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PGM assemblages from the lower ore bodies of the North Kamennik palladium deposit, Kola Region, Russia

A N Ivanov, A V Chernyavsky, N Yu Groshev, E E Savchenko

Geological Institute, Kola Science Centre, Russian Academy of Sciences, Apatity, Russia

nikolaygroshev@gmail.com

Abstract. The low-sulfide palladium deposit North Kamennik is confined to the North platinum-bearing reef in the West Pana intrusion of the Paleoproterozoic Fedorova-Pana layered complex of the Kola Peninsula. The main ore body of this deposit is accompanied by underlying ore bodies, which is not typical of other sites of the North Reef (e.g., Kievey deposit). The lower ore bodies, differing from the main one in composition of the host rocks and geochemical characteristics, are divided into three types. The conducted mineralogical studies allow us to determine each ore type according to the PGM assemblage — stannide-telluride (type 1), arsenide-sulfide-telluride (type 2) and sulfide-telluride (type 3). Mineralogical finds have been made within the ore bodies of stannide-telluride and arsenide-sulfide-telluride PGM assemblages and are presented by arsenopalladinite, isomertieite and kojonenite (new minerals for the North Reef).

1. Introduction

The Fedorova-Pana Palaeoproterozoic layered complex is located in the central part of the Kola Peninsula and contains several low-sulfide palladium deposits discovered in recent years which are similar in their features to other platinum group element (PGE) deposits in layered intrusions [1–6]. A significant part of PGE resources of the complex are concentrated in the North Reef of the West Pana intrusion, in which two deposits have been explored: Kievey and North Kamennik (hereinafter referred to as Kamennik). The geological structure and composition of mineralization from main ore bodies (MOB) are presented in detail in the articles by Korchagin with colleagues [7,8].

The Kamennik deposit (Fig. 1) is located at the western flank of the lower layered horizon (LLH), near the supposed feeding magmatic channel. The geochemical features and mineral composition of the MOB are similar to those of the Kievey deposit [8]. The MOB of the deposit lies within the alternation of gabbronorites and anorthosites within the LLH. An important feature of the Kamennik deposit is an increase of PGE concentrations in the ore body in the places of synform bends of the LLH, which are characterized by the development of a thick sequence of taxitic recrystallized gabbronorites below the alternation of gabbronorites and anorthosites. In this sequence and lower along the section, below the LLH, there are lenticular ore bodies with PGE mineralization (lower ore bodies).

The lower ore bodies of the deposit are often richer in PGE than the MOB and have highly variable geochemical characteristics [9] such as Pd/Pt and Cu/Ni ratios (Fig. 2). Lower ore bodies of the first type are hosted by taxitic gabbronorites (Fig. 2). The second type of these bodies with relatively low concentrations of PGE is localized a few meters below the LLH base. The third type occurs at a depth of more than ten meters from the LLH base as lenses of geochemically homogeneous and relatively rich mineralization.

