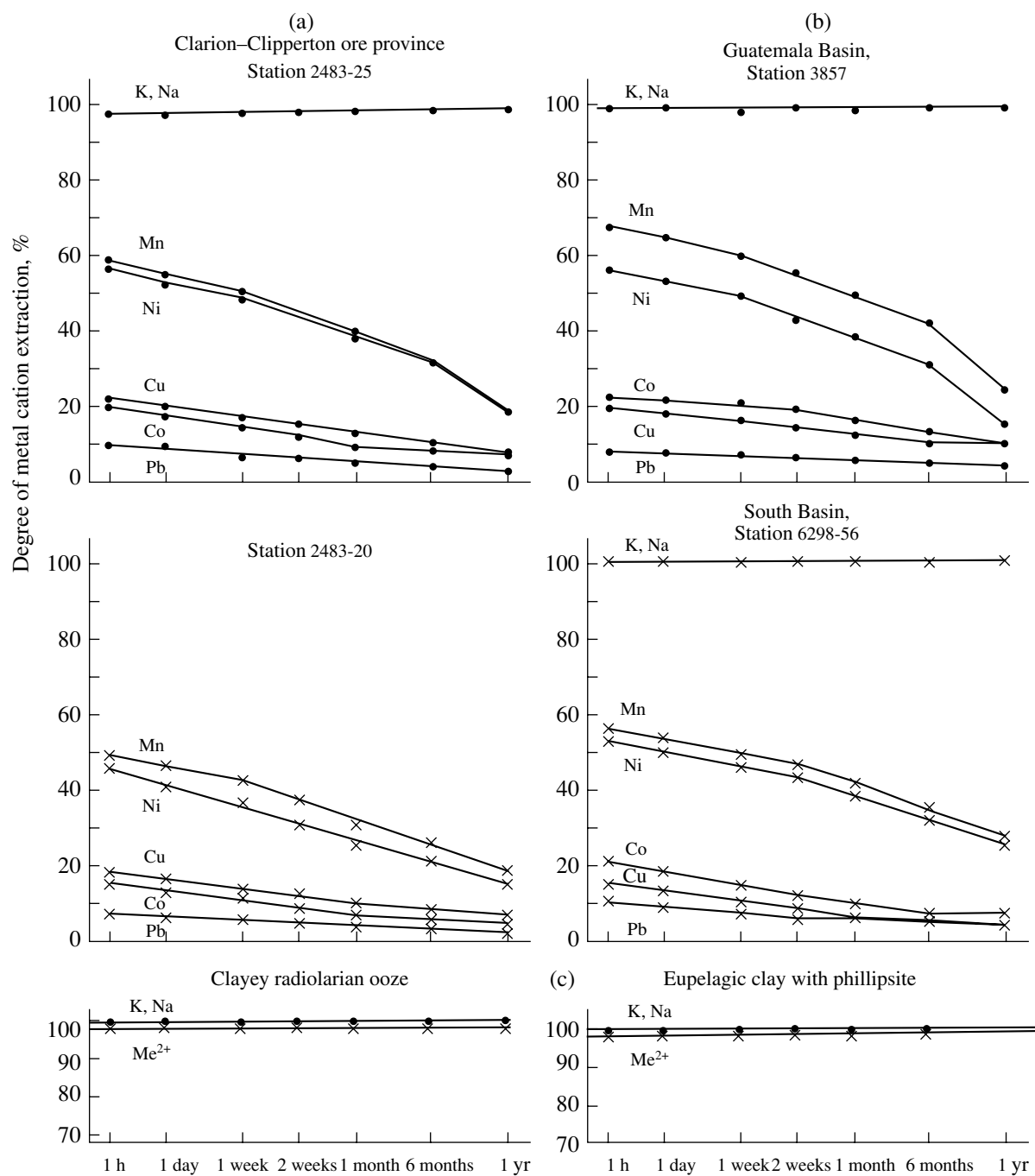


Fig. 3. Degree of metal cation extraction from (a, b) FMN and (c) pelagic sediments vs. time of their ageing during the interaction with natural ocean water. (a, b) Diagenetic and sedimentary nodules, respectively; (c) cations of alkali and heavy metals, respectively.

solutions generally characterized by considerable discrepancies in values of this parameter for different cations.

Hence, we believe that results of the study of sorption of heavy metal cations from the ocean bottom and interstitial waters are very important in the issue of the chemical composition of ferromanganese nodules. Concentrations of the majority of metal ions dissolved

in the ocean water vary significantly depending on the facies setting of the submarine hydrothermal activity. Concentrations of the majority of metal ions (including the heavy metals) in the oceanic and marine waters have been revised many times during the recent 20–25 years because of the refinement of analytical methods and technical devices (primarily, increase in the detection limit of metal ions). Taking into consideration

Table 5. Average concentrations of heavy metal cations in different types of ocean water

Water type	Mn	Cu	Ni	Zn	Cd	Co
Bottom Zn/Me ²⁺	0.1	0.5	0.6	5.0	0.07	–
	50	10	8.3	–	71.4	–
Interstitial Ni/Me ²⁺	56.2	132	370	138	0.27	3.6
	6.6	2.8	–	2.7	1366	102.5

Note: Data on bottom water are adopted from (Baturin et al., 1986); data on interstitial water, from (Baturin, 1993).

certain complications in the determination of negligible concentrations of heavy metal cations (0.0006–126 µg/l) in various types of ocean water (Baturin, 1993; Baturin et al., 1986; Bruland, 1983), particularly after the sorption, we were compelled to increase the concentration of heavy metal cations to their reliable detection limit. Ratio of concentrations is essential for the sorption of metal cations from multicomponent solutions. Therefore, we took into consideration ratios of average concentrations of heavy metal cations in each solution during the preparation of model solutions of various types of ocean water (Table 5). Na⁺ cations, the content of which matched their concentration in ocean water with a salinity of ~35‰, represented the macrocomponent of solutions.

The results obtained show that sorption of heavy metal cations in various associations of nodule-hosted manganese minerals demonstrates certain trends. Irrespective of the type of ocean water and mineral composition of nodules, one can record the collective sorption of all heavy metal cations beginning from the earliest moment of interaction of phases. However, the rate of sorption and the content of metal cations absorbed by manganese minerals are variable (Table 6; Figs. 4, 5). The maximum sorption rate is typical of Co²⁺ and Cd²⁺

cations. Sedimentary nodules (samples 2474-29, 2474-37) composed of Fe-vernadite and Mn-feroxyhyte absorb Co²⁺ completely (100%) from the interstitial and bottom waters in 1 h; diagenetic nodules composed of buserite I and asbolane-buserite (samples 2483-6, 19/t-1), in 3 h. Similar high sorption rate is also typical of Cd²⁺ cations, which are absorbed completely from the interstitial water by buserite and vernadite nodules in the first hour of the interaction of phases. Time required for the complete sorption of heavy metal cations from both types of ocean water is significantly variable. For example, Cd²⁺, Mn²⁺, Cu²⁺, and Ni²⁺ cations are absorbed from the bottom water in 12, 26, 32, and 58 days, respectively. In our experiments, no more than 17% of Zn²⁺ cations were absorbed in 2 months (Fig. 4). Time required for the complete extraction of these metal cations from the interstitial water was much less: 1 day for Cu²⁺, 2 days for Mn²⁺, and 3 days for Ni²⁺ and Zn²⁺. Moreover, metal cations are absorbed on the buserite and vernadite nodules with nearly similar rates (Fig. 5). It should be emphasized that Co²⁺ and Cd²⁺ cations are so rapidly absorbed by the manganese minerals of nodules against the background of high Cu²⁺, Ni²⁺, and Zn²⁺ concentrations that are two to three orders of magnitude higher than Co²⁺ and Cd²⁺ concen-

