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Composition and Genesis of Accessory Mineralization in Manganese Silicate Rocks of the Triassic Sikhote-Alin Chert Formation

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Abstract—Manganese silicate rocks together with silicate–magnetite ores and jaspers (Late Anisian–Ladinian) form lenticular or tabular bodies in the Triassic Sikhote-Alin chert formation. The lower part of the formation (Olenekian–Early Anisian) is enriched in clayey and organic matter. Nickel and cobalt compounds and other ore minerals in the Sikhote-Alin manganese silicate rocks belong to two genetic groups including minerals of the valence and ultimately reduced Ni, Co, and other metals. Minerals of the valence species of Ni, Co (sulfoantimonides, sulfoarsenides, sulfides, antimonides, arsenides, tellurides, and silicates), and other metals (galena, sphalerite, chalcopyrite, arsenopyrite, wolframite, scheelite, molybdenite, cassiterite, stannite, cinnabar, stibnite, boulangerite, jamesonite, bournonite, löllengite, bismuthite, fahlore, altaite, native Sb and Bi, etc.) formed from the protolith material during metamorphism under the same conditions as the rock-forming minerals. The presence of minerals of ultimately reduced Ni, Co (maucherite, native Ni, Ni phosphide, Ni and Co chromides, disordered solid solutions, and intermetallic compounds of Ni with Cu, Zn, Sn, and Pb), and other metals (native Pb, Zn, Fe, Sn, Se, Au, Pt, "cupriferous gold", and intermetallic compounds of Cu, Sn, Pb, Sb, Al, and Zn) in the manganese silicate rocks is due to the influence of the organic matter of the underlying carbonaceous silicites. During metamorphism, the most volatile components (first of all, poorly bound water and hydrocarbons) were released from the heated carbonaceous rocks; as a result, a metal-enriched fluid with highly or ultrahighly reducing properties appeared, which migrated along fractures into other rocks. The manganese silicate rocks are the products of contact metamorphism of siliceous rhodochrosite rocks formed through the diagenesis of biogenic siliceous muds enriched in Mn oxides and organic matter. Erosion of the weathering crust of islands composed of gabbroids of the Kalinovka, Vladimiro-Aleksandrovskoe, and Sergeevka complexes (in the late Middle Triassic–Late Triassic) played the leading role in the formation of metalliferous sediments. Manganese silicate rocks localized in the stratigraphic column above the carbonaceous silicites of the Triassic chert formation are enriched in Au (up to 35.38 ppm), Pt (11.27 ppm), and Pd (5.33 ppm). They contain noble-metal minerals and a wide spectrum of native elements and intermetallic compounds. The presence of Au–Pd–Pt–Ni–Co association (typomorphic for basic and ultrabasic rocks) in the Triassic protoliths of the manganese silicate rocks and carbonaceous silicites is probably due to the sorption of these elements by Mn and Fe hydroxides and organic matter during the exogenous weathering of the ancient Sikhote-Alin gabbroids.

Keywords: nickel, cobalt, PGE, mineralogy, manganese silicate rocks, carbonaceous silicites, Triassic, Sikhote-Alin

INTRODUCTION

The main goal of the research was study of the mineralogy and genesis of Co–Ni mineralization in the manganese silicate rocks of the Taukhe and Samarka terranes.

The lower part (Olenekian–Early Anisian) of the Triassic Sikhote-Alin chert formation is enriched in clayey and organic matter (hereafter, it is called an argillaceous–siliceous unit). It is composed of siliceous, argillaceous–siliceous, and siliceous-argillaceous rocks, has interbeds of carbonaceous silicites (Volokhin et al., 2003), and is conformably overlain by a unit (Late Anisian–Norian) of light gray platy cherts (hereafter, a chert unit). This formation was found in the Sikhote-Alin only as fragments in melange complexes of Jurassic and Early Cretaceous accretionary prisms of the Samarka (and its analog, Nadan'khada–Bikin) and Taukhe terranes, respectively.

Manganese silicate rocks were studied in the Shirokaya Pad', Mokrusha, and Sadovaya areas in the Ol'ga and Dal'negorsk ore districts (Taukhe terrane) and in the Gornaya area in the Malinovka ore district (Samarka terrane). Manganese silicate rocks and silicate–magnetite ores form lenticular and sheet bodies few tens of centimetres to few meters in thickness and tens to few hundreds of meters in length. They are localized in the lower part of the chert unit in all studied areas (Kazachenko and Sapin, 1990; Kazachenko, 2002). Together with jaspers (Late Anisian–Ladinian) and stratified silicate–magnetite ores, they form a common member (Fig. 1) or replace each other as facies along the strike. The outcrops of Triassic metalliferous sediments, grouped in series of extended linear zones parallel to the

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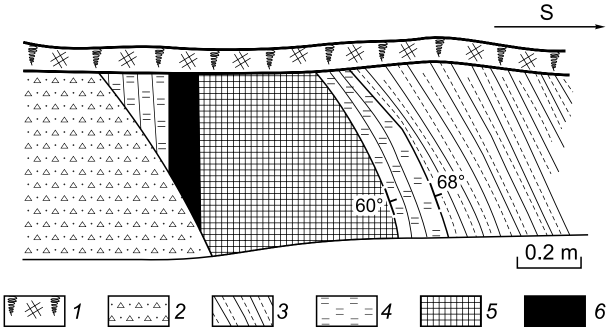

Fig. 1. The occurrence and structure of ore-bearing member in the Shirokaya Pad' area of the Ol'ga district, after Kazachenko and Sapin (1990), supplemented and modified. *1,* soil–vegetation bed; *2*, deluvium; *3*, siliceous–argillaceous rocks; *4*, jaspers; *5*, manganese silicate rocks; *6*, silicate–magnetite ores.

strike of the host rocks, mark the outcrops of a folded Mn-bearing horizon (Fig. 2). Some zones are traceable by separate outcrops at a distance of up to 4.3 km. Manganese silicate rocks are found only in the contact aureoles of granitoid intrusions of the East Sikhote-Alin volcanointrusive belt in the Taukhe terrane and of the Khungari-Tatibe intrusive complex in the Samarka terrane, beyond which they give rise to siliceous rhodochrosite rocks.

Manganese silicate rocks (usually microcrystalline) have a massive, banded, or spotted structure. The banded structure, expressed as alternation of bands enriched in pyroxenoids, quartz, spessartine, feldspars, rhodochrosite, and other minerals, is due to the initial bedding of sediments. The manganese silicate rocks contain (wt.%): 18.20–47.33 MnO, 32.30–67.56 SiO_2, up to 4.30 Al_2O_3, 9.90 CaO, 4.56 MgO, 11.83 FeO, 7.15 Fe_2O_3, 1.45 (Na_2O + K_2O), 0.29 TiO_2, and 0.28 P_2O_5 (Perevoznikova, 2010). A specific feature of the manganese silicate rocks of the Samarka terrane, compared with the rocks of the Taukhe terrane, is lower contents of Ca and Fe and higher contents of alkalies. According to the ICP-MS data, manganese silicate rocks are enriched in Ba, REE, Ni, Co, Pb, Zn, Cu, As, Nb, Sb, Sn, Mo, and other elements (Table 1). The results of assay, ICP-MS, and AAS analyses show that the manganese silicate rocks localized above the argillaceous-siliceous unit in the stratigraphic column are enriched (ppm) in Au (up to 35.38), Pt (11.27), and Pd (5.33). They contain noble-metal minerals and a wide range of native elements and intermetallic compounds (Kazachenko et al., 2008).