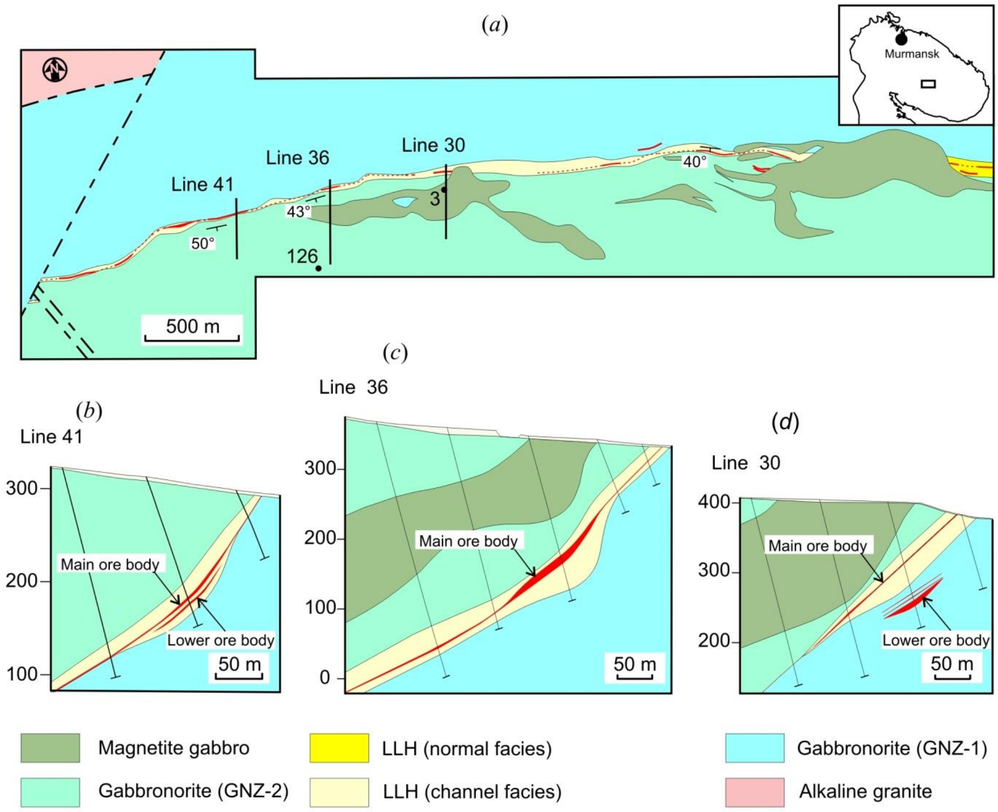

Figure 1. Schematic geological map (a) and cross-sections (b, c) of the Kamennik palladium deposit, modified after [8]. Red lines shows ore bodies, dashed red lines refer to sites with grades below the cut-off. Black dashed lines are faults and tectonized margin of the West Pana intrusion. Abbreviations: GNZ-1and GNZ-2, gabbronorite subzones 1 and 2; LLH, lower layered horizon.

The purpose of this study is to identify the features of the mineral composition of the lower ore bodies of the Kamennik deposit, in particular in relation to the mineral assemblages of platinum group minerals (PGM), as well as to compare them with the MOB.

2. Materials and research methods

The lower bodies were studied in 8 polished sections sampled from drill holes 126 and 3 in the western part of the deposit (Fig. 1 and 2). The mineralization of the first and second type is presented by drill hole126, whereas the third type is found in drill hole 3. The mineral composition was studied on a scanning electron microscope Leo-1450 with a Bruker XFlash-5010 X-ray energy dispersive spectrometer and Quantax-200 software (GI KSC RAS). In total, in order to identify PGM, 528 BSE images were taken and 222 noble metal minerals were analyzed in the non-standard mode using the following characteristic lines: Mα for Pt, Ir, Os, Re, Au, Bi, Pb, Hg; Lα for Pd, Ag, Rh, Te, As, Se, Sn, Sb, Mo; Kα for S, Fe, Ni, Co, Cu. A list of identified PGM is given in Tables 1 and 2. A table of mineral chemical compositions is available on request from the authors.

3. Results

3.1. PGM in the lower ore bodies of the Kamennik deposit

The first type of mineralization is represented by irregular, in places nesting (in pegmatoid and coarse-grained gabbronorites) dissemination with sulfide content from 0.3 to 10 vol.%. Sulfides are interstitial with respect to plagioclase and pyroxene. Chalcopyrite, the amount of which varies from 50 to 75% of the sulfide total amount, dominates in the pyrrhotite-pentlandite-chalcopyrite dissemination. 462 PGM grains were found in this type of mineralization. PGM grain size ranges from 1 to 40 microns. 80% of PGM are included in silicates; about 15% of the minerals are intergrowths with sulfides and are located at the silicate/sulfide interface; 5% of the grains are included in sulfides. According to the relative volume abundance, the main minerals (>10 vol.% of all PGM) are rustenburgite, moncheite, and kotulskite, which determine the stannide-telluride association of PGM. The morphology and interrelations of PGM with other minerals are shown in Fig. 3, a–c.