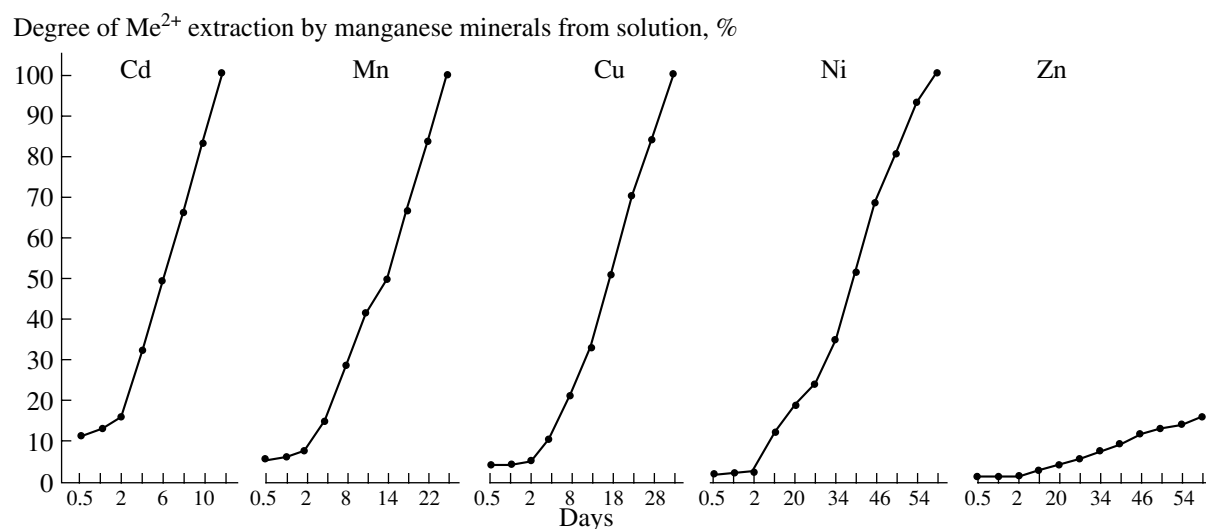


Fig. 4. Kinetic plots of the sorption of heavy metal cations by diagenetic buserite I and asbolane-buserite nodules from model solution of bottom water (sample 666-8).

Table 6. Distribution of heavy metal cations between manganese minerals of nodules and different types of ocean water

Mineral association, sample no.	Me ⁿ⁺ cation concentrations in the initial solution, µg/ml	Sorption time, days	Equilibrium coefficient (K _e), (mg-equiv/g)/(mg-equiv/ml)					
			Co	Mn	Cd	Cu	Ni	Zn
Bottom water								
Bs I, A-bs, (sample 2483-6)	Zn, 5000; Ni, 600; Cu, 500; Mn, 100; Cd, 70.0; Co, 1.0 Na, 10.8 × 10 ³ ; pH 6.40	2	8.50 × 10 ³	81.8	200	53.3	22.0	3.53
		10	—	113	1.0 × 10 ⁶	78.2	20.0	3.66
		26	—	1.10 × 10 ⁵	—	282	22.5	4.64
		32	—	—	—	3.10 × 10 ⁶	25.0	4.66
		58	—	—	—	—	4.50 × 10 ⁵	13.8
Fe-V, Mn-F (sample 2474-29)	Solution composition is the same	2	8.50 × 10 ³	93.9	230	56.0	24.0	3.73
		12	—	225	3.50 × 10 ⁵	93.0	29.0	3.80
		22	—	1.15 × 10 ⁵	—	200	44.2	3.75
		32	—	—	—	5.00 × 10 ⁵	97.5	7.86
		48	—	—	—	—	3.72 × 10 ⁵	7.38
Interstitial water of pelagic sediments								
Bs I, A-bs (sample 19/t-1)	Ni, 100; Zn, 40.0; Cu, 35.0; Mn, 15.0; Co, 1.0; Cd, 0.10; Na, 10.8 × 10 ³ ; pH 7.45	1	8.50 × 10 ³	1.90 × 10 ³	9.0 × 10 ³	2.72 × 10 ⁶	259	200
		2	—	8.23 × 10 ⁴	—	—	1.10 × 10 ³	5.80 × 10 ³
		3	—	—	—	—	3.30 × 10 ⁵	3.70 × 10 ⁵
Fe-V, Mn-F (sample 2474-37)	Solution composition is the same	1	8.50 × 10 ³	2.10 × 10 ³	9.0 × 10 ³	2.80 × 10 ⁶	266	245
		2	—	7.60 × 10 ⁴	—	—	1.00 × 10 ³	7.10 × 10 ³
		3	—	—	—	—	3.20 × 10 ⁵	3.00 × 10 ⁵
Mineral association, sample no.	Me ⁿ⁺ cation concentrations in the initial solution, µg/ml	Sorption time, days	Amount of heavy metal cations absorbed by manganese minerals of FMN, mg/g					
			Co	Mn	Cd	Cu	Ni	Zn
Bottom water								
Bs I, A-bs, (sample 2483-6)	Zn, 5000; Ni, 600; Cu, 500; Mn, 100; Cd, 70.0; Co, 1.0 Na, 10.8 × 10 ³ ; pH 6.40	2	1.0 (3 h)	7.42	11.24	25.44	12.90	17.33
		10	—	41.80	70.0	161.53	68.66	106.92
		26	—	100.0	—	382.21	140.27	248.87
		32	—	—	—	500.0	172.84	311.98
		58	—	—	—	—	600.0	781.86
Fe-V, Mn-F (sample 2474-29)	Solution composition is the same	2	1.0 (1 h)	8.52	12.92	26.71	14.09	18.31
		12	—	53.90	70.0	162.80	84.23	109.55
		22	—	100.0	—	326.56	160.25	201.76
		32	—	—	—	500.0	261.47	311.97
		48	—	—	—	—	600.0	575.51
Interstitial water of pelagic sediments								
Bs I, A-bs (sample 19/t-1)	Ni, 100; Zn, 40.0; Cu, 35.0; Mn, 15.0; Co, 1.0; Cd, 0.10; Na, 10.8 × 10 ³ ; pH 7.45	1	1.0 (3 h)	9.62	0.10 (1 h)	35.0	20.54	6.54
		2	—	15.0	—	—	60.75	35.0
		3	—	—	—	—	100.0	40.0
Fe-V, Mn-F (sample 2474-37)	Solution composition is the same	1	1.0 (1 h)	10.45	0.10 (1 h)	35.0	21.13	7.85
		2	—	15.0	—	—	61.63	35.92
		3	—	—	—	—	100.0	40.0

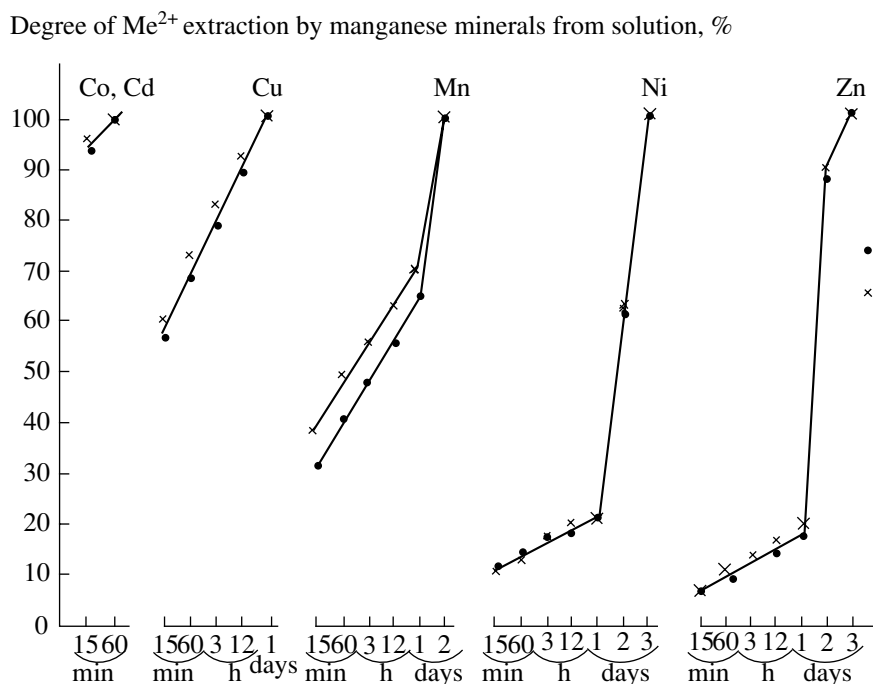


Fig. 5. Kinetic plots of the sorption of heavy metal cations by (1) diagenetic buserite I and asbolane-buserite nodules (sample 19/t-1) and (2) sedimentary Fe-vernadite and Mn-feroxyhyte nodules (sample 2474-37) from model solution of bottom water.

trations. Hence, the manganese minerals of nodules demonstrate a higher selectivity to Co^{2+} and Cd^{2+} cations than to other heavy metal cations. This is supported by the considerably higher values of their equilibrium distribution coefficient (K_d) (Table 6). The K_d value of Cu^{2+} is at least three orders of magnitude higher than the K_d value of other metals only during the sorption of metal cations from the interstitial water. In accordance with the K_d values obtained in our experiments, metal cations make up the following series (with respect to increase in affinity to the manganese minerals of nodules):

for the bottom water:

$\text{Na} \ll \text{Zn} < \text{Ni} < \text{Cu} < \text{Mn} < \text{Cd} < \text{Co}$;

for the interstitial water: $\text{Na} \ll \text{Zn} < \text{Ni} < \text{Mn} < \text{Cd} < \text{Co} < \text{Cu}$.