The manganese silicate rocks are composed of rhodonite, pyroxmangite, quartz, and spessartine. Tephroite, bustamite, manganactinolite, Mn-rich amphiboles of the cummingtonite–grünerite series, manganpyrosmalite, pyrophanite, and manganaxinite are scarcer. Also, V-containing varieties of spessartine and pyrophanite, hyalophane, celsian, and Ni- and Ba-containing phlogopite are present. Secondary, accessory, and rare minerals are magnetite, titanite, apatite, monazite, baddeleyite, thorianite, uraninite, zircon, alabandite, rhodochrosite, barite, etc.

Table 1. Limiting and average contents (ppm) of minor elements in the metamorphosed Triassic Sikhote-Alin metalliferous sediments

Element	Area		
	Gornaya	Shirokaya Pad'	
	Manganese silicate rocks		Silicate–magnetite ores
V	6.88 – 131.79* 49.80**	2.06 – 172.71 52.39	7.45 – 125.98 40.93
Cr	0.76 – 24.48 4.44	0.53 – 49.09 9.34	3.94 – 46.03 13.04
Co	8.50 – 109.76 55.98	2.01 – 221.27 57.31	3.82 – 45.85 20.13
Ni	13.65 – 442.95 127.21	3.19 – 421.32 92.06	8.94 – 349.18 76.87
Cu	0.00 – 110.62 9.42	0.00 – 588.21 88.00	0.80 – 350.88 107.61
Zn	0.00 – 0.3336 232.29	78.97 – 4628.26 1389.12	65.66 – 1103.21 483.90
Ge	0.64 – 9.99 3.71	1.53 – 5.32 2.73	0.87 – 4.79 2.78
As	1.97 – 242.57 31.79	2.35 – 402.11 62.65	3.40 – 86.33 22.26
Nb	0.08 – 2.36 0.88	0.08 – 15.27 2.45	0.21 – 13.06 3.42
Mo	0.60 – 53.77 10.34	0.28 – 9.67 4.98	0.17 – 5.84 1.05
Cd	0.01 – 4.85 0.32	0.00 – 20.98 3.47	0.00 – 1.01 0.29
In	0.00 – 0.64 0.05	0.03 – 21.74 1.67	0.07 – 4.04 1.03
Sb	0.00 – 23.64 4.47	1.92 – 35.84 7.55	1.89 – 16.68 7.67
Ta	0.00 – 1.02 0.10	0.00 – 1.74 0.24	0.04 – 1.50 0.36
W	0.30 – 21.84 2.22	0.03 – 44.87 9.42	1.25 – 39.35 12.72
Hg	0.00 – 1.82 0.17	0.00 – 5.77 1.02	0.03 – 4.91 1.60
Tl	0.02 – 0.15 0.08	0.00 – 0.32 0.08	0.01 – 3.00 0.29
Pb	0.99 – 160.54 7.81	6.28 – 11273.40 943.27	2.80 – 538.42 64.74
Sn	0.00 – 146.20 6.12	0.75 – 145.03 31.57	10.60 – 257.79 89.35
Number of samples	31	18	12

*Limiting contents.
**Average content.

The manganese silicate rocks are products of contact metamorphism of siliceous rhodochrosite rocks formed during the diagenesis of biogenic siliceous silts enriched in Mn oxides and organic matter (Perevoznikova, 2010) in the water areas around islands. The metalliferous sediments formed mostly through the late Middle Triassic–Late Triassic ero-

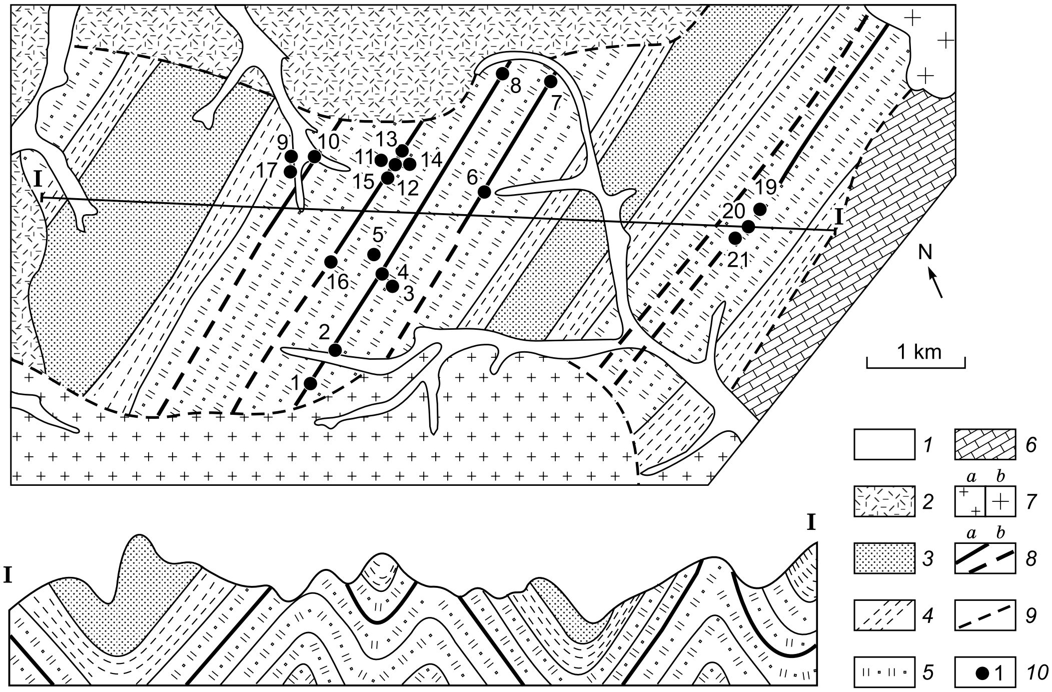

Fig. 2. Schematic geologic structure of the Shirokaya Pad' area, after Kazachenko (2002), modified and supplemented. *1*, Quaternary deposits; *2*, volcanics of the East Sikhote-Alin volcanic belt; *3*, sandstone unit (K_1?); *4*, pelite–siltstone unit with horizons of tuffites, siliceous rocks, and sandstones (J_{2-3}); *5*, Middle–Late Triassic argillaceous–siliceous units; *6*, Carboniferous–Permian siliceous–argillaceous sediments and reef limestones; *7*, granites of the Shirokaya Pad' (*a*) and Vladimir (*b*) massifs (Late Cretaceous); *8*, ore-bearing member (manganese silicate rocks, silicate–magnetite ores, and jaspers): *a*, opened deposit, *b*, predicted deposit; *9*, faults; *10*, outcrops of manganese silicate rocks and numbers of ore occurrences (Kazachenko and Sapin, 1990).

sion of weathering crust on the islands composed of the gabbroids of the Kalinovka, Vladimiro-Aleksandrovskoe, and Sergeevka complexes (Kazachenko et al., 2015, 2016). In the Taukhe terrane, contact metamorphism of cherts with dispersed rhodochrosite, connected with granitoid massifs of the East Sikhote-Alin volcanointrusive belt, occurred in the Late Cretaceous–Paleogene. The manganese silicate rocks of the Samarka terrane formed in the Early Cretaceous, during the formation of the large granitoid bodies of the Khungari–Tatibe complex. The complex mineral composition of the manganese silicate rocks was due to the presence (along with Mn, Si, and Al) of chemical impurities (Mg, Ca, Fe, alkalies, Ti, Ba, etc.) in the initial sediments, regional variations in the chemical composition of sediments, and a decrease in the temperature of mineral formation with distance from the contacts of intrusions and as the intrusions cooled down (Kazachenko, 2002).

METHODS

Samples for the preparation of thin sections and polished sections and samples for geochemical studies (~1.5 kg) were taken by the hand ore sampling method. The contents of minor elements (Table 1) were determined by ICP-MS on a Elan DRC II PerkinElmer (US) mass spectrometer at the Khabarovsk Innovation Analytical Center of the Institute of Tectonics and Geophysics. Acid digestion of the samples was performed in the microwave field.