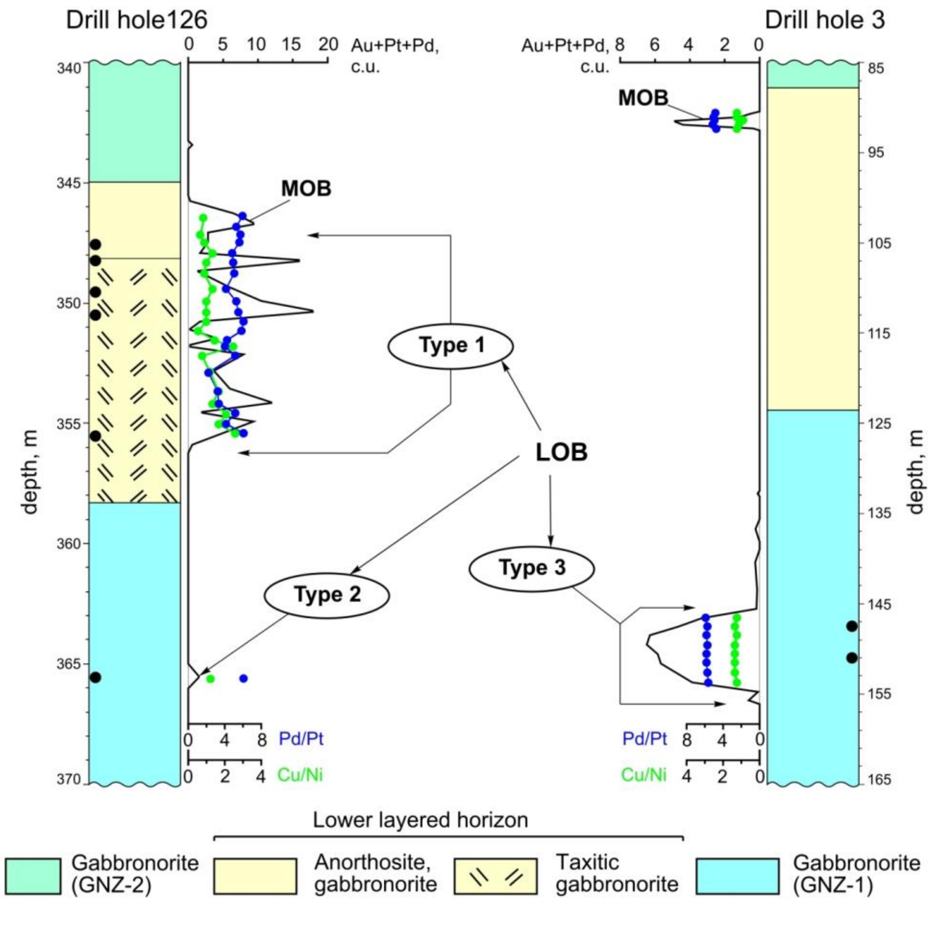

Figure 2. Mineralization of the Kamennik deposit on drill hole geological columns with variations of PGE and Au concentrations (black line) and Pd/Pt (blue circles) and Cu/Ni (green circles) ratios in ores, data from [9]. Black circles show a location of polished sections of this study. Abbreviations: GNZ-1 and GNZ-2, gabbronorite subzones 1 and 2; MOB, main ore body; LOB, lower ore body; c.u., conventional units.

The PGM assemblage in the first type of the lower ore bodies shows the enrichment in tin relative to the MOB. In addition to rustenburgite, the mineralization contains four more minerals and one mineral phase with the tin specification: paolovite, atokite, palarstanide, kojonenite, and MPh-2 phase (Tables 1 and 2). Kojonenite $(Pd_{6.5}Fe_{0.1})_{6.6}Sn_{1.1}Te_{2.3}$, recently discovered mineral from the Stillwater Complex [10], is the first find in the North Reef (Fig. 3, k). The same applies to the mineral phase MPh-2 $(Pd_{1.2}Ag_{0.8})_{2.0}(Te_{0.6}Sn_{0.2}Se_{0.2})_{1.0}$ associated with kojonenite [11]. In addition, as an impurity, tin is noted in tornroozite (up to 5.1 wt.%), stillwaterite (up to 4.7 wt.%), vincentite (up to 6.1 wt.%) and keithconnite (to 3.9 wt.%). Probably, tin impurity was originally present also in the moncheite, in which rustenburgite forms the exsolution structure (Fig. 3, b).

Minerals of gold and silver, including their native minerals, belong to a group of often found minerals in this type of the lower ore bodies. (Table 1). Among the PGM, there are minerals with the silver specification — telargpalite, sopcheite, lukulaysvaaraite, and MPh-2 mineral phase belonging to the category of rare. Silver minerals are represented by hessite, acanthite, naumannite, argentopentlandite (Fig. 4, d). Admixture of silver is noted in paolovite (up to 6.58 wt.%) and merenskyite (up to 4.21 wt.%), admixture of gold is found in laflammeite (up to 1.17 wt.%), distinguishing this type of mineralization from the others.

In addition to tin, gold and silver, lead can be pertained to typomorphic impurities in PGM from mineralization of the first type. The concentration of lead reaches 2.1 wt.% in kotulskite, 1.6 wt.% in moncheite and 11.8 % in telargpalite (Fig. 4, d). Minerals with the lead specification are represented by rare PGE sulfide laflammeite $(Pd_{3.0}Pt_{0.2}Au_{0.1})_{3.3}(Pb_{1.9}Bi_{0.3})_{2.2}S_{1.6}$ and mineral phase Mph-11 $Pd_{3.2}(Pb_{1.4}Bi_{0.5})_{1.9}$.