The series are constructed based on results of the analysis of equilibrium solid phase in the first 2 days for the bottom water and 1 day for the interstitial water.

Despite the simultaneous sorption of heavy metal cations, the equilibrium exchange capacity of the manganese minerals of nodules is primarily realized at the expense of Cu^{2+} and Ni^{2+} cations in the interstitial water and Cu^{2+} and Zn^{2+} cations in the bottom water. In the latter case, however, we should take into consideration the following fact; concentration of Zn^{2+} cation is nearly one order of magnitude higher than that of Ni^{2+} cations. Sorption of Ni^{2+} and Zn^{2+} cations by various manganese minerals increases drastically only after the

complete sorption of Cu^{2+} cations from any ocean water. Time required for the achievement of equilibrium capacity of manganese minerals was commonly slightly more than 2 days (50–54 h). Series of the concentration of heavy metal cations in manganese minerals are as follows (compiled similarly as the series presented above):

for the bottom water: $\text{Co} < \text{Mn} < \text{Cd} < \text{Ni} < \text{Zn} < \text{Cu}$;

for the interstitial water: $\text{Cd} < \text{Co} < \text{Zn} < \text{Mn} < \text{Ni} < \text{Cu}$.

The chemical analysis of sorption products revealed extremely low contents of Na^+ , K^+ , and Ca^{2+} cations (no more than 0.05 wt %) in various manganese minerals. Hence, we can draw the following important conclusion: Na^+ cations contained in each type of ocean water do not influence the sorption of heavy metal cations by manganese minerals; i.e., Na^+ cations are not competitive ones for the heavy metal cations.

It is no less important to elucidate compositional variations in equilibrium solid phases during their further interaction with the ocean water. For this purpose, we took equilibrium (2-days-old) samples of diagenetic (sample 19/t-1) and sedimentary (sample 2474-37) nodules that interacted with the interstitial water of composition similar to that in the previous case. The purpose of such investigations was to elucidate the relationship between the time of nodule ageing and the reactivity of sorbed heavy metal cations. The results demonstrated that the distribution pattern of metal cations is similar for both diagenetic and sedimentary nodules.

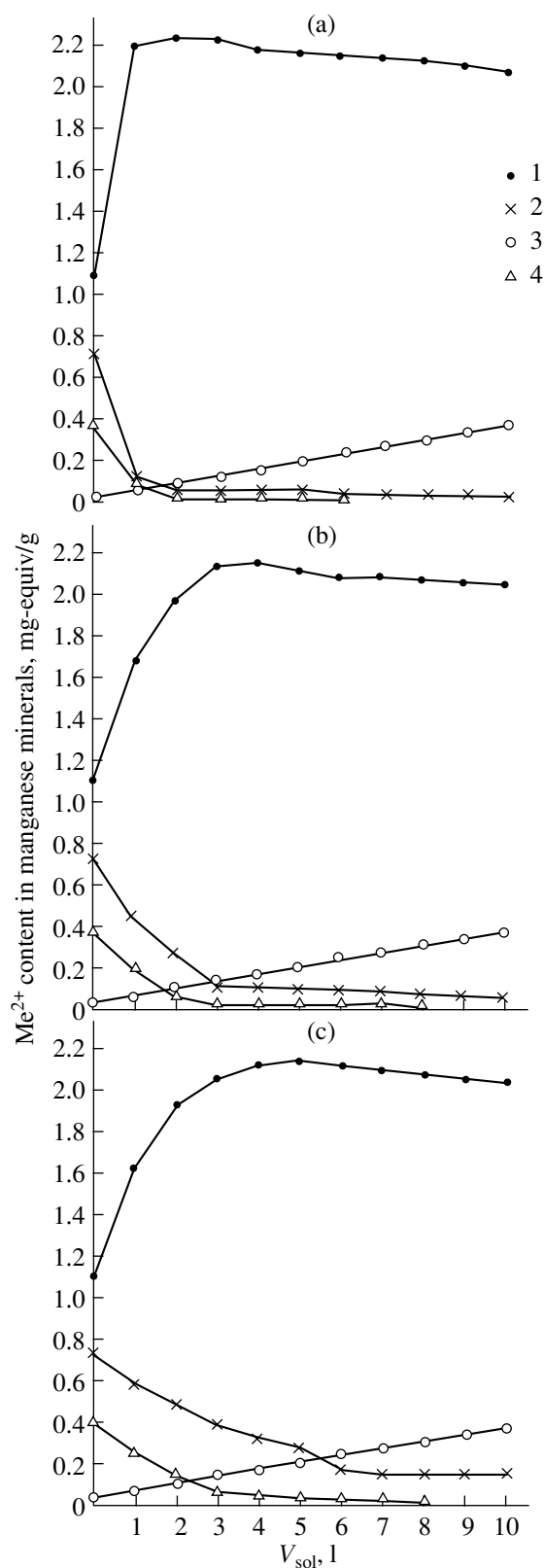


Fig. 6. Contents of sorbed heavy metal cations in sedimentary Fe-vernadite and Mn-feroxyhyte nodules (sample 2474-37) vs. volume of the transmitted model solution of interstitial water during the ageing of nodules for (a) 5 days, (b) 6 months, and (c) 1 yr. (1) Cu; (2) Ni; (3) Co; (4) Mn.

Interaction of manganese minerals saturated with heavy metal cations with the interstitial water fosters the additional sorption of Cu²⁺ and Co²⁺ cations due to the displacement of Ni²⁺, Mn²⁺, Zn²⁺, and Cd²⁺ cations into the solutions (Fig. 6). In our experiments, Co²⁺ cations were constantly absorbed by manganese minerals only up to certain values. The maximum capacity of buserite and vernadite nodules was 2.00 and 2.24 mg-equiv/g, respectively. Like Ni²⁺, Zn²⁺, and other cations, Cu²⁺ cations began to pass into the solutions after the achievement of the equilibrium capacity of manganese minerals. Isotherms of the exchange of heavy metal cations on manganese minerals of the FMN reported in (Chelishchev et al., 1992) suggest that Cu²⁺ cations are primarily displaced by Co²⁺ cations, and the exchange between these cations is only partial (no more than 10%). This regularity is also typical of samples with different ageing periods (the samples were preserved in the air-dry state until the continuation of experiments).

The process discussed above is also characterized by the specific behavior of Ni²⁺ cations: the rate of their transfer into the liquid phase has negative correlation with the duration of nodule ageing. The content of Ni²⁺ cations in buserite and vernadite nodules is similar (0.01 mg-equiv/g) at the ageing period of 5 days; 0.13 and 0.17 mg-equiv/g, respectively, at the ageing period of 6 months; and 0.06 and 0.10 mg-equiv/g, respectively, at the ageing period of 1 yr. Discrepancy in the Ni²⁺ content in the buserite and vernadite nodules is likely to be caused by different degrees of the filling of sorption-active centers in structures of the studied minerals. Hence, if we increase the ageing period of nodules, the content of reactive Ni therein will probably decrease. In addition, as was shown in (Chelishchev et al., 1991), the presence of sorbed Ni²⁺ cations in buserite I promotes its gradual partial recrystallization into asbolane-buserite. Ni²⁺ cations are displaced from the asbolane-buserite to a lesser extent than from buserite I (Chelishchev et al., 1992). In contrast to Ni²⁺ cations and irrespective of residence time in the manganese minerals of nodules, Cd²⁺, Zn²⁺, and Mn²⁺ cations are intensely driven into the solutions by other heavy metal cations. In this process, the maximum reactivity is typical of Cd²⁺ and Zn²⁺. It is also worth mentioning that variation in the exchange capacity of buserite and vernadite nodules during the entire experimental period did not exceed ± 0.10 mg-equiv/g of the value established for the equilibrium (2-days-old) solid phases; i.e., the capacity remained virtually constant. The experimental results indicate that manganese minerals are characterized by both collective and selective sorption of heavy metal cations, leading to variation in their chemical composition even at low concentrations of metal cations in solutions.