Analyses of minerals (in polished sections) (Tables 2–7) were carried out on a JXA8100 microprobe with three wave spectrometers and an INCAx-sight energy-dispersive spectrometer (accelerating voltage 20 kV, current 1×10^{-8} A) at the Far East Geological Institute, Vladivostok. Since ore minerals have small grains, the results of their analysis often fall in the region including other (usually silicate) compounds. In this case, the contents of alien elements were not taken into account during the calculation of chemical formulas.

RESULTS

Manganese silicate rocks in all studied areas contain a large group of Ni- and Co-minerals or minerals with a significant isomorphous impurity of these elements. The group includes native elements and intermetallic compounds, sulfoantimonides, sulfoarsenides, sulfides, antimonides, arsenides, tellurides, and silicates (Table 8). Native elements and intermetallic compounds are typical mostly of manganese silicate rocks in the Shirokaya Pad' and Gornaya areas. These are native nickel, Ni-containing copper and bismuth,

Table 2. Results of analyses of Ni- and Co-minerals from manganese silicate rocks of the Shirokaya Pad' area (wt.%)

No.	O	Si	S	Ca	Mn	Fe	Co	Ni	Sb	As	Te	Total	Mineral	Formula
1		0.4	35.59	–	3.61	0.43	–	59.58	–	0.75	–	100.36	Millerite	$Ni_{0.95}(S_{1.04}As_{0.01})_{1.05}$
2	15.90	9.89	–	1.42	10.70	1.11	–	24.97	24.09	11.92	–	100	Breithauptite	$Ni_{1.06}(Sb_{0.51}As_{0.41})_{0.92}$
3	5.28	2.66	17.24	–	0.29	3.1	14.42	16.35	2.99	40.46	–	102.79	Gersdorffite	$(Co_{0.45}Ni_{0.51})_{0.96}(As_{1.00}Sb_{0.05})S_{0.99}$
4	37.96	32.29	–	–	1.22	0.41	–	7.44	–	0.48	17.69	97.85	Imgreite	$Ni_{0.93}(Te_{1.02}As_{0.05})_{1.07}$
5	26.07	16.17	5.28	3.87	18.26	2.6	2.68	8.42	8.22	8.67	–	100.24	(Co, Ni)(As, Sb)S	$(Co_{0.25}Ni_{0.80})_{1.05}(Sb_{0.38}As_{0.65})_{1.03}S_{0.92}$
6	11.84	8.54	–	1.7	11.24	0.96	–	16.62	13.55	–	31.99	96.94	$Ni_3(Te, Sb)_4$	$Ni_{3.07}(Te_{2.72}Sb_{1.21})_{3.93}$
7	10.05	6.71	–	1.06	9.65	0.72	–	17.7	16.23	1.09	38.02	102.98	$Ni_2(Te, Sb, As)_3$	$(Ni_{2.00}Pb_{0.06})_{2.06}(Te_{1.97}Sb_{0.88}As_{0.10})_{2.95}$
8	16.17	8.39	11.86	2	10.25	2.02	15.32	8	–	25.67	2.24	102.82	Cobaltite	$(Co_{0.69}Ni_{0.36})_{1.05}(Te_{0.05}As_{0.91})_{0.96}S_{0.99}$
9	21.06	14.7	–	2.65	17.03	1.42	–	10.99	7.82	0.92	20.32	97.50	$Ni_3(Te, Sb, As)_4$	$Ni_{3.10}(Te_{2.63}Sb_{1.06}As_{0.20})_{3.89}$

Note. Samples: 1, 2, F-79-32; 3, 4, R-80-11; 5–9, R-80-15. Contents of other elements: 4, 0.36 P; 6, 0.5 Mg; 7, 1.75 Pb; 8, 0.9 P; 9, 0.59 Mg.

Table 3. Results of analyses of minerals of ultimately reduced Ni and Co species from manganese silicate rocks of the Shirokaya Pad' area (wt.%)

No.	O	Si	Mn	Fe	Zn	Cu	Ni	Sn	W	Total	Mineral	Formula
1	25.31	17.17	18.88	2.31	11.49	17.36	3.49	–	–	100.84	$(Cu, Ni)_2Zn$	$(Cu_{1.61}Ni_{0.35})_{1.96}Zn_{1.04}$
2	8.96	4.14	–	4.68	–	–	2.09	–	74.64	96.24	Tungsten	$W_{0.86}Ni_{0.08}Co_{0.06}$
3	2	1.22	0.29	1.49	–	–	93.92	–	–	98.92	Nickel	$Ni_{1.00}$
4	28.16	35.4	–	4.98	–	19.08	3.75	1.57	–	97.05	Copper	$Cu_{0.80}Ni_{0.17}Sn_{0.03}$
5	11.18	16.18	1.6	0.37	23.24	36.38	7.3	–	–	97.78	$(Cu, Ni)_2Zn$	$(Cu_{1.62}Ni_{0.35}Mo_{0.03})_2Zn_{1.00}$
6	24.41	2.61	14.48	1.4	13.57	34.06	5.03	–	–	98.44	$(Cu, Ni)_3Zn$	$(Cu_{2.59}Ni_{0.41})_{3.00}Zn_{1.00}$
7	5.5	1.61	3.73	5.76	6.73	9.46	67.28	–	–	101.47	Nickel	$Ni_{0.82}Cu_{0.11}Zn_{0.07}$
8	1.63	1.54	2.56	81.4	–	–	0.45	–	–	98.15	$(Fe, Ni)_7Cr$	$(Fe_{6.99}Ni_{0.04})_{7.03}Cr_{0.97}$

Note. 1, sample R-80-60; 2, R-80-11; 3–6, R-80-60; 7, R-80-15; 8, K-80-2. Contents of other elements: 1, 0.83 Mg and 4.00 Ca; 2, 1.73 Co; 4, 3.08 Cr and 1.03 S; 5, 0.49 Al and 1.04 Mo; 6, 2.01 Al, 0.47 Ca, and 0.40 K; 7, 1.4 Al; 8, 10.57 Cr.

Table 4. Results of analyses of Ni- and Co-minerals from manganese silicate rocks of the Mokrusha area (wt.%)

No.	O	Si	S	Mn	Fe	Co	Ni	As	W	Total	Mineral	Formula
1	9.77	4.01	18.05	4.47	1.05	28.06	–	34.26	–	100.32	Cobaltite	$Co_{0.95}As_{0.92}S_{1.13}$
2	20.98	7.34	22.67	12.64	32.45	2.02	1.62	–	–	100.65	Pyrrhotite	$(Fe_{0.82}Co_{0.05}Ni_{0.04})_{0.91}S_{1.00}$
3	16.9	12.41	15.75	17.67	7.63	17.21	9.89	–	–	99.97	(Co, Ni)S	$(Co_{0.61}Ni_{0.36})_{0.97}S_{1.03}$
4	1.95	0.62	19.18	2.66	0.37	31.53	3.41	39.91	–	99.63	Cobaltite	$(Co_{0.93}Ni_{0.10})_{1.03}As_{0.93}S_{1.04}$
5	2.25	1.48	14.13	3.63	–	22.59	3.68	0.67	–	102.85	Costibite	$(Co_{0.86}Ni_{0.14})_{1.00}(Sb_{1.00}As_{0.02})_{1.02}S_{0.98}$
6	3.26	0.62	19.41	1.94	1.67	30.07	3.94	40.66	–	101.57	Cobaltite	$(Co_{0.89}Ni_{0.11})_{1.00}As_{0.95}S_{1.05}$
7	15.93	4.7	–	10.81	0.44	0.58	–	–	65.58	99.41	Tungsten	$W_{0.97}Co_{0.03}$

Note. 1, 0.65 Al; 2, 3, 0.93 and 2.51 Ca, respectively; 5, 54.42 Sb; 7, 1.37 Ca.

