

Distribution of Noble Metals in Ore Mineral Assemblages of the Volkovsky Gabbroic Pluton, Central Urals

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Abstract—Relationships between noble-metal and oxide–sulfide mineralization during the origin of the Volkovsky gabbroic pluton are discussed on the basis of geochemical data and thermodynamic calculations. The basaltic magma initially enriched in noble metals (NM) relative to their average contents in mafic rocks, except for Pt, is considered to be a source of Pd, Pt, Au, and Ag in the gabbroic rocks of the Volkovsky pluton. The ores were formed with a progressive gain of NM in the minerals during the fractionation of the basaltic magma. The active segregation of NM in the form of individual minerals (palladium tellurides and native gold) hosted in titanomagnetite and copper sulfide ore occurred during the final stage of gabbro crystallization, when the residual fluid-bearing melt acquired high concentrations of Cu, Fe, Ti, and V, along with volatile P and S. Copper sulfides—bornite and chalcopyrite—are the major minerals concentrating NM; they contain as much as 22.65–25.20 ppm Pd and 0.74–1.56 ppm Pt; 4.39–8.0 ppm Au, and 127.2–142.6 ppm Ag, respectively. The copper ore and associated NM mineralization were formed at a relatively low sulfur fugacity, which was a few orders of magnitude (attaining 5 log units) lower than that of the pyrite–pyrrhotite equilibrium. The low sulfur fugacity and the close chemical affinity of Pd and Pt to Te precluded the formation of pyrrhotite, pyrite, and PGE disulfides. The major ore minerals and NM mineralization were formed within a wide temperature range (800–570°C), under nearly equilibrium conditions. Foreign elements (Ni, Co, and Fe) affected the thermodynamic stability of Pd and Pt compounds owing to the difference in their affinity to Te and to elements of the sulfur group (S, Se, and As). The replacement of Pd with Ni and Co and, to a lesser extent, with Pt and the replacement of Te with S, As, and Se diminish the stability field of palladium telluride. Comparison of Pd tellurides from copper sulfide ores at the Volkovsky and Baronsky deposits showed the enrichment of the former in Au, Sb, and Bi, while the latter are enriched in Pt, Ni, and Ag. The enrichment of Pd tellurides at the Baronsky deposit in Ni is correlated with the analogous enrichment of the host gabbroic rocks.

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INTRODUCTION

A survey of the literature on noble metal contents in mafic and ultramafic complexes and related ore mineralization [1–7] indicates that titanomagnetite and associated copper sulfide ores are still studied much more poorly than chromite, copper–nickel, massive sulfide, and porphyry copper deposits. The literature on noble metals (NM) in titanomagnetite deposits is largely focused on the geological, petrological, and mineralogical aspects of ore formation, which can be only provisionally correlated with formation of Fe and Cu ores proper. Therefore, genetic models of the NM mineralization associated with titanomagnetite and copper sulfide ores remain inadequately developed. The only exception is [4], in which the concentration of NM is explained by ferritization and sulfurization of mafic melts, processes that give rise to the formation of ferritic and sulfide liquids. These processes are thought to proceed under variable redox conditions, controlled by variations in the oxygen partial pressure. The authors emphasize a much closer chemical affinity of NM to

elements of the sulfur group (Se, Te) than to oxygen. In other words, NM accumulation in mafic melts is predetermined by the ability of sulfide liquid to extract these metals from a crystallizing melt, as was demonstrated in numerous experiments [8–11]. As concerns the formation of PGE- and sulfide-bearing magmas, some researchers highlight the effects of immiscibility and separation of sulfide liquid [5–7], whereas others attach importance to transmagmaic fluids and fluid–magma interaction (sulfurization) [12, 13]. It should be noted that both points of view are based on experimental evidence.

In this paper, we consider the NM behavior in rocks and ores related to the Volkovsky gabbroic pluton, which provides insights into the possible physicochemical conditions of NM concentration in titanomagnetite and copper sulfide ores. The Pd, Pt, Au, and Ag distribution in the process of ore formation is interpreted by using thermodynamic analysis. The published experimental data on the interaction of volatiles with mafic melts are attracted to elucidate the role of immiscibility and fluid–magma interaction in the formation of apa-



Fig. 1. Schematic geological map of the Volkovsky gabbro pluton (modified from materials of the Krasnoyarsk Geological Exploration Team). (1) Quaternary loose sediments; (2) Upper Silurian–Lower Devonian volcano-sedimentary rocks; (3) pyroxene–plagioclase hornfels and blastomylonite; (4) rocks of the Kushva monzodiorite–syenite complex; (5) quartz and quartz-bearing diorites of Chernovsky pluton; (6) gabbrodiorite; (7) normal and olivine-bearing gabbro; (8) biotite-bearing gabbro; (9) pyroxenite and olivinite; (10) ore zones (numerals in the figure): 1—apatite–titanomagnetite and copper sulfide ores of the Volkovsky deposit, 2—titanomagnetite ore of the Baronsky group of deposits; (11) ore occurrences: 3—Mount Listvennaya, 4—Mount Zherebtsovaya, 5—Klyuevsky; (12) faults; (13) strike and dip of banding and planar orientation of minerals.

tite–titanomagnetite and copper sulfide ores and associated NM mineralization.

GEOLOGY OF THE VOLKOVSKY PLUTON

The Volkovsky gabbroic pluton is situated in the Central Urals, in the Tagil Tectonic Zone. The pluton is exposed over an area of $15 \times 9 \text{ km}^2$ and is elongated in the NNW direction. The age of the pluton is sug-

gested to be late Ludlowian. The geology and composition of this pluton were studied by many geologists, and the most comprehensive descriptions were given in [14–20].

The pluton consists of three adjoining concentrically zoned intrusive bodies (Fig. 1), as is emphasized by the banding of gabbro (alternation of leucocratic bands enriched in feldspar and bands enriched in mafic minerals) and by the frequently visible planar orientation of the latter. The northern funnel-shaped body is the largest; its vertical extent is estimated at 2.5 km from gravity measurements and magnetometric data. The outer zone of this body is composed of crudely layered and alternating mesocratic amphibole–pyroxene, olivine-bearing and olivine gabbros with plagioclase of bytownite, labradorite, and less abundant anorthite compositions, typically of gabbroic and ophitic texture. Anorthite gabbro largely occurs in the lower portion of the intrusion, while labradorite gabbro is widespread at the northeastern periphery. In the east and southwest, the gabbroic rocks are rimmed by gabbrodiorite grading into gabbro. The central zone is occupied by quartz and quartz-bearing biotite–amphibole diorites (Chernovsky intrusion), which cut through the gabbro and gabbrodiorite. The Volkovsky deposit of complex V-bearing titanomagnetite and copper sulfide ores is localized at the northeastern margin of the northern intrusive body. The ores are hosted in taxitic olivine-bearing bytownite and less frequent anorthite and labradorite gabbro; the anorthite variety occurs in the lower and middle parts of the vertical section, while the labradorite gabbro is confined to the upper part of the section. The ore occurrences of Mount Listvennaya and Mount Zherebtsovaya in the western and southern marginal parts of the pluton consist of gabbroic rocks with sporadic disseminations of titanomagnetite and bornite.

Similar disseminated mineralization also occurs in two other (northwestern and southern) concentric intrusive bodies of taxitic gabbro attaining 1.5 km in vertical extent. These rocks also reveal a poorly expressed compositional layering. The northwestern body consists of normal and hypersthene–biotite labradorite gabbro. The banding and trachytoid texture are parallel to the outer contours of the body and dip inward at angles of 35° – 55° . The southern intrusion is composed of amphibole and amphibole–pyroxene bytownite and labradorite gabbro, with small gabbrodiorite bodies located in the center of this intrusions. Olivine-bearing pyroxenite of the deepest level of the pluton crops out in the west and hosts the titanomagnetite ore of the Baronsky deposit. The Au–Pd occurrence, which probably will prove economic, was discovered recently in immediate proximity to the titanomagnetite ore [21]; this mineralization is hosted in apatite olivinite and pyroxenite. The Au–Pd mineralization of the Klyuchevsky occurrence is the target of current exploration at the southern continuation of the Baronsky area [22].

The average chemical compositions given in Table 1 characterize gabbroic rocks from the upper, apical portion of the Volkovsky pluton, which hosts the complex titanomagnetite and copper sulfide ores of the Lavrovo–Nikolaevsky area (southern flank of the Volkovsky deposit), from the intermediate and middle parts of the vertical section (Northwestern area of the Volkovsky deposit, Mounts Listvennaya and Zherebtsovaya), and from the deepest level of the Baronsky deposit of titanomagnetite ore.

As follows from these data, the ore-bearing rocks are distinguished by elevated Al_2O_3 and P_2O_5 contents, along with moderate MgO and relatively low TiO_2 and alkalis contents. The gabbroic rocks of the lower level are generally enriched in Ni, Co, and Cr. The relatively low ratios of $\text{Mg}/(\text{Mg} + \text{Fe}) \leq 0.55$, $\text{Ni}/\text{Co} = 0.34\text{--}1.70$, and $\text{Cr}/\text{V} = 0.10\text{--}0.32$ clearly indicate that the ore-bearing gabbroids are crystallization products of evolved rather than primary mantle-derived magma (MORB is characterized by $\text{Mg}/(\text{Mg} + \text{Fe}) = 0.65\text{--}0.70$, $\text{Ni}/\text{Co} > 1$, and $\text{Cr}/\text{V} \gg 1$) [23].

The average contents of NM, except Pt, in the barren gabbroic rocks of the Volkovsky pluton (Table 2) are appreciably higher than the global mean contents in mafic and ultramafic rocks [24]. The elevated Pd, Au, and Ag contents testify to the initial enrichment of the gabbroic melt in these metals; the reasons for depletion in Pt remain uncertain. It might be suggested that the ore-bearing gabbroic rocks represent the crystallized residual melts that were produced by the fractionation of pyroxene and chromite. At the parameters of the magmatic process ($P = 5$ kbar and $T = 1300\text{--}1100^\circ\text{C}$), these minerals are characterized by relatively high partition coefficients for Pt ($K_p \geq 1.0$), whereas for Pd $K_p \leq 1.0$ [25]. As a result, the fractionation of these minerals, especially chromite, could have led to substantial depletion of mafic melt in Pt, so that the Pd content in the residual liquid would exceed the Pt content. This suggestion could be proved by the occurrence of chromite-bearing pyroxenite with Pt mineralization in the lower part of the gabbroic pluton.

In order to estimate the physicochemical conditions under which the Volkovsky gabbroic pluton crystallized, we carried out a series of model calculations that simulate the fractional crystallization of the parental mafic melt under isobaric conditions, and specified external parameters (pressure, $f\text{O}_2$, and H_2O content) by using the hydrous version of the KOMAGMAT computer program [26]. The matching of the calculated and empirical (natural) trends of major components were accepted as a plausibility criterion of the estimates of fractionation conditions. According to the results of our computer simulations, the gabbroic rocks were formed as a result of fractional crystallization of olivine tholeiitic melt of elevated alkalinity, with a high (6–8 wt %) water content, under reducing conditions of the CCO buffer, within a temperature range of $\approx 1150\text{--}915^\circ$ and ~ 5 kbar pressure [27].

Table 1. Chemical composition (wt %) of gabbroic rocks in the Volkovsky pluton

Component	Volkovsky deposit		Ore occurrence of Mount Listvennaya	Ore occurrence of Mount Zherebtsovaya	Baronsky deposit
	Lavrovo-Nikolaevsky area	Northwestern area			
	1	2			
SiO_2	44.91	42.01	42.25	41.42	48.84
TiO_2	0.89	1.12	0.89	1.01	0.97
Al_2O_3	18.16	17.61	17.46	16.28	14.50
Fe_2O_3	5.35	5.81	6.01	7.15	8.33
FeO	4.77	7.77	5.46	3.57	2.73
MnO	0.16	0.11	0.16	0.17	0.17
MgO	6.38	5.97	7.22	6.70	6.91
CaO	13.28	12.75	14.84	13.37	11.30
Na_2O	2.43	1.89	1.03	2.23	2.12
K_2O	0.29	0.51	0.22	0.69	0.61
P_2O_5	0.78	1.08	1.19	1.93	0.40
LOI	1.87	1.68	1.93	5.58	1.56
Total	99.27	98.31	98.66	100.1	98.44
Mg#	0.54	0.46	0.54	0.54	0.55
S	0.03	0.06	–	–	0.03
Cu	0.06	0.09	–	–	–
Ni*	22	30	26	–	87
Co*	48	–	76	–	51
V*	816	922	456	259	546
Cr*	90	92	105	41	176
<i>n</i>	25	36	14	3	7

Note: (1) pyroxene gabbro; (2) olivine-bearing pyroxene gabbro; (3) leucocratic pyroxene gabbro; (4) pyroxene gabbro; Mg# = $\text{MgO}/(\text{MgO} + \text{FeO}_{\text{tot}})$, mol %; *element contents are given in ppm. Analyses were performed at the Institute of Geology and Geochemistry, Uralian Division, RAS, analysts N.P. Gorbunova, L.A. Tatarinova, and V.P. Vlasov; *n* is number of samples; dash denotes not analyzed.