Thus, results of the sorption of very small amounts of heavy metals from model solutions, in which cation

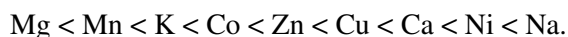
ratios are close to those in the natural ocean water, indicate the principle possibility of sorption in various facies settings of the World Ocean according to the mechanism considered above. This statement is primarily related to the diagenetic and sedimentary nodules in the oceanic pelagic region, where the content of Ni^{2+} and Cu^{2+} cations is considerably higher than contents of the majority of other cations of heavy, rare, and other metals.

Pelagic Sediments

It is known that sorption capacity of sediments is governed by their grain size distribution, as well as the mineral and organic constituents of the absorbing complex. The sediments studied are mainly composed of the pelite fraction (>85%). The content of organic carbon does not exceed 0.36 wt % (Table 2). Hence, ion exchange capacity of sediments is mainly controlled by the clay minerals.

Interaction of various types of bottom sediments with aqueous solutions of metal salts is related to exchange reactions between metal cations of the solid and liquid phases. Hence, all sediment types studied in the present paper can be considered natural cation exchangers. However, they have different degrees of sorption capacity with respect to both separate metal cations and the entire spectrum of metals. The exchange capacity of sediments varies from 0.01 to 1.58 mg-equiv/g (Table 3). Metal cations primarily manifest the differential reactivity in the course of their displacement into solution.

Exchange reactions with metal cations of solutions involve cations of the alkaline, alkaline earth, and heavy metals of sediments. Data in Table 3 show that Na^+ and Ca^{2+} have the maximum reactivity in all types of sediments, whereas the minimum reactivity is typical of Mg^{2+} and Mn^{2+} . In addition, all sediment types demonstrate a high degree of Ni^{2+} extraction (33.4–40.3%). In the phillipsite-bearing eupelagic clays, the highest extraction is typical of Cu^{2+} cations (35.5%). The degree of extraction of heavy metal cations (Zn, Co, and Cu) from various sediments types is similar (18.3–24.7%). A slightly higher extraction of other metal cations from the studied bottom sediments is recorded for Cu^{2+} and Pb^{2+} cations. Based on the degree of extraction of metal cations, they make up the following series of increase in reactivity:



Location of Cu^{2+} before Ni^{2+} in this series in eupelagic clays is the sole difference from the general regularity.

Hence, these cations are located in minerals in the sorbed form, and they can easily be extracted during their interaction with aqueous solutions of metal salts. In this process, the contribution of each metal to the total capacity of sediments is different. The share of

Na^+ and Ca^{2+} cations varies within the range of 0.19–0.29 and 0.15–0.25 mg-equiv/g, respectively (Table 3), which corresponds to 60–75% of the total capacity of sediments. All sediment types are characterized by the following common regularity: the share of Na^+ in the total capacity of sediments is 0.08–0.12 mg-equiv/g higher during the sorption of Cu^{2+} and Pb^{2+} cations relative to other metal cations. Moreover, the amount of Ca^{2+} cations transferred into the solution during the sorption of Cu^{2+} exceeds the amount of Na^+ cations by 0.03 mg-equiv/g in clayey radiolarian oozes (station 2474-3) and 0.05 mg-equiv/g in miopelagic clays (station 3855). Table 3 shows that the contribution of K^+ , Mg^{2+} , and Mn^{2+} to the total capacity of sediments varies from 0.3 to 0.16 mg-equiv/g. However, results of the sorption of Pb^{2+} indicate a higher degree of Mg^{2+} extraction from the diatom-containing clayey radiolarian oozes (0.18 mg-equiv/g, station 3833-6) and miopelagic clays (0.25 mg-equiv/g, station 3855). The extraction of K^+ cations from the eupelagic clays is also higher (0.35 mg-equiv/g, station 6298-6; 0.38 mg-equiv/g, station 6298-55). The contribution of heavy metal cations into the capacity of various sediments is no more than 0.01 mg-equiv/g. Thus, the exchange complex of sediments mainly consists of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} (major cations of ocean water), whereas heavy metal cations play a subordinate role.

Ion exchange reactions in various types of oceanic sediments are characterized by the equivalent exchange of the sum total of exchange cations of sediment and the sorbed metal cation irrespective of the nature of the latter cation. The amount of sorbed cation is either equal to the amount of exchange cations of sediment transferred into the solution or the discrepancy between these values is no more than $\pm(0.03\text{--}0.07\text{ mg-equiv/g})$. Among all exchange reactions studied in our case, we can mark the reaction with the participation of Cu^{2+} cations in the miopelagic clayey radiolarian ooze from the Guatemala Basin (station 3855). The capacity of such sediments for Cu^{2+} cations is 0.22 mg-equiv/g higher than the sum total of exchange cations transferred to the solution. Exchange equivalence in this case is retained owing to the transfer of H^+ protons into the solution. This is evident from decrease in the pH value of the equilibrium solution by 0.15, relative to the pH value of the prepared solution (Table 4). In reactions marked by inverse correlation, the exchange equivalence is retained owing to the sorption of H^+ protons, in addition to metal cations, leading to the formation of equilibrium solutions with the pH value higher than that of the initial solutions by approximately 0.10. However, processes of sorption and desorption of H^+ in both cases are not probably crucial for ion exchange reactions in sediments of various types.

Data presented in Table 3 show that the capacity of various types of sediments is rather similar during the sorption of metal cations from 1.0–0.01 N solutions

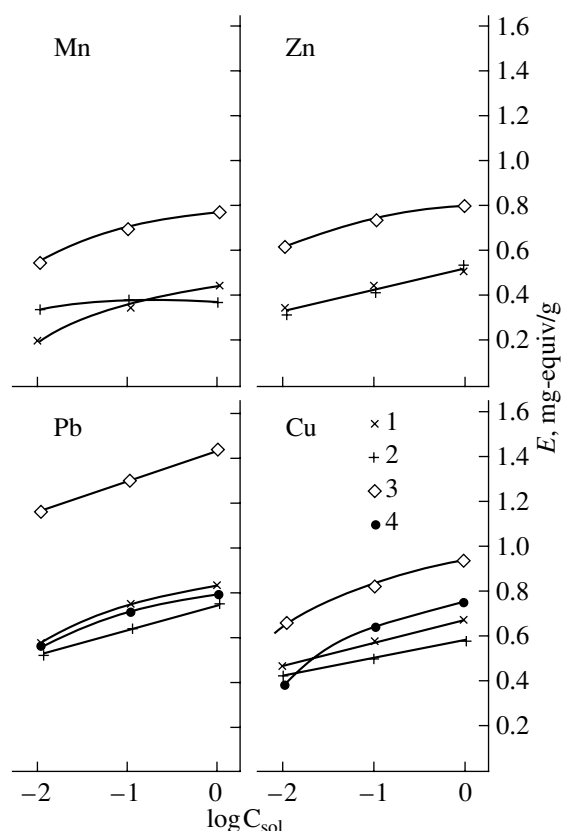


Fig. 7. Exchange capacity of clay minerals in sediments vs. concentration of metal salt solution (C_{sol}). (1) Clayey radiolarian ooze; (2) radiolarian clay; (3) eupelagic clay; (4) clayey radiolarian ooze with diatoms.

(discrepancy is 0.03–0.12 mg-equiv/g). However, the value is 1.25–1.65 times lower (except for alkali metal cations) during the sorption from diluted solutions (0.01 N). At the same time, the capacity of sediments shows virtually linear correlation with the concentration of the sorbed metal cation in solution (Fig. 7). Similarity of the capacity of sediments is related to the prevalence of clay minerals in them (smectite, hydromica, mixed-layer illite-smectite, chlorite, and kaolinite). Despite different ratios of minerals in each specific type of sediments, the sorption capacity of sediments is generally similar (Table 3). However, exceptions from the general regularity are observed in some cases.

