

Transformations of Ore Minerals in Genetically Different Oceanic Ferromanganese Rocks

G. V. Novikov and O. Yu. Bogdanova

Shirshov Institute of Oceanology, Russian Academy of Sciences, Nakhimovskii pr. 36, Moscow, 117997 Russia

e-mail: novibog@ocean.ru

Received September 20, 2006

Abstract—Results of thermic transformations of ore minerals from genetically different oceanic ferromanganese rocks in the course of their heating up to 1000°C are considered. Manganese minerals with various types of crystalline lattice have different grades of thermic stability. Layered manganese minerals (buserite I, asbolane-buserite, and birnessite) are stable up to 120–150°C; asbolane up to 180°C; vernadite, up to ~500°C; todorokite and pyrolusite (minerals of the tunnel group), up to 600 and 670°C, respectively. Sorbed cations of heavy metals govern the transformation temperature and mineral composition of products of the calcination of ferromanganese rocks. Study of birnessite and todorokite demonstrated that genesis of ferromanganese rocks do not affect thermic properties of minerals in them.

DOI: 10.1134/S0024490207040013

By the beginning of the 20th century, researchers have accumulated a large body of mineralogical–geochemical data pertaining to the chemical composition of oceanic ferromanganese rocks. High contents of Ni, Cu, and Co in nodules and crusts suggest that these rocks can be considered raw material for nonferrous metals and manganese (ferromanganese). However, crystallochemical, physicomachanical, and mechanical features of ore minerals in these rocks are insufficiently studied.

Data on the behavior of manganese and iron minerals from oceanic ferromanganese rocks in aqueous solutions of electrolytes are presented in several publications (Chelishchev et al., 1991, 1992; Giovanoli, 1980; Golden et al., 1986; Gorshkov et al., 1992; Gribanova and Shatskaya, 1988; Gunneriusson, 1994; Lysyuk, 1991; Novikov, 1988, 1996; Novikov and Baturin, 1997; Novikov and Cherkashov, 2000; Novikov and Murdmaa, 2007; Novikov and Shatskaya, 1990; Novikov et al., 2006; Pivovarov, 2001, 2004; Pivovarov and Lakshtanov, 2003; Takematsu, 1979; Varentsov et al., 1988; and others). Results of these investigations show a significant chemical and structural stability of ferromanganese rocks in ion exchange reactions in the course of basic and acid treatments. Phase transformations of layered manganese minerals (buserite I, asbolane-buserite, birnessite, and vernadite) into each other in the reactions (Chelishchev et al., 1991, 1992; Gorshkov et al., 1992; Gribanova and Shatskaya, 1988; Novikov and Shatskaya, 1990; Novikov, 1996; Novikov et al., 2005) support previous theoretical conclusions about the similarity of these minerals (Chukhrov et al., 1989).

The thermic analysis provides new insight into the general picture of structural transformations of layered manganese minerals in oceanic nodules and crusts. The behavior of manganese minerals during heating depends on reducing processes accompanied by the release of oxygen. Phase transformations usually proceed in a wide temperature range. Identification of products of the calcination of nodules and crusts is hampered by the similarity of diffractometric characteristics of newly formed manganese and iron oxides. Moreover, data on the chemical composition of newly formed phases are absent. Therefore, data on the X-ray phase analysis can only suggest the prevalence of certain phases during their heating to more than 500°C.

The aim of the present work was to study thermic transformations of (a) ore minerals in genetically different ferromanganese rocks and (b) cationic products of ion exchange reactions in the course of successive calcination of rocks up to 1000°C.

EXPERIMENTAL

Characteristics of the initial material. We studied genetically different ferromanganese rocks (diagenetic and sedimentary nodules, crusts, crustal nodules, and low-temperature hydrothermal manganese crusts from different regions of the World Ocean). The mineral composition of the ferromanganese rocks is represented by the typical association of manganese minerals.

Diagenetic nodules contain the following typical minerals: buserite I, asbolane-buserite (samples 666-5, 2483-12, 19/t-1: Clarion–Clipperton ore province in the Pacific; sample 1352-30: Central Basin in the

Table 1. Contents of metal cations (wt %) in genetically different ferromanganese rocks

Station no.	Fe	Mn _{tot}	Mn ²⁺	Ni	Co	Cu	Zn	Pb	Mo	Cd	Ca	Mg	Na	K	Mn/Fe
Diagenetic nodules															
666-6	6.85	28.25	1.56	1.30	0.18	1.10	0.16	0.035	0.037	1.4	1.34	2.06	1.50	0.72	4.86
2483-12	5.52	26.16	1.47	1.24	0.20	1.06	0.12	0.035	0.037	1.4	1.36	1.88	1.47	0.74	4.74
19/t-1	4.56	26.80	1.65	1.08	0.22	1.05	0.14	0.060	0.045	4.0	1.45	1.75	1.81	0.72	5.88
19/t-2	4.76	28.40	1.75	1.22	0.20	0.96	0.12	0.060	0.038	3.0	1.34	1.68	1.76	0.78	5.98
2520-25/2	6.63	21.90	0.87	0.98	0.10	0.66	0.041	0.054	0.022	1.7	0.97	1.50	1.22	0.35	3.35
6A-124-2	7.42	24.82	1.12	1.21	0.038	0.46	0.071	0.048	0.048	1.5	1.30	1.54	1.83	0.35	3.34
3852-1	4.26	37.60	1.82	0.80	0.024	0.47	0.24	0.0057	0.018	1.5	1.88	2.23	2.38	0.86	8.83
3857	1.36	40.86	1.86	0.67	0.016	0.40	0.25	0.013	0.025	1.6	1.06	2.44	2.10	0.55	30.0
1352-30	4.24	26.90	1.52	1.20	0.16	1.43	0.19	0.048	0.038	1.0	1.05	2.15	1.24	0.64	6.34
1370-1.5	4.66	34.88	1.72	1.30	0.10	1.14	0.14	0.042	0.056	2.6	1.94	2.16	1.68	0.82	7.48
6742-13	5.67	26.38	1.30	0.94	0.15	0.98	0.16	0.086	0.032	2.2	1.44	1.52	1.48	0.43	4.41
Sedimentary nodules															
2520-17	9.30	17.96	0.41	0.65	0.28	0.47	0.065	0.057	0.018	1.5	1.32	1.26	1.85	0.71	1.93
6298-56	15.34	15.61	0.48	0.28	0.48	0.44	0.15	0.18	0.032	1.4	0.94	1.27	1.56	0.33	1.02
6754-5	11.55	17.00	0.35	0.51	0.22	0.36	0.092	0.071	0.022	1.3	1.82	1.60	1.64	0.46	1.47
43-63	19.00	16.95	0.26	0.42	0.40	0.18	0.054	0.060	0.036	11.0	1.03	1.15	1.84	0.45	0.90
Sedimentary crusts and crustal nodules															
9-124	10.50	17.85	0.38	0.45	0.56	0.13	0.044	0.18	0.041	2.6	1.66	0.82	0.78	0.24	1.70
11-298	11.16	17.95	0.36	0.43	0.48	0.15	0.064	0.19	0.038	2.5	4.00	0.92	1.27	0.26	1.61
9-77	10.90	17.06	0.36	0.38	0.48	0.14	0.044	0.17	0.034	1.8	2.28	0.72	0.85	0.29	1.64
Low-temperature hydrothermal manganese crusts															
285-1	0.56	39.60	1.08	0.025	0.017	0.023	0.084	0.0080	0.0010	1.4	2.04	1.40	2.58	0.40	70.7
415-2	3.33	42.30	1.62	0.30	0.067	0.067	0.042	0.043	<0.0010	<1.0	2.13	2.02	1.75	0.90	12.70
415-4	2.45	56.20	0.082	0.051	0.017	0.097	0.018	0.028	<0.0010	<1.0	1.05	0.58	0.85	0.20	20.50

Note: The Cd content is given in ppm.

Indian Ocean; sample 6742-13: East Indian Ridge); asbolane-buserite, birnessite (sample 19/t-2: Clarion-Clipperton ore province; sample 2520-25/2: Central Basin of the Pacific); buserite I, birnessite (samples 6A-124-2, 3857: Peru and Guatemala basins, respectively, in the Pacific; sample 1370-1.5: Central Basin in the Indian Ocean); todorokite, asbolane-buserite (sample 3852-1: Guatemala Basin). The nodules contain the following admixtures: birnessite, buserite II, todorokite, and Fe-free vernadite.

Sedimentary rocks are mainly composed of Fe-vernadite and Mn-feroxyhyte. Sedimentary nodules were taken from the Pacific (samples 2520-17, 6298-56: Central and South basins, respectively), Indian (sample 6754-5: West Australian Basin), and Atlantic (sample 43-63: Brazil Basin) oceans. Crusts (samples 9-124, 11-298) and crustal nodules (sample 9-77) were taken from the Magellan Mountains of the Pacific.

Low-temperature hydrothermal manganese crusts were taken from the East Pacific Rise (sample 285-1, nearly 100% birnessite) and the East Indian

Ridge (sample 415-2, >90% todorokite; sample 415-4, pyrolusite). Table 1 presents their chemical compositions. These samples are typical for each morphogenetic type of ferromanganese rocks. Diagenetic nodules are characterized by high contents of Mn_{tot}, Mn²⁺, Ni, Cu, Zn, and Mo; sedimentary nodules, by high contents of Fe, Co, and Pb; and low-temperature hydrothermal crusts, by very low contents of all cations of heavy metals.