Our data testify to the magmatic origin of the hydrous fluid. The saturation of the basaltic melt with water and other volatile components (Cl and F) occurred most likely between the generation of basaltic magma and its crystallization at a depth of 13.5–15.0 km (judging from the modeled pressure of 5 kbar). However, the geological data indicate that the real depth of the gabbroic pluton crystallization did not exceed 3–5 km and 1.5–2.0 kbar pressure. Hence, the gabbroic rocks crystallized at a fluid pressure that was much higher than the lithostatic loading of rocks. Analogous situations are known from the literature. A high fluid pressure was recorded in melt and fluid inclusions captured by minerals of volcanic rocks at continental

Table 2. PGE contents (ppm) in barren gabbroids of the Volkovsky pluton and mean contents in mafic and ultramafic rocks

Component	Volkovsky deposit		Mount Listvennaya	Baronsky deposit [2]	Mean contents [24]	
	pyroxene gabbro (8)	gabbrodiorite (2)	pyroxene gabbro (2)	amphibole-pyroxene gabbro (1)	mafic rocks	ultramafic rocks
	1	2	3	4	5	6
Pt	$\frac{0.018}{0.00-0.03}$	$\frac{0.012}{0.01-0.014}$	0.020	<0.010	0.02	0.08
Pd	$\frac{0.03}{0.025-0.10}$	$\frac{0.10}{0.10-0.10}$	$\frac{0.05}{0.04-0.06}$	0.05	0.02	0.02
Au	$\frac{0.06}{0.05-0.08}$	$\frac{0.12}{0.05-0.18}$	$\frac{0.07}{0.06-0.08}$	0.02	0.004	0.005
Ag	$\frac{1.38 (4^*)}{0.4-3.50}$	$\frac{2.0}{2.0-2.0}$	–	–	0.10	0.06

Note: numerators are arithmetic means; denominators are ranges; numbers of samples are given in parentheses. Analyses in columns 1, 3, and 4 were carried out with the chemical-spectroscopic method at the Institute of Geology and Geochemistry, Uralian Division, RAS; in column 2, with atomic absorption spectroscopy at the Central laboratory of the Nevskgeologiya Enterprise and at the Institute of Testing and Certification of Mineral Raw Materials at the Ural State Mining and Geological Academy; (4*) analyses were performed with ICP/HR-MS. Detection limits, ppm: Pt—0.005, Pd—0.01, Au—0.02, Ag—0.1; dash denotes not analyzed.

margins and the oceanic floor [28]. In particular, hydrous fluid inclusions under pressures varying from 2–3 to 10 kbar were reported. A high fluid pressure appreciably exceeding the lithostatic loading was also determined at some rare-metal and gold deposits [28]. Thus, the formation of the Volkovsky gabbroid pluton under a high pressure of magmatic fluid is not an extraordinary event. Similar estimates of temperature characterizing the formation of gabbroic rocks were obtained by Fominykh [29] from coexisting clinopyroxene–plagioclase and amphibole–plagioclase pairs. According to these data, the olivine-bearing pyroxene gabbroic rocks were formed at 850–950°C, while the amphibolized gabbro crystallized at 700–800°C.

The igneous rocks of the Volkovsky pluton are classed with the dunite–clinopyroxenite–gabbro association (mainly, by Uralian geologists [2, 20]), anorthosite–pyroxenite–gabbro [4], or gabbro–syenite association. According to [4], the ore-bearing gabbro and associated titanomagnetite and copper sulfide ores of this pluton are counterparts of the Early Proterozoic Chinei pluton in the southern Siberian Platform, which is the most promising for exploration for noble metals among all known Ti-bearing gabbroic plutons with V-bearing magnetite and copper sulfide ores. In our opinion, the Volkovsky pluton is much more similar to the Early Paleozoic Nomgon troctolite–anorthosite–gabbro pluton in Mongolia [32] rather than to the Chinei pluton [31], which is characterized by the pyrite–pyrrhotite–chalcopyrite type of the ore mineralization with insignificant amounts of bornite and the prevalence of Pt over Pd ($Pd/Pt \leq 1$). The Nomgon pluton is more similar with the Volkovsky pluton in the composition of gabbroic rocks, sulfide mineralization [pre-

dominant bornite and chalcopyrite with a high $Cu/(Cu + Ni) = 0.90-0.97$], and the prevalence of Pd over Pt ($Pd/Pt = 1.9-3.4$). Such plutons apparently belong to an unusual type of ore-bearing gabbroic rocks that have elevated Cu contents combined with low Ni and Cr contents (Table 1), below the mean global level [24], and often with high concentrations of Fe and P.

The Volkovsky and Baronsky deposits are the most important areas with NM mineralization in the Volkovsky pluton, with the Baronsky deposit localized at a lower level than the Volkovsky deposit [20].

The Volkovsky deposit is composed of pyroxene, olivine–pyroxene, and, to a lesser extent, biotite–pyroxene and pyroxene–amphibole gabbro of massive and taxitic textures. The deposit embraces a series of *en echelon* ore zones from a few tens to 500 m in extent, which gradually change their strike from the northwestern in the north to the near-meridional in the south and dip to the west at angles from 30°–50° to 75°. The ore zones are composed of richly impregnated and less frequent massive apatite–titanomagnetite, chalcopyrite–bornite, and chalcopyrite–bornite–titanomagnetite ores hosted in taxitic gabbro. The orebody boundaries are gradual and are delineated only based on the results of sampling. The ores are complex; along with V-bearing titanomagnetite, bornite, and chalcopyrite, they contain P in the form of apatite, PGE, largely as Pd tellurides, and native Au. The structural relationships between bornite as the major Cu-bearing mineral and other minerals are rather intricate. Tiny bornite inclusions are detected in crystals of fresh twinned plagioclase and in clinopyroxene with a magnetite exsolution network. Bornite mosaic also occurs at the intersections of cleavage planes in pyroxene. The formation of this mode of

bornite occurrence was likely synchronous with the onset of amphibolization. Graphic bornite–digenite intergrowths occur in plagioclase and pyroxene. Another major mineral—titanomagnetite—is observed as rounded inclusions (ore droplets) in pyroxene, plagioclase, and apatite [14] and also makes up graphic intergrowths with ilmenite and gangue minerals (pyroxene and amphibole). The above modes of bornite and titanomagnetite occurrence are their earliest, high-temperature modifications, which are not abundant. Disseminations with a grain size varying from fractions of a millimeter to 5 mm hosted in gabbro are the predominant mode of occurrence of these minerals that make up the bulk of titanomagnetite and copper sulfide ores formed during the final stage of the fluid–magmatic differentiation of gabbroic magma. The structural and textural relationships between ore minerals and their temporal compositional trends indicate the following sequence of mineral formation with decreasing temperature during this stage: titanomagnetite, ilmenite, bornite, digenite, bornite + chalcopyrite, chalcopyrite, covellite, and pyrite. Chalcopyrite, the second most abundant sulfide, also occurs in all varieties of the gabbro, commonly in the form of disseminations as large as 4 mm. Schlieren and vein-shaped segregations 0.5–15 cm in size of bornite, bornite–chalcopyrite, and chalcopyrite, sporadically with coarse-grained titanomagnetite, are the latest products of ore formation. The absence of near-sulfide alteration is a distinctive feature of such segregations. Veinlets as thick as 2–3 cm filled with fine-grained aggregates of chalcopyrite, pyrite, quartz, and calcite are quite abundant at the southern flank of the deposit. This mineral assemblage is genetically related to the emplacement of quartz and quartz-bearing diorites of the Chernovsky pluton and is superimposed on the gabbroic rocks and ore hosted therein. Saussurite aggregates, epidote, chlorite, and prehnite developed along fractures in the gabbro.

The NM mineralization associated with copper ore consists of palladium tellurides and small grains of native gold. According to [21], the total PGE and Au grade of the Cu sulfide ore with 0.6–4.6 wt % Cu and 1.0–1.5 wt % S is 1–7 g/t, whereas the Cu sulfide–apatite–titanomagnetite ore (0.3–0.7 wt % Cu and 0.5–1.2 wt % S) contains 0.1–0.3 g/t PGE and Au. As has been shown by our own and previous investigations [21, 33–35], merenskyite PdTe_2 , kotulskite PdTe , and keithconnite Pd_{3-x}Te that contain variable amounts (from fractions of percent to 1–2 wt %) of Pt, Au, and Ag are the most abundant palladium tellurides. These minerals occur as inclusions, 0.001–0.025 mm in size, in sulfides (bornite and chalcopyrite), titanomagnetite, and pyroxene. Hessite $(\text{Ag,Pd})_2\text{Te}$ is detected sporadically. It was pointed out that Pd tellurides commonly occur in bornite intergrown with titanomagnetite and pyroxene rather than with plagioclase. This indicates that some amount of NM was initially dispersed in mafic minerals and subsequently extracted when the Pd tellurides were formed. The bulk of NM is coeval in

formation with the rich impregnations, schlieren, and veined segregations of bornite and chalcopyrite.

The currently developed genetic models for the deposits are set forth within the scope of the magmatic [14, 16, 19, 20] and metasomatic [36] concepts. Following Zavaritsky [37], most of researchers, including the authors of this paper, ascribe the Volkovsky deposit to the late magmatic type and regard titanomagnetite and copper sulfide mineralization as formed during the final stages of crystallization of the residual S-, Cl-, F-, and CO_2 -bearing melt enriched in ore components. The sulfur isotopic composition ($\delta^{34}\text{S} = -0.15\%$) testifies to a homogeneous mantle source of sulfur.

The Baronsky Au–Pd deposit discovered in 1985 [21] is confined to a relatively large ($4.5 \times 0.7 \text{ km}^2$) ultramafic body in the southwestern part of the Volkovsky pluton (Fig. 1) and is composed of alternating olivine clinopyroxenite, apatite olivinite, and wehrlite. Olivine is mostly replaced by serpentine, chlorite, and talc, and plagioclase is saussuritized. All rocks contain clinopyroxene, titanomagnetite, and apatite in amounts varying from scarce grains to 25% and more. Pyroxenite with high-grade titanomagnetite disseminations and massive segregations makes up titanomagnetite ore that extends as a discontinuous belt throughout the entire ultramafic body and was known long ago as the Baronsky group of low-Ti titanomagnetite deposits of the Kachkanar type [38]. A thin (0.5–2.0 m) unit of tectonized and metamorphosed apatite olivinite, wehrlite, and olivine clinopyroxenite that hosts gold–palladium ore mineralization was found and traced in the close proximity to this belt. This mineralization was first thoroughly described in [21, 33]. According to these data, the NM grades are variable and decrease with depth from ~20 g/t near the surface (the rocks contain 16.9 g/t Pd, 0.42 g/t Pt, and 3.22 g/t Au to a depth of 8 m) to 6 g/t at deeper levels (at a depth of 50 m, the average Pd, Pt, and Au grades are 5.23, 0.20, and 0.62 g/t, respectively). The bulk of NM is associated with chalcopyrite and bornite that are contained in amounts of 0.1–1.0%, locally to 3%, in apatite olivinite and other rocks; other minerals are chalcocite, carrollite, and pyrite. The list of NM minerals includes merenskyite, kotulskite, and keithconnite and their Ni- and Cu-bearing varieties, Bi- and Pd-bearing native Au. The highest NM contents (up to 40 g/t NM sum) are related to the secondary enrichment and occur in oxidation zones as local, 1–5 cm thick zones of intense antigorization, chloritization, and phlogopitization of host rocks. The primary nature of NM mineralization at the Baronsky deposit remains unknown.