Co- or Ni-containing tungsten (Tables 3, 4, and 6), maucherite (Tables 6 and 7), Ni-containing Fe chromide (Table 3) and Co chromide, Ni phosphide (Table 6), and intermetallic compounds of Ni, Cu, Zn, and Sn (Tables 3, 6, and 7). Native nickel with Co (and, possibly, Fe) impurity and tungsten with Co (or Co and Ni) impurity occur as grains few micrometers in diameter in organic-matter segregations or as inclusions in rock-forming minerals in the immediate vicinity of these segregations. Maucherite, found in manganese silicate rocks from the Gornaya and Sadovaya areas, occurs as individual acicular crystals in rock-forming minerals, also associated with organic matter. The rocks from the Gornaya area contain phosphide $Ni_{11}P_2$ (Table 6) along with native Sn, Ni, Sb, and Pb, maucherite, Cu_3Sn_2, $(Cu,Ni)_3Zn_2$, and other minerals. Phosphorus and nickel form various compounds: Ni_5P, Ni_4P, Ni_5P_2, Ni_2P, NiP_2, NiP_3, etc. Many of them are metastable and are absent from the phase diagram. By now, only rhabdite (nickelphosphide), an essentially nickel variety of schreibersite $(Fe,Ni)_3P$, has been found in nature. Phosphide from the Gornaya area is intermediate in composition between Ni_5P and Ni_6P and is probably a variety of one of them. Manganese silicate rocks

Table 5. Results of analyses of sulfoarsenides, sulfoantimonides, and sulfobismuthides of Ni and Co from manganese silicate rocks of the Gornaya area (wt.%)

No.	O	Si	S	Mn	Fe	Co	Ni	Sb	As	Pb	Bi	Total	Mineral	Formula
1	7.66	1.63	12.3	0.61			27.98		27.76	20.27		98.21	As-parkerite	$(Ni_{2.51}Pb_{0.52})_{3.03}As_{1.95}S_{2.02}$
2	24.39	15.34	3.46	21.3	0.75		9.88	0.77			22.64	100.28	Parkerite	$Ni_{3.01}(Bi_{1.94}Sb_{0.12})_{2.06}S_{1.93}$
3	3.44	0.93	18.54	1.34		5.75	29.03	1.46	42.51			103.00	Gersdorffite	$(Ni_{0.85}Co_{0.17})_{1.02}(As_{0.97}Sb_{0.02})_{0.99}S_{0.99}$
4	14.44	6.44	6.33	13.11			17.23				41.77	100.92	Parkerite	$Ni_{2.93}(Bi_{2.00}Te_{0.10})_{2.10}S_{1.97}$
5	3.16	0.45	27.56	3.2	0.59	1.18	50.71		15.16			102.01	As-hauchecor-nite	$(Ni_{4.00}Co_{0.09})_{4.09}As_{0.94}S_{3.98}$
6	25.61	8.47	9.91	20.54	0.69	1.37	19.28	1.87	1.5		10.56	101.20	Hauchecornite	$(Ni_{3.96}Co_{0.29})_{4.25}(Bi_{0.61}As_{0.24}Sb_{0.19})_{1.04}S_{3.72}$
7	2.5	1.69	18.29	3.13		16.1	16.04		44.44			102.19	Cobaltite–gersdorffite	$(Ni_{0.48}Co_{0.48})_{0.96}As_{1.04}S_{1.00}$
8	4.09	1.36	22.25	5.59	0.53	6.31	34.97	8.24	10.5		8.83	102.67	As-hauchecor-nite	$(Ni_{3.25}Co_{0.58})_{3.83}(As_{0.77}Sb_{0.37}Bi_{0.23})_{1.37}S_{3.79}$
9	9.24	1.69	10	5.75			24.57	3.29			47.08	102.48	Parkerite	$Ni_{2.98}(Bi_{1.61}Sb_{0.19})_{1.80}S_{2.22}$
10	5.07	2.47	21.81	6.74	0.7	3.74	38.11	13.43	1.57	1.34	6.6	101.58	Tucekite	$(Ni_{3.74}Co_{0.37}Pb_{0.04})_{4.15}(Sb_{0.64}Bi_{0.18}As_{0.12})_{0.94}S_{3.92}$

Note. 1, 2, sample Ev-01-24; 3–4, Ev-93-210; 5–9, Ev-93-206; 10, Ev-93-213. Contents of other elements: 2, 0.56 Mg and 1.19 Ca; 4, 0.29 Ca and 1.31 Te; 6, 0.83 Mg and 0.57 Ca; 9, 0.42 Mg and 0.44 Al.

Table 6. Results of analyses of sulfides, arsenides, antimonides, and other minerals from manganese silicate rocks of the Gornaya area (wt.%)

No.	O	Si	S	Mn	Fe	Zn	Cu	Co	Ni	Sb	As	W	Total	Mineral	Formula
1	17	16.87	9.84	0.61	–	–	–	–	40.4	–	15.29	–	100.01	$Ni_4(S,As)_3$	$Ni_{4.02}(S_{1.79}As_{1.19})_{2.98}$
2	19.37	20.51	19.34	0.88	0.6	–	26.41	–	11.17	–	–	–	98.28	(Cu,Ni)S	$(Cu_{0.69}Ni_{0.31})_{1.00}S_{1.00}$
3	19.74	16.58	16.53	2.94	–	–	–	2.64	31.27	8.58	1.72	–	100	Millerite	$(Ni_{0.90}Co_{0.08})_{0.98}(S_{0.87}Sb_{0.12}As_{0.04})_{1.03}$
4	8.99	6.86	20.71	10.16	0.39	–	–	–	51.04	2.37	2.84	–	103.36	Ni_4S_3	$Ni_{3.87}(S_{2.87}As_{0.17}Sb_{0.08})_{3.12}$
5	7.99	3.43	2.04	8.23	0.44	–	–	–	28.28	47.33	3.34	–	101.08	Breithauptite	$Ni_{0.98}(Sb_{0.79}As_{0.09}S_{0.13})_{1.01}$
6	–	0.61	–	–	–	–	–	–	49.09	0.95	48.03	–	98.68	Ni_4As_3	$Ni_{3.94}(As_{3.02}Sb_{0.04})_{3.06}$
7	6.08	2.95	–	6.14	0.39	–	–	–	54.61	0.88	28.96	–	100.01	Orcelite	$Ni_{4.92}(As_{2.04}Sb_{0.04})_{2.08}$
8	2.42	3.28	16.1	–	–	–	–	–	54.22	10.82	9.87	–	96.71	$Ni_4(S,As,Sb)_3$	$Ni_{3.93}(S_{2.14}As_{0.56}Sb_{0.38})_{3.08}$
9	1.72	0.34	35.08	1.73	2.34	–	–	8.76	50.14	–	–	–	100.11	Millerite	$(Ni_{0.80}Co_{0.14}Fe_{0.04})_{0.98}S_{1.02}$
10	2.85	1.1	0.67	4.94	–	–	–	–	40.15	5.09	47.86	–	102.66	Niccolite	$Ni_{0.99}(As_{0.92}Sb_{0.06}S_{0.03})_{1.01}$
11	6.46	3.55	–	6.78	–	–	–	–	75.4	–	–	–	99.23	$Ni_{11}P_2$	$Ni_{11.00}P_{2.00}$
12	13.13	10.44	0.47	0.82	–	–	–	1.09	39.41	0.64	32.93	–	98.93	Maucherite	$(Ni_{2.92}Co_{0.08})_{3.00}(As_{1.91}Sb_{0.02}S_{0.07})_{2.00}$
13	17.13	14.93	0.36	1.71	–	26.45	40.01	–	0.62	–	–	–	101.21	$(Cu,Ni)_3Zn_2$	$(Cu_{3.01}Ni_{0.05})_{3.06}Zn_{1.94}$
14	2.67	1.96	–	5.19	–	–	–	–	2.65	–	–	–	101.21	Bismuth	$Bi_{0.90}Ni_{0.10}$
15	33.66	16.75	–	1.94	–	–	–	1.29		–	–	21.89	96.92	Tungsten	$W_{0.84}Co_{0.16}$
16	12.47	4.63	–	8.98	–	–	–	–	72.16	–	–	–	100.73	Nickel	$Ni_{1.00}$