It was shown in (Chelishchev et al., 1991; Novikov, 1996; Novikov and Baturin, 1997; Novikov and Murdmaa, 2007; Novikov et al., 1995, 2005, 2006) that exchange reactions between metal cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, and Mn²⁺) in ore minerals of ferromanganese rocks and metal cations (Cu²⁺, Co²⁺, Ni²⁺, and others) in solutions yield cationic forms of these minerals (Cu-, Co-, Ni-rich species, and others) used in the present communication. Contents of sorbed metal cations in respective mineral species (Table 2) are much higher than their contents in initial samples of ferromanganese rocks, except for the low-temperature

Table 2. Contents of metal cations (wt %) in respective cationic forms of ore minerals in ferromanganese aggregates ($C_{\text{sol}} = 1 \text{ N}$; $T = 20^\circ\text{C}$)

Sample no.	Sorbed metal cation												
	Na	Cs	Sr	Y	Ni	Zn	Cd	Co	Cu	Ba	Pb	Mo	W
666-5	3.61	12.2	6.56	4.65	5.85	6.18	10.2	6.60	8.03	15.2	22.8	4.30	2.80
2483-12	3.20	12.0	5.95	4.27	5.85	5.87	9.73	6.23	7.86	14.8	22.5	3.92	2.13
19/t-1	4.04	12.5	5.83	4.44	6.02	5.96	9.90	6.11	7.84	14.9	22.5	4.10	2.45
19/t-2	3.87	12.0	5.40	3.70	4.98	4.17	6.75	4.26	6.60	9.77	14.9	1.75	2.15
2520-25/2	3.22	11.2	4.86	3.46	4.33	3.70	6.20	3.66	5.60	8.74	13.8	1.4	1.96
6A-124-2	4.08	12.6	6.58	–	6.55	6.60	11.6	8.17	8.80	17.4	26.3	4.58	–
3852/1	4.86	13.5	2.40	–	3.38	2.95	3.78	3.73	5.17	8.70	13.3	0.90	–
3857	4.74	16.3	7.92	5.77	6.42	6.80	10.9	9.43	10.3	20.7	32.3	5.33	2.94
1352-30	3.10	10.4	5.82	4.38	5.78	5.68	9.33	5.61	7.57	12.7	19.4	3.21	2.67
1370-1.5	4.21	14.0	7.58	5.62	7.05	7.04	11.9	8.76	10.3	20.5	31.4	5.19	2.82
6742-13	3.73	12.6	6.12	4.40	5.55	5.85	9.95	6.10	7.66	14.3	21.4	4.14	2.40
2520-17	3.81	10.6	6.30	4.85	5.33	5.62	9.45	6.50	7.27	15.5	23.6	5.96	3.52
6298-56	3.56	10.4	5.38	4.33	4.33	5.19	8.22	6.00	6.80	13.2	20.2	5.28	3.22
6754-5	3.69	11.0	6.35	4.82	5.32	5.70	9.84	6.35	7.36	14.8	22.3	5.68	3.40
43-63	4.23	12.9	5.40	4.66	4.44	5.05	8.37	6.14	6.54	14.2	21.8	5.57	3.44
9-124	2.48	9.30	7.00	5.21	5.58	6.20	10.8	6.90	6.87	15.1	23.3	7.72	3.77
9-77	2.73	10.2	6.80	5.04	5.37	6.06	10.7	6.60	6.56	14.4	22.1	7.76	3.62
11-298	3.15	10.4	7.25	5.33	6.40	6.27	11.7	8.00	9.18	18.8	29.8	8.52	3.84
285-1	5.52	–	–	–	8.30	9.07	13.9	12.6	11.1	21.0	33.7	5.45	–
415-2	3.68	–	–	–	2.88	2.60	3.15	2.84	4.65	–	9.78	0.77	–
415-4	1.82	–	–	–	0.84	0.97	1.12	0.76	1.56	–	4.70	0.26	–

Note: (–) no data.

hydrothermal crust (sample 415-4) composed of pyrolusite. Among all associations of manganese minerals, this sample has the lowest absorption capacity for metal cations.

Thermic investigations of ferromanganese rocks were carried out with a MOM-102 derivatograph (rate of sample heating $10^\circ/\text{min}$). At maximal temperatures of endothermic and exothermic effects recorded on DTA curves, the rock samples were additionally heated for 2 h. Calcination products of natural products and their cationic forms were identified by the TEM method using a JEM-100C electron microscope equipped with goniometer and energy-dispersive KEVEX-5100 device (Laboratory of Crystal Chemistry, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Moscow) and the X-ray powder diffraction method (DRON-2, CuK_α , monochromatized beam, 40 kV, 30 mA, scanning rate $1^\circ/\text{min}$). In order to determine the content of metal cations in the oceanic ferromanganese rocks, their cationic forms, and calcination products, the weighed samples were decomposed in a mixture of concentrated $\text{HCl} + \text{H}_2\text{O}_2$ solutions in the course of boiling for 5–7 min. Concentra-

tions of metal cations in respective solutions were determined by the flame atomic absorption method (Perkin-Elmer 503, Analytical Laboratory of the Shirshov Institute of Oceanology, Moscow).

RESULTS

Thermic investigations revealed that **diagenetic nodules** composed of various associations of layered manganese minerals are characterized by monotype character of reactions. Their DTA curves show a number of endothermic effects with maximums at 120–150, 210–230, 400–415, and 590–600°C (Fig. 1). Results of investigations are given in this paper with sample 19/t-1 as example. Relative to nodules composed of busserite I and asbolane-busserite, DTA curves of nodules composed of busserite I and birnessite or asbolane-busserite and birnessite are characterized by slightly more intense maximums of endothermic effects at 130–140 and 215–230°C. The endothermic effect at 120–150°C is related to the thermic dehydration of busserite I and its transformation into birnessite. It should be mentioned that, according to (Chukhrov et al., 1989), busserite I is recognized at 100–110°C. The greatest losses of mass

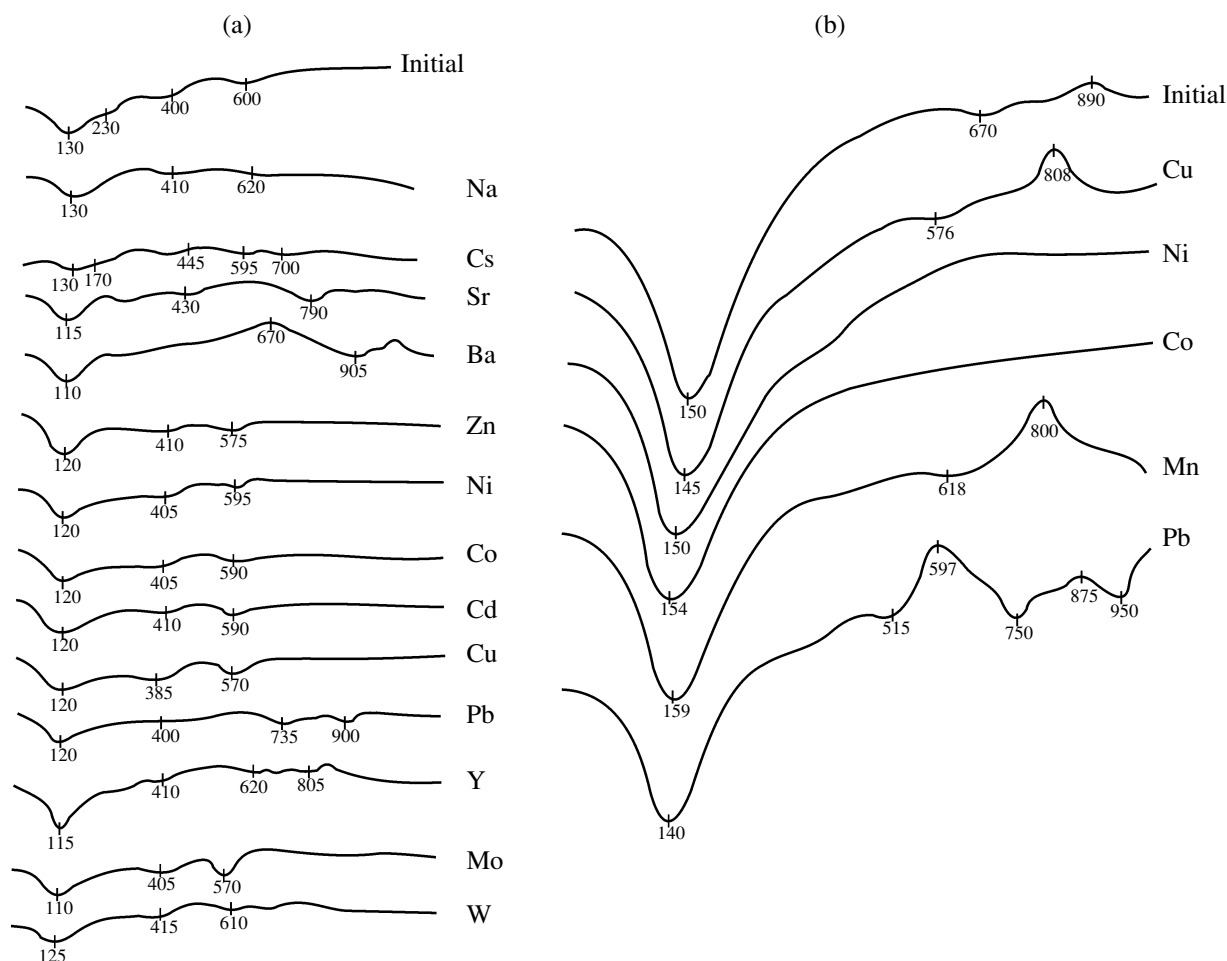


Fig. 1. DTA curves. (a) Diagenetic nodules with busenite I, asbolane-busenite (sample 19/t-1); (b) sedimentary crusts with Fe-vernadite, Mn-feroxyhyte (sample 9-124) and their cationic forms.

corresponding to loss of interlayer water are recorded at these temperatures (Table 3).

Thus, busenite I in the diagenetic nodule sample shows a weak thermic stability. However, issue of reversibility of this phase transformation is not discussed in (Chukhrov et al., 1989) devoted to identification of busenite I. Previous experiments (Chelishchev et al., 1991) demonstrated that the busenite I–birnessite phase transformation is an irreversible process, because birnessite is not recovered after its treatment with water ($T \sim 80^\circ\text{C}$) and aqueous solution of tetramethylammonium bromide (TMABr), which is dissociated in water into a large TMA^+ cation and Br^- . However, this treatment changes significantly the diffraction image of the basal reflection of birnessite with $d = 7.20 \text{ \AA}$: the diffuse weak maximum becomes prominent, testifying to the formation of the well-developed mineral crystal. After heating under temperatures mentioned above, the nodules are composed of birnessite (major component) and asbolane. Thus, we obtained effect analogous to that recorded during the reaction of nodules with solutions of mineral acids (Chelishchev et al., 1991), sug-

gesting similar nature of the given phase transformation.