GENETIC MODEL OF OXIDE–SULFIDE ORES

Discussing the possible origin of the NM mineralization in the Volkovsky pluton, it is necessary to analyze some genetic features of the spatially and genetically associated titanomagnetite and copper sulfide

Table 3. Variation of some petrochemical parameters of gabbroic rocks at the Volkovsky deposit versus the intensity of ore mineralization and contents of volatile components

Parameter	1	2	3	4	5
Q ^{Mt}	6.28 (25)	8.59 (53)	11.95 (51)	15.73 (18)	27.38 (13)
TiO ₂	0.89 (25)	1.17 (53)	1.41(51)	2.09 (18)	3.59 (1)
Cu	0.06 (5)	0.31 (25)	0.47 (26)	0.60 (10)	1.22 (5)
S	0.03 (5)	0.17 (25)	0.34 (26)	0.19 (18)	0.29 (5)
P	0.34 (25)	0.76 (53)	0.99 (51)	1.72 (18)	3.59 (13)
<i>Fem</i>	30.09	35.02	37.11	34.60	25.78
<i>Fem/Pl</i>	0.64	0.86	0.97	1.55	2.29
<i>Pl</i> ^{An}	0.73	0.78	0.80	0.84	0.91

Note: Q^{Mt} is the amount of magnetite calculated from the equation $Fe^{Mt} = 0.963Fe_{tot} - 4.708$, wt % [43]; *Fem* is the sum of normative dark-colored minerals (*Ol* + *Di* + *Hy*), wt %; *Pl* is plagioclase; *Pl*^{An} is the amount of anorthite end member in plagioclase composition. Columns: (1) barren gabbro, (2) low-grade ore gabbro; (3–5) gabbroic rocks with economic Cu grade, wt %. Numerals in parentheses are numbers of analyses.

ores. According to the commonly adopted concept, the initial basaltic magma was generated by the decompression melting of the upper mantle [6, 39, 40] or under the effect of mantle fluids [41, 42]. The basaltic magma derived from a deep-seated mantle source was undersaturated with respect to sulfur and probably remained so during the formation of magma chambers within the crust. Available empirical material (Tables 1, 3, columns 1) testifies to the undersaturation of gabbroic melt in sulfur relative to its experimentally determined solubility in silicate melts [6, 25]; the sulfur contents are comparable to the mean concentration in mafic rocks (0.025 wt %) [24]. The sulfur solubility in the model system K₂O–SiO₂–FeO–FeS–volatile component at 750–850°C and within a pressure range of 1–10 kbar varies from 0.1 to 0.8 wt %; in the fluid-bearing normal basaltic melt at $T = 1100$ – 1250 °C and $P \leq 5$ kbar, the sulfur solubility does not exceed 0.28 wt % [25]. It is important to note that inverse relationships were established between the sulfur solubility and pressure; i.e., a degree of undersaturation with sulfur increases with the ascent of basaltic melt toward the surface.

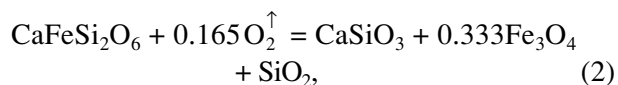
It is fairly difficult to estimate the equilibrium solubility of copper because of the lack of experimental data. According to [44], the copper solubility in experimental melts of 40Ab20An40Di composition at 1300°C and oxygen fugacity of 10^{-6} – 10^{-8} atm is only 0.01–0.04 wt % and decreases with diminishing oxygen fugacity. The Cu content in barren gabbroic rocks (Tables 1, 3) is generally higher than both this value and the global average for mafic rocks (0.009 wt %) [24]. Thus, the mantle-derived basaltic magma served as a source of Cu and S in gabbroids of the Volkovsky pluton.

According to the currently adopted concept, the formation of magmatic copper sulfide ore is related to the fractionation of an ore-bearing magma with the separation of immiscible sulfide and titanomagnetite liquids during a certain stage of the evolution of the fluid-bearing

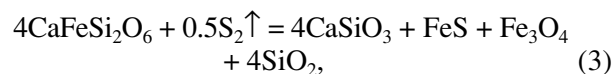
melt. The separation of ore melts is accompanied by their pronounced enrichment in PGE. As is suggested in [4], the concentration of NM at the titanomagnetite deposits is favored by ferritization and sulfurization of silicate melts, which are controlled by the partial pressures of oxygen and sulfur. The interaction of basaltic melt with components of the fluid phase, first of all, oxygen and sulfur, should lead to the depletion of the crystallizing melt in Fe, Ti, and probably other ore components with the formation of an ore liquid and its subsequent crystallization as oxide–sulfide mineral assemblages. This process may be described as the following schematic reactions, calculated from thermodynamic data [45, 46]:



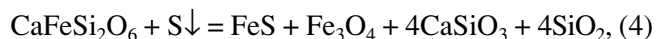
where $\Delta G^0 = -19.319$ kcal/mol and $\Delta S^0 = -8.325$ entropy units.



where $\Delta G^0 = -16.248$ kcal/mol and $\Delta S^0 = -4.82$ entropy units.



where $\Delta G^0 = -35.130$ kcal/mol and $\Delta S^0 = -11.565$ entropy units.



where $\Delta G^0 = -25.513$ kcal/mol and $\Delta S^0 = -7.91$ entropy units.

The relatively high negative ΔG^0 values, and on the contrary, small ΔS^0 values highly probably indicate that the reactions proceed from left to right within a wide temperature interval. The higher the value of the entropy difference ΔS^0 , the more intense oxidation with decreasing temperature. In this case, the oxidizing

effect of sulfur on metals of variable valence is even stronger than that of oxygen. To our knowledge, the oxidizing role of sulfur was pointed out for the first time by Kullerud and Yoder [47]. According to these considerations, the residual melt should become more leucocratic during its crystallization. As follows from the reactions presented above and from experimental data on the interaction of fayalite with hedenbergite at 800°C and 2 kbar pressure [47], the formation of oxide–sulfide assemblages must be accompanied by a decrease in the Fe/(Fe + Mg) ratio of the silicates and the formation of quartz. Judging from the optical examination of gabbroic rocks from the Volkovsky pluton conducted by Yu.P. Kraeva, the Fe/(Fe + Mg) ratio of pyroxene actually decreases in the sequence: olivine gabbro ($N_g = 1.720$ and $N_p = 1.695$) → pyroxene gabbro → ($N_g = 1.705$ and $N_p = 1.690$) → magnetite gabbro ($N_g = 1.696$ and $N_p = 1.685$) → ore gabbro ($N_g = 1.695$ and $N_p = 1.670$). This trend may be regarded as a consequence of fluid–magmatic interaction.

The immiscibility of sulfide and silicate melts [6, 25] should arise when the melt becomes saturated with volatile components. However, as was mentioned above, the gabbroic rocks of the Volkovsky pluton are undersaturated with sulfur. Therefore, taking into account the high sulfur solubility (2.2–2.4 wt %) in hydrous high-Fe melts of basaltic andesite at 5 kbar and 1250°C [25], it is reasonable to suggest that the effect of immiscibility was hardly likely to arise during fractional crystallization of ore-bearing magma. As concerns the possible role of phosphorus as a component that promotes immiscibility, available experimental data [25, 48] indicate that immiscibility in P-bearing basaltic melts arises at a relatively high P content (>1 wt % P_2O_5). Hence, it may be suggested that the P contents in the gabbroic rocks (Tables 1, 3) are quite sufficient for the separation of a Fe-rich liquid enriched in Cu, Ti, S, and P. Therefore, it is hardly accidental that the highest contents of all ore-forming elements are related to relatively mafic rocks with calcic plagioclase. In any event, the direct correlation of phosphorus in ore-bearing gabbroids with intensity of Fe, Ti, and Cu ore mineralization and *Fem/Pl* ratio of silicate rocks (Table 3) does not contradict this model. The formation of oxide–sulfide ore was accompanied by the deposition of apatite with variable Cl and F contents. The highest Cl content (1.22–1.70 wt %) is typical of apatite from the melanocratic ore gabbro, whereas the lowest Cl content (0.67–0.70 wt %) was detected in apatite from diorite. The F content in apatite is rather stable within a range of 0.98–1.53 wt %. It is possible to discern, at least locally, vertical zoning in the Cl and F distribution in apatite. Thus, the Cl and F contents in apatite sampled at a depth of 180 m are within ranges of 0.2–0.5 and 1.2–2.3 wt %, respectively, and are equal to 1.4–1.6 and 0.9–1.3 wt % at a depth of 550 m. The total

content of these elements tends to increase with depth [49]. Similar results were reported previously [50].

The enrichment of titanomagnetite–Cu sulfide ore in P (apatite) and Cl and F, respectively, obviously testifies to participation of these volatile components in the formation of magma-derived fluids. The ore is a product of crystallization of a fluid-bearing melt during a late fractionation stage of the ore-bearing gabbroic magma. Naturally, a high fluid content of such a melt was favorable for autometasomatic processes and assembling recrystallization with the formation of taxitic gabbro and metasomatic appearance of rocks and ores.

Finally, the role of Cu in sulfide–silicate immiscibility cannot be ruled out. According to experimental data on the model FeS–CaO–FeO_x system at 1300°C [51], the effect of immiscibility with the formation of a sulfide liquid that crystallized as bornite (!) was observed only when no less than 1 wt % Cu₂S, i.e., 0.8 wt % Cu and 0.2 wt % S, was added. In the absence of Cu₂S, only a homogeneous oxide–sulfide melt of variable composition is formed. To our knowledge, this feature was previously overlooked.

The temperature of copper sulfide formation during the final stage of ore formation may be estimated from the sulfide compositions (Table 4).

(1) Bornites from the Volkovsky and Baronsky deposits contain, respectively, about 1.10 and 0.4 wt % S more (in recalculation to 100%) than is required by the stoichiometry of this mineral. This difference is most likely caused by the effect of temperature. Judging from experimental data on phase relations in the Cu–Fe–S system and on solvus curves in the CuFeS_{2-x}–Cu₅FeS₄ and the Cu_{9,2}S₅–Cu₅FeS₄ systems [52, 53], the mutual solubility of these compounds increases with temperature, so that continuous solid solutions are formed. At 400°C, bornite contains sulfur in the amount that fits the stoichiometric formula, while at 700°C, the sulfur content increases by 0.8 wt %. In application to the ore, this implies that the bornite solid solution at the Volkovsky deposit could have been formed at a temperature of ~800°C and higher, while the temperature at the Baronsky deposit was about 550°C.

(2) In compliance with the Cu–Fe–S diagram [54], the field of chalcopyrite stability as a solid solution markedly expands at a temperature above 570°C at the expense of enrichment in iron. Under these conditions, chalcopyrite is stable along with digenite–bornite solid solution and at 739°C makes up an equilibrium assemblage with pyrite and pyrrhotite; below 570°C bornite is equilibrated with digenite–pyrite assemblage. Judging from the average composition, chalcopyrite at this deposit could have been formed at a temperature of no lower than 620°C. According to [54], the chalcopyrite solid solutions varying in composition from Cu_{0.58}Fe_{0.42} to Cu_{0.30}Fe_{0.70} (in Cu–Fe coordinates) are stable at a temperature of no lower than 743°C. Some chalcopy-

Table 4. Chemical composition (wt %) of copper sulfides at the Volkovsky and Baronsky deposits

No.	Mineral	Cu	Fe	S	Σ
Volkovsky deposit					
1	<i>Bn</i> (11)	$\frac{62.76}{57.94-69.80}$	$\frac{10.02}{6.61-12.05}$	$\frac{26.67}{24.13-29.00}$	99.58
2	<i>Cp</i> (7)	$\frac{34.64}{33.63-35.82}$	$\frac{30.71}{29.41-32.46}$	$\frac{34.56}{34.25-34.72}$	99.91
3	<i>Dg</i> (3)	$\frac{80.19}{79.77-80.94}$	$\frac{0.13}{0.10-0.18}$	$\frac{20.89}{20.41-21.14}$	101.21
Baronsky deposit					
4	<i>Bn</i> (3)	$\frac{63.13}{60.00-64.80}$	$\frac{10.30}{9.90-10.80}$	$\frac{25.70}{23.30-28.00}$	99.13
5	<i>Cp</i> (5)	$\frac{35.88}{33.90-37.00}$	$\frac{29.46}{28.70-30.00}$	$\frac{35.10}{34.20-36.00}$	100.44
6	<i>Dg</i> (1)	80.20	0.40	19.80	100.40

Note: Here and hereafter: *Bn*—bornite, *Cp*—chalcopyrite, *Dg*—digenite. Numbers of analyses are given in parentheses. In addition to the authors' data, the data taken from [34] were used for calculation of average composition of minerals at the Volkovsky deposit. The data on the Baronsky deposit were taken from [33].

Crystal chemical formulas of an average mineral composition and entropy values (S_{ss}^0 , cal/mol degree), calculated with Latimer's method [45]; entropy values for stoichiometric compositions are given in parentheses. (1) Bornite $Cu_{4.94}Fe_{0.897}S_{4.16}$, $S_{ss}^0 = 83.48$ (84.40); (2) chalcopyrite $Cu_{1.00}Fe_{1.01}S_{1.98}$, $S_{ss}^0 = 31.23$ (30.80); (3) digenite $Cu_{9.22}Fe_{0.02}S_{4.76}$, $S_{ss}^0 = 123.58$ (122.50); (4) bornite $Cu_{5.02}Fe_{0.93}S_{4.05}$, $S_{ss}^0 = 84.14$ (84.40); (5) chalcopyrite $Cu_{1.03}Fe_{0.96}S_{2.01}$, $S_{ss}^0 = 31.58$ (30.80); (6) digenite $Cu_{9.36}Fe_{0.05}S_{4.58}$, $S_{ss}^0 = 124.51$ (122.50).

rites from the Volkovsky deposit have the formula $Cu_{0.48}Fe_{0.52}$, i.e., fall within this interval. Thus at least some chalcopyrite solid solutions could have been formed at a similar temperature, which does not seem to be overestimated, if one takes into account that a pressure increase by 1000 bar raises the upper stability limit of sulfide assemblages by 10–15°C [54]. As was shown previously [27], gabbroids of the Volkovsky pluton crystallized under a total pressure of 5 kbar, so that sulfides could have started to form at a temperature 50–75°C higher than 743°C, i.e., at ~800°C.