The second type is characterized by thin irregular emulsion sulfide dissemination. Sulfides are barely noticeable, their amount does not exceed 0.5 vol.%. The main sulfide minerals are pyrrhotite, millerite and chalcopyrite; pentlandite refers to accessory minerals. According to the chemical composition 929 PGM grains were diagnosed in the mineralization. The grain size varies from 2 to 20 microns. 82% of PGM are inclusions in silicates. Of these, 55% are separate grains and 27% are intergrowths of PGM among themselves. About 17% of minerals are noted in the intergrowth with sulfides and there are only single grains in the form of inclusions in sulfides. According to the relative volume abundance, the main group of PGM (> 10 vol.%) includes stillwaterite, tornroosite, vysotskite, and kotulskite (Table 1; Fig. 3, d – f), therefore the ores belong to the arsenide-sulfide-telluride mineral assemblage.

Platinum and palladium tellurides from the mineralization of the second type (unlike the first one) are characterized by a composition close to stoichiometric (Fig. 4, b and c). Minor impurities of tin and antimony are in stillwaterite $(Pd_{8.0\text{-}8.5}Pt_{0\text{-}0.1})_{8.0\text{-}8.5}(As_{2.4\text{-}3.0}Te_{0\text{-}0.2}Sn_{0\text{-}0.4}Sb_{0\text{-}0.2})_{2.5\text{-}3.0}$ and tornroosite $(Pd_{11.0\text{-}11.3}Pt_{0\text{-}0.2}Bi_{0\text{-}0.1})_{11.0\text{-}11.4}(As_{1.6\text{-}2.2}Sn_{0\text{-}0.2})_{1.7\text{-}2.3}(Te_{1.4\text{-}1.8}Sb_{0\text{-}0.5})_{1.5\text{-}1.9}$, that is characteristic for the Pd–As system in general. The mineral phase MPh-2 $(Pd_{1.3\text{-}1.8}Ag_{0.3\text{-}0.8})_{2.0\text{-}2.1}(Te_{0.3\text{-}0.5}Sn_{0.3\text{-}0.4}Se_{0.1}As_{0\text{-}0.1})_{0.9}$ has the highest tin concentration. It should be noted that some silver-bearing minerals (sopcheite, MPh-2) are found here more often than in the first type of mineralization (Tables 1 and 2).

Arsenopalladinite $Pd_{8.0}(As_{2.6}Sib_{0.4})_{3.0}$ and isomertieite $Pd_{11.0\text{-}11.2}(Sb_{1.5\text{-}1.6}Te_{0.3})_{1.8\text{-}1.9}As_{2.1}$ in the second type of mineralization are minerals that were not observed earlier in the North Reef (Fig. 3, l and m).

The third type of mineralization is represented by a regular sulfide dissemination with a sulfide content of 5–7 vol.%. Pyrrhotite, pentlandite and chalcopyrite predominate in the dissemination. The share of chalcopyrite, as in MOB, is 40–50% of the total volume of sulfides. PGM grain size found in the amount of 51 grains ranges from 1 to 10 microns. 64% of grains are located in silicates; 24% of grains are at the silicate/sulfide interface; 12% of the grains are included in sulfides. The sulphide-telluride assemblage of PGM, due to the set of the main minerals according to their relative volumetric abundance (kotulskite, moncheite, and vysotskite), is close to the MOB assemblage (Table 1; Fig. 3, g–j). Besides, PGM from this type of mineralization do not contain impurities and the composition of minerals is close to stoichiometric.

3.2. Comparison of the main and lower ore bodies of the Kamennik deposit

Detailed studies of the MOB mineral composition, carried out at the Kievey and Kamennik deposits [8,12], showed a close spatial and genetic relationship of PGM with base metal sulfides. More than 70% of PGM grains larger than 10 microns are included in sulfides or are located on the border of sulfide and silicate minerals. For the PGM grains of a lower size, this indicator decreases to 50%. The third type of the lower ore bodies is closest to the MOB, since it has the same PGM assemblage and

36% of the PGM grains are in direct contact or included in sulfides. Other side, the number of PGM closely related with sulfides in the ores of the first and second types does not exceed 20%.