In contrast to busenite I, the asbolane constituent of the mixed-layer asbolane-busenite remains stable at the given calcination temperature. At 175°C , oceanic nodules composed of busenite I and asbolane-busenite (sample 19/t-1) and asbolane-busenite and birnessite (sample 19/t-2) were additionally calcined. Analysis of their calcination products showed that the asbolane phase is absent in sample 19/t-1 and is preserved in sample 19/t-2 (Table 4). Hence, decomposition of asbolane probably depends on the degree of its structural ordering. At the same time, the DTA curve remains smooth. In calcination products of nodules at 230°C , we do not see birnessite formed at $\sim 100^\circ\text{C}$ (sample 19/t-1), birnessite of the initial sample 19/t-2, and asbolane remaining stable at 110 and 175°C . Instead, we only see vernadite, which is stable until $\sim 500^\circ\text{C}$. Endothermic effect in the $340\text{--}350^\circ\text{C}$ interval with maximum at 400°C is related to the removal of water from vernadite.

Table 3. Phase composition of diagenetic nodules and their cationic forms at different calcination temperatures

Cationic form of nodules	Association of prevalent minerals at 20°C	Total hydrothermal manganese crusts weight loss, wt %	Temperature of the onset and termination of thermochemical reaction, °C						Mineral composition at 1000°C	Content of metal cations (wt %) at			
			30–200		200–270		340–450			530–660		20°C	1000°C
			weight loss, wt %	major mineral phase at 130°C	weight loss, wt %	major mineral phase at 230°C	weight loss, wt %	major mineral phase at 400°C		weight loss, wt %	major mineral phase at 590°C		
Initial (sample 19/t-1) Na Zn Ni Co Cu Cd Pb	Bs I, A-bs (B)	26.40	12.15	B, A	4.00	V	2.00	V	M	Mn—26.80 Fe—4.56	Mn—40.55 Fe—6.08		
	Bs I, A-bs (B)	26.25	12.63	B, A	—	V	2.15	V	M	4.04	4.40		
	Bs I, A-bs (B)	25.00	16.82	B, A	—	V	2.50	V	J, Bb	6.15	6.50		
	Bs I, Ni-A (B)	25.57	14.07	B, Ni-A	—	V	3.00	V	M	5.72	6.12		
	Bs I, Co-A (B)	24.08	15.06	B, Ni-A	—	V	2.80	V	J, Bb	6.10	6.56		
	Bs I, A-bs (B)	23.62	13.55	B, A	—	V	2.95	V	M, Bb	7.85	9.67		
	Bs I, A-bs (B)	24.55	16.55	B, A	—	V	2.30	V	M, J, Bb	9.90	11.92		
	Bs I, A-bs (B)	19.05	12.04	B, A	—	V	0.40	V	Cr	22.54	6.70		
	Bs I, B	27.70	16.44	B	1.33	V	1.75	V	Bb, J	Mn—40.86 Fe—2.04	Mn—62.20 Fe—2.95		
	Bs I, B	27.44	16.75	B	0.80	V	2.00	V	Bb, J	4.74	5.10		
Initial (sample 3857) Na Zn Ni Co Cu Cd Pb	Bs I, B	26.20	19.40	B	—	V	2.45	V	Hr, (J)	6.80	7.10		
	Ni-A, B	27.25	18.30	Ni-A, B	—	V	2.75	V	Bb, (J)	6.42	6.94		
	Co-A, B	26.00	18.55	Co-A, B	—	V	2.50	V	Bb, (J)	9.46	10.15		
	Bs I, B	25.75	18.20	B	—	V	2.75	V	Bb, J	10.33	12.10		
	Bs I, B	26.45	19.25	B	—	V	2.30	V	Bb, J	10.96	12.66		
	Bs I, B	21.30	16.15	B	—	V	0.65	V	Cr	32.33	33.10		
	A-bs, B	27.10	14.85	A, B	5.60	V	2.40	V	J	Mn—28.40 Fe—4.76	Mn—42.20 Fe—6.40		
	A-bs, B	27.00	15.05	A, B	5.25	V	2.65	V	J	3.87	4.25		
	A-bs, B	25.65	17.20	A, B	2.30	V	2.87	V	J, Bb	3.52	3.90		
	Ni	26.20	15.55	A, B	3.60	V	3.26	V	M, Bb	4.83	5.15		
Initial (sample 19/t-2) Na Zn Ni Co Cu Cd Pb	A-bs, B	25.80	16.30	A, B	2.85	V	3.03	V	M, Bb	4.26	4.64		
	A-bs, B	25.55	15.15	A, B	2.60	V	2.47	V	M, Bb	6.27	7.90		
	A-bs, B	26.80	17.15	A, B	2.40	V	3.74	V	J, Bb	5.40	6.83		
	A-bs, B	19.65	14.65	A, B	0.73	V	0.50	V	Cr	14.87	15.04		

Note: (A) Asbolane; (A-bs) asbolane-buserite; (B) birnessite; (Bs I) buserite I; (V) vernadite; (Bb) bixbyite; (Br) braunite; (H) hausmannite; (Hr) heterolite; (K) krentolite; (Cr) coronadite; (M) magnetite; (Fr) franklinite; (J) jacobssite.

Table 4. Mineral composition of diagenetic nodules and their cationic forms after low-temperature calcination (up to 200°C)

Cationic form	Heating temperature, °C	Diagnostic peaks												Mineral composition
		<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>	
Initial (sample 19/t-1)	–	9.70	4	7.22	1	4.85	3	–		2.44	2	1.41	1	Bs I, A-bs, (B)
Calcined	110	9.43	2	7.13	3	4.74	2	3.57	2	2.45	2	1.42	1	B, A
	110; H ₂ O	9.20	2	7.22	2	4.75	1	3.60	1	2.44	2	1.41	1	B, A
	110; TMABr	9.20	2	7.17	4	–		3.58	2	2.44	2	1.41	1	B, A
	175	–		7.17	2	–		3.57	1	2.45	2	1.41	1	B
Cu	–	9.60	3	7.23	1	4.78	3	–		2.44	2	1.41	1	Bs I, A-bs, (B)
	110	9.43	2	7.10	3	4.76	2	3.58	2	2.44	2	1.41	1	B, A
	175	–		7.14	2	–		3.59	1	2.45	2	1.41	1	B
Ni	–	9.59	3	7.20	2	4.76	3	–		2.45	2	1.41	1	Ni-A, B
	110	9.40	3	7.14	2	4.73	3	3.56	1	2.44	2	1.41	1	Ni-A, B
	175	9.41	1	7.15	2	4.74	2	3.56	1	2.44	2	1.42	1	Ni-A, B
Co	–	9.55	3	7.18	2	4.78	3	–		2.45	2	1.41	1	Co-A, B
	110	9.35	2	7.14	2	4.72	3	3.56	1	2.45	2	1.42	1	Co-A, B
	175	9.38	1	7.20	2	4.75	2	3.57	1	2.46	2	1.41	1	Co-A, B
Initial (sample 19/t-2)	–	9.55	3	7.18	2	4.77	2	3.58	1	2.43	2	1.41	1	A-bs, B
Calcined	110	9.45	2	7.20	3	4.72	2	3.60	1	2.43	2	1.41	1	A, B
	175	9.40	2	7.16	3	4.70	2	3.58	1	2.42	2	1.41	1	B, A
Cu	–	9.52	3	7.17	2	4.76	2	3.60	1	2.43	2	1.43	1	A-bs, B
	110	9.45	2	7.18	3	4.73	3	3.59	1	2.42	2	1.41	1	B, A
	175	9.40	2	7.14	3	4.70	2	3.57	1	2.41	2	1.42	1	B, A
Ni	–	9.45	3	7.15	2	4.71	3	3.58	1	2.42	2	1.41	1	A-bs, B
	110	9.40	3	7.16	3	4.72	3	3.59	1	2.43	2	1.42	1	A, B
	175	9.40	2	7.20	3	4.71	2	3.60	1	2.44	2	1.41	1	B, A
Co	–	9.40	3	7.17	2	4.70	3	3.58	1	2.42	2	1.42	1	A-bs, B
	110	9.35	3	7.18	3	4.68	3	3.59	1	2.42	2	1.41	1	A, B
	175	9.38	2	7.15	3	4.69	2	3.57	1	2.43	2	1.42	1	B, A

Note: Abbreviations of minerals are as in Table 3.

Calcination of vernadite at more than 500°C is accompanied by its decomposition with the release of oxygen ($7\text{MnO}_2 \rightarrow 2\text{Mn}_2\text{O}_3 + \text{Mn}_3\text{O}_4 + 2\text{O}_2\uparrow$) and the formation of phases with the spinel-type structure. Identification of calcination products of nodules at high temperatures is rather difficult because of the formation of complex oxides of systems $\text{Mn}_2\text{O}_3\text{--Fe}_2\text{O}_3$ and $\text{Mn}_3\text{O}_4\text{--Fe}_3\text{O}_4$. Magnetite (FeFe_2O_4) formed in the 530–660°C interval (maximum at 600°C) is transformed into jacobsonite (MnFe_2O_4) at further heating to 1000°C (Table 3). Formulas presented above show that these minerals belong to the $\text{Mn}_3\text{O}_4\text{--Fe}_3\text{O}_4$ system, which is also composed of hausmannite and vredenburghite (intergrowth of jacobsonite and magnetite). Contents of Mn (40.55 wt %) and Fe (6.08 wt %) in the calcined nodules (sample 19/t-1) suggest that the terminal

product of thermochemical reaction of busserite nodules occurs as a phase dominated by manganese oxides, i.e., hausmannite (MnMn_2O_4). This is indirectly confirmed by data reported in (Rode, 1952), according to which hausmannite is the calcination product of all manganese minerals at a temperature of 900°C or more. However, the spinel-type manganese minerals, which form during the recrystallization of ore minerals of nodules at 500–1000°C, are probably weakly crystallized, whereas magnetite and jacobsonite are better crystallized. This is evident in diffractograms of nodules calcined at 600 and 1000°C. The results obtained are consistent with data reported in (Han et al., 1979; Ono et al., 1971; Van Hook and Keit, 1958), according to which the presence of Fe in natural and synthetic manganese oxides is responsible for the their transformation into the spinel-

type minerals at lower temperatures and the formation of complex ferromanganese compounds. Influence of the sorbed metal cation on the newly forming phases and temperature of their phase transformations are very important for understanding sequential alterations of manganese and iron minerals. This issue has become more urgent after the establishment of high chemical and structural stability of manganese minerals and their cationic products in aqueous solutions of electrolytes. Experiments with cationic forms of synthetic birnessite testify to the influence of sorbed metal cation on the mineral composition of its calcination products (Golden et al., 1986).