(3) On the contrary, digenite Cu_9S_5 , is characterized by appreciable depletion in S and enrichment in Cu with an admixture of Fe in comparison with stoichiometric proportions. The composition of this mineral fits the Dg–Cc (chalcocite) solid solution in the Cu_9S_5 – Cu_5FeS_4 pseudoternary (binary) system [55].

As may be deduced from the material discussed above, the evolution of the ore-magmatic system may be outlined as a sequence of the following events. After the emplacement of fluid- and ore-bearing basaltic magma into the Earth's crust, a poorly layered fluid-magmatic chamber was formed at hypabyssal or mesoabyssal level; its vertical extent was no less than 2.5 km. This is confirmed by the gradual transitions between gabbroic rocks with various silica contents and by the formation of relatively leucocratic gabbrodioritic rocks

near the roof of pluton. Fluid–magmatic fractionation resulted in localization of the most melanocratic mafic melt enriched in Fe, Ti, Cu, P, S, Cr, and Ni in the deep portion of the magmatic chamber. The crystallization of this melt gave rise to the segregation of a residual melt, which was progressively enriched in fluids (which depressed its crystallization temperature). The high content of a hydrous fluid with P, S, Cl, and F dissolved therein was favorable for the formation of taxitic gabbroids and associated oxide–sulfide ore mineralization and the development of autometasomatic processes.

The crystallization of basaltic melt was accompanied by the separation of immiscible ore liquids enriched in Fe, Cu, and P. This is indicated by small globular inclusions of ore minerals (titanomagnetite, bornite, and chalcopyrite) in the major minerals (pyroxene, apatite, and plagioclase). According to [56], the ore droplets were segregating in the magmatic chamber within the entire temperature range of melt crystallization. Conceivably, the separation of ore droplets on the liquidus of the crystallizing basaltic melt and their subsequent crystallization as small schlieren during the early stage of gabbroic melt fractionation might have been provoked by a fluid component. The bulk of the oxide–sulfide ore crystallized within a temperature range of approximately 800–570°C from a fluid-bearing residual melt.

BEHAVIOR OF NOBLE METALS DURING ROCK
AND ORE FORMATION
AND THEIR CONCENTRATION CONDITIONS

Elevated NM contents are detected in virtually all ore-bearing areas of the Volkovsky pluton. Bornite and chalcopyrite are the main NM concentrators with the prevalence of Pd over Pt and of Ag over Au. Pyroxene, titanomagnetite, and pyrite contain NM in much smaller quantities (Table 5). The occurrence of NM in pyroxene and accessory titanomagnetite indicates that physicochemical conditions favorable for the incorporation of NM into crystallizing silicates and oxides were created already during early stages of basaltic melt crystallization. During the fractionation of basaltic magma, noble metals were gradually accumulated in minerals. The abrupt increase in the concentrations of Pd and Au occurred during the deposition of titanomagnetite and copper sulfide ores owing to the crystallization of residual melt enriched in ore components. The maximum in the accumulation of NM was achieved during the final stage of melt crystallization, along with the formation of schlieren and vein-shaped segregations. The Pd and Ag and, to a lesser extent, Pt and Au contents in titanomagnetite increase with increasing intensity of ore mineralization (Table 5): they are the lowest in the barren gabbro, higher in mineralized gab-

bro, and are much higher in sulfide–titanomagnetite schlieren and veined segregations. A similar tendency is also recognizable in major ore minerals: bornite and chalcopyrite. Pyrite genetically related to the quartz diorite of the Chernovsky pluton is characterized by low contents of all NM except Ag.

The NM distributions in various minerals are shown in Figs. 2 and 3. The unimodal bar charts of Pd, Pt, and Au testify to the common origin of these elements. The NM contents are widely variable; however, their arithmetic means and modes change in line with the mode of occurrence of the host ore minerals. Accessory and disseminated titanomagnetites contain equal modal amounts of Pd and Pt: <1.0 and 0.01–0.02 ppm, respectively; titanomagnetite from schlieren commonly contains 2–3 ppm Pd and 0.02–0.03 ppm Pt. The bornite disseminations contain 8–12 ppm Pd and <0.2 ppm Pt, whereas 4–8 ppm Pd and <0.4 ppm Pt are contained in bornite from schlieren and veins. Chalcopyrites from pockets and veins contain 4–8 ppm Pd and <0.20 ppm Pt. Pyrite commonly contains 0.1–0.2 ppm Pd and 0.01–0.02 ppm Pt. Similar proportions are characteristic of Au and Ag. The accessory titanomagnetite contains <0.2 ppm Au and <2.0 ppm Ag, while impregnations in ore gabbro contain 0.2–0.4 and 2–4 ppm, respectively. The maximum Au and Ag contents in tita-

Table 5. Precious metal contents (ppm) in minerals at the Volkovsky deposit

Mineral	Mode of occurrence	Pd	Pt	Au	Ag
<i>Px</i> (2)	Rock-forming mineral of unaltered gabbro	$\frac{0.07}{0.03-0.11}$	0.011 (1)	$\frac{0.08}{0.05-0.12}$	3.5 (1)
<i>Px</i> (1)	Rock-forming mineral of ore gabbro	0.23	0.011	0.33	7.3
<i>TiMt</i> (6)	Accessory mineral of unaltered gabbro	$\frac{0.06}{0.01-0.09}$	$\frac{0.012}{0.009-0.017}$	$\frac{0.18}{<0.05-0.40}$	$\frac{0.3}{0.2-0.4}$
<i>TiMt</i> (3)	Disseminations in ore gabbro	$\frac{1.01}{0.01-1.88}$	$\frac{0.01}{0.010-0.011}$	$\frac{0.77}{0.27-1.63}$	$\frac{2.7}{2.6-3.0}$
<i>TiMt</i> (7)	Massive aggregate in sulfide-titanomagnetite schlieren and veins	$\frac{1.84}{0.06-4.83}$	$\frac{0.025}{0.010-0.062}$	$\frac{0.22}{0.09-0.33}$	$\frac{3.5}{0.8-7.6}$
<i>Bn</i> (3)	Disseminations in ore gabbro	$\frac{8.55}{6.40-9.87}$	$\frac{0.075}{0.020-0.130}$	$\frac{2.56}{0.70-4.09}$	$\frac{91.4}{14.0-168.8}$
<i>Bn</i> (9)	Massive aggregate in sulfide-titanomagnetite schlieren and veins	$\frac{9.64}{2.97-22.65}$	$\frac{0.32}{0.04-0.740}$	$\frac{1.61}{0.05-8.0}$	$\frac{80.4}{9.0-127.2}$
<i>Cp</i> (1)	Disseminations in ore gabbro	8.50	–	1.00	–
<i>Cp</i> (14)	Massive aggregate in sulfide-titanomagnetite pockets and veins	$\frac{7.46}{0.04-25.20}$	$\frac{0.42}{0.010-1.556}$	$\frac{1.15}{<0.05-4.39}$	$\frac{65.4}{4.0-142.6}$
<i>Py</i> (11)	From veinlets in diorite	$\frac{0.20}{0.07-0.58}$	$\frac{0.03}{0.015-0.083}$	$\frac{0.08}{<0.05-0.15}$	$\frac{39.8}{0.7-124.5}$

Note: *Px*—pyroxene, *TiMt*—titanomagnetite, *Py*—pyrite; see Table 4 for other symbols; number of analyses are given in parentheses. Numerators are the arithmetic means, denominators are the ranges. Monomineralic fractions were analyzed for Pt and Pd by atomic absorption spectroscopy at the Central Laboratory of the Nevskgeologiya Enterprise and for Au and Ag at the Institute of Testing and Certification of Mineral Raw Materials at the Ural State Mining and Geological Academy. Detection limits (ppm): Pt—0.005, Pd—0.01, Au—0.05, Ag—0.1; dash means not analyzed.

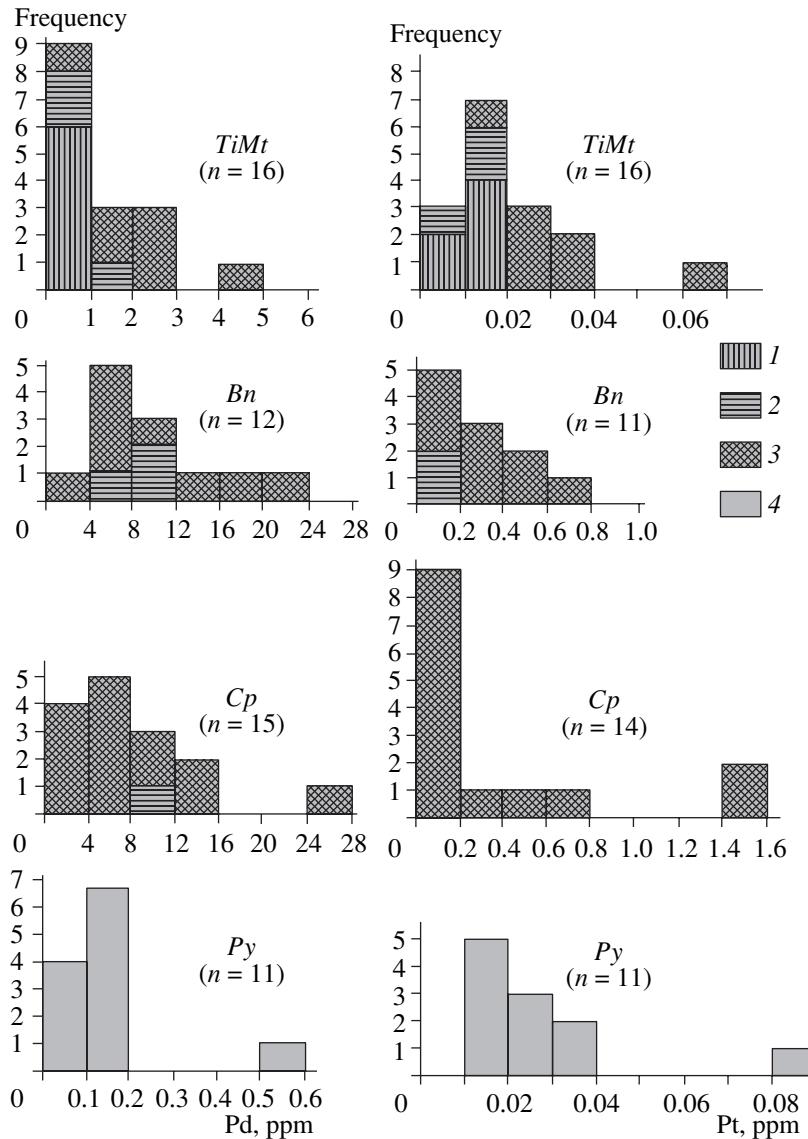


Fig. 2. Bar charts of Pd and Pt distribution in minerals from the Volkovsky deposit. (1) Accessory titanomagnetite in the barren gabbro, (2) disseminated titanomagnetite and copper sulfide ore, (3) schlieren and vein-shaped segregations, (4) veinlets in diorite. *n* is number of samples.

nomagnetites from schlieren and veins are 0.2–0.4 and 2–4 ppm, respectively. No systematic modal values of Au and Ag contents were established in bornite impregnations from ore gabbro, most likely, because of the insufficient number of analyses. Bornite of large schlieren and vein-shaped segregations contains <1.0 ppm Au and 80–100 ppm Ag. The modal Au and Ag contents in chalcopyrites from pockets and veins are <1.0 and <20 ppm, respectively. Pyrite contains <0.1 ppm Au and <20 ppm Ag. It is worth noting the polymodal distribution of Ag (bar charts with two or three peaks), apparently, as a result of repeated Ag deposition. As follows from the data presented above, proportions of NM turn out to be clearly differentiated in the process of fluid-bearing and ore-forming melt evolution, along

with a change in the concentrations of major ore components and their mineral speciation (Figs. 4a, 4b). Three fields with different NM proportions in ore minerals and barren gabbroic rocks can be clearly recognized in Fig. 4a: (A) barren gabbroids, pyroxene and accessory titanomagnetite, (B) gabbroids with ore disseminations, and (C) ore gabbroids with schlieren and veinlets. In each field, minerals display characteristic geochemical features. The barren gabbroids are noted for the lowest Pd/Au ratio and by a relatively high Pt and Ag percentage of total NM. The highest Pd/Au ratio is typical of ore gabbroids with schlieren and vein-shaped segregations. All major ore minerals (titanomagnetite, bornite, and chalcopyrite) make up a compact group that corresponds to the paragenetic assem-