Note. 1, sample Ev-01-24; 2, Ev-93-210; 3–8, Ev-93-206; 9, Ev-93-213; 10, Ev-93-203; 11–13, Ev-93-210; 14, 15, Ev-93-206; 16, Ev-93-203. Contents of other elements: 11, 7.04 P; 14, 88.74 Bi; 15, 0.29 Na, 5.42 Al, 8.24 K, 1.37 Ti, and 6.07 Cr; 16, 0.43 Mg, 0.57 Ca, and 1.49 Al.

from the Gornaya, Shirokaya Pad', and Sadovaya areas contain intermetallic compounds of Cu, Zn, and Ni. The analyzed compositions of some of them can be recalculated to ideal formulas Cu_5NiZn_3, Cu_7NiZn_3, Cu_3NiZn_3, and Cu_4NiZn_3. These minerals are probably Cu- and Ni-ordered analogs of compounds $(Cu,Ni)_4Zn_3$, $(Cu,Ni)_5Zn_3$, $(Cu,Ni)_2Zn$, and $(Cu,Ni)_8Zn_3$. In addition, intermetallic compounds of Cu and Ni as well as Cu, Sn, Pb, and Ni are widespread in the Shirokaya Pad' and Sadovaya areas.

Cobaltite–gerdsdorffite solid solution is the most common Ni–Co mineral in manganese silicate rocks of all the studied areas. Its Co- and Sb-rich varieties (Fig. 3*a*, *b*, Table 2), along with As-rich ulmanite, are widespread in the Shirokaya Pad' area. These minerals with the general formula (Ni,Co)(As,Sb)S are characterized by a wide isomorphism between the As and Sb end-members. Members of the cobaltite–gerdsdorffite series (Fig. 3*c*), sometimes with a small impurity of Sb (Table 5) the only minerals

Table 7. Results of analyses of Ni- and Co-minerals from manganese silicate rocks of the Sadovaya area (wt.%)

No.	O	Si	S	Ca	Mn	Fe	Co	Ni	As	Total	Mineral	Formula
1	23.9	17.82	8.76	10.76	2.34	8.52	9.95	1.22	14.97	98.24	Cobaltite	$(Co_{0.87}Ni_{0.11})_{0.98}As_{1.02}S$
2	10.41	5.44	–	0.62	0.62	4.08	–	0.55	–	100.89	$(Cu, Ni)_3Sn$	$(Cu_{2.88}Ni_{0.04})_{2.92}Sn_{1.09}$
3	10.62	6.19	–	0.79	7.21	–	–	39.40	35.81	100.02	Maucherite	$Ni_{2.92}As_{2.08}$
4	–	–	40.11	–	2.43	5.74	28.79	22.9	–	99.97	Siegenite	$(Ni_{1.22}Co_{1.53}Fe_{0.32})_{3.07}S_{3.92}$
5	4.07	0.81	35.01	–	33.12	0.72	5.77	17.52	–	100.48	Millerite	$(Ni_{0.65}Co_{0.21}Zn_{0.11})_{0.97}S_{1.03}$
6	–	0.24	32.32	–	2.15	21.61	4.71	38.14	–	99.17	Pentlandite	$(Ni_{5.20}Co_{0.64}Fe_{3.10})_{8.94}S_{8.06}$
7	–	–	40.71	–	2.68	3.81	25.73	28.36	–	101.29	Polydymite	$(Ni_{1.50}Co_{1.35}Fe_{0.21})_{3.06}S_{3.94}$
8	2.52	1.33	18.45	–	3.8	0.62	0.57	33.32	40.69	102.78	Gersdorffite	$(Ni_{1.00}Co_{0.02})_{1.02}(As_{0.95}Sb_{0.02})_{0.97}S_{1.01}$
9	20.06	10.08	–	–	27.27	1.36	–	19.52	23.55	102.76	Niccolite	$Ni_{1.02}\ (As_{0.96}Sb_{0.02})_{0.97}$
10	–	0.46	31.19	–	3.06	23.32	–	38.74	0.85	97.62	Pentlandite	$(Ni_{5.44}Fe_{3.44})_{8.88}(S_{8.02}As_{0.09})_{8.11}$

Note. 1, 2, sample Sd-06-1(2); 3–10, Sd-06-1(1). Contents of other elements: 2, 0.32 Al, 46.25 Cu, and 32.6 Sn; 5, 0.25 Al and 3.21 Zn; 8, 9, 1.48 and 0.92 Sb, respectively.

with the general formula (Ni,Co)(As,Sb)S, that are present in the Gornaya area. In the Sadovaya area, this mineral (Table 7) is almost free of Sb, and Co-rich varieties are rare (Fig. 3*d*). In the Mokrusha area, there are Sb-free Co-richest varieties of this mineral (Fig. 3*d*), associated with costibite, a Sb-containing analog of cobaltite (Table 4).

Other complex compounds of Ni and Co in the manganese silicate rocks are parkerite and its As-containing analog, hauchecornite, tucekite, and their As-containing analog. A specific feature of these minerals is the presence of Pb and a low content of Co (Table 5). Parkerite contains some Sb or (seldom) Te. This group of minerals is found only in manganese silicate rocks of the Gornaya area.