For example, the miopelagic clayey radiolarian ooze from the Guatemala Basin (station 3855) has a higher exchange capacity for heavy metal cations, relative to analogous sediments from the Central Basin and other regions. This is explained by the higher content of micronodules in sediments of the Guatemala Basin relative to other regions, manganese minerals from which intensely absorb heavy metal cations, such as Cu^{2+} and Pb^{2+} (Novikov and Svalnov, 1999). Relative to other sediment types, eupelagic clays (station 6298-6, 6298-55) have the maximal capacity for Cd (1.00 mg-equiv/g) and alkali metals (0.62–0.68 mg-equiv/g). The

capacity for Pb (1.40 mg-equiv/g) is similar to that of sediments in the Guatemala Basin. The capacity of eupelagic clays for alkali metals is two to three times higher than that of other sediment types due to the presence of phillipsite, which has a high capacity for alkali metal cations (Chelishchev et al., 1984) and, probably, for Pb^{2+} and Cd^{2+} cations as well.

Zaitseva (1959, 1966) reported values of the capacity of surface sediments, in general, and sediments of <0.001 mm fraction, in particular, for the northwestern, southeastern, and central tropical sectors of the Pacific. In all studied areas, the capacity of sediments is virtually similar (mg-equiv/g): 0.076–0.30, 0.14–0.24, and 0.44–0.46, respectively (0.40–0.58 and 0.60–0.62, respectively, for fraction <0.001 mm). Comparison of literature and our data obtained for the sediments, in general, from 1 N solutions of metal salts (Table 3) shows that the sorption capacity range of our sediments is similar to that of <0.001 mm fraction. Hence, the sorption capacity of sediments is governed by their fine pelite fraction.

It is known that clay minerals are marked by variable exchange capacity (mg-equiv/g): kaolinite 0.03–0.25; smectite group minerals (montmorillonite, nontronite) 0.8–1.2; beidellite 0.6–0.65; and hydromica 0.20–0.40 (Brouwer et al., 1983; Comans et al., 1991; Dunaeva and Mironenko, 2000; Gorbunov, 1956; Kokotov, 1980; Tarasevich and Ovcharenko, 1975; Wahlberg and Fishman, 1962; Zaitseva, 1959, 1966). The pelite fraction of sediments from sites 2474 and 2520 is composed of hydromica (average content 49 and 52%, respectively) with a subordinate amount of smectite (37 and 31%, respectively) and chlorite (14 and 16%, respectively). At Site 2483, the relationship is reverse: 49% of smectite, 39% of hydromica, and 12% of chlorite (Chudaev and Sval'nov, 1986). The capacity of clayey radiolarian ooze, radiolarian clay, and miopelagic clay for alkali and heavy metals (except Cu and Pb) varies from 0.40 to 0.61 mg-equiv/g (Table 3). This capacity range is intermediate between values for hydromica and smectite group minerals. The higher capacity of sediments for Cu^{2+} and Pb^{2+} is likely related to the higher selectivity of hydromicas and smectite for these metals than for other metal cations. The data obtained for exchange capacity of sediments from the Clarion–Clipperton zone (sites 2474, 2483) and Central Basin (Site 2520) coincide with the data on the sorption of metal cations on sediments from the northwestern Pacific mainly composed of hydromica minerals and smectite (Zaitseva, 1959). Eupelagic clays of the South Basin (Site 6298) are characterized by the prevalence of smectite and mixed-layer illite-smectite and the presence of phillipsite, resulting in their elevated sorption capacity relative to other sediment types.

Among the spectrum of studied elements, Mo is marked by exchange capacity of 0.01–0.10 mg-equiv/g (Table 3) in the majority of sediment types, except miopelagic clays (station 3855), which have the capacity of

0.19–0.28 mg-equiv/g during the sorption of Mo from 1.0–0.1 N solutions. This is probably caused by the presence of X-ray amorphous manganese hydroxides or manganese micronodules on the surface of sediments (Mn 2.32 wt %). Such low values of the exchange capacity of sediments for Mo can be related to the following fact: clay minerals are cation exchangers, whereas Mo is absorbed from solution as molybdate ion (MoO_4^{2-}). Mo is probably absorbed by sediments according to the mechanism of isomorphic replacement of exchange cations at the surface. Analogous result was also obtained for the oceanic low-temperature hydrothermal minerals composed of silicates (opal and quartz) and nontronite (Novikov and Cherkashev, 2000). Sediments absorb simultaneously Mo anions and K^+ cations, but capacity values are similar to those for the sorption of K^+ cations from the KCl solution (Table 3). The clayey radiolarian ooze, radiolarian clay, and miopelagic clay show the following single series of increase in capacity:

$\text{Mo} < \text{K} \sim \text{Na} < \text{Cd} \sim \text{Co} < \text{Mn} < \text{Ni} < \text{Zn} < \text{Cu} < \text{Pb}$.

For the eupelagic clay, the series is as follows:

$\text{Mo} < \text{Ni} < \text{Co} < \text{Na} \sim \text{K} < \text{Mn} < \text{Zn} < \text{Cu} < \text{Cd} < \text{Pb}$.

In terms of exchange capacity (Table 3), metals are divided into four groups. Group 1 includes Mo characterized by the minimum exchange capacity in various sediment types. Group 2 includes alkali metals (except eupelagic clays). Group 3 comprises Co, Cd, Ni, and Zn. Group 4 includes Cu and Pb that are always marked by the higher exchange capacity relative to other metals. In some places, elements of group 3 are rearranged due to similar values of exchange capacity, but the geochemical regularity is unaltered. However, the exchange capacity of each sorbed metal cation increases slightly from the clayey radiolarian ooze to the eupelagic clay (Fig. 5).

Investigations of the kinetics of desorption of metal cations absorbed from sediments revealed two regularities: (i) the lack of relationship between the ageing period of cationic forms in sediments and the transfer of sorbed metal cations into solution; (ii) the sorbed metal cations are transferred to solution irrespective of the nature of the applied gegenion (alkali or heavy metal). Interaction between cationic forms of various types of sediments during the whole exposition period (from 1 day to 1 yr) and the distilled water results in an insignificant (2.65–2.90%) displacement of the sorbed metal cations, whereas interaction with the NaCl solution and ocean water results in their virtually complete (97.2–99.6%) displacement (Fig. 3b). The interactions are characterized by equivalent exchange between Na^+ cations (major cations in the ocean water) and the sorbed metal cation in sediment. In the case of ocean water, more Na^+ and Ca^{2+} cations are absorbed than Mg^{2+} and K^+ cations. Hence, Na^+ and Ca^{2+} should contribute more to the exchange capacity of sediments during the subsequent sorption of heavy metal cations.

Thus, results of exchange reactions (sorption–desorption) of metal cations on surface sediments of the Pacific show that the sediments are natural ion exchangers with distinctly expressed cation exchange properties. Their exchange complex includes Na^+ , Ca^{2+} , Mg^{2+} , and K^+ cations, which are the major regulators of exchange capacity of sediments. Cations of heavy metals (Mn, Ni, Cu, Co, and Zn) account for no more than 3–5% of the total capacity. Despite different proportions of clay minerals, their capacity for each metal or the entire spectrum of studied metals has similar values. At the same time, the presence of manganese minerals and/or phillipsite in the sediments enhances their sorption capacity for separate heavy (Cu, Pb, Cd) and alkali (Na, K) elements.

COMPARATIVE ANALYSIS OF ION EXCHANGE PROPERTIES OF MANGANESE MINERALS IN NODULES AND CLAY MINERALS IN SEDIMENTS

As was shown above, manganese minerals of nodules and aluminosilicate (clay) minerals of sediments have ion exchange properties relative to various metal ions. In the ion exchange process, manganese minerals exhibit properties of amphotolyte, which can absorb metal cations and anions from solutions, while clay minerals serve as cation exchangers. Ion exchange properties of both mineral types (Table 7) show general regularities and discrepancies in the sorption and desorption of metal ions.