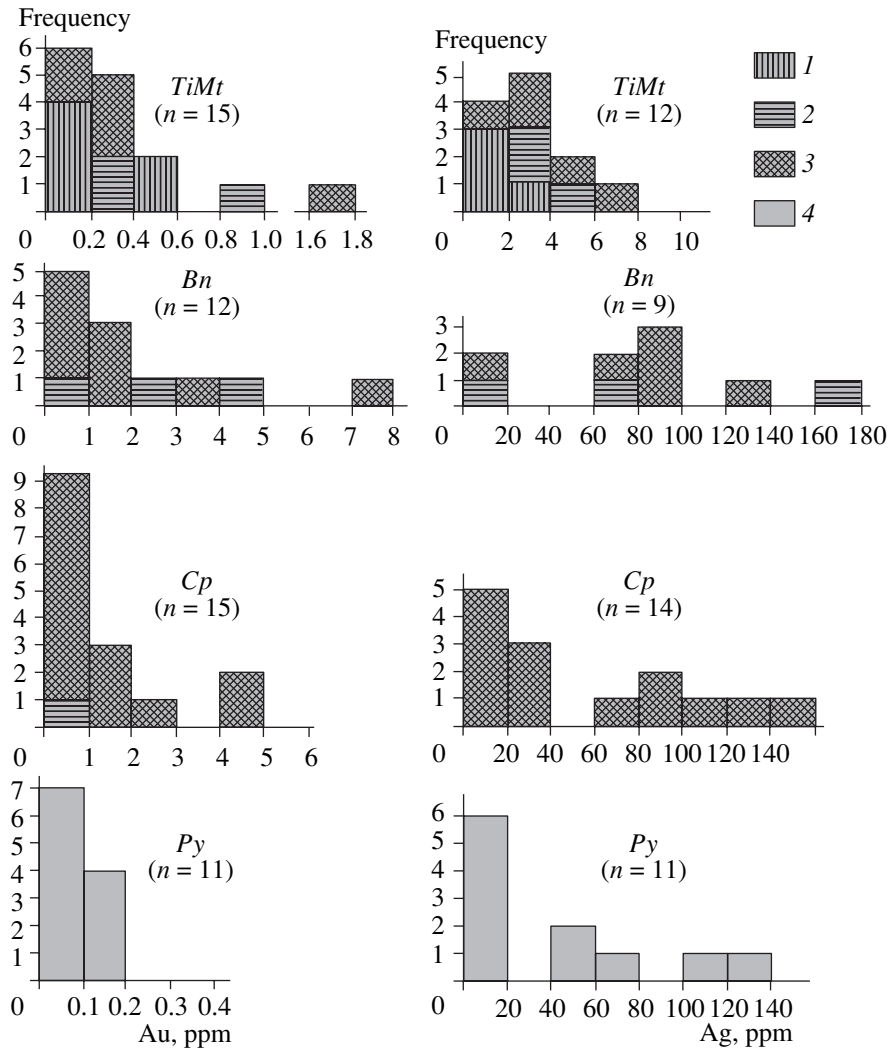


Fig. 3. Bar charts of Au and Ag distribution in minerals from the Volkovsky deposit. See Fig. 2 for legend.

blage. Gabbro with ore disseminations occupies a transitional position in the diagram. Copper sulfides and titanomagnetite plot separately and are characterized by appreciably different proportions of NM (Fig. 4b). The Ag and Pd percentage of total NM increases with increasing intensity of ore mineralization in the series of accessory–disseminated–schlieren and veined titanomagnetite. Copper sulfides (bornite and chalcopyrite) are characterized by a strong prevalence of Ag over other NM as a result of the high extracting ability of Cu sulfides with respect to Ag.

The opposite tendencies in the Pd distribution between coexisting minerals are observed in various equilibrium mineral assemblages (Table 6 and Fig. 5). For example, in schlieren and vein-shaped segregations, the enrichment of titanomagnetite in Pd is accompanied by depletion of bornite in this element, whereas the chalcopyrite–titanomagnetite pair is characterized by enrichment of both coexisting ore phases in Pd and Pt. The compositional variations of meren-

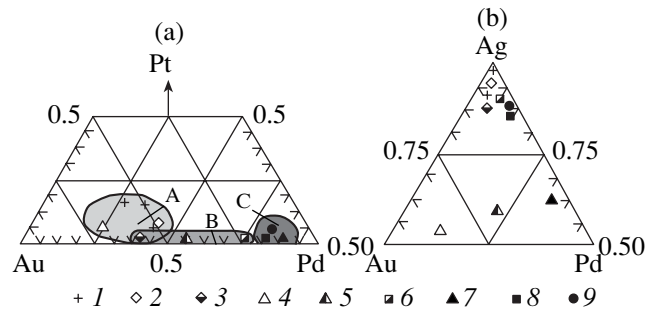


Fig. 4. Proportions of precious metals in rocks and ore minerals of the Volkovsky deposit. (a) Au–Pd–Pt system; (b) Au–Pd–Ag system. (1) Barren gabbro, (2) pyroxene from barren gabbro, (3) pyroxene from ore gabbro, (4) accessory titanomagnetite, (5) titanomagnetite from gabbro bearing disseminated oxide–sulfide ore mineralization, (6) bornite from gabbro bearing disseminated oxide–sulfide ore mineralization, (7) titanomagnetite from schlieren and vein-shaped segregations, (8) bornite from schlieren and vein-shaped segregations, (9) chalcopyrite from schlieren and vein-shaped segregations. Diagrams were compiled from the data presented in Tables 2 and 5.

Table 6. Precious metal contents (ppm) in coexisting minerals at the Volkovsky deposit

Sample number	Rock	Mineral	Pd	Pt	Au	Ag
41/p-92	Unaltered gabbro	<i>Px</i>	0.03	–	0.05	–
		<i>TiMt</i>	0.05	0.012	0.06	–
V1-6-93	Unaltered gabbro	<i>Px</i>	0.11	0.011	0.12	3.5
		<i>TiMt</i>	0.09	0.010	<0.05	0.3
V1-19-01	Slightly mineralized gabbro	<i>TiMt</i>	0.01	0.010	0.10	0.4
		<i>Bn</i>	9.40	0.130	4.09	168.8
42/p-92	Ore gabbro	<i>TiMt</i>	1.88	0.011	0.27	3.0
		<i>Bn</i>	9.87	0.020	0.07	14.0
V1-65-01	Ore gabbro	<i>TiMt</i>	0.25	0.010	0.87	2.6
		<i>Bn</i>	6.40	–	2.88	–
		<i>Cp</i>	8.50	–	1.00	–
<i>Titanomagnetite-bornite-chalcopryrite assemblage</i>						
7/p-00	<i>TiMt-Bn-Cp</i> schlieren in gabbro	<i>TiMt</i>	2.20	–	–	–
		<i>Bn</i>	8.40	0.110	1.68	96.9
V1-30-01	<i>TiMt-Bn-Cp</i> schlieren in gabbro	<i>TiMt</i>	0.09	0.017	0.09	–
		<i>Bn</i>	17.60	0.350	1.07	–
8/p-00	<i>TiMt-Bn-Cp</i> schlieren in gabbro	<i>TiMt</i>	0.06	0.017	0.16	0.8
		<i>Cp</i>	5.10	0.190	1.65	–
V1-35-01	<i>TiMt-Bn-Cp</i> vein-shaped segregation in gabbro	<i>TiMt</i>	3.00	0.062	0.33	5.5
		<i>Cp</i>	25.20	0.460	4.09	19.0
V1-70-01	<i>TiMt-Bn-Cp</i> vein-shaped segregation in gabbro	<i>TiMt</i>	0.88	0.010	0.32	2.8
		<i>Cp</i>	14.40	0.098	2.91	4.1
29/p-92	<i>TiMt-Bn-Cp</i> vein-shaped segregation in gabbro	<i>TiMt</i>	4.83	0.027	0.20	7.6
		<i>Cp</i>	11.42	0.220	0.05	142.6

Note: See Table 5.

skyite inclusions and host mineral are conjugated (Table 7). In the merenskyite–bornite pair, the Pd/Pt and Fe/Cu ratios are inversely correlated with the Fe/Cu ratio of bornite (Figs. 6a, 6b); the merenskyite–chalcopryrite pair reveals a direct correlation between these ratios (Figs. 6c, 6d).

These empirical relationships are consistent with thermodynamic calculations. The relationship between Fe and Cu in the copper sulfides, on the one hand, and in palladium tellurides, on the other, may be represented as the following equilibrium: $2\text{CuTe} + 2\text{CuFeS}_2 + \text{Cu}^0 \rightleftharpoons \text{Cu}_5\text{FeS}_4 + \text{FeTe}_2$. The Gibbs free energy and entropy difference calculated for this equilibrium by using data from [45, 55] are $\Delta G^0 = -6.55$ kcal/mol and $\Delta S = 7.25$ entropic units. The equilibrium constant of this reaction is $K = (\alpha_{\text{Cu}_5\text{FeS}_4} \alpha_{\text{FeTe}_2}) / [(\alpha_{\text{CuTe}})^2 (\alpha_{\text{CuFeS}_2})^2 \alpha_{\text{Cu}}]$. For the sake of visual presentation, this constant may be written

with a certain approximation as $\alpha_{\text{MeTe}}^{\text{MeTe}} = [K \alpha_{\text{Fe/Cu}}^{2\text{Cp}} \alpha_{\text{Cu}}^{\text{Bn}}] / \alpha_{\text{Fe/Cu}}^{\text{Bn}}$, where MeTe is Pd telluride. As follows from this equation, the ratio of Fe and Cu activities in Pd tellurides should be in a direct (more specifically, power) dependence on the Fe/Cu ratio in coexisting chalcopryrite and in an inverse dependence on the Fe/Cu ratio in bornite. Thus, our results clearly demonstrate that the oxide–sulfide mineral assemblages and associated precious metals were formed under physico-chemical conditions close to equilibrium.

The effect of temperature on the Fe and Cu contents in Pd tellurides as foreign components may be deduced from the following schematic reaction: $2\text{CuTe} + \text{Fe}^0 \rightleftharpoons \text{FeTe}_2 + 2\text{Cu}^0$, where $\Delta G^0 = -2.913$ kcal/mol and $\Delta S = -8.01$ entropic units; equilibrium constants ($\log K$) at 500 and 900°C are equal to -0.2511 and 0.7631 , respectively. Hence, the Fe/Cu ratio in palladium tellurides at a relatively constant Fe/Cu ratio

in the mineral-forming medium should increase with decreasing temperature. This conclusion is consistent with the compositions of such palladium minerals as keithconnite $\text{Pd}_{3-x}\text{Me}_x\text{Te}_{1-y}\text{A}_y$, kotulskite $\text{Pd}_{1-x}\text{Me}_x\text{Te}_{1-y}\text{A}_y$, and merenskyite $\text{Pd}_{1-x}\text{Me}_x\text{Te}_{2-y}\text{A}_y$ (Me = Pt, Cu, Fe, Ni, etc. and A = As, S, Se, Sb, etc.) from the Baronsky Au–Pd deposit [33]; these minerals were formed during a decrease in the temperature of the ore-forming process (Fig. 7). The formation of merenskyite at a lower temperature in comparison with other Pd minerals—kotulskite and keithconnite—may also be deduced from equilibrium constants calculated by using thermodynamic data [57] for the reaction $\text{PdTe} + \text{Te}^0 \longleftrightarrow \text{PdTe}_2$. The equilibrium constants at 500 and 900°C are $\log K^{500} = 0.491$ and $\log K^{900} = 0.464$, respectively.

It is interesting to analyze the behavior of Ni and Cu in Pd tellurides as a function of temperature. Thermodynamic analysis suggests two types of reactions: (1) $\text{Cu}^0 + \text{NiTe} \longleftrightarrow \text{CuTe} + \text{Ni}^0$, whose free energy ΔG^0 is equal to 6.313 kcal/mol and the entropy difference is $\Delta S^0 = 1.05$ entropic units; the equilibrium constants at 500 and 900°C are $\log K^{500} = -1.467$ and $\log K^{900} = -0.801$ and (2) $\text{CuS} + \text{NiTe} \longleftrightarrow \text{CuTe} + \text{NiS}$, $\Delta G^0 = -2.625$ kcal/mol and $\Delta S^0 = -3.44$ entropic units; $\log K_p = 0.280$ for 500°C and $\log K_p = -0.072$ for 900°C. As follows from these data, the Cu and Ni redistribution in tellurides that proceeds with decreasing temperature should be accompanied by a decrease in the Cu/Ni ratio in the first case and by an increase in this ratio in the second case. Judging from [33], the formation of Pd tellurides in the series keithconnite–kotulskite–merenskyite in nature proceeds according to reaction (1) and is accompanied by enrichment of these minerals in Ni from 0.07 wt % in keithconnite to 0.34 wt % in kotulskite and 2.83 wt % in merenskyite (on average), together with depletion in Cu from 13.63 wt % in keithconnite to 5.47 wt % in kotulskite and 2.84 wt % in merenskyite; the Cu/Ni ratio decreases from 80.06 in keithconnite to 16.08 in kotulskite and 1.00 in merenskyite. The opposite character of Cu and Ni distribution in the Pd tellurides is clearly seen from Fig. 8, which demonstrates an increase in the Ni content and a decrease in the Cu content in the keithconnite–kotulskite–merenskyite series.