DTA curves of cationic forms of diagenetic nodules with different mineral compositions are generally similar to those of initial nodules. However, they show the following distinctive features (Fig. 1a). The interlayer water is removed from the cationic forms in one stage at 30–350°C. Study of the thermic behavior of Cu-, Ni-, and Co-rich species of manganese minerals during their calcination at 110 and 175°C revealed the following. Their diffractograms are analogous to those of initial busserite nodules (sample 19/t-1), but one can see a number of distinctions (Table 4). Diffractograms of all cationic forms of manganese minerals calcined at 110°C show a shift of the basal reflection with $d = 9.70 \text{ \AA}$ toward higher Θ values and variation in the intensity of major reflections depending on the sorbed metal cation. For example, the Cu-rich species is characterized by a drastic attenuation of reflections with $d = 9.43$ and $4.75 \text{ \AA}$, while the intensity of reflection with $d = 7.10 \text{ \AA}$ is drastically intensified. In contrast, the Ni- and Co-rich species show a weak reflection with $d = 7.12$ and $7.14 \text{ \AA}$. Intensity relationship of basal reflections I_{001} and I_{002} is shifted toward the second reflection similarly as in the case of unheated forms of these species (Chelishchev et al., 1991). As in the case of primary nodules, temperature rise to 175°C destroys the asbolane phase in the calcined Cu-rich species. In contrast, this phase is retained in the Ni- and Co-rich species. Birnessite also remains stable in all calcined cationic forms.

Thus, the comparative analysis of mineral compositions of calcined busserite nodules and their cationic forms showed that sorbed cations Ni^{2+} and Co^{2+} have a stabilizing influence on the Ni- and Co-asbolanes produced by ion exchange. Asbolane is the major mineral in calcination products of Ni- and Co-rich species. Other cations of heavy metals (Cu^{2+} , Zn^{2+} , and Cd^{2+}) do not have such impact upon manganese minerals.

As in the case of initial nodules, the endothermic effect at 530–660°C is related to the breakdown of minerals, the release of oxygen, and the consequent formation of complex manganese and iron oxides. This process is characterized by a specific DTA pattern of the Pb-rich variety of nodules. The curve lacks the endothermic effect at ~600°C, but includes two endothermic effects at 735 and 900°C accompanied by a slight loss of weight (Fig. 1a). The high content of Pb cations (25–

33 wt %) in calcination products of Pb-rich species affects the dissociation of manganese oxides. This is reflected in the shift of endothermic effects toward the higher-temperature region.

As in the case of initial nodules, issue of the identification of newly formed high-temperature phases deserves special attention. Identification of calcination products of cationic forms of manganese minerals is difficult, because one should take into consideration the content of not only Mn and Fe cations, but also sorbed metal cation. At high calcination temperatures, contents of oxides of heavy metals become very significant and range from 8.5 wt % NiO in the Ni-rich variety to 35 wt % PbO in the Pb-rich variety of nodules (Table 3). These oxides make up solid solutions with the major components of phases (manganese and iron oxides). In this case, the $\text{Mn}_3\text{O}_4\text{--Fe}_3\text{O}_4$ system is transformed into the more complex $\text{Mn}_3\text{O}_4\text{--Fe}_3\text{O}_4\text{--M}_x\text{O}_y$ system, where M_x are cations of heavy metals. Zinc is characterized by the following system (Mason, 1947): calcination products of the Zn-rich species are represented by franklinite (ZnFe_2O_4) and hetaerolite (ZnMn_2O_4); products of the Pb-rich species, by kentrolite ($3\text{PbO} \cdot 2\text{Mn}_2\text{O}_3 \cdot 3\text{SiO}_2$). The absence of reliable data on this class of oxides with Cu, Ni, Co, Cd, and other cations of heavy metals is related to the fact that calcination products of the respective cationic forms are identified as braunite ($\text{Mn}^{2+}\text{Mn}^{4+}\text{O}_3$) and magnetite. Most probably, manganese phases formed at 1000°C (with cations of heavy metals) have a structure close to that of braunite and hausmannite. One can also see an additional distinction: diffractograms of calcination products of all cationic forms of manganese minerals contain typical lines of both manganese and iron phases, whereas diffractograms of initial nodules mainly contain iron phases. This fact indicates a higher degree of crystallization and ordering of the structure of manganese minerals in the presence of cations of heavy metals.

Based on the hydrothermal acid treatment of busserite I (sample 19/t-1), we synthesized birnessite, more exactly, its hydrogenous variety H-f₁₁ (Chelishchev et al., 1991). Reproduction mechanism of this phase mimics to a certain extent the natural formation of low-temperature hydrothermal birnessite (Corliss et al., 1978; Lonsdole et al., 1980; Shterenberg et al., 1987). However, the chemically produced birnessite virtually lacks cations of Fe^{3+} and heavy metals, except cations of Co^{3+} located in octahedra of MnO_6 . Therefore, study of the behavior of synthetic birnessite and asbolane of initial nodules during their thermic treatment is of specific interest.

Relative to the generally similar diagenetic nodules composed of busserite I and asbolane-busserite (sample 19/t-1), the DTA curve of birnessite (H-f₁₁) is distinguished by the lack of endothermic effects at 230 and 400°C and the presence of an additional weak endothermic effect with maximum at 950°C. Endothermic

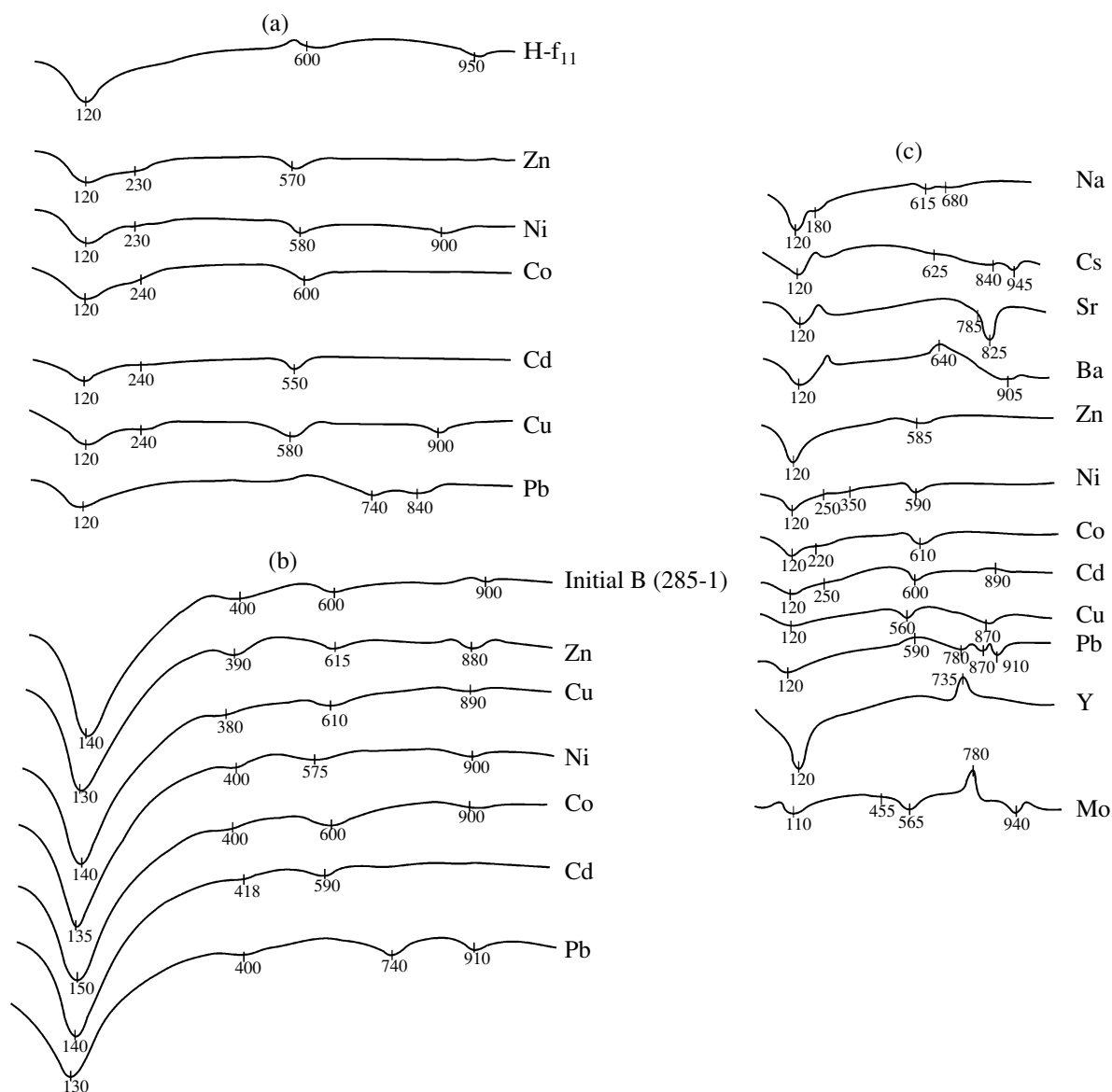


Fig. 2. DTA curves. (a) Acid modified (H-f₁₁) and (b) acid-alkali modified (Na-f) nodules with birnessite and asbolane; (c) low-temperature hydrothermal birnessite (sample 285-1) and their cationic forms.

effects at 120 and 600°C are retained in H-f₁₁ as in the initial sample (Fig. 2a). The chemically obtained birnessite has a weak thermic stability. At 120°C, it is transformed into vernadite that becomes the major phase in the calcined H-f₁₁. Asbolane, a stable phase in hydrosulfuric acid solutions (Chelishchev et al., 1991), is transformed into birnessite (Table 5). The theoretical substantiation of this transformation is given in (Chelishchev et al., 1991). Alterations of the mineral composition of H-f₁₁ in nodules at temperatures up to 200°C are accompanied by the maximal loss of interlayer water from the mineral structure (Table 5). Vernadite is the sole mineral of phase H-f₁₁ during its additional calcination at 230 and 400°C.