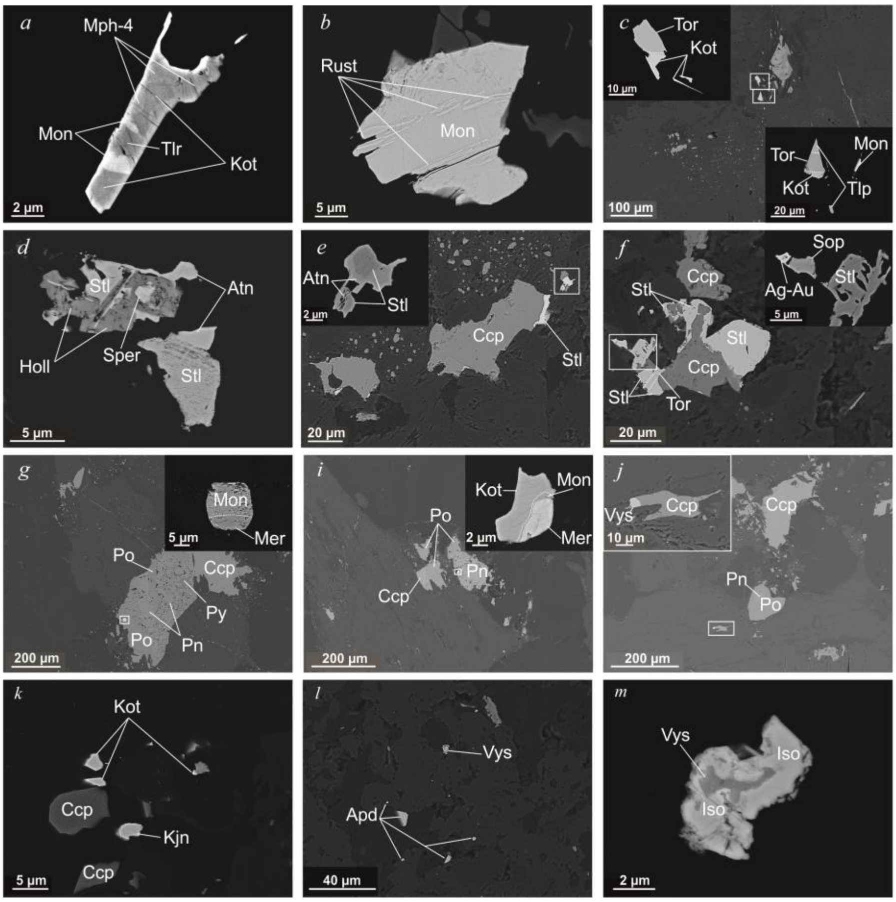

Figure 3. Morphology of PGM grains from different types of lower ore bodies of the Kamennik deposit (a–c, 1 type; d–e, 2 type; g–j, 3 type) and new PGM for the North Reef (k, kojonenite; l, arsenopalladinite; m, isomertieite). Mineral abbreviations see tabl. 1, except: Ag-Au, silver and gold alloy; Ccp, chalcopyrite; Mph, mineral phase; Po, pyrrhotite; Pn, pentlandite; Py, pyrite. BSE images.

The MOB at both deposits, at the Kievey and Kamennik, is characterized by the predominance of PGE sulphides and tellurides, represented by braggite, vysotskite, moncheite, kotulskite and merenskyite (Table 1). V. Subbotin with colleagues [12] note that the composition of the dominant PGE tellurides corresponds to stoichiometric. As Table 1 shows, despite a relatively small number of the found PGM grains, the third type of lower ore bodies has the same mineral assemblage of noble metals as the MOB. It should be noted that PGE tellurides from the third type of mineralization also do not contain impurities (Fig. 4, d).

The similarity of the mineral composition of the MOB and the lower ore body of the third type leads us to the assumption that this type of ores was formed as a result of migration of the PGE-rich sulfide liquid into the underlying cumulate. Apparently, this became possible due to the local partial melting of the latter (at the level of the intercumulus space) with increasing temperature due to intrusion of the first additional portions of the ore-bearing magma, which is associated with the formation of LLH [13,14]. The locality of melting was determined by the gradients of the flow velocity and temperature in overlying magma. These gradients are most likely responsible for the formation of synformic bends and recrystallized taxitic gabbronorites in the channel LLH facies [9].