To elucidate genetic relations between minerals of oxide–sulfide ore and NM mineralization and to clarify the effects of geological factors on their formation, we compared the composition of Pd tellurides and Cu sulfides at the Volkovsky and Baronsky deposits, which are distinguished by the composition of the host rocks and the depth of ore formation. As follows from Tables 8 and 9, Pd tellurides at the Volkovsky deposit are enriched in Sb, Bi, and Au and depleted in Pt, Ni, and Ag in comparison with the same minerals at the Baronsky deposit. Furthermore, as can be seen from Fig. 9, the Au content in merenskyite increases with decreasing Fe/Cu ratio.

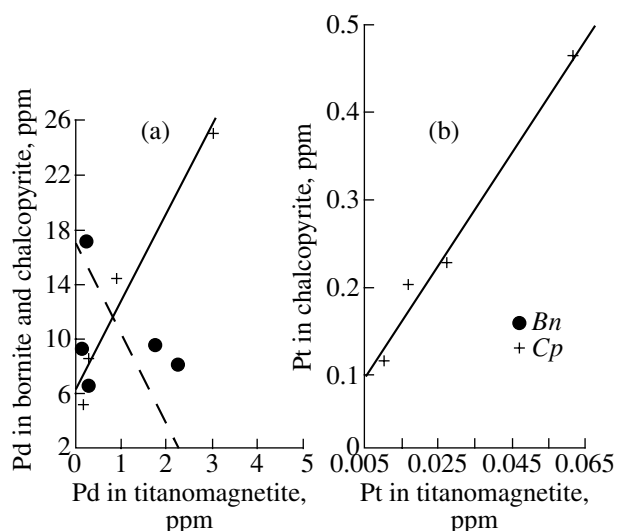


Fig. 5. Partition of (a) Pd and (b) Pt between coexisting bornite (*Bn*), chalcopyrite (*Cp*), and titanomagnetite in ore of the Volkovsky deposit.

The aforementioned thermodynamic calculations have shown that this ratio in merenskyite is inversely correlated with temperature. Therefore, merenskyite at the Volkovsky deposit should be regarded as a higher tem-

Table 7. Chemical compositions (wt %) of coexisting copper sulfides and merenskyite inclusions therein in ore of the Volkovsky deposit

No.	Mineral	Cu	Fe	S	Pd	Pt	Te
1	<i>Bn</i>	69.80	6.61	24.75	–	–	–
	<i>Me</i>	3.00	1.07	1.74	21.80	0.22	66.04
2	<i>Bn</i>	57.94	10.73	29.00	–	–	–
	<i>Me</i>	4.92	0.70	1.25	23.93	7.40	65.57
3	<i>Bn</i>	61.73	8.97	27.94	–	–	–
	<i>Me</i>	2.79	0.68	0.46	27.93	0.52	68.04
4	<i>Bn</i>	60.61	9.13	28.55	–	–	–
	<i>Me</i>	6.22	1.10	1.82	27.90	0.42	63.64
5	<i>Bn</i>	57.94	10.73	29.00	–	–	–
	<i>Me(?)</i>	–	0.44	–	15.64	19.54	63.24
6	<i>Cp</i>	34.92	29.53	34.72	–	–	–
	<i>Me</i>	1.06	0.64	0.11	24.38	0.16	58.30
7	<i>Cp</i>	35.11	29.45	34.25	–	–	–
	<i>Me</i>	4.95	2.42	1.99	22.37	0.29	64.59
8	<i>Cp</i>	35.82	29.41	35.34	–	–	–
	<i>Me</i>	4.90	0.72	1.24	28.40	0.59	67.61

Note: *Me* is merenskyite. Analyses were performed at the Institute of Geology and Geochemistry, Uralian Division, RAS, on a JXA-5 microprobe, analysts Yu.S. Shagalov and L.K. Voronina. Dash denotes not analyzed.

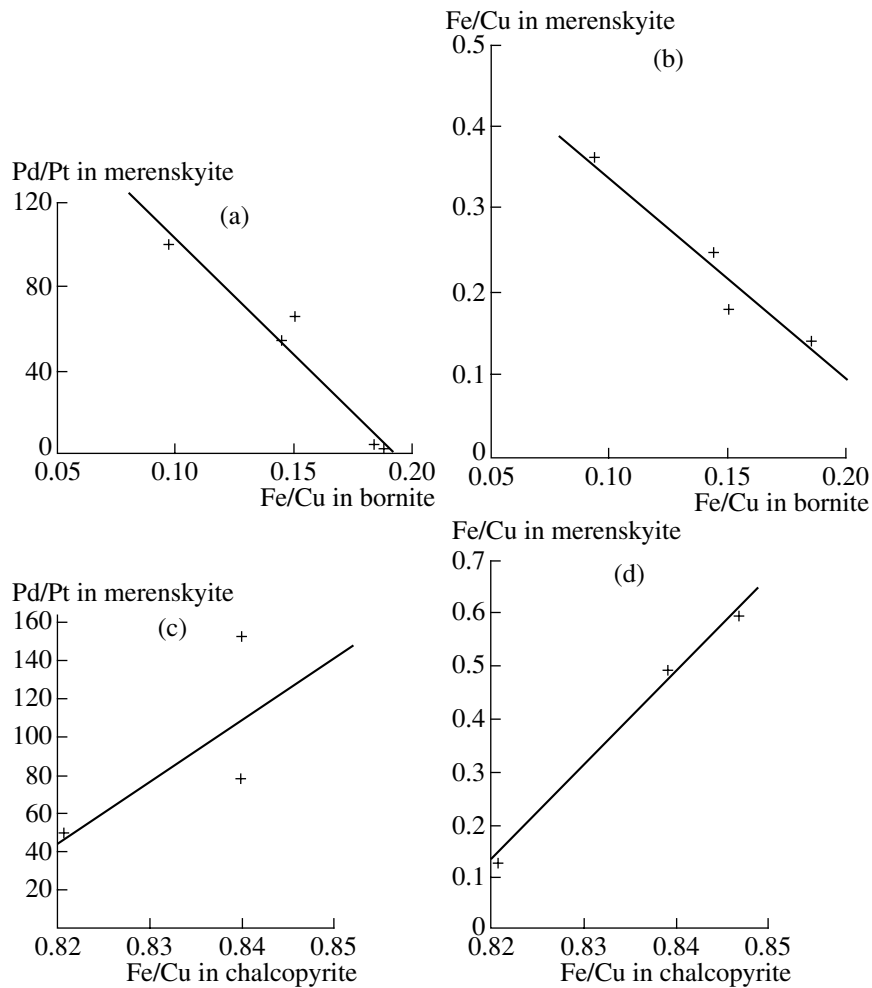


Fig. 6. Pd/Pt and Fe/Cu in merenskyite versus the composition of host sulfides.

perature mineral relative to merenskyite from the Baronsky deposit, and this is corroborated by the higher fineness of the associated native gold.

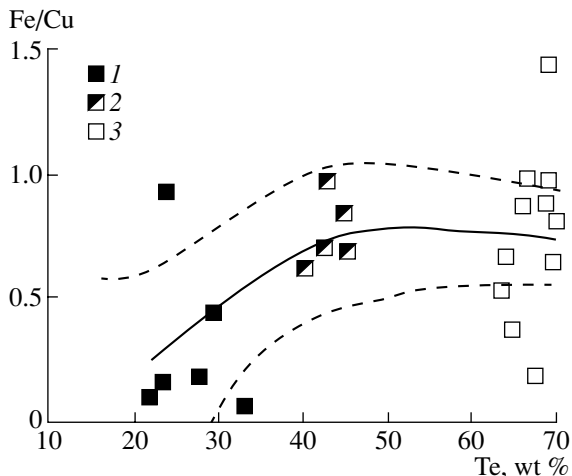


Fig. 7. Distribution of Fe/Cu ratio in (1) keithconnite, (2) kotulskite, and (3) merenskyite at the Baronsky deposit. The dashed lines are boundaries of the confidence interval. The diagram has been compiled by using the data from [33].

The elevated Ni content in Pd tellurides at the Baronsky deposit is correlated with the enrichment of the host gabbroids in Ni (Table 1). Thus, the composition of NM minerals depends on both the composition of the host mineral and the host rock.

The correlation between compositions of sulfides (Table 4) and NM (Tables 8, 9) at the Volkovsky and Baronsky deposits reveal some specific compositional features that are correlated with some thermodynamic parameters, in particular, with the entropy. As can be seen from the crystal chemical formulas of the minerals in question, all of them are characterized by compositions close to the stoichiometric ones, with an insignificant prevalence of cations (C) over anions (A). Bornite and probably keithconnite are the only exceptions. It is worth noting that the C/A ratio in these minerals is correlated with the entropy calculated for them as solid solutions (S_{ss}^0) by using Latimer's method [45, 46]. When $C > A$ relative to the stoichiometric composition, the calculated S_{ss}^0 values are also higher than the entropy of this mineral of stoichiometric composition.

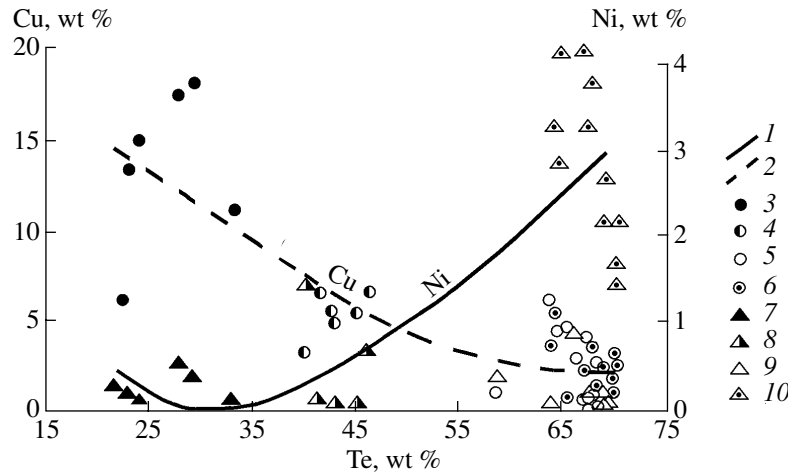


Fig. 8. Variations in the (1) Ni and (2) Cu contents in the keithconnite–kotelusite–merenskyite series. (3–5) Cu content in keithconnite, kotelusite, and merenskyite, respectively; (5, 6) Cu content in merenskyite from (5) Volkovsky and (6) Baronsky deposits; (7–10) Ni content in keithconnite, kotelusite, and merenskyite, respectively; merenskyite from (9) Volkovsky and (10) Baronsky deposits. The diagram has been compiled taking into account the data from [33, 35].

If $C < A$, S_{ss}^0 is also lower than the entropy of the mineral of stoichiometric composition. As can be seen from the comparison of the solid-solution entropy in the digenite–bornite–chalcopyrite series, which characterizes the consecutive change of ore phases during the ore formation, the entropy per one atom of chemical elements in the sulfide formulas (S_{ss}^0/Σ_{C+A}) diminishes. Thus, this series is characterized by the following values of reduced entropy (S_{ss}^0/Σ_{C+A}): 8.83–8.35–7.82 cal/mol degree at the Volkovsky deposit and 8.90–8.41–7.79 cal/mol degree at the Baronsky deposit. A similar relationship is established by normalizing the entropy to one anion (S_{ss}^0/Σ_A): 25.96–20.07–14.76 and 27.18–20.77–15.50 cal/mol degree at the Volkovsky and Baronsky deposits, respectively. It is worth noting that, according to our and previously published data, a decrease in the entropy normalized to one cation (S_{ss}^0/Σ_C) also holds for Pd tellurides: the minerals formed later are characterized by lower values of the normalized entropy. For example, for merenskyite that occurs as inclusions in chalcopyrite $S_{ss}^0/\Sigma_C = 12.97$ cal/mol degree, while for merenskyite in bornite, it is 13.18 cal/mol degree. According to [35], the normalized entropy of the same minerals is 12.87 and 12.94 cal/mol degree, respectively. As can be seen from the crystal chemical formulas of merenskyites, these features are related to the partial contributions of cations to the entropy of the minerals. Merenskyite hosted in bornite contains more foreign elements replacing palladium than that in chalcopyrite. As could be expected, merenskyite from the Baronsky deposit, which contains less impurities than its Cu–Ni counterpart, is also character-

ized by a lower normalized entropy ($S_{ss}^0/\Sigma_C = 13.65$ and 14.87 cal/mol degree, respectively). Kotelusite and keithconnite have the highest normalized entropy: 30.20 and 43.86 cal/mol degree. Thus, these features are in agreement with principles of chemical thermodynamics. Because the crystallization of minerals is an exothermic reaction, the process is accompanied by a decrease in the entropy of the newly formed phases. This implies that the merenskyite–bornite and merenskyite–chalcopyrite are paragenetic assemblages, which were formed under conditions close to equilibrium. Judging from our data, the formation of sulfides and NM at the Volkovsky deposit developed within a temperature range of 800°–570°C. The possible formation of merenskyite within this temperature interval is supported by experimental results. According to [58], PdTe₂ and PdTe crystallize congruently in the Pd–Te system at 752 and 746°C, respectively.