The exchange complex of manganese and clay minerals is primarily composed of the major cations of ocean water (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}). Their total content accounts for 90–95% of the total capacity. Among them, Na^+ and Ca^{2+} are the major contributors to the capacity of manganese and clay minerals, while the role of K^+ cations is minimal. The group of major exchange cations also includes Mn^{2+} cations that can significantly contribute to the exchange capacity of both manganese minerals and clay minerals in sediments (up to 0.5 and 0.15 mg-equiv/g, respectively). The contribution of the remaining heavy metal cations (Cu, Ni, Co, and others) to the capacity of minerals of both types usually does not exceed $n\%$ (no more than 0.1 and 0.01 mg-equiv/g, respectively). The role of H^+ protons in exchange reactions is presumably insignificant.

The exchange capacity of manganese and clay minerals in the studied spectrum of metals increases in a similar sequence: from the alkali to heavy metals during the sorption from concentrated (1 N) metal salt solutions and from Mo to heavy metals during the sorption from 0.1–0.01 N solutions (the maximum capacity is recorded with respect to Cu^{2+} , Pb^{2+} , and Co^{2+} cations). The exchange capacity of manganese minerals is at least 1.5–2 times higher than that of clay minerals (Table 3).

Diagrams based on results of the sorption of metal ions from the 1 N solution (Fig. 8) show that the type of

Table 7. Ion exchange characteristics of manganese minerals of nodules and clay minerals of sediments

Characteristics	Manganese minerals in nodule	Clay minerals of sediments
Mineral texture	Layered, tunnel	Layered and expanding
Mechanism of metal cation sorption	Alkali metals: equivalent reversible; heavy metals: equivalent (Ni, Zn, Cd, Mn) or superequivalent (Co, Pb, Cu) partly reversible (no more than 10–15%)	Alkali and heavy metals: equivalent reversible
Composition of exchange complex	Major: Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} ; secondary: Ni^{2+} , Zn^{2+} , Cu^{2+}	Major: Na^+ , K^+ , Ca^{2+} , Mg^{2+} ; secondary: Mn^{2+} , Ni^{2+} , Cu^{2+}
Reactivity of metal cations	$\text{Pb} < \text{Co}^{2+} < \text{Zn}, \text{Ni}, \text{Cu} < \text{K} < \text{Mn}^{2+} \leq \text{Mg} < \text{Ca} \leq \text{Na}$	$\text{Mg} < \text{Mn}^{2+} < \text{K} < \text{Co} < \text{Zn} < \text{Cu} < \text{Ca} < \text{Ni} \leq \text{Na}$
Exchange capacity (mg-equiv/g)	For alkali metals: 0.65–1.24; for heavy metals: Ni, Zn, Cd, Mn: 0.77–2.68, Co, Pb, Cu: 1.20–3.43, Mo_1 : 1.20–4.26, Mo_2 : 0.37–1.02, $\text{Mo}_1 < \text{Na}, \text{K} < \text{Ni} < \text{Zn} \sim \text{Cd} < \text{Mn} < \text{Co} < \text{Pb} < \text{Cu} < \text{Mo}_2$	For alkali metals: types CR, RC, MCP: 0.10–0.37, type ECZ: 0.47–0.66. For heavy metals: types CR, RC, MCR: Cd, Co, Mn, Zn, Ni, Cu, Pb 0.20–1.58, Mo 0.02–0.28, type ECZ: Cd, Co, Mn, Zn, Ni, Cu, Pb 0.32–1.40, Mo 0.02–0.09, types CR, RC, MCZ: Mo < K, Na < Cd ~ Co < Mn < Zn < Cu < Pb, type ECZ: Mo < Ni < Co < Na, K < Mn < Zn < Cu < Cd < Pb

Note: (Mo_1 , Mo_2) based on results of Mo ion sorption from diluted and concentrated solutions, respectively.

nodule-enclosing sediment does not influence the exchange capacity of manganese minerals in nodules. Variation in the capacity is insignificant for each sorbed metal cation. The variation range is generally 1.60–2.40 mg-equiv/g for heavy metal cations. However, the capacity is more variable for diagenetic nodules composed of different associations of manganese minerals. For example, buserite I and birnessite nodules lying in the miopelagic clay from the Guatemala Basin have a greater capacity for all metal cations, relative to buserite I and asbolane-buserite nodules lying in clayey radiolarian oozes of the Clarion–Clipperton ore province. Discrepancies in the capacity of manganese minerals in nodules from these regions are related to compositions and properties of manganese minerals (sorbents) rather than sediment types (Dymond et al., 1984).

The exchange capacity of sedimentary (vernadite) nodules lying in the clayey radiolarian ooze or radiolarian clay of the Clarion–Clipperton ore province and Central Basin is slightly higher than that of nodules lying in the eupelagic clay of the South basin characterized by the lowest sedimentation rate (<0.5 mm/ka). Under such conditions, in contrast to nodules of the radiolarian belt (Skorniyakova and Murdmaa, 1992), the nodules described above can only be formed by the sedimentary mechanism (*Zhelezomargantsevy...*, 1976).

Hence, discrepancies in ion exchange properties of manganese minerals of cognate nodules lying in different types of sediments are significantly governed by differences in facies settings of sedimentation (Murd-

maa, 1987) rather than only sorptional processes in sediments and nodules. This statement is also supported by the calculated coefficients of nodule enrichment relative to the underlying sediment, $K_{\text{enr}} = E_{\text{FMN}}/E_{\text{sed}}$ (Table 8). The K_{enr} value is maximal for Mo in diagenetic and sedimentary nodules irrespective of the sediment type. In the diagenetic FMN, this parameter varies from 12.2 (miopelagic clay) to 42.6 (clayey radiolarian ooze); in sedimentary FMN, from 34.2 (eupelagic clay with phillipsite) to 46.3 (clayey radiolarian ooze). The minimum value recorded for Pb varies from 1.40 (eupelagic clays) to 3.00 (clayey radiolarian oozes). Hence, cations mentioned above will mainly be absorbed by manganese minerals of nodules during the influx of bottom or interstitial waters, which contain heavy metal cations, to the contact surface of nodule-hosted manganese minerals and sediment-hosted clay minerals.

Significant discrepancies in ion exchange properties of minerals in nodules and sediments are related to different mechanisms of the sorption of metal cations, which primarily depend on crystallochemical features of minerals and the nature of the sorbed metal cation. Clay minerals of sediments are characterized by the equivalent reversible sorption of metal cations irrespective of their nature and residence period in minerals. According to (Tarasevich and Ovcharenko, 1975), substitution of Si^{4+} by Al^{3+} (in tetrahedral layers within the crystal structure of aluminosilicates) and Al^{3+} by cations with lower valence (in octahedral layers) produces in the crystal lattice uncompensated negative charges