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Table 1. Minerals of platinum metals, gold and silver of the North Kamennik deposit

Mineral	Abbreviation	Formula	MOB[1]	Lower ore bodies		
				Type 1	Type 2	Type 3
Elements						
Gold	Au	Au	••	•••		••
Silver	Ag	Ag	•	•••	••	
Tellurides-Bismuthides						
Hessite	Hes	Ag_2Te	•	••		
Telargpalite	Tlr	$(Pd,Ag)_3Te$	••	••		
Kotulskite	Kot	$Pd(Te,Bi)_{2-x}$	••••	••••	••••	••••
Michenerite	Mch	$(Pd,Pt)BiTe$	•			
Merenskyite	Mer	$PdTe_2$	••••	••		••••
Moncheite	Mon	$Pt(Te,Bi)_2$	••••	••••	••	••••
Telluropalladinite	Tlp	Pd_9Te_4	•	•••		
Keithconnite	Keit	$Pd_{20}Te_7$	••	•		
Sopcheite	Sop	$Ag_4Pd_3Te_4$	••	••	•••	
Lukkulaisvaaraite	Luk	$Pd_{14}Ag_2Te_9$		•[2]?	•[2]?	
Tornroosite	Tor	$Pd_{11}As_2Te_2$	••	•••	••••	
Kojonenite*	Kjn	$Pd_{7-x}SnTe_2$		••		
Temagamite	Tmg	Pd_3HgTe_3	•			
Sobolevskite	Sob	$PdBi$	••			
Intermetallides-Arsenides-Sulfoarsenides						
Hongshiite	Hng	$PtCu$	•			
Paolovite	Plv	Pd_2Sn	•	••		
Atokite	Atk	$(Pd,Pt)_3Sn$	•	••		
Zvyagintsevite	Zvg	Pd_3Pb	•			
Palarstanide	Pls	$Pd_5(Sn,As)_2$	•			
Isoferroplatinum	Ifp	Pt_3Fe	•	•		
Rustenburgite	Rust	$(Pt,Pd)_3Sn$	•	••••		
Arsenopalladinite*	Apd	$Pd_8(As,Sb)_3$			•••	
Mertieite-1	Mrt	$Pd_{11}(Sb,As)_4$	•	•		
Isomertieite*	Iso	$Pd_{11}Sb_2As_2$			•••	
Sperrylite	Sper	$PtAs_2$	••	••	•••	••
Vincentite	Vin	Pd_3As	•	•		
Atheneite	Atn	$Pd_2(As_{0.75}Hg_{0.25})$			•••[2]	
Palladoarsenide	Pal	Pd_2As	•			
Stillwaterite	Stl	Pd_8As_3	••	••	••••	
Hollingworthite	Hol	$RhAsS$	•		•••	
Irarsite	Irs	$(Ir,Ru,Rh,Pt)AsS$	•			
Menshikovite	Men	$Pd_3Ni_2As_3$		•[2]		
Sulfides-selenides						
Acanthite	Akn	Ag_2S	•	••		
Argentopentlandite	Apn	$Ag(Fe,Ni)_8S_8$	•	••		
Braggite	Br	$(Pt,Pd,Ni)S$	•••	•••	•••	
Vysotskite	Vys	$(Pd,Pt,Ni)S$	••••	•••	••••	••••
Laflammeite	Lfl	$Pd_3Pb_2S_2$		•[2]		
Laurite	Lrt	$(Ru,Os)S_2$	•			
Malanite	Mln	$Cu(Pt,Ir)S_4$	•	•		
Naumannite	Nau	Ag_2Se	•	••		
Coldwellite	Cdw	Pd_3Ag_2S		•[2]		

Note: •, single grains; ••, rare; •••, often found; ••••, the main mineral; *, the first find in the North Reef; [1,2], data from [12] and [8] respectively; MOB, main ore body.

Table 2. Mineral phases of platinum metals of the Kamennik deposit.

Phase	Formula	MOB[1]	Lower ore bodies	
			Type 1	Type 2
MPh-1	Pd_2Te			••
MPh-2	$(Pd, Ag)_2(Te, Sn)$		•	••
MPh-3	$(Cu,Pt,Rh)_2S_3$			•
MPh-4	$(Pd,Ag)_3(Ag,Pb)(Te,Se)$		••	
MPh-5	$(Re,Cu,Pt)S_2$	•		
MPh-6	$Pd_{2-x}(Bi,Pb)(S,Se)$	•		
MPh-7	$(Pd,Au)_{2+x}(As,Sn)$	•		
MPh-8	Pt_5Te_7	•		
MPh-9	$(Ni,Fe,Cu,Co)_2(Rh,Pt)S_4$		•[2]	
MPh-10	$(Pd,Ag)_7Se_5$		•[2]	
MPh-11	$Pd_3(Pb,Bi)_2$		•	

Note: see table 1.