In spite of rather detailed investigations [34, 35, and many others], PGE sulfides have never been found at the Volkovsky and Baronsky deposits, and neither sulfides proper (PdS, PtS, etc.) nor sulfospinel (CuPt₂S₄, etc.) are known there. The absence of sulfide species of these metals seems to be strange at first glance, because Pd mineralization is here closely related to Cu sulfide ore. However, thermodynamic calculations indicate that Pd reveals closer chemical affinity to Te than to S. As is shown in Fig. 10a, PdTe₂ is stable at a lower fugacity of PdS₂ than S₂, and this controls the stability of PdS₂. Platinum makes up the most stable compound with arsenic (Fig. 10b). These diagrams clearly demonstrate different effects of foreign anions and cations on the thermodynamic stability of various Pd and Pt compounds. For example, the most volatile (least stable) compounds of these metals are those with O and Cl,

Table 8. Chemical composition (wt %) of merenskyite and native gold inclusions in copper sulfides at the Volkovsky deposit

No.	Pd	Pt	Au	Ag	Fe	Cu	Ni
1	$\frac{24.54}{15.64-27.93}$	$\frac{0.34^*}{0.22-7.40}$	$\frac{0.30}{0.11-0.46}$	–	$\frac{1.31}{0.44-3.87}$	$\frac{3.99}{2.79-6.22}$	$\frac{0.18}{0.0-0.82}$
2	$\frac{25.05}{22.37-28.40}$	$\frac{0.35}{0.16-0.59}$	$\frac{0.22}{0.16-0.28}$	–	$\frac{1.26}{0.64-2.42}$	$\frac{3.01}{1.06-4.95}$	–
3	0.03	0.06	89.98	10.34	0.42	0.17	–
4	$\frac{26.62}{26.09-27.58}$	$\frac{1.89}{0.0-3.31}$	$\frac{0.33}{0.17-0.53}$	–	$\frac{0.22}{0.10-0.38}$	$\frac{0.63}{0.38-0.78}$	$\frac{0.30}{0.07-0.74}$
5	$\frac{27.83}{26.96-29.00}$	–	–	–	$\frac{0.48}{0.30-0.59}$	$\frac{0.86}{0.67-1.08}$	$\frac{0.07}{0.07-0.08}$
No.	Co	Te	Bi	Sb	Se	S	Total
1	–	$\frac{65.24}{63.24-68.4}$	$\frac{0.11}{0.08-0.15}$	$\frac{1.06}{0.81-1.21}$	$\frac{2.02}{1.70-2.46}$	$\frac{1.40}{0.46-1.82}$	100.49
2	–	$\frac{63.50}{58.30-67.61}$	$\frac{0.16}{0.12-0.19}$	$\frac{0.96}{0.91-0.97}$	$\frac{2.08}{1.77-2.38}$	$\frac{1.11}{0.11-1.99}$	97.70
3	–	–	–	–	–	0.05	101.05
4	$\frac{0.13}{0.12-0.13}$	$\frac{68.27}{67.88-68.82}$	$\frac{0.10}{0.06-0.12}$	$\frac{0.61}{0.55-0.64}$	–	$\frac{0.16}{0.09-0.26}$	99.26
5	$\frac{0.13}{0.10-0.16}$	$\frac{67.85}{67.50-68.14}$	$\frac{1.29}{0.92-1.98}$	$\frac{0.64}{0.62-0.66}$	–	$\frac{0.21}{0.12-0.35}$	99.36

Note: (1) merenskyite in bornite (average of 5 analyses); (2) merenskyite in chalcopyrite (average of three analyses); (3) gold in chalcopyrite (one analysis); (4) merenskyite in bornite (average of 3 analyses); (5) merenskyite in chalcopyrite (average of three analyses); (4, 5) were taken from [35]. Numerators are the arithmetic means, denominators are the ranges; * anomalous contents were omitted from the calculation of the arithmetic mean. Dash denotes not analyzed. Analyses were conducted at the Institute of Geology and Geochemistry, Uralian Division, RAS on a JXA-5 microprobe at an accelerating voltage of 20 kV, current of 30 mA, and counting time of 10 s. Analyst E.S. Shagalov.

The crystal chemical formulas of average mineral compositions and entropy values (S_{ss}^0 , cal/mol degree), calculated with Latimer's method [45]; entropy values for stoichiometric compositions are given in parentheses.

$$(1) (\text{Pd}_{0.752}\text{Pt}_{0.029}\text{Au}_{0.005}\text{Cu}_{0.205}\text{Ni}_{0.010}\text{Fe}_{0.076})_{1.077}(\text{Te}_{1.667}\text{Bi}_{0.002}\text{Sb}_{0.028}\text{Se}_{0.083}\text{S}_{0.143})_{1.923}, S_{ss}^0 = 41.55 (28.50).$$

$$(2) (\text{Pd}_{0.807}\text{Pt}_{0.006}\text{Au}_{0.004}\text{Cu}_{0.164}\text{Ni}_{0.0}\text{Fe}_{0.077})_{1.058}(\text{Te}_{1.705}\text{Bi}_{0.003}\text{Sb}_{0.027}\text{Se}_{0.090}\text{S}_{0.119})_{1.940}, S_{ss}^0 = 41.93 (28.50).$$

$$(3) \text{Au}_{0.808}\text{Ag}_{0.213}(\text{Pd,Pt})_{0.001}\text{Cu}_{0.005}\text{Fe}_{0.013}\text{S}_{0.003}, S_{ss}^0 = 15.29 (15.30).$$

$$(4) (\text{Pd}_{0.906}\text{Pt}_{0.035}\text{Au}_{0.006}\text{Cu}_{0.036}\text{Ni}_{0.018}\text{Co}_{0.008}\text{Fe}_{0.014})_{1.023}(\text{Te}_{1.938}\text{Bi}_{0.002}\text{Sb}_{0.018}\text{Se}_{0.028})_{1.976}, S_{ss}^0 = 43.95 (28.50).$$

$$(5) (\text{Pd}_{0.937}\text{Pt}_{0.00}\text{Au}_{0.00}\text{Cu}_{0.048}\text{Ni}_{0.004}\text{Co}_{0.008}\text{Fe}_{0.031})_{1.028}(\text{Te}_{1.906}\text{Bi}_{0.022}\text{Sb}_{0.019}\text{Se}_{0.024})_{1.971}, S_{ss}^0 = 43.67 (28.50).$$

whereas the compounds with As, Te, and Se are the least volatile and most stable. It should be noted that PtAs_2 and probably PdAs_2 are characterized by the lowest As activity and, therefore, are probably the most stable compounds over a wide temperature interval; the field of their stability expands toward lower temperatures. Palladium telluride in form of merenskyite PdTe_2 should be the most stable among various palladium compounds with other anions (Fig. 10a).

It is interesting to examine the effects of elements of the S group (S, As, Se) and Fe group (Fe, Co, Ni) on the stability of Pd and Pt tellurides. The replacement of Te by S, As, and Se and Pd by Ni, Co, and, to a lesser extent, Pt must reduce the stability fields of Pd tellurides in a wide temperature range (Figs. 10a and 10c).

Gold should occur mainly as a native metal in the association with palladium tellurides devoid of impurities at high temperatures and as gold tellurides in the relatively low-temperature region ($\approx 700^\circ\text{C}$ and lower).

Under still lower temperature (no higher than $\approx 400^\circ\text{C}$) of the hydrothermal solutions [57], the stability fields of Pd and Pt sulfides and tellurides largely correspond to the stability regions of oxide-sulfide ore assemblages (magnetite, pyrite, and pyrrhotite) and depend on the acidity-alkalinity of hydrothermal solutions that controls speciation of S and Te anions in solution. In low- and moderate-alkaline solutions (pH 8–12), they occur as HS^- and HTe^- , whereas in slightly acid and more acidic solutions ($\text{pH} \leq 8$), as H_2S^0 and H_2Te^0 . Thermodynamic calculations [59] show that, regardless

Table 9. Chemical composition (wt %) of NM minerals in apatite olivinite at the Baronsky deposit

No.	Pd	Pt	Au	Ag	Fe	Cu
1	$\frac{21.90}{20.0-25.10}$	$\frac{0.75}{0.49-1.21}$	$\frac{0.11}{0.06-0.24}$	$\frac{0.05}{\text{Cl.}-0.10}$	$\frac{1.92}{1.46-2.61}$	$\frac{2.19}{1.03-3.14}$
2	$\frac{22.67}{20.10-26.0}$	$\frac{1.08}{0.55-2.10}$	$\frac{0.15}{0.0-0.47}$	$\frac{0.10}{0.0-0.20}$	$\frac{2.07}{0.29-3.90}$	$\frac{3.38}{0.75-5.48}$
3	$\frac{39.87}{37.80-42.10}$	$\frac{0.67}{0.05-2.40}$	$\frac{0.20}{0.0-0.61}$	$\frac{0.16}{0.0-0.31}$	$\frac{4.59}{3.88-5.77}$	$\frac{5.47}{3.41-6.60}$
4	$\frac{52.80}{41.80-66.89}$	$\frac{0.47}{0.0-1.25}$	$\frac{0.13}{0.0-0.63}$	$\frac{0.14}{0.0-0.42}$	$\frac{2.64}{0.50-7.26}$	$\frac{13.61}{5.72-18.54}$
5	$\frac{0.10}{0.05-0.14}$	–	$\frac{85.00}{84.6-85.4}$	$\frac{12.70}{12.20-13.20}$	–	–
No.	Ni	Te	Sb	Bi	Total	
1	$\frac{1.98}{1.42-2.61}$	$\frac{69.52}{69.09-70.0}$	$\frac{0.23}{0.11-0.31}$	$\frac{0.04}{0.0-0.10}$	98.69	
2	$\frac{3.55}{2.80-4.11}$	$\frac{65.80}{64.0-67.60}$	$\frac{0.23}{0.13-0.32}$	$\frac{0.03}{0.0-0.19}$	99.06	
3	$\frac{0.34}{0.0-1.40}$	$\frac{43.00}{40.0-46.10}$	$\frac{0.06}{0.0-0.12}$	–	94.36	
4	$\frac{0.17}{0.0-0.47}$	$\frac{27.06}{22.0-33.00}$	$\frac{0.08}{0.0-0.13}$	–	97.10	
5	–	–	–	$\frac{0.46}{0.25-0.67}$	98.26	

Note: (1) merenskyite, average of 5 analyses; (2) Cu-Ni-merenskyite, average of 6 analyses; (3) Cu-kotulskite, average of 6 analyses; (4) Cu-keithconite, average of 6 analyses; (5) native gold, average of 2 analyses. Numerators are the arithmetic means, denominators are the ranges. Dash denotes not analyzed. The table is compiled from the data reported in [33]. Analyses were performed at the Institute of Geology and Geochemistry, Uralian Division, RAS, on an JXA-5 microprobe. Analyst L.V. Voronina.

Crystal chemical formulas of average mineral composition and entropy values (S_{ss}^0 , cal/mol degree), calculated with Latimer's method [45]; entropy values for stoichiometric compositions are given in parentheses.

(1) $(\text{Pd}_{0.744}\text{Pt}_{0.014}(\text{Au,Ag})_{0.004}\text{Cu}_{0.125}\text{Ni}_{0.122}\text{Fe}_{0.125})_{1.134}(\text{Te}_{1.860}\text{Sb}_{0.007}\text{Bi}_{0.001})_{1.868}$, $S_{ss}^0 = 43.15$ (28.50).

(2) $(\text{Pd}_{0.720}\text{Pt}_{0.019}(\text{Au,Ag})_{0.003}\text{Cu}_{0.180}\text{Ni}_{0.204}\text{Fe}_{0.125})_{1.251}(\text{Te}_{1.742}\text{Sb}_{0.006}\text{Bi}_{0.001})_{1.749}$, $S_{ss}^0 = 42.48$ (28.50).