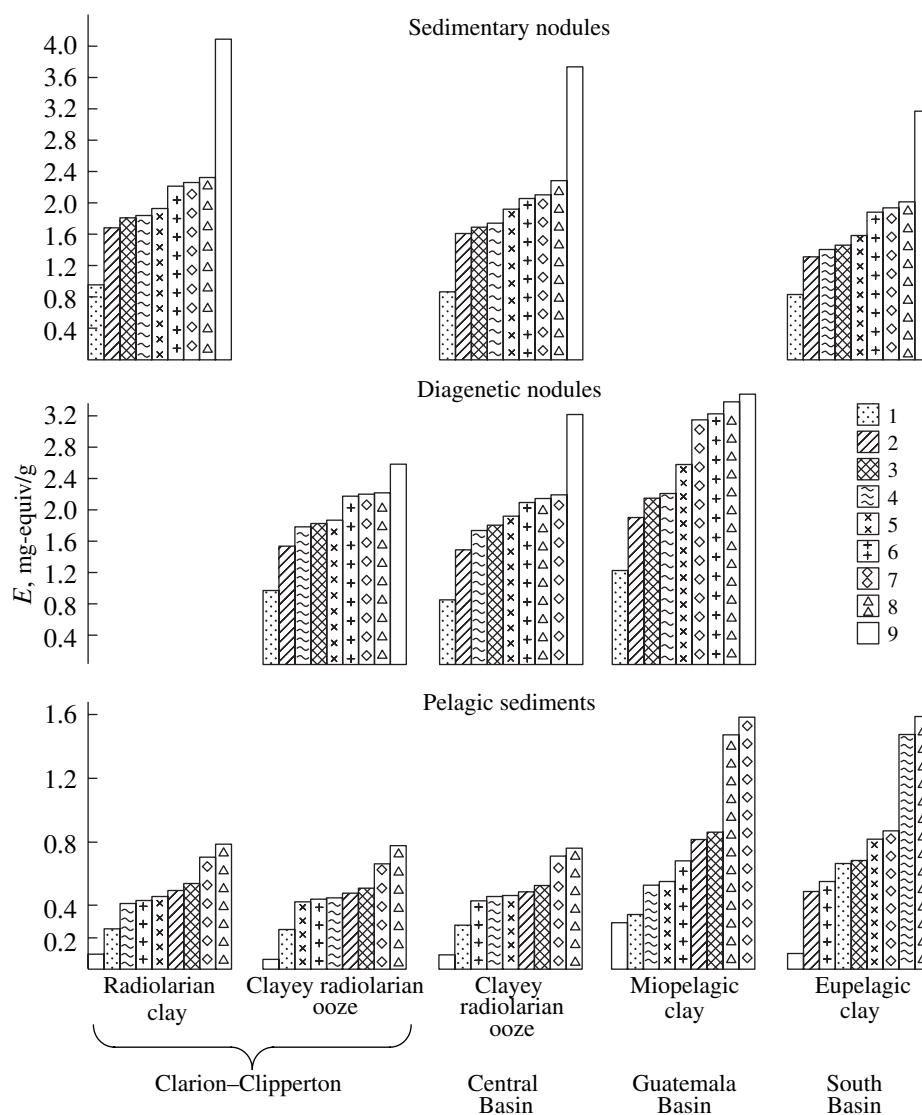


Fig. 8. Exchange capacity of manganese minerals in nodules and clay minerals in nodule-hosting sediments. Sorbed metal ions: (1) Na, (2) Ni, (3) Zn, (4) Cd, (5) Mn, (6) Co, (7) Cu, (8) Pb, (9) Mo.

that can be compensated by nonstructural exchange cations mainly located on basal planes of clay mineral particles. Rupture of chemical bonds in tetrahedral and octahedral layers of crystals in clay minerals can produce hydroxyl groups on their lateral edges. Hydrogen of the hydroxyl groups can provoke cation exchange reactions under certain thermodynamic conditions of the environment. Our original data indicate that different metal cations (Na^+ , Ca^{2+} , Cu^{2+} , Co^{2+} , and others) probably occupy the same positions in minerals. However, energy of the chemical bond of these cations with the major elements of the mineral structure is low. Therefore, they can easily participate in ion exchange reactions.

Mechanism of the sorption of metal cations by manganese minerals of nodules is governed by the nature of cations and their arrangement in the structure of specified minerals. Cations of alkali and heavy metals

occupy different sorption-active positions in the manganese minerals of nodules (Chukhrov et al., 1989). This is consistent with variable strength of the bond of sorbed cations with the major elements in mineral structure. Under certain physicochemical constraints, the crystal chemistry of manganese minerals and their affinity with a specified metal cation foster the complete or partial translation of the sorbed metal cation (Na, K, Ca, Mg, Ni, Cu, Zn, and others) to the solution or its chemically bonded form in the specified crystallochemical position of a mineral (Co^{3+}). Like clay minerals of sediments, manganese minerals absorb alkali metal cations according to the ion exchange mechanism characterized by the equivalent reversible sorption, while the sorption of heavy metal cations is accomplished by a complex mechanism in several stages: the equivalent ion exchange (for all metal cations) and the

Table 8. Coefficients of FMN enrichment with metal cations (relative to enclosing sediments) after sorption

Region	Sedi- ment type	Mineral composition of nodules	Sorbed metal cation									
			Mn	Ni	Co	Cu	Zn	Cd	Pb	Mo	Na	K
Guatemala Basin	MC	Bs I, B	4.85	2.49	4.78	2.00	2.48	4.06	2.05	12.2	3.14	3.65
Clarion–Clipperton ore province	CR	Bs I, A-bs (B, Bs II, V)	4.18	3.19	5.07	3.16	3.53	4.00	2.92	42.6	3.46	3.80
	RC	Fe-V, Mn-F (Bs I, A-bs)	3.78	3.04	4.72	3.18	3.00	3.83	2.70	45.0	3.19	3.44
Central Basin	CR	Fe-V, Mn-F (A-bs, B)	4.00	3.27	5.10	3.00	3.17	3.75	3.00	46.3	2.93	3.22
South Basin	ECZ	Fe-V, Mn-F	2.00	2.70	3.37	2.18	1.89	1.37	1.40	34.2	1.30	1.24

Note: Legends of sediment types and manganese minerals are as in Tables 3 and 4.

superequivalent partial reversible (not more than 15%) sorption of heavy metal cations (Cu, Co, Pb) relative to cations of the exchange complex of minerals (Chelishchev et al., 1992). Subsequently, depending on the type of sorbed metal cation, one can see either the hydrolytic precipitation of cations (Ni^{2+} , Co^{2+}) in the interlayer space of manganese minerals leading to the formation of the newly formed asbolane (Novikov et al., 2005) or the replacement by the preliminarily sorbed Co^{2+} and Pb^{2+} (subordinate component) cations in the structure of minerals in accordance with the solid phase oxidation–reduction reaction (Morozov et al., 2001). These specific features of manganese minerals provide insight into the high reactivity of alkali metal cations and rate of their exchange with any other gegenion, whereas heavy metals virtually do not exchange cations with the alkaline and alkaline earth metals. Manganese minerals demonstrate selectivity to certain cation(s) of metals (primarily, Cu^{2+} , Pb^{2+} , and Co^{2+}) during the interexchange of heavy metal cations.

ROLE OF ION EXCHANGE REACTIONS IN PROCESSES OF FERROMANGANESE MINERAL FORMATION

Our original data on ion exchange properties of manganese minerals and the available hypotheses of their formation make it possible to explain why the manganese minerals do not realize all of their sorption potentials in the oceanic environment.

Realization of the process of sorption requires the fulfillment of the following two obligatory conditions. First, the ocean water should contain reactive forms of element at the contact with unaltered manganese and iron phases (at the initial stage of nodule formation) or with nodules developed to a certain extent. Second, the rate of delivery of these phases to the reaction zone is limited by the radius of hydrated gegenions, the dimension of which virtually does not exceed 10 Å. This parameter is likely the major factor governing the initiation of ion exchange reaction.

Sorption of metal cations from the ocean water begins immediately after the formation of manganese oxide (hydroxide) phases and continues over the whole period of nodule growth irrespective of their mineral composition and genetic type. At the initial stage of the formation of manganese minerals, the degree of their crystallochemical perfection is low and the structure of minerals probably plays the crucial role. This is suggested by experimental data on the sorption of heavy metal cations on the newly formed low-temperature manganese oxides (hydroxides) represented by different phases: layered poorly or slightly ordered Fe-free vernadite, buserite I, birnessite, asbolane-type phase, tunnel cryptomelane, and hausmannite (tetragonal-distorted type of normal spinel) (Morozov et al., 2001; Novikov et al., 2005, 2006). Sorption activity of these phases increases in the following series: cryptomelane < hausmannite < asbolane-type phase < birnessite < vernadite < buserite I. This case shows complete analogy with the natural manganese minerals of nodules, the exchange capacity of which increases from minerals with well ordered tunnel structure (todorokite) to minerals with disordered layered structure (vernadite, buserite I).

Interaction of the newly formed manganese phases, which entrap Na, K, Ca, and Mg cations in the course of precipitation, or the nodules of various mineral compositions and ocean water fosters the ion exchange reaction. Consequently, exchange cations of manganese minerals are transferred to water, while heavy metal cations contained in the water are absorbed. This is confirmed by data on the sorption of metal cations from model solutions of ocean water and data reported in (Novikov, 1985). Kinetic parameters of the sorption of cations of alkali (Na, K, Cs) and heavy (Cu, Ni, Co, Zn, Cd, Pb) metals testify to the virtually similar mode of exchange reactions on the buserite, vernadite, and birnessite nodules (Novikov, 1998; Chelishchev et al., 1992). Irrespective of the mineral composition of nodules, time required for the ion exchange equilibrium of alkali metal cations is 3–6 h in 0.0001–1.0 N solutions; for heavy metal cations, 2.0–4.5 days in 1.0–0.001 N

solutions and 3.5–6.5 days in 0.0001 N solutions. High rates of exchange reactions in manganese minerals suggest that the ion exchange equilibrium should be achieved instantly (in the geological time scale) if the nodule grains have a small dimension, on the one hand, and the concentration of heavy metal cations in ocean water is negligible, on the other hand. Obviously, nodules could be enriched in the heavy metal cations in accordance with their capacity parameters only if such cations are constantly delivered to the exchange reaction microzone. However, this process is not observed under natural conditions owing to several reasons.