At 600°C, calcination products of H-f₁₁ contain manganese (bixbyite) and subordinate iron (jacobsonite) phases. Table 5 shows that they only contain manganese phases (hausmannite and braunite) at 1000°C. This is probably caused by the following fact: despite the low Fe content (0.33 wt %) in birnessite-asbolane nodules, diffractograms of calcination products contain still sufficiently distinct reflections related to iron phases at 600°C, whereas they are transformed into amorphous phases at 1000°C. However, manganese oxides with highly ordered structures are crystallized at 1000°C. This is manifested as intense distinct reflections of H-f₁₁ in diffractograms of their calcination products.

Table 5. Results of the thermic analysis of diagenetic nodules after the acid salt and acid-alkali salt modification

Cationic form of nodules	Association of prevalent minerals at 20°C	Total weight loss, wt %	Temperature of the onset and termination of thermochemical reaction, °C								Mineral composition at 1000°C	Content of metal cations (wt %) at	
			30–200		200–270		340–450		530–660			20°C	1000°C
			Weight loss, wt %	Major mineral phase at 120°C	Weight loss, wt %	Major mineral phase at 230°C	Weight loss, wt %	Major mineral phase at 400°C	Weight loss, wt %	Major mineral phase at 590°C			
H-f ₁₁ ¹	B, A	26.8	23.0	V, B	–	V	–	V	2.30	Bb, J	Br, H	Mn—48.20	Mn—73.70
Zn	B, A	24.5	16.5	V	0.30	V	–	V	3.00	Bb, J	Br, Hr	2.98	3.23
Ni	B, A	26.5	18.2	V	0.30	V	–	V	2.50	Bb, M	Br, H	2.26	2.42
Co	B, A	25.5	17.3	V	0.20	V	–	V	3.50	Bb	Br, H	2.88	3.20
Cu	B, A	25.0	17.3	V	0.20	V	–	V	2.60	Bb, M	Br, H	3.60	3.92
Cd	B, A	24.5	16.5	V	0.20	V	–	V	3.00	Bb, J	Br, H	6.10	6.88
Pb	B, A	19.0	10.0	V	–	V	–	V	1.30	Cr	Br, K	21.4	24.75
Na ²	B, A	28.3	14.7	V	6.40	V	–	V	2.25	Bb	Br, H	4.26	4.48
Zn	B, A	28.5	21.7	V	–	V	–	V	3.40	Bb	Hr, Br	7.30	7.74
Ni	B, A	26.7	16.2	V	2.80	V	2.65	V	3.00	Bb, M	Br, J	6.75	6.95
Co	B, A	25.2	12.6	B, Co-A	4.85	V	–	V	3.80	Bb	H	7.60	8.46
Cu	B, A	24.2	14.1	V	–	V	–	V	2.65	Bb	Br	7.80	10.04
Cd	B, A	23.4	12.5	V	3.55	V	–	V	3.20	Bb	Br	14.30	15.70
Pb	B, A	18.6	11.3	V	–	V	–	V	0.60	Cr	K	26.00	31.10

Note: Mineral abbreviations are as in Table 3. ^{1,2} H-f₁₁, Na-f, and their cationic forms are taken from (Novikov et al., 2006).

Investigations of the thermic behavior of cationic forms of birnessite nodules obtained during the treatment of H-f₁₁ with salt solutions of heavy metals show that the sorbed heavy metal cation has a certain influence on thermochemical reactions even its content is low (Table 5). Although generally similar to the DTA curve of H-f₁₁, DTA curves of cationic forms of birnessite-asbolane nodules are characterized by some specific features (interval 2a). For example, they contain not only Pb-rich species, but also a weak endothermic effect with maximums at 230–240°C due to the release of additional portion of water from the cationic forms of manganese minerals. DTA curves of Ni- and Cu-rich species show a weak endothermic effect at 900°C, whereas this effect is observed in H-f₁₁ at 950°C. In the Zn-, Co-, and Cd-rich species, this effect is missing. The DTA curve of the Pb-rich species is characterized by weak endothermic effects at 740 and 840°C. We recorded previously the endothermic effect in the Pb-rich species of busenite-asbolane nodules with maximum at 740°C (sample 19/t-1).

The mineral composition of calcination products of all cationic forms of acid modified nodules virtually coincides with the H-f₁₁ composition. At ~500°C, they are composed of vernadite. At 590°C, they consist of bixbyite and jacobsonite (or magnetite), which represent

end calcination products of braunite and hausmannite. The calcination product of the Pb-rich species is coronadite at 600°C and kentrolite at 1000°C (Table 5).

The DTA curves of the natural hydrothermal low-temperature birnessite (sample 285-1) and its cationic forms (Fig. 2b) slightly differ from those of analogous curves of the synthetic birnessite (H-f₁₁) in the low-temperature region (up to 500°C), whereas they are nearly identical at high temperatures. First, removal of interlayer water from the oceanic birnessite and its cationic forms is accompanied by a very strong endothermic effect with maximums at 130–150°C. At these temperatures, the loss of sample mass is as much as 13.7–18.8 wt %, the total loss of mass being 20.4–27.6 wt %. Second, the DTA curve of the hydrothermal birnessite lacks the endothermic effect at 230–250°C, which was typical of birnessite obtained by the chemical method. Endothermic effects with maximums in the ~400° and high-temperature regions are less intense.

Like the synthetic variety, the low-temperature hydrothermal birnessite demonstrates a low thermic stability. At 130–150°C, the mineral is transformed into vernadite, which retains stability up to ~500°C according to the previous scenario. At high temperatures, calcination products of vernadite with various cations of heavy metals are represented by the spinel-type manga-

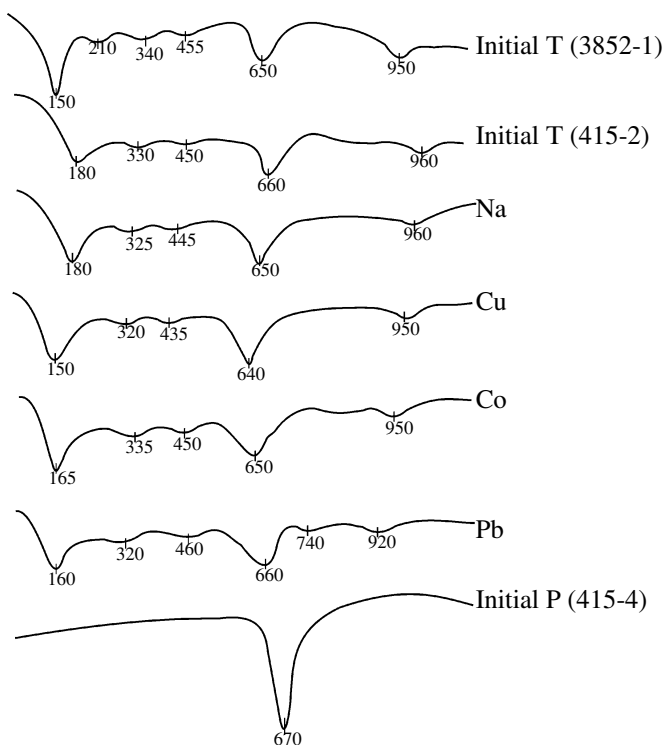


Fig. 3. DTA curves of diagenetic nodules (sample 3852-1) mainly composed of todorokite T_1 and low-temperature hydrothermal crusts composed of todorokite T_2 (sample 415-2) and pyrolusite P (sample 415-4).

nese minerals similar to those in the busserite-asbolane, busserite-birnessite, and asbolane-birnessite nodules. Iron phases are absent in both the initial (low-temperature) and final high-temperature ($\sim 1000^\circ\text{C}$) regions of the birnessite DTA curve. They occur only in the calcination product (magnetite) at $\sim 600^\circ\text{C}$.

Thus, the results obtained testify to a similar thermic behavior of both natural and synthetic birnessite species. This is additional evidence in favor of the hydrothermal origin of birnessite obtained in our experiment (Chelishchev et al., 1991). Results of thermic investigations of the hydrothermal birnessite usually match the data presented in (Corliss et al., 1978; Londshore et al., 1980; Shterenberg, 1987), whereas data on the synthetic birnessite are consistent with those in (Golden et al., 1986).

The alkaline treatment of acid modified nodules and the subsequent reaction of acid-alkali modified nodules (Na-rich species) with solutions of metal salts (Table 5) do not virtually affect the thermic behavior of birnessite and asbolane. DTA curves of the Na- and other cationic forms of birnessite-asbolane nodules are sufficiently similar to those of H-f_{11} and its cationic products (Fig. 2c). However, our new data show the following significant distinction relative to previous experiments: at 120°C , birnessite in the Na- and Co-rich species and

asbolane in the Co-rich species are more stable than H-f_{11} and its Co-rich species. Birnessite and asbolane are transformed into vernadite in the remaining cationic forms (Table 5). The endothermic effect observed in the Na-rich species of birnessite at 180°C corresponds to the loss of water and transition to vernadite. At this temperature, Co-asbolane is transformed into vernadite and its DTA curve shows a smooth pattern. Weak endothermic effects recorded at 220 – 250°C in the Ni-, Co-, and Cd-rich species are related to the loss of water from vernadite. Vernadite formed at 120 – 180°C remains stable up to 500°C in all cationic forms of the acid-alkali modified nodules. In other words, we see a complete analogy with the thermic behavior of busserite I and asbolane-busserite of diagenetic nodules. At 560 – 640 and 1000°C , calcination products of the acid-alkali modified nodules are represented by manganese-iron and manganese oxides, respectively, similar to those in the case of acid modified nodules. Iron phases are only recorded in calcination products of the Ni-rich species represented by magnetite at 590° and jacobsonite at 1000°C (Table 5).

DTA curves of diagenetic nodules mainly composed of todorokite (sample 3852-1) and the low-temperature hydrothermal manganese crust composed of nearly 100% todorokite (sample 415-2) show numerous different-intensity endothermic effects with maximums at 160 – 180 , 330 – 340 , 450 – 455 , 650 – 660 , and 950 – 960°C (Fig. 3). In addition, the DTA curve of todorokite from diagenetic nodules contains a moderate endothermic effect with maximum at 210°C related to the release of water during the decay of asbolane-busserite.

