

Metal Cation Exchange Reactions of Ore Minerals in Fe–Mn Crusts of the Marcus Wake Rise (Pacific Ocean) in Aqueous–Salt Solutions

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Abstract—It is shown that the reaction ability of metal cations of ore minerals in Fe–Mn crusts of the Marcus Wake Rise increases in the following manner: $(\text{Co}^{2+} < \text{Cu}^{2+} < \text{Ni}^{2+}) < (\text{Mg}^{2+} < \text{Mn}^{2+} < \text{K}^+ \approx \text{Ca}^{2+} \approx \text{Na}^+)$. The composition of the exchange complex of the ore minerals is constant and includes these metal cations. Ca^{2+} and Na^+ are major contributors to the exchange capacity of the ore minerals. The capacity of the ore minerals by cations of alkali and base metals is 0.43–0.60 and 2.08–2.70 mg-equiv/g, respectively. The exchange capacity of the ore minerals by cations of base metals increases linearly with the increase in the MnO_2 content of the crust and does not depend on the geographical locations of the Marcus Wake guyots.

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At present, the Co-bearing Fe–Mn crusts (hereafter, crusts), which are abundant on seamounts of the World Ocean, are considered promising ore for Co, Ni, Cu, and Mn [1–3]. At the same time, it was established from the example of the crusts of the Magellan, Mid-Pacific, and Marcus–Necker Seamounts that they are natural highly selective sorbents for the metal cations indicated above [4, 5]. Study of them is topical, because Russia will continue geological exploration works for crusts in the northern sector of the Pacific Ocean in the next 10–15 years. The mode of occurrence of the crusts of the Marcus Wake Rise, their age, and mineral and chemical composition were studied previously [2, 3], whereas their physicochemical (in particular, sorption) properties were unknown. Thus, the task of our work is to study the behavior of metal cations of ore minerals of the crusts of the Marcus Wake Rise in ionic exchange reactions in order to assess their sorption properties.

The Datton (st. 12D215), Lawrie (st. 12D247), and Hemler (st. 12D263) guyots are located in the southwestern part of the rise, and the Batissa Guyot

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(st. 12D298, 12D301) is situated in its southern part. The surface of the Datton, Lawrie, and Batissa guyots is covered by the crusts, whereas that of the Hemler guyot is covered by crust–nodular aggregates. The crusts are platy and irregular; their transverse size varies from 10 to 30 cm, and the thickness is mostly 5–8 cm [3]. In spite of the different location of the crusts, their structure, texture, and mineral composition are similar, stable, and homogeneous. They are mostly composed of finely disperse and ultrafinely intergrown aggregates of poorly crystallized Mn and Fe minerals.

The crusts and crust–nodular aggregates were prepared for the study following the method of [6], which included crushing, grinding, sieving according to coarseness classes, washing of each class from the dust fraction, and drying at room temperature. In the experiments, we used the samples 0.25–0.10 mm in size.

The mineral composition of the crusts and crust–nodular aggregates was studied by electron microdiffraction on a JEM-100C transmitting electron microscope equipped with a goniometer (which provides an inclination of $\pm 60^\circ$) at an accelerating voltage of 100 kV. The major ore minerals of the samples are Fe-vernadite and Mn-feroxyhyte. Subordinate minerals include well crystallized vernadite and goethite; the amount of mixed-layer asbolane–buserite with a disordered structure is no more than 3–4%. All these minerals are finely intergrown, and their portion in the ore component of the samples is ~95%.

Table 1. Content (wt %) of elements of Co-bearing Fe–Mn crusts of the Marcus Wake Rise prior to and after sorption