(3) $(\text{Pd}_{0.869}\text{Pt}_{0.008}\text{Au}_{0.002}\text{Ag}_{0.003}\text{Cu}_{0.199}\text{Ni}_{0.013}\text{Fe}_{0.191})_{1.285}(\text{Te}_{0.782}\text{Sb}_{0.001})_{1.783}$, $S_{ss}^0 = 23.64$ (23.10).

(4) $(\text{Pd}_{2.528}\text{Pt}_{0.012}\text{Au}_{0.003}\text{Ag}_{0.007}\text{Cu}_{0.109}\text{Ni}_{0.015}\text{Fe}_{0.241})_{2.915}(\text{Te}_{1.081}\text{Sb}_{0.003})_{1.084}$, $S_{ss}^0 = 47.55$ (48.50).

(5) $\text{Au}_{0.708}\text{Ag}_{0.213}\text{Pd}_{0.003}\text{Bi}_{0.004}$, $S_{ss}^0 = 13.66$ (15.30).

of the state of the ore-forming solution, Pd and Pt are characterized by still greater differences in their chemical affinity to Te and S than in the case when they occur as a gas phase: $\text{PdTe}_2 + \text{S}_2 \uparrow = \text{PdS}_2 + \text{Te}_2 \uparrow$, where $\Delta G^0 = 3.720$ kcal/mol and $\Delta S^0 = 0.27$ entropic units and $\text{PtTe}_2 + \text{S}_2 \uparrow = \text{PtS}_2 + \text{Te}_2 \uparrow$, where $\Delta G^0 = -2.164$ kcal/mol and $\Delta S^0 = -1.53$ entropic units. The large positive values of the change of the Gibbs free energy (ΔG^0) in reactions: $\text{PdTe}_2 + 2\text{H}_2\text{S}_{\text{sol}} = \text{PdS}_2 + 2\text{H}_2\text{Te}_{\text{sol}}$ ($\Delta G^0 = 50.47$ kcal/mol and $\Delta S^0 = 0.1$ entropic units) and $\text{PtTe}_2 + 2\text{H}_2\text{S}_{\text{sol}} = \text{PtS}_2 + 2\text{H}_2\text{Te}_{\text{sol}}$ ($\Delta G^0 =$

44.607 kcal/mol and $\Delta S^0 = -1.7$ entropic units) indicate that equilibrium shifts to the left, whereas the very small values of the entropy change (ΔS^0) testify to the high stability of Pd and Pt tellurides in comparison with their sulfide analogues in a wide temperature range. As follows from the diagram in Fig. 11, the formation of Pd and Pt sulfides is possible at a relatively high sulfur fugacity, close to the pyrite–pyrrhotite equilibrium. The sulfide ore at the Volkovsky deposit is composed mostly of bornite and chalcopyrite in association with titanomagnetite, digenite, and chalcocite. Pyrrhotite is virtu-

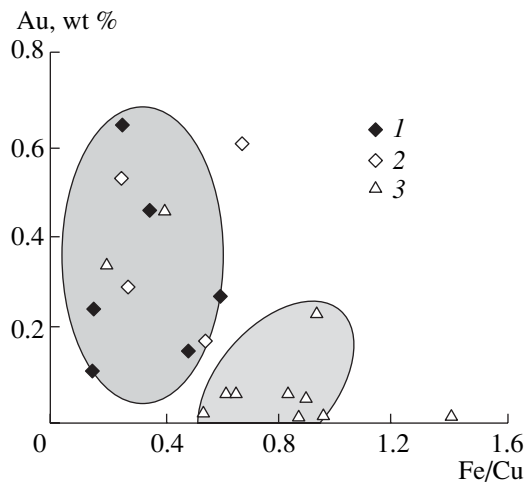


Fig. 9. Au content versus the Fe/Cu ratio in merenskyite from the Volkovsky deposit. (1, 2) Volkovsky deposit: (1) authors' data, (2) after [35]; (3) Baronsky deposit, after [33].

ally absent, and pyrite is a postore mineral. Therefore, it may be supposed that the sulfide ore and related NM mineralization were formed at a very low sulfur fugacity, several orders of magnitude (up to five log units) lower than the pyrite–pyrrhotite equilibrium. The high chemical affinity of Pd and Pt to Te and the low S fugacity during the formation of the Cu sulfide ore and related NM mineralization are the main reasons for the absence of pyrrhotite, pyrite, and such PGE disulfides as PdS₂ and PtS₂ from the ore mineral assemblage at the Volkovsky deposit.

Thus, on the basis of the material reported above, we come to the conclusion that, during the crystallization of magmatic melt, NM most likely concentrated as isomorphous components in pyroxene, titanomagnetite, and probably also in amphibole and biotite. On the one hand, the enrichment of the rocks and ores in NM took place during an early stage of gabbroic melt fractionation, related to crystallization of rock-forming minerals, largely pyroxene and titanomagnetite, and, on the other hand, was caused by the gain of Cu and Te during the evolution of the ore–magmatic system. Later during the magmatic fractionation, when Cu, S, Te, and NM were accumulated in the melt, the latter were precipitated in copper sulfides both as native Au and Pd tellurides with admixture of Pt, Au, and Ag. This conclusion is fully consistent with experimental results, which indicate that sulfide liquid has the greatest extracting ability [9, 25]. The role of fluids in the transfer and extraction of NM was substantial but not crucial. This is supported by the experimental data [9, 25], according to which the coefficients of NM partition between a fluid phase and coexisting silicate melt, sulfide liquid, and rock-forming minerals are commonly less than unity at the parameters of the magmatic process.

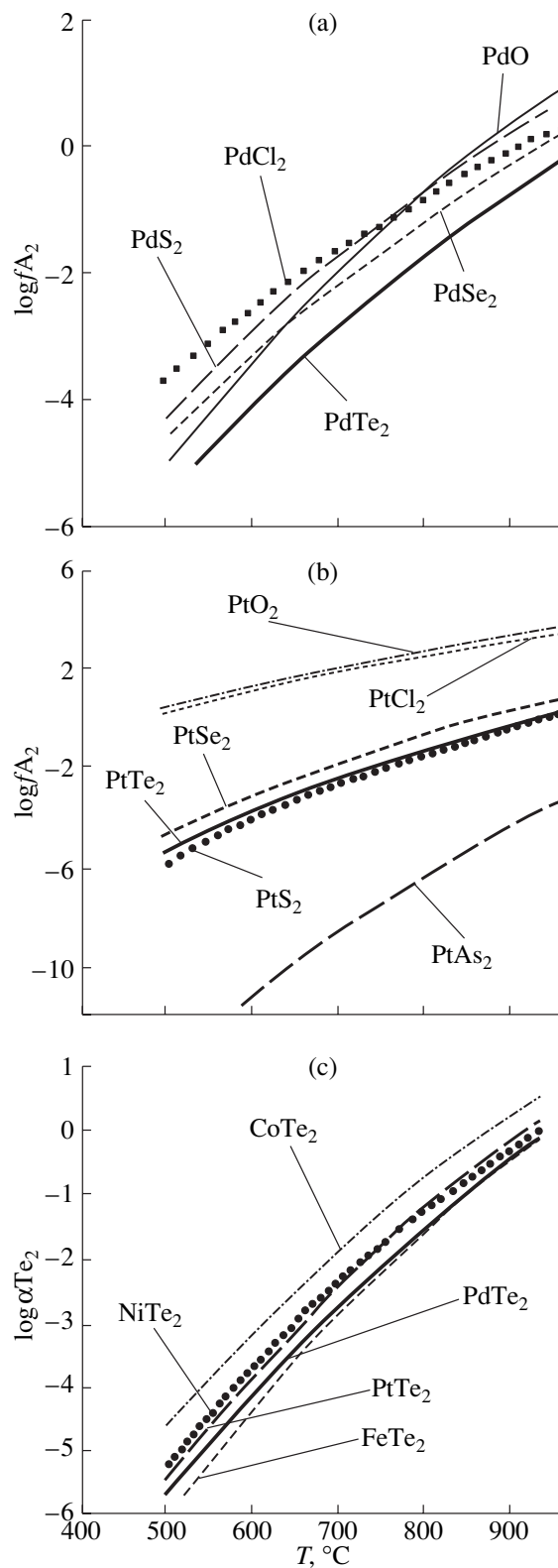


Fig. 10. Fugacity $\log f A_2$ (S₂, Cl₂, Se₂, O₂, and Te₂) versus temperature for Pd and Pt compounds and tellurides of Fe-group elements. The equilibrium curves have been calculated by using thermodynamic constants given in [45, 57].

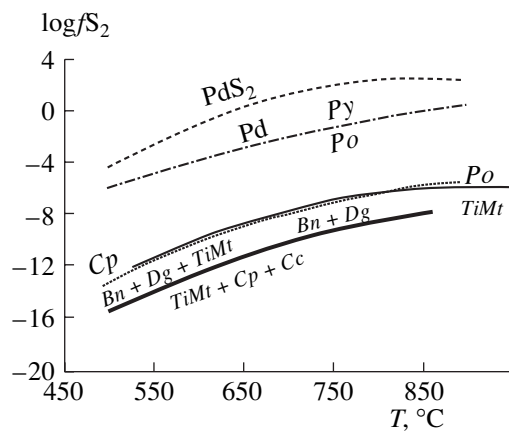


Fig. 11. Sulfur fugacity $\log fS_2$ versus temperature for oxide–sulfide mineral assemblages. Sulfur fugacity in equilibrium reactions with the participation of magnetite was calculated taking into account the oxygen fugacity $\log fO_2$ determined from the computer simulations of crystallization differentiation in the gabbroic series of the Volkovsky pluton by using COMAGMAT program [26]. Thermodynamic data reported by Barton [52] and in [45, 57] were used in calculations. Symbols: *Bn*—bornite, *Cc*—chalcocite, *Cp*—chalcopyrite, *Dg*—digenite, *TiMt*—titanomagnetite, *Po*—pyrrhotite, and *Py*—pyrite.

CONCLUSIONS

(1) The basaltic magma initially enriched in noble metals, except Pt, served as a source of Pd, Pt, Au, and Ag contained in the gabbroic rocks of the Volkovsky pluton. These elements were components of the magmatic melt, and their speciation was controlled by the evolution of the ore-bearing melt and the physicochemical conditions of titanomagnetite and copper sulfide ore formation. Mineralogical and geochemical data on the rocks and ores indicate that the formation of complex titanomagnetite and copper sulfide ores and associated precious-metal mineralization was a result of crystallization differentiation, which gave rise to the formation of melanocratic gabbroids with titanomagnetite and copper sulfide disseminations, and of fluid–magmatic differentiation, which led to the segregation of oxide and sulfide droplets and schlieren.

(2) The formation of the ores was characterized by the progressive enrichment of minerals in NM during the process of basaltic magma fractionation. The physicochemical conditions favorable for the incorporation of NM into minerals, mainly pyroxene and titanomagnetite, were created during an earlier stage of magma crystallization. The massive precipitation of Pd tellurides and native Au occurred during the final stages of gabbro crystallization in areas where disseminated titanomagnetite and copper sulfide ores were formed. The maximum NM gain was related to the formation of schlieren and vein-shaped segregations derived from the residual melt enriched in ore and volatile components.

(3) The copper sulfide ore and related NM mineralization were formed at a relatively low sulfur fugacity, approximately 5 log units below the pyrite–pyrrhotite equilibrium. According our calculation results, $\log fS_2$ varied within the range of -6 to -16 and $\log fTe_2$ ranged from -1 to 6 at temperatures of 800 – 570°C . The low sulfur fugacity in combination with high chemical affinity of Pd and Pt to Te predetermined the absence of pyrrhotite, pyrite, and PGE disulfides from the ore mineral assemblage at the Volkovsky deposit.

(4) The major ore minerals and NM were formed within a wide temperature range (800 – 570°C), under conditions close to the equilibrium. As a result, the compositions of merenskyite inclusions and host mineral are correlated. The Cu content in the keithconnite–kotulskite–merenskyite series increased with decreasing temperature, while the Ni content simultaneously decreased.

The admixtures of Ni, Co, and Fe affected the thermodynamic stability of Pd telluride because of their different chemical affinity to Te and elements of S group (S, Se, As). The replacement of Pd by Ni, Co, and, to a lesser extent, Pt, as well as the replacement of Te by S, As, and Se reduce the stability field of Pd telluride.

(5) Comparison of Pd tellurides hosted in Cu sulfide ore at the Volkovsky and Baronsky deposits demonstrates the enrichment of the former in Au, Sb, and Bi and of the latter in Pt, Ni, and Ag. The elevated Ni content in Pd telluride at the Baronsky deposit is clearly correlated with enrichment of the gabbroids in Ni.

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