The data obtained suggest that maximums of the endothermic effect (except the effect at 950°C) of todorokite are shifted relative to analogous effects of layered manganese minerals toward higher temperatures. The loss of todorokite mass (sample 415-2) at 160 – 180 , 330 – 340 , 450 – 455 , and 650 – 660°C was equal to 9.40, 6.20, 3.30, and 1.05 wt %, respectively. The total loss of sample mass was 22.10 wt %. Loss of mass at 100 – 600°C is related to the complete removal of the sorptional and molecular water from todorokite (stable up to 600°C), because the electronogram and diffractogram of calcination products at this temperature coincided with analogous data on unheated samples. Our data on both diagenetic and hydrothermal species of todorokite are similar to those reported in (Chudaev et al., 1983). These data testify to the stability of the hydrothermal todorokite in oceanic nodules up to a temperature of 700°C . Hence, todorokite has a higher thermic stability than the layered manganese minerals (busserite I, asbolane-busserite, asbolane, and birnessite).

Calcination of todorokite at 650°C leads to the formation of Mn_2O_3 (α -kurnakite), which is the major phase in calcination products of the studied samples. One can also see bixbyite related to the presence of Fe in the initial samples (Table 1). Final calcination prod-

ucts of todorokite at 1000°C (hausmannite and braunite) are similar to those of other manganese minerals. The absence of iron phases suggests their complete amorphization.

DTA curves of cationic forms of todorokite in the low-temperature hydrothermal crust (sample 415-2) are virtually similar to those of the initial sample (Fig. 3). However, curves in the former case are characterized by a relatively higher intensity and lower values (150–165°C) of the temperature maximum (except for the Na-rich species) owing to the presence of sorbed metal cations and, consequently, a high content of sorption water in water. DTA curves of calcination products of Na-, Cu-, and Co-rich todorokite are also characterized by lower values of maximum temperature (640–650°C) relative to the initial sample. DTA curves of the Pb-rich todorokite include a weak endothermic effect at a maximum temperature 740°C, which is probably typical of manganese minerals enriched in Mn cations. Structural transformations of todorokite with various cations of heavy metals at high-temperature calcination are similar to those of other manganese minerals of diagenetic nodules.

The DTA curve of pyrolusite from the low-temperature hydrothermal crust (sample 415-4) differs drastically from curves of layered manganese minerals and todorokite. In the former case, one can see gradual change up to ~640°C and at ~720–1000°C. An intense endothermic effect is recorded at 640–720°C with the maximum at 670°C (Fig. 3). This effect is related to the reduction of MnO_2 to Mn_2O_3 . As in the case of other manganese minerals, the terminal product of pyrolusite calcination (at 1000°C) is represented by hausmannite. Our DTA data on the low-temperature hydrothermal pyrolusite are nearly identical to the respective data on pyrolusite from ores of the Nikopol Basin reported in (Bazilevskaya, 1976). DTA curves of cationic forms of pyrolusite are identical with those of the initial sample; i.e., sorbed metal cations do not affect thermic properties of this mineral.

Investigation of thermic properties of sedimentary ferromanganese rocks composed of only Fe-vernadite, Mn-feroxyhyte, and their cationic forms revealed that their thermochemical transformations follow a single scenario as in the case of diagenetic nodules. DTA curves of initial samples (43-63, 9-124, 11-298, and 9-77) are identical: they show one strong endothermic effect with maximum at 140–160°C and one exothermic effect (sample 9-124) with maximum at 890–900°C (Fig. 1b). In the low-temperature region (up to 500°C), we recorded dehydration of minerals and release of 25.5–26.4 wt % water. Identification of calcination products of sedimentary rocks at 150°C suggests the thermic stability of vernadite at this temperature. At 150°C, asbolane-buserite contained in crustal nodular formations (sample 9-77) is transformed into asbolane-buserite due to the loss of water from buserite packages of the mineral. At 180°C, as in the case of diagenetic

nodules (sample 19/t-2), the asbolane component of asbolane-birnessite is decomposed, but birnessite remains stable.

At 500°C, diffractograms of calcination products of these minerals include two diffuse reflections (100 and 110) related to vernadite and reflections with $d = 2.534$, 2.640, 2.680, 2.508, and 2.098 Å with intensity close to that of reflection with $d = 2.414$ Å. The presence of reflections with d values indicated above testifies to initiation of the formation of iron minerals (jacobite, magnetite, and hematite). At >500°C, decomposition of vernadite is accompanied by the release of oxygen and the subsequent crystallization of manganese and iron oxides. The total loss on ignition is 28.4–29.6 wt %.

Diffractograms of sedimentary rocks calcined at 900°C (maximum of the second endothermic effect) and 1000°C (final calcination temperature) are characterized by reflections of two different oxide groups. Reflections with $d = 2.530$, 1.488, 2.950, 1.621, and 2.907 Å (in decreasing order of reflection intensity) belong to hausmannite (Mn_3O_4), jacobite (MnFe_2O_4), and magnetite (FeFe_2O_4). Reflections with $d = 2.683$, 1.653, and 1.824 Å belong to hematite ($\alpha\text{-Fe}_2\text{O}_3$). Intensity of reflections of the first group is much stronger than that of hematite. This tendency is intensified in the terminal calcination products. Initial samples of sedimentary rocks mainly contain vernadite. In contrast, their calcination products only contain iron phases because of a lower (relative to manganese minerals) recrystallization temperature of the initially X-ray amorphous iron minerals into minerals with the spinel-type structure. We observed a similar effect in diagenetic nodules: at 500°C, vernadite formed from 10 Å manganese minerals and birnessite was recrystallized into manganese oxides with the spinel-type structure. Hence, the thermic behavior of vernadite is similar irrespective of its origin (primary manganese mineral in nodules and crusts or product of other layered minerals). Vernadite remains stable up to 500°C. At higher temperatures, the mineral is decomposed and recrystallized into complex oxides.

DTA curves of cationic forms of vernadite from crusts (sample 11-298) and nodules (sample 43-63) are identical, but they show some distinctions from DTA curves of initial samples (Fig. 1b). All cationic forms of vernadite demonstrate an intense endothermic effect with the maximum at 135–160°C. DTA curves of the Ni- and Co-rich species include only one strong endothermic effect at 150–155°C and lack the effect at ~900°C. Curves of both species are characterized by gradual changes. DTA curves of the Cu- and Mn-rich species show a weak endothermic effect at 570–590°C (this effect is missing in the Mn-rich variety in sample 43-63) and more intense (relative to the initial samples) exothermic effect at 800–810°C. The greatest changes (relative to the initial samples) are recorded in the Pb-rich species: their DTA curves show distinctly four endothermic effects (with maximums at 135–140, 515,

750, and 950°C) and two exothermic effects (at 595 and 860–875°C). Thus, DTA curves of cationic forms of rocks suggest that the sorbed cation of heavy metal governs the thermic transformation of manganese and iron rocks.

Investigation of calcination products of the cationic forms of sedimentary ferromanganese rocks in the low-temperature (up to ~500°C) region shows that Fe-vernadite is the major mineral in them. Asbolane is retained and birnessite is recorded in the crustal nodular formations (sample 9-77). Moreover, reflection with $d = 7.20 \text{ \AA}$ in the diffractogram of calcination products of the cationic forms is more intense relative to the calcined initial sample. Analogous effect was also observed in reflections at 2.76 and 2.66 Å. Relative to diffractograms of calcined minerals, diffractograms of calcined Zn-, Ni-, Mn-, Cu, and Pb-rich species contain an additional diffuse reflection with $d = 4.62\text{--}4.80 \text{ \AA}$, which probably belongs to the Mn-spinel (Mn_3O_4). The only cationic form distinguished from other species is represented by the Co-rich species (Co-asbolane and vernadite). Thus, we can assume that the absorbed cations of heavy metals affect the thermic behavior of minerals in the low-temperature region.

Despite the similarity with diffractograms of initial samples, diffractograms of high-temperature (1000°C) calcination products of the cationic forms of sedimentary ferromanganese rocks are subjected to significant alterations. First, diffractograms of all cationic forms of crustal nodular formations lack reflections typical of berthierite. Second, sufficiently intense reflections with $d = 4.2\text{--}4.4 \text{ \AA}$ are present in all calcination products of cationic forms of crusts and absent in crustal nodular formations. Third, oxides of the jacobsonite–magnetite group are the main phases in calcination products of cationic forms (except the Mn-rich variety), as suggested by reflections with $d = 2.94, 2.53, 1.484$, and $1.610 \text{ \AA}$. The narrow sharp shape of these peaks and their high intensity indicate a high degree of crystallization of iron oxides. Diffractograms of the calcination products also contain weak reflections with $d = 2.68\text{n}, 2.69\text{n}, 1.65\text{n}$, and $1.830 \text{ \AA}$ that are characteristic of hematite.

Thus, reflections of phases of the jacobsonite–magnetite group and hematite in calcination products of initial sedimentary rocks are characterized by virtually similar intensity. However, reflections of phases of the first group are much more intensive (relative to reflections of hematite) in calcination products of their cationic forms. Diffractograms of the calcined Cu-rich species of crusts, as well as the Co-, Pb-, and Mn-rich crustal nodular formations contain not only Fe phases, but also sufficiently intense reflections with $d = 2.74, 2.33$, and $2.14 \text{ \AA}$, suggesting the presence of well-crystallized bixbyite ($\text{Mn,Fe})_2\text{O}_3$.

The wide diffuse reflections with $d = 4.65\text{--}4.80 \text{ \AA}$, which was recorded in calcination products of the cationic forms at 150°C and referred to the Mn-spinel, is

also distinctly recorded in calcination products of the cationic forms at 1000°C. However, the reflection is characterized by a narrow peak with $d = 4.72$ and low intensity.

Calcination of the Co-rich variety in sedimentary ferromanganese rocks at 150°C yields two phases (vernadite and Co-asbolane), whereas its high-temperature calcination product does not differ anyhow from other calcined cationic forms and is represented by both feruginous and mixed Mn–Fe phases.