Fe	Mn _{total}	Mn ²⁺	Co	Ni	Cu	Ca	Mg	Na	K	Mn/Fe
Datton guyot, Fe–Mn crusts, station 12D215, <i>n</i> = 13										
10.55	19.58	0.34	0.54	0.44	0.15	2.25	0.93	1.16	0.28	1.86
10.48	19.64	6.80	7.96	6.54	8.20	0.03	0.44	0.02	0.02	
Coefficient of enrichment		19.0	13.7	13.8	53.6					
Lawrie guyot, Fe–Mn crusts, station 12D247, <i>n</i> = 11										
12.33	21.04	0.41	0.62	0.41	0.13	1.66	0.82	1.22	0.27	1.70
12.42	20.88	7.23	8.48	6.93	8.65	0.02	0.40	0.02	0.02	
Coefficient of enrichment		16.6	12.7	15.9	65.5					
Hemler guyot, crust–nodular aggregates, station 12D263, <i>n</i> = 5										
12.54	18.77	0.52	0.60	0.41	0.12	2.20	0.84	0.88	0.24	1.50
12.42	18.92	6.71	7.67	5.98	7.94	0.03	0.41	0.02	0.02	
Coefficient of enrichment		11.9	11.7	13.6	65.2					
Batissa guyot, Fe–Mn crusts, station 12D298, <i>n</i> = 10										
11.16	20.34	0.44	0.57	0.43	0.15	2.42	0.92	1.36	0.26	1.82
11.13	20.44	7.12	8.23	6.77	8.45	0.02	0.42	0.02	0.02	
Coefficient of enrichment		15.2	13.4	14.7	55.3					
Batissa guyot, Fe–Mn crusts, station 12D301, <i>n</i> = 24										
10.84	19.85	0.36	0.58	0.42	0.12	2.30	0.87	1.18	0.31	1.83
10.77	19.73	6.90	8.15	6.62	8.23	0.03	0.43	0.02	0.02	
Coefficient of enrichment		18.2	13.0	14.7	67.6					

The first and second lines after the guyot title are the element content prior to and after sorption, respectively.

The chemical composition of the samples prior to and after the experiments was determined using atomic absorption analysis (AAA) on a Varian 220FS spectrometer. The air-dried samples were dissolved in a boiled mixture of concentrated solutions of HCl and H₂O₂ for 3–5 minutes using standard samples OOPE-604 (old name SDO-7, Fe–Mn crusts). The concentrations extracted from the solid phase of cations of alkali, alkali earth, and heavy metals were controlled by equilibrium solutions. The accuracy of determination of metal cations was 3–5 relative percent. The content of two valent Mn was analyzed by AAA after its extraction from an individual crust sampling by a 2-% H₂SO₄ solution [7] similarly to other metal cations.

According to the chemical analysis of the crusts and crust–nodular aggregates of the Marcus Wake Rise, they are hydrogenetic in origin: their Mn module (Mn/Fe ratio) is 1.50–1.86 (Table 1). The mean content (hereafter, content, wt %) of cations of base and lithogenic metals is stable and varies insignificantly: 0.54–0.62 Co_{total}(Co²⁺ + Co³⁺), 0.41–0.44 Ni²⁺, 0.12–0.15 Cu²⁺, 1.66–2.42 Ca²⁺, 0.82–0.93 Mg²⁺; 0.88–1.36 Na⁺, 0.24–0.31 K⁺ (Table 1).

The ionic exchange properties of ore minerals were studied following the recommendations of [6]. The metal cations were sorbed from aqueous chloride

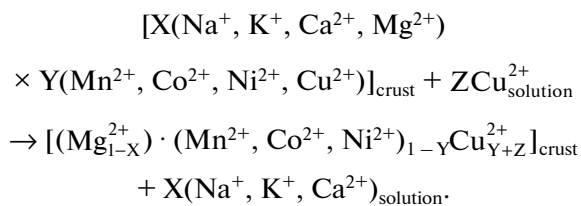
0.25–1.00 M/l solutions of Na⁺ and K⁺ salts and 0.25–0.50 M/l solutions of Co²⁺, Ni²⁺, and Cu²⁺ salts in the static regime at room temperature, with the proportion of liquid (L) and solid (S) phases of 100, and under constant mixing. The period of sorption of the cation forms of ore minerals (mineral assemblages) of the crusts and crust–nodular aggregates was 12–14 days, which, according to the previous experimental data on oceanic crusts [8, 9], was sufficient for ionic exchange equilibrium. The reproducibility of results in sorption experiments was 95–98%.

The interaction of crusts with aqueous chloride solutions of metal salts changes the chemical composition of their ore minerals (Table 1). A common differentiated reaction ability is established for the cations of alkali, alkali earth, and base metals. In exchange reactions between cations of alkali metals of solutions and cations of metals of ore minerals, there is a complete reversible transition of Na⁺ and K⁺ to solution: Na⁺_{solution} → K⁺_{crust} or K⁺_{solution} → Na⁺_{crust}. The degree of extraction of these cations from the minerals is 97.3–99.7%. The amount of Na⁺ and K⁺ extracted to the solution is almost constant. In addition, these cations insignificantly exchange with Ca²⁺, Mg²⁺, and Mn²⁺, the degree of extraction of which is ~18, 5, and 10%, respectively. The total extraction of Cu²⁺, Ni²⁺, and Co²⁺ from ore minerals is less than 3–4%.