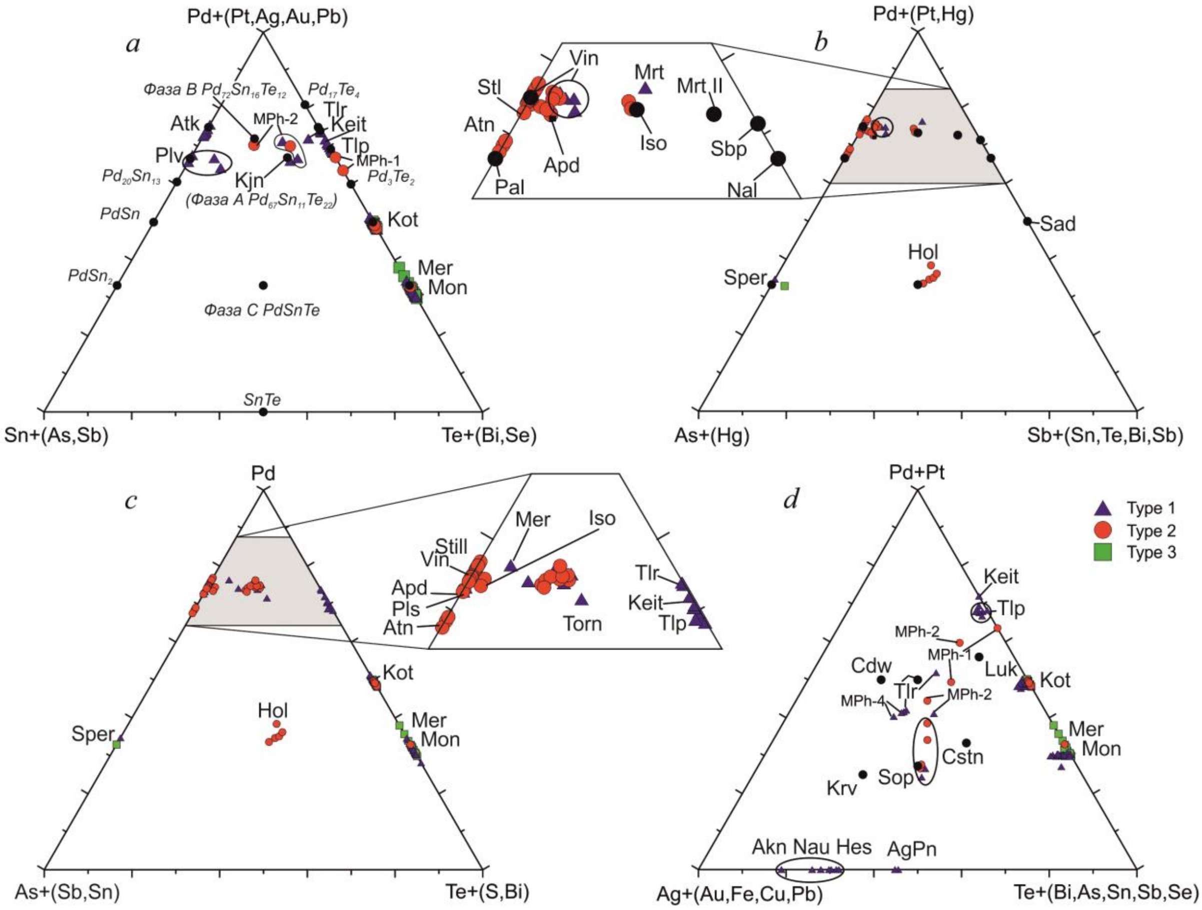

Figure 4. Ternary diagram (at. %) Pd-Sn-Te (*a*), Pd-As-Sb (*b*), Pd-As-Te (*c*), Pd-Ag-Te (*d*) systems. Black dots indicate ideal compositions of known minerals and mineral phases. Color icons represent data from this study. Synthetic mineral phases from [15] are italicized. Mineral abbreviations see tabl. 1, except: AgPn, argentopentlandite; Cstn, chrisstanleyite; Krv, kravtsovite; Mrt II, mertieite II; Nal, naldrettite; Nau, naumannite; Sad, sudburyite; Sbp, stibiopalladinite.