The sedimentary growth mechanism of nodules, like the sorption of metal cations by them, depends on several factors. According to (Cronan, 1980), the velocity of bottom currents and the character of bottom waters are among such factors. In other words, nodules can grow only if the bottom water is constantly furnished with new portions of solution at the contact with nodules. According to (Baturin et al., 1991), the daily mean velocity of bottom currents is 5–8 cm/s. Dynamic experiments performed under the constant inflow of fresh portions of solution through a column filled with nodules demonstrated that heavy metal cations are completely (nearly 100%) extracted from the multi-component solution at the solution inflow rate equal to $1.65\text{--}1.80 \times 10^{-3}$ cm/s. Comparison of rates shows that the experimental sorption rate is three orders of magnitude lower than the velocity of bottom currents. Hence, the newly formed manganese phases or minerals of growing nodules extract an insignificant amount of heavy metal cations from the boundary layer of bottom water.

Relative to the bottom water, the interstitial water is virtually immobile. Therefore, the latter can remain in contact with the nodule surface for a much longer time. Consequently, heavy metal cations can be absorbed more intensely by manganese minerals of diagenetic nodules. The sorption of heavy metal cations in the course of the diagenetic growth of nodules depends, in particular, on their diffusion flux from the interstitial water into the layer of semiliquid active sediment. Manganese minerals of nodules and micronodules form on the surface and in the thin subsurface zone of such sediments. Heavy metal cations can also be delivered to the interstitial water from clayey minerals of sediments. Results presented above concerning desorption of heavy metal cations from sediments by the natural ocean water confirm this statement. The interstitial water is enriched with heavy metal cations as the result of its cation exchange reactions with the sediment-hosted clay minerals. The interstitial water should be depleted in heavy metal cations due to their sorption by manganese minerals of nodules during the subsequent interaction with the surface of nodules.

Density of sediment beneath the nodules is an important factor that can influence the intensity of sorption process during the diagenetic growth of nodules. For example, the highly porous clayey radiolarian ooze, which is developed, for example, in the Clarion–Clip-

perton ore province and can readily be rewashed by bottom waters, is favorable for the rapid delivery of new portions of interstitial water to the surface of nodules. However, the layer of semiliquid active mud represents a zone of not only the microbial and abiogenic decay of the major part of organic matter, but also the dissolution of biogenic carbonates (beneath the carbonate compensation depth) containing heavy metal cations. Dissolution of these components leads to enrichment of the interstitial water with heavy metal cations, which can subsequently be absorbed by manganese minerals of nodules according to the process described above. However, we should take into consideration the existence of various microorganisms that can absorb the dissolved forms of metal cations from the ocean water and, thus, serve as biosorbents, which compete with manganese minerals of nodules.

As was shown in (Chelishchev et al., 1992; Gribanova and Kuklina, 1987; Novikov, 1985; and the present work), manganese minerals of nodules are characterized by two types of sorption (collective and selective). Concentrations of heavy metal cations dissolved in the oceanic (particularly, bottom) water are extremely low, and they are probably subjected to collective sorption by the manganese minerals of nodules owing to the following reasons. First, the amount of sorbed cations (Cu, Ni, Co, and others) is appreciably smaller than that of exchange cations remaining in the nodules (Na, K, Ca, and Mg). Second, the degree of growth and crystallization of manganese and ferromanganese minerals in microlayers of nodules is likely to increase more rapidly than the input of heavy metal cations from ocean water into the exchange reaction microzone; i.e., a large number of sorption-active centers is created in minerals. At the same time, this process should not provoke the complete termination of sorption, because the ocean water will continue to percolate in the nodules owing to their high porosity (Novikov, 1996a).

The selective sorption of metal cations may take place only during diagenesis owing to higher concentrations of elements in the interstitial water relative to the bottom water. This process can also be promoted by a more prolonged interaction between the interstitial water and nodule surface relative to the sedimentary growth of nodules. At the same time, appreciable variations in concentrations of components in solutions (Table 6) can lead to different degrees of sorption by manganese minerals. The selective sorption of metal cations is marked by specific behavior of Co. Its extraction from manganese minerals of nodules does not exceed 10%. Cobalt transferred to solution is represented by the bivalent variety, whereas the remaining portion of this element enters octahedral layers of manganese minerals and naturally does not take any part in exchange reactions.

The process of sorption of heavy metal cations by manganese minerals of nodules can be influenced by forms of their occurrence in ocean water. It is known that heavy metals occur in the ocean water in both suspended and dissolved forms. The bottom and interstitial

waters contain metals mainly in the dissolved form, such as free hydrated cations (M_{aq}^{2+}), positively charged chloride and hydroxyl complexes ($MeCl^+$, $MeOH^+$), neutral carbonate complexes ($MeCO_3$), and metalloorganic complexes (Baturin et al., 1986; Bruland, 1983; Demina, 1982; Pushkina et al., 1977; Shishkina, 1979). Free hydrated cations and chloride complexes of metal cations are most preferential for ion exchange reactions. However, Putilina and Varentsov (1986, 1987) have shown the principle possibility of the sorption of heavy metal cations by manganese hydroxides from the dissolved metalloorganic complexes.

CONCLUSIONS

Results of the experimental study of ion exchange properties of various manganese minerals in nodules and clay minerals in enclosing sediments from the Pacific abyssal pelagic zone suggest the following conclusions.

(1) Manganese minerals of nodules and clay minerals have ion exchange properties relative to cations of alkali, alkali earth, and heavy metals. The manganese minerals represent an ampholyte with cation and anion exchange properties, while the clay minerals are prominent cation exchangers.

(2) The exchange complex of various types of sediments is almost totally composed of the major cations of ocean water (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}). In addition, the exchange complex of manganese minerals also includes Mn^{2+} cations, which significantly enhances the exchange capacity of manganese minerals, particularly in diagenetic nodules. Exchange cations account for 90–95% in the total capacity of minerals in sediments and nodules. Both types of oceanic ionites are characterized by a single series of increase in the share of cations in the capacity of minerals:

$(Pb, Co, Zn, Cu, Ni) < (K < Mn^{2+} \sim Mg) < (Ca < Na)$.

The succession matches the series of increase in their reactivity.

(3) The exchange capacity of manganese minerals of nodules is at least 1.5–3 times higher than that of clay minerals from any type of nodule-enclosing sediments.

(4) Clay minerals are characterized by the equivalent reversible sorption of cations, which suggests that exchanged (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) and sorbed (Cu^{2+} , Ni^{2+} , Co^{2+} , and so on) metal cations occupy same positions in the minerals.

(5) Authigenic manganese minerals of nodules absorb alkali metal cations according to the ion exchange mechanism characterized by the equivalent reversible exchange, whereas heavy metal cations are absorbed in several stages: equivalent ion exchange and superequivalent, partly reversible (relative to exchange cations) sorption of heavy metal cations. Cations of alkali and heavy metals occupy different sorption-

active positions in manganese minerals. Therefore, heavy metals virtually do not exchange cations with alkali or alkali earth metals. In the case of their mutual exchange, the manganese minerals exhibit selectivity to certain metal ions (first of all, Cu^{2+} , Pb^{2+} , and Co^{2+}).

(6) Manganese minerals of diagenetic and sedimentary nodules are sharply undersaturated with heavy metal cations (especially, Cu , Ni , and Co) relative to their sorption capacities, probably, because of the deficit of dissolved forms of metals in the reaction microzone at the contact of growing nodules with the bottom (sedimentary nodules) or interstitial (diagenetic nodules) waters. Hence, the ore-grade concentration of heavy metals is primarily controlled by the rate and mechanism of the delivery of metal cations to the microzone of exchange reactions, modes of their occurrence in ocean water, and rate of nodule growth.

(7) Our experimental data indicate that ion exchange reactions play an important role in the oceanic ferromanganese mineral formation. At certain moment of time, the manganese (ferromanganese) minerals of nodules almost completely extract cations of heavy, rare, and other metals from the boundary zone of nodule surface. The metals are tightly fixed in the minerals and taken out from the process of further exchange reactions.

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