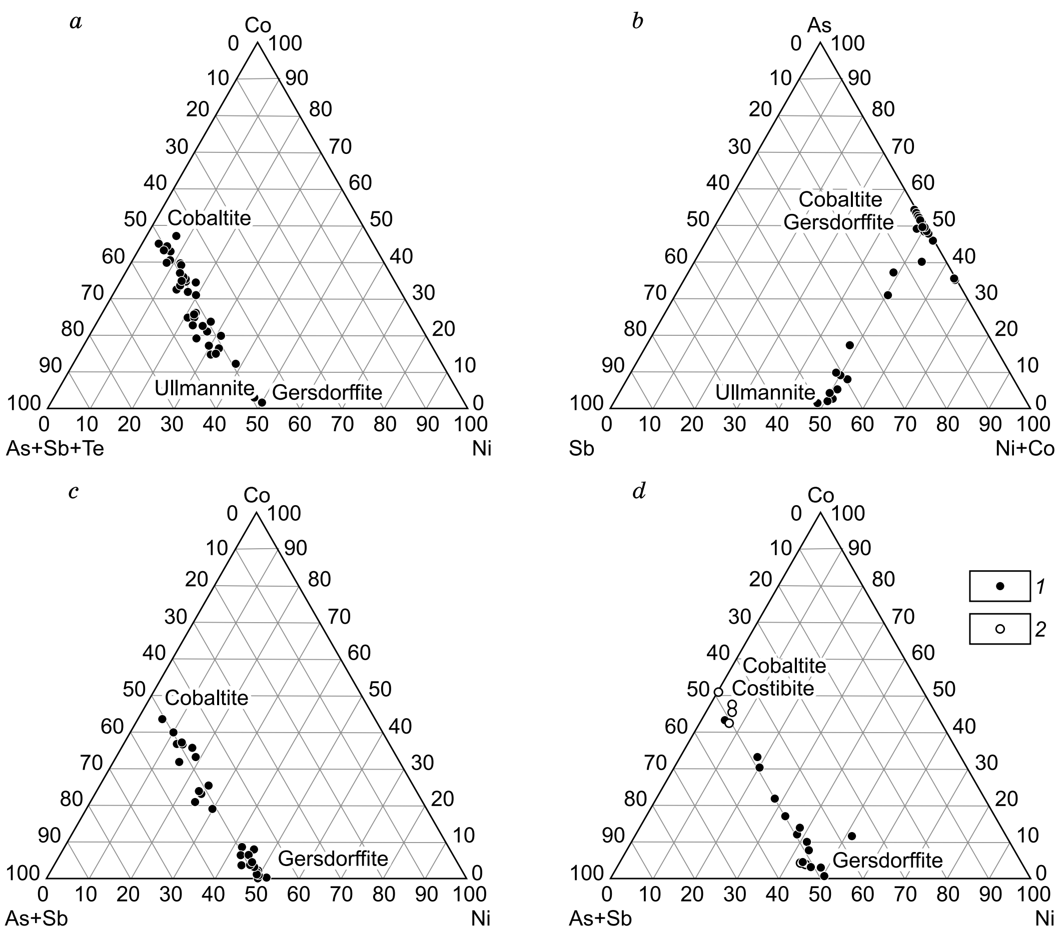

Fig. 3. Composition of (Ni, Co)(As, Sb, Te)S minerals from Sikhote-Alin manganese silicate rocks. *a*–*d*, areas: *a*, *b*, Shirokaya Pad', *c*, Gornaya, *d*, Sadovaya (*1*), Mokrusha (*2*).

Table 8. Mineralogy of Ni and Co in the Sikhote-Alin manganese silicate rocks

Minerals	Area			
	Shirokaya Pad'	Mokrusha	Gornaya	Sadovaya
Nickel	+	–	+	–
Ni-containing copper	+	–	–	–
Ni-containing bismuth	–	–	+	–
Co-containing tungsten	+	+	+	–
Maucherite	–	–	+	+
$(Cu, Ni)_2Zn$	+	–	+	–
$(Cu, Ni)_3Zn$	+	–	–	–
$(Cu, Ni)_3Zn_2$	–	–	+	–
$(Cu, Ni)_4Zn_3$	–	–	+	–
$(Cu, Ni)_5Zn_3$	–	–	–	+
Cu_4Ni	+	–	–	–
$Cu_{11}Ni_3$	+	–	–	–
NiCuSn	+	–	–	–
$(Cu, Ni)_3Sn$	–	–	–	+
$(Cu, Ni)_2(Sn,Pb)$	–	–	–	+
Co_3Cr	+	–	–	–
$(Fe, Ni)_7Cr$	+	–	–	–
$Ni_{11}P_2$	–	–	+	–
Ni-containing pyrite	–	–	–	+
Ni-containing pyrrhotite	+	+	–	–
Millerite	+	–	+	+
Siegenite	–	–	–	+
Pentlandite	–	–	–	+
Polydymite	–	–	–	+
(Co, Ni)S	–	+	–	–
(Cu, Ni)S	–	–	+	–
Ni_4S_3	–	–	+	–
$Ni_4(S, As)_3$	–	–	+	–
$Ni_4(S, As, Sb)_3$	–	–	+	–
Ni_4As_3	–	–	+	–
Orcelite	–	–	+	–
Gersdorffite	+	–	+	+
Cobaltite	+	+	+	+
Ni(As, Sb)S	+	–	–	–
(Co, Ni)(As, Sb)S	+	–	–	–
Ulmannite	+	–	–	–
Costibite	–	+	–	–
As-hauchecornite	–	–	+	–
Tucekite	–	–	+	–
Hauchecornite	–	–	+	–
$Ni_{12}As_4S_{13}$	–	–	+	–
As-parkerite	–	–	+	–
Parkerite	–	–	+	–
Breithauptite	+	–	+	–
Niccolite	+	–	+	+
Imgreite NiTe	+	–	–	–
$Ni_2(Te, Sb, As)_3$	+	–	–	–
$Ni_3(Te, Sb)_4$	+	–	–	–
$Ni_3(Te, Sb, As)_4$	+	–	–	–
Ni-containing cummingtonite	–	–	+	–
Ni-containing phlogopite	–	–	+	–

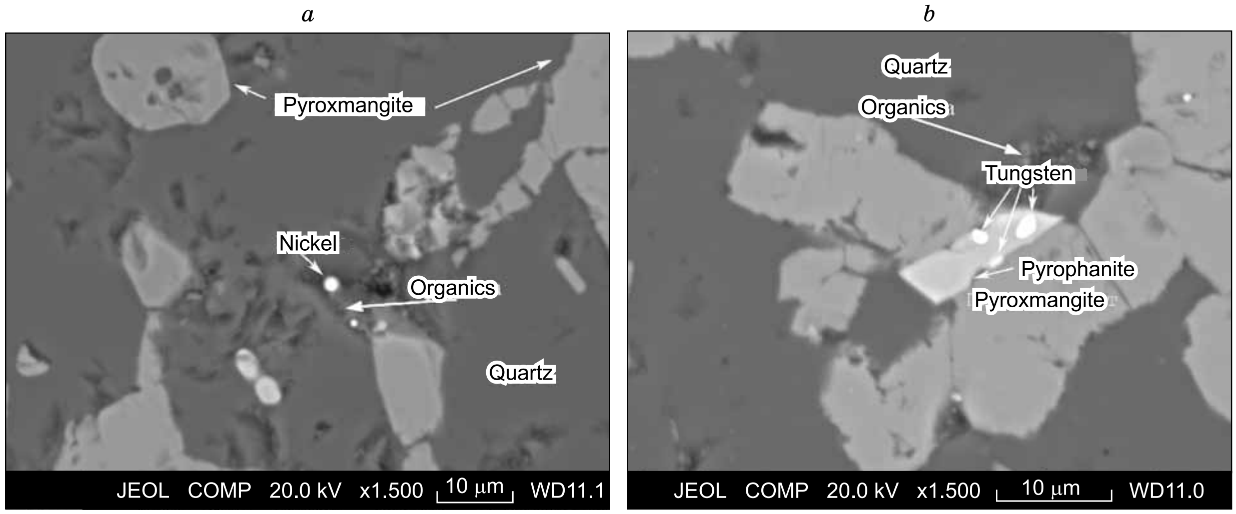

Fig. 4. Native nickel (sample Ev-01-24) (*a*) and Co-containing tungsten (Ev-93-203) (*b*) in manganese silicate rocks from the Gornaya area.