Among all high-temperature (1000°C) calcination products of the cationic forms of sedimentary ferromanganese rocks, the Mn-rich variety is characterized by the presence of only intense narrow sharp reflections with $d = 2.489, 2.766$, and $1.547 \text{ \AA}$ related to hausmannite. Hence, sorbed Mn^+ cations foster the formation of well-crystallized manganese oxides. It should be noted that jacobsonite, magnetite, and bixbyite, which were recorded as the major phases in other cationic forms, occur as traces in calcination products of the Mn-rich variety. Therefore, we can assume that high-temperature manganese and iron phases were fractionated in the course of their crystallization.

Results of the investigation of thermic properties of ore minerals in the oceanic ferromanganese rocks suggest the following inference concerning the transformation of minerals in continental manganese ores. As is well known, the major ore minerals of the oceanic ferromanganese rocks of different genetic types (buserite I, buserite II, birnessite, asbolane-buserite, asbolane, vernadite, todorokite, goethite, feroxyhyte, and ferrihydrite) are formed at water temperature equal to 2–6°C. Layered manganese minerals can be transformed into each other or todorokite in aqueous solutions of electrolytes (Novikov et al., 2005; Chelishchev et al., 1991). Reduction of Mn (IV) and Fe (III) to Mn (II, III) and Fe (II), respectively, in the solid substance requires significant alteration of physical and chemical parameters of the external medium. Such alternations are missing at sites of the oceanic ferromanganese nodules and crusts, suggesting that the minerals described above are sufficiently stable compounds. This is indicated by numerous data on the mineral composition of ferromanganese rocks from different-facies settings of the World Ocean. Based on the finding of varieties of sedimentary nodules in the South Basin (Pacific) with crystalline pyrolusite, braunite, hematite, subordinate vernadite, and rare todorokite, Andrushchenko et al. (1975) suggested that such nodules are products of the metamorphism of sediments by the postvolcanic hydrothermal processes.

In continental manganese deposits, the major ore minerals are represented by bixbyite, hausmannite, pyrolusite, braunite, and associated iron minerals, such as jacobsonite, magnetite, and hematite (Jimenez-Millan and Velilla, 1997; Jorge et al., 1998; Karimov, 1967; Amouric et al., 1991; Kavun, 1967; Kazachenko and Kiselev, 2004; Perseil Sur, 1991; Von Bezing and

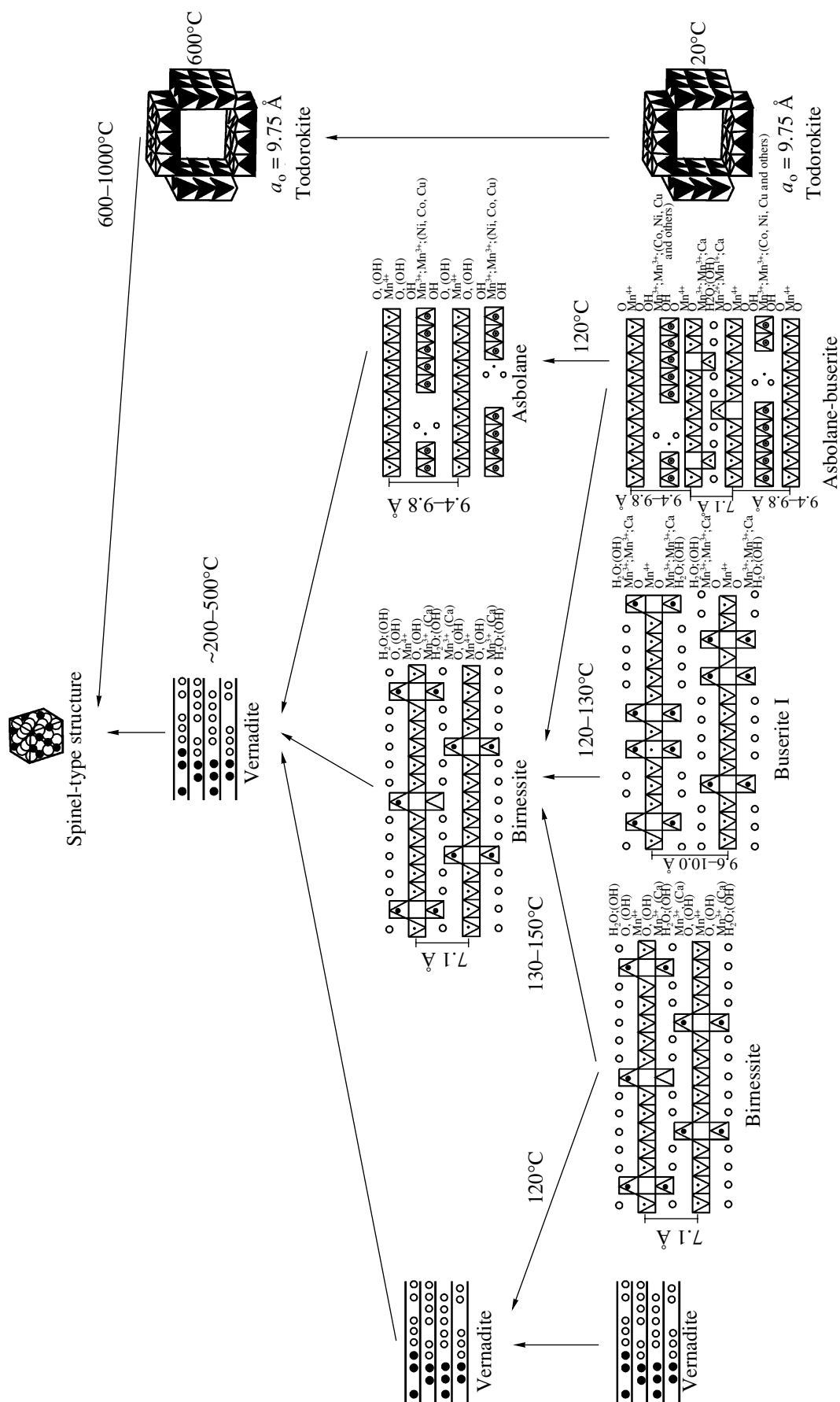


Fig. 4. Scheme of transformations of manganese minerals in oceanic ferromanganese rocks during heating. Models of structures are adopted from (Chukhrov et al., 1989).

Gutzmer, 1991, 1994a, 1994b). The formation of all minerals (with the spinel-type structure) mentioned above is a function of two simultaneous factors: high-temperature (>400–500°C) and reducing environment. However, manganese minerals typical of the oceanic ferromanganese rocks are only represented by small amounts of todorokite, birnessite, and rare pyrolusite. Researchers mentioned above and others believe that continental manganese ores are usually metamorphosed products irrespective of their primary (hydrothermal, volcanosedimentary, or sedimentary) origin.

Thus, comparison of mineral compositions of the oceanic ferromanganese rocks and continental manganese ores with experimental data on thermal transformations of manganese minerals suggests that buserite I, asbolane-buserite, birnessite, vernadite, and todorokite could serve as the protolith for the formation of hausmannite, bixbyite, pyrolusite, and other ore minerals.

CONCLUSIONS

Results of the investigation of thermic properties of ore minerals in the oceanic ferromanganese rocks of different genetic types suggest the following conclusions.

Thermic stability is low (up to 120–150°C) for the layered manganese minerals (buserite I, asbolane-buserite, and birnessite), slightly higher (up to 180°C) for asbolane, and maximal (up to ~500°C) for vernadite (Fig. 4). Their thermic stability does not depend on their origin (component of primary oceanic ferromanganese rocks or product of their modification). Thermal transformations of the layered manganese minerals at 120–200°C indicate their structural similarity.

Relative to the layered manganese minerals, minerals with the tunnel structure (todorokite and pyrolusite) show much higher thermic stability (up to 600 and 670°C, respectively).

The formation of high-temperature manganese and iron oxides does not depend on the primary mineral composition of ferromanganese rocks. This is suggested by the complete recrystallization of their ore minerals.

Sorbed cations of heavy metals affect the transformation temperature and mineral composition of calcination products of the ferromanganese rocks.

Data on birnessite and todorokite indicate that genesis of ferromanganese rocks does not affect thermic properties of their mineral constituents.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 06-05-64614.

REFERENCES

- Amouric, M., Parc, S., and Nahon, D., High-Resolution Transmission Electron Microscopy Study of Mn-Oxyhydroxide Transformations and Accompanying Phases in a Lat-eritic Profile of Moanda, Gabon, *Clays Clay Miner.*, 1991, vol. 39, no. 3, pp. 254–263.
- Andrushchenko, P.F., Gradusov, V.P., Eroshchev-Shak, V.A., et al., Composition and Structure of Metamorphic Ferromanganese Nodules, Vein-Filling Neogenic Manganese Hydroxide Minerals, and Host Pelagic Sediments in the Southern Basin of the Pacific Ocean, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1975, no. 1, pp. 91–111.
- Bazilevskaya, E.S., *Chemical-Mineralogical Analysis of Manganese Ores (Nikopol Basin and Nodules in the Pacific Ocean)*, Moscow: Nauka, 1976, issue 287, pp. 35–44.
- Chelishchev, N.F., Novikov, G.V., and Gorshkov, A.I., Transformation of Mn-Minerals in Oceanic Ferromanganese Nodules during Ion Exchange Reactions, *Izv. Akad. Nauk. SSSR. Ser. Geol.*, 1991, no. 6, pp. 87–101.
- Chelishchev, N.F., Gribova, N.K., and Novikov, G.V., *Sorbtsionnye svoystva okeanicheskikh zhelezomargantsevykh konkretov i korok* (Sorption Properties of Oceanic Ferromanganese Nodules and Crusts), Moscow: Nedra, 1992.
- Chudaev, O.V., Skorniyakova, N.S., and Pushcharovsky, D.Yu., Mineral Composition of Ferromanganese Nodules in the Central Pacific, *Dokl. Akad. Nauk SSSR*, 1983, vol. 369, no. 6, pp. 1444–1448.
- Chukhrov, F.V., Drits, V.A., and Gorshkov, A.I., Structural Transformations of Manganese Oxides in Oceanic Fe–Mn Nodules, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1987, no. 1, pp. 3–14.
- Chukhrov, F.V., Gorshkov, A.I., and Drits, V.A., *Gipergennye okisly margantsa* (Supergene Manganese Oxides), Moscow: Nauka, 1989.
- Corliss, T., Lyle, M., and Dymond, F., The Chemistry of Hydrothermal Mounds Near the Galapagos Rift, *Earth Planet. Sci. Lett.*, 1978, vol. 40, no. 1, pp. 12–24.
- Giovanoli, R., On Natural and Synthetic Nodules, *Manganese*, Budapest, 1980, vol. 1, pp. 160–202.
- Golden, D., Dixon, J., and Chen, C., Ion Exchange, Thermal Transformation and Oxidizing Properties of Birnessite, *Clays Clay Mineral.*, 1986, vol. 34, no. 5, pp. 511–520.
- Gorshkov, A.I., Drits, V.A., Putilina, V.S., et al., Natural and Synthetic Birnessite, *Litol. Polezn. Iskop.*, 1992, vol. 27, no. 6, pp. 67–81.
- Gribova, N.K. and Shatskaya, N.S., Behavior of Vernadite in Electrolyte, Solutions, in *Metody polucheniya i ispol'zovaniya modifitsirovannykh prirodnykh sorbentov* (Methods for the Production and Use of Modified Natural Sorbents), Moscow: Inst. Mineral. Geokhim. Redk. Elemen. Akad. Nauk SSSR, 1988, pp. 86–97.
- Gunneriusson, L., Composition and Stability of Cd (II)-Chloro and -Hydroxo Complexes at Goethite (α -FeOOH)/Water Interface, *Clays Clay Mineral.*, 1994, vol. 163, pp. 484–492.
- Han, K., Hoover, M., and Fuerstenau, D.W., The Effect of Temperature on the Physicochemical Characteristics of Deep-Sea Manganese Nodules, *Mar. Miner.*, 1979, vol. 2, nos. 1/2, pp. 131–149.