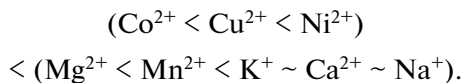
The interaction of the solutions of Co, Ni, and Cu salts with ore minerals leads both to preservation of the high reaction ability of Na⁺ and K⁺ and a significant increase in the reaction ability of Ca²⁺, Mg²⁺, and Mn²⁺. The content of Na⁺, K⁺, Ca²⁺, and Mg²⁺ in ore minerals after sorption of Co²⁺, Cu²⁺, and Ni²⁺ is hundreds of portions of a percent and 0.40–0.44 wt %, respectively (Table 1). The degree of extraction of Ca²⁺ from ore minerals is 97.8–99.5%. Na⁺, K⁺, and Ca²⁺ are extracted to the solutions irrespective of the sorbed cations of base metals, whereas extraction of Mg²⁺ and Mn²⁺ is affected by a sorbed metal cation. During sorption of Co²⁺ and Cu²⁺ and Ni²⁺ and Mn²⁺, Mg²⁺ is extracted to solutions by 52.0–53.5, 43.5–45.0, and 68.7–69.4%, respectively. Sorption of Co²⁺ and Cu²⁺ results in maximum extraction of Mn²⁺ to the solutions, the degree of extraction of which is 95.7–100% (73.4–76.7% during sorption of Ni²⁺). These results indicate a high reaction ability of Mn²⁺ in solutions of salts of base metals, which exceeds that of Mg²⁺.

Among the cations of base metals of ore minerals of the crust, the highest and lowest reaction ability is typical of Ni²⁺ and Co²⁺, the degree of extraction of which is 6–8 (during sorption of Cu²⁺ and Co²⁺) and 1–2%, respectively.

Thus, the following ionic exchange reactions are observed between the metal cations of minerals and cations of base metals of solutions (on example of Cu²⁺):



Our results allow the following series of increase in the reaction ability of metal cations of ore minerals of the crusts and crust–nodular aggregates:



Significant extraction of cations of alkali and alkali earth metals from ore minerals of crust–nodular aggregates is accompanied by intense sorption of Co²⁺, Cu²⁺, Ni²⁺, and Mn²⁺, the content of which in minerals increases up to a few percent by each. As a result of exchange reactions, the crusts and crust–nodular aggregates of the Marcus Wake Rise are significantly enriched in these metals: from 11.7 to 67.6 times by Co and Cu, respectively (Table 1).

The exchange capacity of ore minerals of the crusts by the cations of heavy metals is 2.08–2.70 mg-equiv/g (Table 2). In comparison, the capacity of minerals by Na⁺ and K⁺ is considerably lower:

Table 2. Mean values of exchange capacity (mg-equiv/g) of ore minerals of the crusts of the Marcus Wake Rise by metal cations

Guyot, number of station	MnO ₂ , wt %	Na ⁺	K ⁺	Mn ²⁺	Ni ²⁺	Co ²⁺	Cu ²⁺
Datton, 12D215	30.45	0.55	0.55	2.35	2.08	2.52	2.55
Lawrie, 12D247	32.63	0.54	0.53	2.50	2.22	2.67	2.70
Hemler, 12D263	28.87	0.44	0.46	2.25	1.90	2.40	2.46
Batissa, 12D298	31.48	0.60	0.59	2.43	2.16	2.62	2.65
Batissa, 12D301	30.85	0.57	0.58	2.38	2.11	2.57	2.60

This table presents data on the capacity after sorption of metal cations from 1 M solutions.

0.43–0.60 (0.54, on average) mg-equiv/g. The narrow range of capacity values of ore minerals by Na⁺ and K⁺ indicates that their sorption ability is almost constant and that the cations occupy strict positions in the structure of ore minerals. The series of increase in the exchange capacity of ore minerals of the crust is as follows:



The results of exchange reactions show that the composition of the exchange complex of ore minerals of the crust is constant and includes two (conditionally) groups of metal cations: main (Na⁺, K⁺, Ca²⁺, Mg²⁺, and Mn²⁺) and subordinate (Cu²⁺, Co²⁺, Ni²⁺, and probably, other cations of base metals too). The total contribution of major exchange metal cations to the capacity of minerals is 97.7–99.3% with the greatest portion of Ca²⁺ and Na⁺.