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The position of the lower ore bodies of the first and second types in the section indicates the possibility of their formation also in the process of sulfide liquid percolation down from the level of the moving magmatic flow. The differences with the MOB in the mineral composition (Tables 1 and 2), as well as the enrichment of PGM with tin and other impurities, can be explained by the processes of reworking of the early sulfide impregnation as a result of a series of additional ore-bearing magmatic pulses. Judging by the number of rhythmic units in the LLH at the Kievey deposit [7], there were at least four such pulses during its formation.

4. Conclusion

The mineralogical studies confirm the division of the lower ore bodies of the North Kamennik deposit into three types and make it possible to distinguish them by the PGM assemblages — stannide-telluride, arsenide-sulfide-telluride and sulfide-telluride. When studying the first two mineral assemblages, we found three new minerals for the North Reef: arsenopalladinite, isomertieite and kojonenite. These assemblages are promising for the discovery of new mineral species in the Pd–Sn–Te system.

Acknowledgments

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References

[1] Irvine T N, Keith D W and Todd S G 1983 The J-M platinum-palladium reef of the Stillwater complex, Montana: II. Origin by double-diffusive convective magma mixing and implications for the Bushveld complex *Econ. Geol.* **78** 1287-334

[2] Barnes S-J and Maier W D 2002 Platinum-group Elements and Microstructures of Normal Merensky Reef from Impala Platinum Mines, Bushveld Complex *J. Petrol.* **43** 103-28

[3] Grobler D F, Brits J A N, Maier W D and Crossingham A 2019 Litho- and chemostratigraphy of the Flatreef PGE deposit, northern Bushveld Complex *Miner. Depos.* **54** 3-28

[4] Groshev N Y, Rundkvist T V, Karykowski B T, Maier W D, Korchagin A U, Ivanov A N and Junge M 2019 Low-Sulfide Platinum-Palladium Deposits of the Paleoproterozoic Fedorova-Pana Layered Complex, Kola Region, Russia *Minerals* **9** 764

[5] Oberthuer T, Cabri L J, Weiser T J, McMahon G and Mueller P 1997 Pt, Pd and other trace elements in sulfides of the Main Sulfide Zone, Great Dyke, Zimbabwe; a reconnaissance study *Can. Min.* **35** 597-609

[6] Holwell D A, McDonald I and Armitage P E B 2006 Platinum-group mineral assemblages in the Platreef at the Sandsloot Mine, northern Bushveld Complex, South Africa *Mineral. Mag.* **70** 83-101

[7] Korchagin A U, Subbotin V V, Mitrofanov F P and Mineev S D 2009 Kievey PGE-bearing deposit in the West-Pana layered intrusion *Strateg. Miner. Resour. Lapland, Apatity* 12-32

[8] Korchagin A U *et al* 2016 Geology and composition of the ores of the low-sulfide North Kamennik PGE deposit in the West-Pana intrusion *Ores and Metals* **1** 42-51

[9] Ivanov A N, Groshev N Y and Korachagin A U 2018 Transgressive structures of the Lower Layered Horizon in the area of North Kamennik low-sulfide PGE deposit *Tr. FNS* **15** 124-7

[10] Stanley C J and Vymazalová A 2015 Kojonenite, a new palladium tin telluride mineral from the Stillwater Layered Igneous Intrusion, Montana, U.S.A. *Am. Mineral.* **100** 447-50

[11] Chernyavsky A V, Groshev N Y, Korchagin A U and Shilovskikh V V 2018 Minerals of platinum group elements through the South Reef, West-Pana intrusion *Tr. FNS* **15** 392-5

[12] Subbotin V V., Korchagin A U, Savchenko E E *et al* 2012 Platinum mineralization of the Fedorova-Pana ore node: types of ores, mineral compositions and genetic features *Vestn. Kola Sci. Cent. Russ. Acad. Sci. Apatity* **1** 54-65

[13] Korchagin A U, Subbotin V V., Mitrofanov F P and Mineev S D 2009 Kievey PGE-bearing

deposit of the West-Pana layered intrusion: geological structure and ore composition *Strategic Mineral Resources of Lapland – Base for the Sustainable Development of the North.* (Apatity: KSC RAS) 12-33

[14] Latypov R M, Mitrofanov F P, Alapieti T T and Halkoaho T A A 1999 Petrology of the lower layered horizon of the Western Pansky Tundra intrusion, Kola Peninsula *Petrology* **7** 482-508

[15] Vymazalová A and Drábek M 2010 The system Pd-Sn-Te at 400°C and mineralogical implications. II. the ternary phases *Can. Min.* **48** 1051-8