- Jimmenez-Millan, J. and Velilla, N., Hausmannite and Braunitz Nodules from the Aracena Area (Iberian Massif, SW Spain), *Mineral. Mag.*, 1997, vol. 61, no. 6, pp. 898–902.
- Jorge, R.C., Barriga, F.J., and Relvas, J.M., Soloviejo Manganese Deposit: Mineralogy and Geochemistry, Progress Report, *Comun. Inst. Geol. Miner.*, 1998, vol. 84, no. 1, pp. 103–106.
- Karimov, A.G., Manganese Potential of the Lower–Middle Ordovician Tasobina Formation in Northern Kazakhstan, in *Margantsevye mestorozhdeniya SSSR* (Manganese Deposits of the USSR), Moscow: Nauka, 1967, pp. 332–336.
- Kavun, V.I., Main Regularities in the Distribution of Manganese Ores in the Karadzhai Ore Field, in *Margantsevye mestorozhdeniya SSSR* (Manganese Deposits of the USSR), Moscow: Nauka, 1967, pp. 294–304.
- Kazachenko, V.T. and Kiselev, V.V., Manganese Mineral Associations: Indicators of Redox Conditions during the Metamorphism of Metalliferous Deposits, *Tikhookean. Geol.*, 2004, vol. 23, no. 5, pp. 81–100.
- Londsdole, P., Burns, V., and Fisk, M., Nodules of Hydrothermal Birnessite in Caldera of a Young Seamount, *J. Geol.*, 1980, vol. 88, no. 5, pp. 611–618.
- Lysyuk, G.N., *Mineralogiya okeanicheskikh zhelezomargantsevykh konkretov* (Mineralogy of Oceanic Ferromanganese Nodules), St. Petersburg: Nauka, 1991.
- Mason, B., Mineralogical Aspects of the System Fe_3O_4 – Mn_3O_4 – ZnMn_2O_4 – ZnFe_2O_4 , *Am. Mineral.*, 1947, vol. 32, pp. 426–438.
- Novikov, G.V., Modified Oceanic Ferromanganese Nodules: Highly Selective Sorbent of Metals, in *Metody polucheniya i ispol'zovaniya modifitsirovannykh prirodnikh sorbentov* (Methods for the Production and Use of Modified Natural Sorbents), Moscow: Inst. Mineral. Geokhim. Redk. Elemen. Akad. Nauk SSSR, 1988, pp. 61–80.
- Novikov, G.V., Oceanic Ferromanganese Formations as Sorbents of Metal Ions: Chemical–Mineralogical Aspect, *Zap. Vses. Mineral. O-va*, 1996, no. 3, pp. 38–51.
- Novikov, G.V. and Baturin, G.N., Sorption Ability of Oceanic and Marine Ferromanganese Nodules and Crusts of Different Chemical and Mineralogical Composition, *Okeanologiya*, 1997, vol. 37, no. 4, pp. 525–531 [*Oceanology* (Engl. Transl.), 1997, vol. 37, no. 4, pp. 472–478].
- Novikov, G.V. and Cherkashov, G.V., Ion-Exchange Reactions on Low-Temperature Oceanic Hydrothermal Rocks, *Geochem. Int.*, 2000, vol. 38, Suppl. 2, pp. 194–205.
- Novikov, G.V. and Murdmaa, I.O., Ion-Exchange Properties of Oceanic Ferromanganese Nodules and Host Pelagic Sediments, *Litol. Polezn. Iskop.*, 2007, vol. 42, no. 2, pp. 153–186 [*Lithol. Miner. Resour.* (Engl. Transl.), 2007, vol. 42, no. 2, pp. 137–167].
- Novikov, G.V. and Shatskaya, N.S., Stability of Stratified Manganese Minerals of Oceanic Nodules in the Aqueous Solution of Electrolytes, in *Metody polucheniya novykh materialov iz mineral'nogo syr'ya* (Methods for the Production of New Materials from Natural Minerals), Moscow: Inst. Mineral. Geokhim. Redk. Elemen. Akad. Nauk SSSR, 1990, pp. 70–80.
- Novikov, G.V., Andreev, S.I., and Anikeeva, L.I., Sorption Capacity of Ferromanganese Nodules in Ocean, in *Litosfera okeana: sostav, stroenie, razvitiye, prognoz i otsenka mineral'nykh resursov* (The Lithosphere of Ocean: Composition, Structure, Evolution, and Mineral Resource Forecast and Evaluation), St. Petersburg: Vseross. Nauchno-Issled. Inst. Okeangeologiya, 1995, pp. 291–304.
- Novikov, G.V., Kulikova, L.N., and Bogdanova, O.Yu., Mineralogy and Sorption Properties of Low-Temperature Manganese Oxide-Hydroxide Phases, Abstracts of Papers, *Spektroskopiya, rentgenografiya i kristalloghiya mineralov. Mezhdunar. nauchnoi konferentsii* (Int. Sci. Conference on Spectroscopy, X-Ray Analysis, and Crystallochemistry of Minerals), Kazan, 2005, pp. 184–186.
- Novikov, G.V., Vikent'ev, I.V., and Bogdanova, O.Yu., Sorption of Heavy Metal Cations by Low-Temperature Deposits of Pacific Hydrothermal Fields, *Geol. Rudn. Mestorozhd.*, 2006, vol. 48, no. 4, pp. 351–374 [*Geol. Ore Deposits* (Engl. Transl.), 2006, vol. 48, no. 4, pp. 324–325].
- Ono, K. and Ueda, T., Thermodynamic Study of the Iron–Manganese Oxygen System, *Nippon Kinzoku Gakkashi*, 1971, vol. 36, pp. 757–763.
- Perseil, E.-A., Sur, L., Evolution mineralogique des constituents des nodules polymetalliques, *Bull. Mus. Nat. Hist. Nature*, 1991, vol. 13, nos. 1/2, pp. 3–15.
- Pivovarov, S., Adsorption of Cadmium onto Hematite: Temperature Dependence, *J. Colloid Interface Sci.*, 2001, vol. 234, pp. 1–8.
- Pivovarov, S.A., Adsorption of Ions (Cu^{2+} , Zn^{2+} , Cd^{2+} , Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} , CO_3^{2-}) on (Hydro)Oxides of the Trivalent Iron, in *Eksperimental'naya mineralogiya. Nekotorye itogi na rubezhe stoletii* (Experimental Mineralogy: Some Results at the Turn of Centuries), Moscow: Nauka, 2004, pp. 255–272.
- Pivovarov, S.A. and Lakshmanov, L.Z., Absorption of Cadmium on Hematite, *Geokhimiya*, 2003, vol. 41, no. 10, pp. 1105–1120 [*Geochem. Int.* (Engl. Transl.), 2003, vol. 41, no. 10, pp. 1013–1027].
- Rode, E.Ya., *Kislopodnye soedineniya margantsa* (Oxygen Compounds of Manganese), Moscow: Akad. Nauk SSSR, 1952.
- Shterenberg, L.E., Antipov, M.P., and Ilev, A.Ya., Ferromanganese Nodules in the Sea of Okhotsk, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1987, no. 12, pp. 106–115.
- Takematsu, N., The Incorporation of Minor Transition Metals into Marine Manganese Nodules, *J. Oceanogr. Soc. Jap.*, 1979, vol. 35, no. 2, pp. 191–198.
- Van Hook and Keith, M., The System Fe_3O_4 – Mn_3O_4 , *Am. Mineral.*, 1958, vol. 43, pp. 69–83.
- Varentsov, I.M., Putilina, V.S., and Zaitseva, L.V., Study of the Mechanism of Ferromanganese Nodule and Crust Formation in Modern Basins: Communication 1. Experiments with the Synthesis of Fe, Ni, Cu, Co Hydroxide Compounds on Manganese Hydroxides, *Litol. Polezn. Iskop.*, 1988, vol. 23, no. 4, pp. 14–20.
- Von Bezing, K.L. and Gutzmer, J., Das Kalahari Manganerzfeld und Seine Mineralien (I), *Miner. Welt*, 1994a, vol. 5, no. 4, pp. 24–45.
- Von Bezing, K.L. and Gutzmer, J., Das Kalahari Manganerzfeld und Seine Mineralien (II), *Miner. Welt*, 1994b, vol. 5, no. 5, pp. 41–59.
- Von Bezing, K.L., Dixon, R., Pohl, D., and Cavallo, G., The Kalahari Manganese Field: An Update, *Mineral. Rec.*, 1991, vol. 22, no. 4, pp. 279–297.