As a result of our studies, it was established that the exchange capacity of ore minerals by cations of base metals increases similarly with an increase in the MnO₂ content of the crust (Fig. 1). In addition, the capacity of the Fe–Mn crusts and crust–nodular aggregates within the range of indicated concentrations of the salt solutions of metals is almost constant: in comparison with the results given in Table 2, its values decreased by no more than 0.05–0.07 mg-equiv/g. The Fe and Mn contents of the products of cation exchange reactions are in the same range of values as in primary samples of the crusts and crust–nodular aggregates (Table 1), which indicates chemical stability of the ore minerals in these solutions.

The values of the exchange capacity of ore minerals of the crusts located in the southwestern and southern parts of the Marcus Wake Rise are close by the base metal cations and vary insignificantly (Fig. 2).

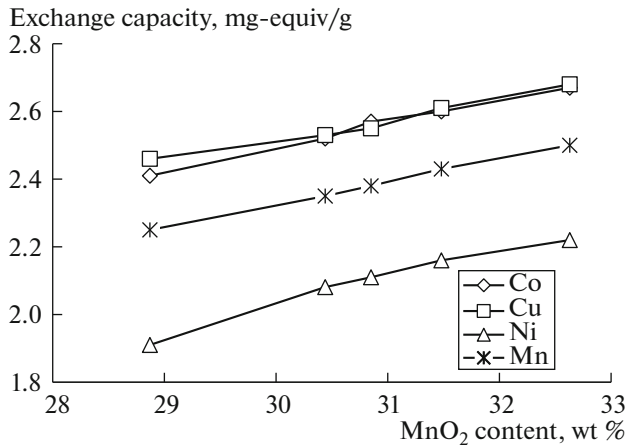


Fig. 1. Correlation between the exchange capacity of ore minerals by base metal cations and the MnO₂ content of crusts.

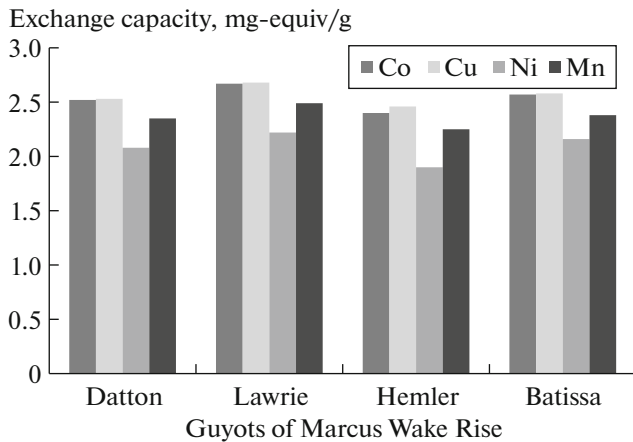


Fig. 2. Exchange capacity of ore minerals of the crusts of the Marcus Wake Rise by base metal cations.

The problem of the mode of occurrence of sorbed metal cations is also important. To solve this problem, the Co-, Cu-, and Ni-forms of crust samples from st. 12D215 (Datton guyot) and 12D298 (Batissa guyot) interacted with the same solutions, which were used for extraction of cation forms of minerals. Na⁺ and K⁺ (0.5 M chloride solutions) provide minor extraction of sorbed base metal cations to the solutions: the maximum degree of extraction is typical of Ni²⁺ (10.5%), whereas, for Co²⁺ and Cu²⁺, it is ~2.5%.

The reaction ability of sorbed base metal cations significantly increases during their mutual exchange. The exchange reaction $\text{Co}^{2+}(\text{Cu}^{2+})_{\text{solution}} \rightarrow \text{Ni}_{\text{sorbed crust}}^{2+}$ is characterized by more intense extraction of Ni²⁺ from the crusts, which are composed of Fe-vernadite and vernadite (st. 12D215) rather than from the crusts, which consist of Fe-vernadite, vernadite,

and asbolane–buserite (st. 12D298): 21.6–24.2 and 17.3–19.8%, respectively. A similar effect was previously determined for the crusts from the Magellan Seamounts [4] and synthetic Mn phases [10]. A low degree of extraction is typical of Co²⁺ (8.85–10.1%), and the highest extraction to the solution is observed during exchange with Cu²⁺. In turn, the Cu²⁺ exchanges with Co²⁺ and Ni²⁺ by 18.0–22.4 and 24.0–28.3%, respectively.