The manganese silicate rocks of the studied areas differ from each other in the set, composition, and abundance of Ni and Co sulfides, antimonides, and arsenides. A specific feature of rocks of the Gornaya area is the presence of millerite containing Co and, more seldom, As or Sb (Table 6) and of sulfide Ni_4S_3, sometimes rich in As and Sb. Nickel-containing pyrrhotite was found in the rocks of the Shirokaya Pad' and Mokrusha areas (up to 0.48 and 1.62 wt.% Ni, respectively) (Table 4). In the Sadovaya area, Ni-containing (up to 1.85 wt.%) pyrite occurs instead of pyrrhotite. Iron sulfides of the Mokrusha and Sadovaya areas are enriched in Co (up to 2.02 and 2.85 wt.%, respectively). The rocks of the Shirokaya Pad' area contain niccolite and breithauptite. These minerals are rare in the Gornaya area, where they are usually enriched in S. Niccolite contains Sb, and breithauptite contains As (Table 6). The same features are specific to these minerals in the metamorphogenic-hydrothermal veins of the Norilsk ore field, which have compositions corresponding to the continuous niccolite–breithauptite isomorphous series (Gritsenko and Spiridonov, 2005). Sulfides, antimonides, and arsenides of the Gornaya area are enriched in Co. There are also Ni-rich arsenides: orcelite and Ni_4As_3. In the Mokrusha and Sadovaya areas, this group of minerals (Tables 4 and 7) is represented by Co-rich or Co-enriched sulfides: millerite (in which Co sometimes dominates over Ni) and siegenite, polydymite, and pentlandite, respectively. The domination of sulfides over arsenides and their enrichment in Co is a specific feature of rocks of the Mokrusha, Sadovaya, and Gornaya areas. Rocks of the Shirokaya Pad' area show, on the contrary, domination of Ni arsenides and antimonides over Ni sulfides and low contents of Co (or its absence) in these minerals (Table 2). Niccolite, breithauptite, and intermediate members of the niccolite–breithauptite solid solution are widespread in this area. In contrast to similar minerals in the Gornaya area, they lack S (for rare exception). A specific feature of the rocks of the Shirokaya Pad' area is the presence of As- and, particularly, Sb-enriched tellurides, whose analyzed compositions are recalculated to the ideal formulas NiTe, Ni_3Te_4, and Ni_2Te_3 (Table 2).

The rock-forming Ni-containing silicates—phlogopites and amphiboles of the cummingtonite–grünerite series (up to 0.87 and 0.22 wt.% NiO, respectively)—occur only in rocks of the Gornaya area.

The considered Ni- and Co-minerals in the Sikhote-Alin manganese silicate rocks are rock-forming (phlogopite and amphiboles) or accessory (other) minerals. Native nickel and cobalt and their intermetallic compounds are found in areas containing organic matter or are present as inclusions in rock-forming minerals in the immediate vicinity of these areas (Fig. 4). Besides them, native Pb, Zn, Fe, Sn, Se, Au, and Pt, "cupriferous gold", disordered solid solutions, and intermetallic compounds of the systems Cu–Sn–Pb, Pb–Sb–Sn, and Cu–Al–Zn are present in intimate association with organic matter in the Sikhote-Alin manganese silicate rocks (Perevoznikova, 2010). Sulfoantimonides, sulfoarsenides, sulfides, antimonides, arsenides, and tellurides of Ni and Co, like many other ore minerals (galena, sphalerite, chalcopyrite, arsenopyrite, wolframite, scheelite, molybdenite, cassiterite, stannite, cinnabar, stibnite, boulangerite, jamesonite, bournonite, löllingite, bismuthine, fahlore, altaite, native Sb and Bi, etc.), intergrow with the rock-forming minerals or inclusions in them without signs of reactive interactions (Fig. 5). Mineral of the cobaltite–gerdsdorffite series occurs as inclusions in pyrite, rhodonite, and parkerite and contains galena and pyrrhotite inclusions. In the Sadovaya area it is found in intergrowth with pentlandite, galena, and sphalerite or as inclusions in polydymite. The cobaltite–gerdsdorffite mineral of the Gornaya area sometimes occurs as crystals with cores formed by granular annabergite. Millerite is present as individual crystals (or their clusters), sometimes with inclusions of hauchecornite group minerals, in the rock-forming minerals. It is also found together with molybdenite or in intergrowths with parkerite and chalcopy-

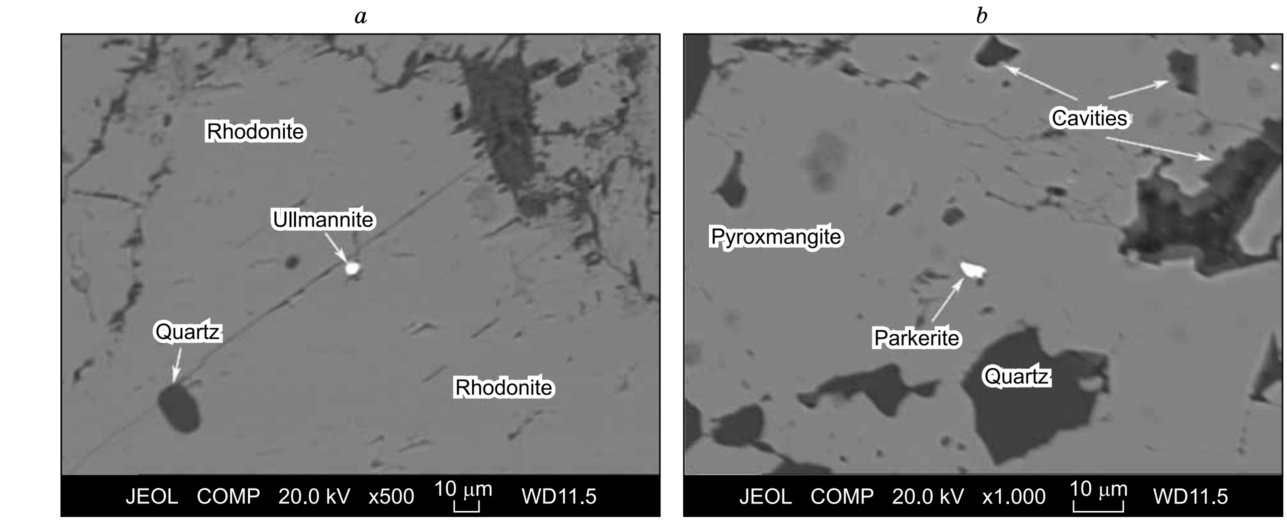

Fig. 5. Ulmanite (sample F-79-32) (*a*) and parkerite (sample Ev-93-203) (*b*) inclusions in manganese silicate rocks from the Shirokaya Pad' (*a*) and Gornaya (*b*) areas.

rite. Hauchecornite group minerals were observed as individual grains, their clusters, or inclusions in millerite. Breithauptite occurs as individual grains, inclusions in nickel arsenide Ni_4As_3, and intergrowths with fluorapatite in rhodonite crystals. Parkerite is sometimes found in intergrowth with millerite. Nickel arsenide Ni_4As_3 often contains breithauptite inclusions. Ulmannite was observed as individual grains (Fig. 5*a*) and together with a mineral of the cobaltite–gersdorffite series and costibite. Sometimes it is intergrown with chalcopyrite or occurs as acicular crystals or their intergrowths with galena in the latter. Telluride NiTe was found in intergrowth with a mineral of the cobaltite–gerdsdorffite series. Costibite occurs together with a mineral of the cobaltite–gerdsdorffite series. Siegenite forms an exsolution "lattice" in pentlandite.

DISCUSSION

Previous studies of the geochemistry and mineralogy of REE and some other minor elements in the manganese silicate rocks made it possible to establish the main events of the early period (middle Devonian–late Triassic) of the Sikhote-Alin geologic history that determined the metallogeny of this structure (Kazachenko et al., 2015). The results of this research provide a better understanding of the prerequisites and mechanisms of formation of deposits of noble and other metals in black-shale strata. Cobalt–nickel mineralization is probably a specific feature of many occurrences of metamorphosed carbonate–siliceous and oxide–carbonate–siliceous Mn-ores. Nickel and cobalt minerals (niccolite, gersdorffite, cobaltite, pentlandite, and violarite) are present, in particular, in contact-metamorphosed oxide–carbonate Mn-ores of many deposits in Japan (Noda-Tamagawa, Kaso, Taguchi, etc.) (Lee, 1955; Watanabe et al., 1973), which are similar in mineral composition, mineral assemblages, geologic environments, and the age of the protoliths to the Sikhote-Alin manganese silicate rocks. Pentlandite was found in the South Urals rhodonite deposits (Brusnitsyn, 2000).

Nickel and cobalt compounds, like other ore minerals of manganese silicate rocks, belong to two groups according to the type of their relations with the rock-forming minerals. The first group includes compounds of the valence species of Ni, Co, and other elements. Cobaltite–gerdsdorffite solid solution is the most abundant among Ni- and Co-minerals of this group, such as sulfoantimonides, sulfoarsenides, sulfides, antimonides, arsenides, tellurides, and silicates. Parkerite, niccolite, millerite, hauchecornite, and some other Ni–Co minerals of manganese silicate rocks are typical of many Pt-mineral deposits. Parkerite was found together with bismuthohauchecornite and other Ni-minerals in the Norilsk ore field (Ponomarenko et al., 1987; Spiridonov et al., 2007) and in other areas. Compound Ni_4As_3 is obviously a natural analog of the known synthetic compound of the same composition. Orcelite has been recently found in serpentinites of the Shlezha ophiolite complex, along with native gold and other Ni arsenides (Delura, 2004). Telluride NiTe is similar in composition to the earlier discredited imgreite. Tellurides Ni_3Te_4 and Ni_2Te_3 are intermediate in composition between imgreite and melonite $NiTe_2$ (sometimes they are described by the formula $NiTe_{2-x}$). It is not ruled out that all tellurides of manganese silicate rocks are the same mineral of varying composition (melonite). Minerals of the hauchecornite group (Gait and Harris, 1972; Just, 1980) belong to the same isomorphic series including the Bi (hauchecornite), Sb (tucekite), As, and Te end-members. Manganese silicate rocks contain essentially Bi (hauchecornite), As, and, most often, Sb (tucekite) varieties of this series. Nickel and cobalt compounds, like other ore minerals (galena, sphalerite, chalcopyrite, arsenopyrite, wolframite, scheelite, molybdenite, cassiterite, stannite, cinnabar, stibnite, boulangerite, jamesonite, bournonite, löllingite, bismuthine, fahlore, altaite, native Sb and Bi, etc.), form inclusions in the rock-forming minerals, showing no signs of reactive relations with them. They crystallized during metamorphism under the same conditions as the host minerals.

The second group includes native Ni, Co, and many other elements and their intermetallic compounds. The Ni- and Co-minerals of this group are maucherite, native nickel, Ni phosphide, Ni and Co chromides, and disordered solid solutions and intermetallic compounds of Ni with Cu, Zn, Sn, and Pb. These minerals, like other native elements (Pb, Zn, Fe, Sn, Se, Au, and Pt), "cupriferous gold", and intermetallic compounds of Cu, Sn, Pb, Sb, Al, and Zn, are closely associated with organic matter and formed during metamorphism under highly and ultrahighly reducing conditions.

A review of the literature data shows that assemblages of minerals formed under highly and ultrahighly reducing conditions are abundant in black-shale formations and associated deposits (Distler et al., 1996), meteorites, ultrabasic rocks and products of their hydrothermal alteration (Delura, 2005), combustion products of coal, kimberlites, diamonds (Gorshkov et al., 2003; Titkov et al., 2006), carbonado (Petrovskii et al., 2004), lunar regolith, coal, and some other rocks. They have been found in manganese silicate rocks for the first time and thus are of particular interest in the mineralogical and genetic aspects.

The protoliths of manganese silicate rocks were initially enriched in ore elements, which contributed to the formation of minerals of the valence species of Ni, Co, and other metals of the first group during metamorphism. A specific feature of noble-metal mineralization of this group is the total absence of "cupriferous gold" and the presence of rather large (up to 0.5 mm in diameter) segregations of native Au in the form of Au–Ag solid solution. Associations of native elements and intermetallic compounds of the second group are often localized in mineralized microcracks and pores (preserved during metamorphism) containing organic matter. This indicates the active participation of C and, probably, H, which ensured the highly and ultrahighly reducing conditions of mineral formation. A specific feature of noble-metal mineralization of the second group is a wide occurrence of "cupriferous gold" and finest (fractions of microns to first microns in diameter) mineral particles. According to the data presented, the redox conditions of metamorphism near microcracks and in the rest rock differed strongly. Probably, minerals of different ultimately reduced metals in manganese silicate rocks, like those in metamorphosed Triassic metalliferous sediments of other types (silicate–magnetite ores and jasper) (Kazachenko et al., 2008; Miroshnichenko and Perevoznikova, 2010), formed under the influence of organic matter of the underlying argillaceous–siliceous unit. Heating of carbonaceous rocks led to the removal of the most volatile components, first of all, weakly bound water and hydrocarbons, and to the appearance of the certain amount of fluid with highly and ultrahighly reducing properties, which migrated along fractures into other rocks. This process is established from the presence of numerous thin (fractions of mm–few mm) veinlets cutting the rocks of argillaceous–siliceous and siliceous units and containing organic matter, noble-metal mineralization, and ultimately reduced metal species. The veinlets bear pyrite, galena, Ni-containing pyrrhotite, sphalerite, chalcopyrite, arsenopyrite, chloanthite–smaltine, $(Ni,Co)As_3$, cinnabar, argentite, V- and Co-containing magnetite, stibnite, molybdenite, scheelite, Ag-rich fahlore, boulangerite, tenorite, bravoite, coloradoite, galenobismuthite, bournonite, and pentlandite. Native Zn, Sb, Bi, Ni, Cu, and Pb are also present. In addition, there are Cd, Cr, Sn, Fe, Al, W, Pt, Au, Ag, "cupriferous gold", and disordered solid solutions and intermetallic compounds of the systems Ni–Cr–Fe, Cu–Ni–Zn, and W–Co–Ti–Mo. Organic matter of the argillaceous–siliceous unit was obviously the source of metals present in the veinlets. This conclusion is confirmed by the high contents of ore elements in carbonaceous silicites (Volokhin and Ivanov, 2007) and by the presence of noble-metal and nickel–cobalt mineralization and ultimately reduced metal species in metamorphosed analogs of carbonaceous rocks (Miroshnichenko and Perevoznikova, 2010). The same ore components and mineralization were later discovered in carbonaceous silicites without obvious signs of metamorphism (Volokhin and Karabtsov, 2016).

CONCLUSIONS

We have established that the presence of various Ni- and Co-minerals in the studied manganese silicate rocks is due to the high contents of these and other ore elements in the initial sediments, temporal and spatial changes in the thermal conditions of metamorphism, regional variations in the chemical composition (contents of ore elements) of the initial sediments, and local highly and ultrahighly reducing conditions of mineral formation.

Nickel and cobalt compounds, like other ore minerals in the Sikhote-Alin manganese silicate rocks, belong to two genetic groups including minerals of valence and ultimately reduced species of Ni, Co, and other metals.

Minerals of the valence species of Ni, Co, and other metals formed from the protolith material during metamorphism under the same conditions as the rock-forming minerals.

The presence of minerals of ultimately reduced Ni, Co, and other metals in the manganese silicate rocks is due to the influence of organic matter of the underlying argillaceous–siliceous unit. Heating of carbonaceous rocks leads to the removal of their most volatile components, first of all, weakly bound water and hydrocarbons, during metamorphism and the appearance of a certain amount of metal-enriched fluid with highly and ultrahighly reducing properties, which then migrated along fractures into other rocks.

The presence of Au–Pd–Pt–Ni–Co association (typomorphic for basic and ultrabasic rocks) in the Triassic protoliths of the studied manganese silicate rocks and carbonaceous silicites is probably due to the sorption of these elements by Mn and Fe hydroxides and organic matter during the exogenous weathering of the ancient Sikhohte-Alin gabbroids.

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