The high intensity and easy extraction of Na⁺, K⁺, Ca²⁺, and Mn²⁺ from ore minerals of the crusts to the metal salt solutions indicate their almost complete sorbed mode of occurrence in minerals. Co²⁺, Cu²⁺, Ni²⁺, and Mg²⁺ are characterized by sorbed and chemically bounded modes, and their extraction to the metal salt solution depends on the affinity of minerals to one metal cation or another, the sorbed metal cation, and crystal chemical features of ore minerals. Our data indicate that the ore minerals of the crusts and crust–nodular aggregates exhibit the greatest and least affinity to Co²⁺ and Ni²⁺, respectively.

The study of the crystal chemical features of ore minerals encounters certain difficulties. Now, the models of the structure are known only for vernadite, asbolane–buserite, and feroxyhyte [11]. Judging from these models, it can be suggested that Na⁺, K⁺, Ca²⁺, and (partly) Mg²⁺ occupy a disordered interlayer position in minerals, which are easily accessible for metal cations to ionic exchange reactions, whereas Mn²⁺, Co²⁺, Cu²⁺, and Ni²⁺ occupy the position of ordered interlayer cations and a vacant position in MnO₆ or FeO₆ octahedra. Our results are in agreement with these models of the structure of the ore minerals of the crusts.

Our experimental data indicate that the crusts and crust–nodular aggregates of the Marcus Wake Rise are natural ionic exchange substances, which explains the high Co²⁺, Cu²⁺, and Ni²⁺ content. Thus, it can be concluded that ionic exchange reactions play an important role in the process of oceanic Fe–Mn crust mineral formation. The high values of the exchange capacity of ore minerals by cations of base metals allow their consideration as a promising sorbent for the solution of technological and ecological tasks, especially because they are chemically stable compounds.

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REFERENCES

1. *Ferromanganese Crusts and Nodules of the Pacific Ocean Underwater Mountains*, Ed. by A. P. Lisitzin (Nedra, Moscow, 1990) [in Russian].
2. *Cobalt-Rich Ores of the World Ocean* (Gramberg All-Russ. Res. Inst. Geol. Miner. Resour. World Ocean, St. Petersburg, 2002) [in Russian].
3. M. E. Mel'nikov, *Deposits of Cobalt-Bearing Manganese Crusts*, (Federal State Unitary Geol. Enterprise State Sci. Center Yuzhmorgeologiya, Gelendzhik, 2005) [in Russian].
4. G. V. Novikov, S. V. Yashina, M. E. Mel'nikov, I. V. Vikent'ev, and O. Yu. Bogdanova, *Lithol. Miner. Resour.* **49** (2), 138–164 (2014).
5. G. V. Novikov, M. E. Mel'nikov, O. Yu. Bogdanova, and I. V. Vikent'ev, *Lithol. Miner. Resour.* **49** (1), 1–22 (2014).
6. G. V. Novikov, *Methods for Estimating Sorption Properties of the World Ocean Ferromanganese Sediments* (Granitsa, Moscow, 2005) [in Russian].
7. E. S. Bazilevskaya, *Ferromanganese Nodules of the Pacific Ocean Central Part* (Nauka, Moscow, 1986), pp. 238–250 [in Russian].
8. G. V. Novikov, *Theory and Practice of Sorption Processes* (Voronezh State Univ., Voronezh, 1998), pp. 141–158 [in Russian].
9. N. F. Chelishchev, N. K. Gribanova, and G. V. Novikov, *Sorption Properties of Oceanic Ferromanganese Nodules and Crusts* (Nedra, Moscow, 1992) [in Russian].
10. G. V. Novikov, L. N. Kulikova, O. Yu. Bogdanova, et al., *Russ. J. Inorg. Chem.* **50** (12), 1847–1855 (2005).
11. F. V. Chukhrov, A. I. Gorshkov, and V. A. Drits, *Supergene Manganese Oxides* (Nauka, Moscow, 1989) [in Russian].

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