

Article

Occurrences of Pd–Pt Bismuthotellurides and a Phosphohedyphane-Like Phase in Sulfide Veins of the Monchepluton Layered Complex, Kola Peninsula, Russia

Andrei Y. Barkov ^{1,*}, Andrey A. Nikiforov ¹, Larisa P. Barkova ¹ and Robert F. Martin ²

¹ Research Laboratory of Industrial and Ore Mineralogy, Cherepovets State University, 162600 Cherepovets, Russia; ultramafic-rock@mail.ru (A.A.N.); larisa-p-barkova@mail.ru (L.P.B.)

² Department of Earth and Planetary Sciences, McGill University, Montreal, QC H3A 0E8, Canada; robert.martin@mcgill.ca

* Correspondence: ore-minerals@mail.ru; Tel.: +7-(8202)-55-65-97

Abstract: We describe occurrences of platinum-group minerals (PGM) and an uncommon mineral enriched in Cl, and provide a brief review of Cl-bearing minerals associated with basic–ultrabasic complexes. An unusual phosphohedyphane-like phase (~30 µm), close to CaPb₄(PO₄)₃Cl, occurs in one of the PGM-bearing veins of massive sulfides in the Monchepluton layered complex, Kola Peninsula, Russia. These veins consist of varying amounts of pyrrhotite, pentlandite, chalcopyrite, pyrite and accessory grains of galena; they are fairly abundant in the heavy-mineral concentrate, as are small (<0.1 mm) grains of PGM: michenerite, sperrylite, Bi-enriched members of the merenskyite–moncheite series and kotulskite, also rich in Bi. The PGE mineralization is attributed to a low-temperature deposition at the hydrothermal stage. The pyromorphite–phosphohedyphane solid solution likely formed as a secondary phase under conditions of a progressive build-up of oxygen fugacity via oxidation reactions of a precursor grain of galena and involving Ca, as an incompatible component of the sulfides, in a medium of residual fluid enriched in Cl.

Keywords: pyromorphite–phosphohedyphane solid solution; chlorine; Cl-rich compounds; platinum-group minerals; massive sulfide veins; basic–ultrabasic complexes; layered intrusions; Fennoscandian Shield; Kola Peninsula; Russia



Citation: Barkov, A.Y.; Nikiforov, A.A.; Barkova, L.P.; Martin, R.F.

Occurrences of Pd–Pt Bismuthotellurides and a Phosphohedyphane-Like Phase in Sulfide Veins of the Monchepluton Layered Complex, Kola Peninsula, Russia. *Minerals* **2022**, *12*, 624.

<https://doi.org/10.3390/min12050624>

Academic Editor:

Maria Economou-Eliopoulos

Received: 25 April 2022

Accepted: 7 May 2022

Published: 14 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

A detailed investigation of ore veins sampled at the site of long-abandoned mine adits in the Monchepluton layered basic–ultrabasic complex has led to the discovery of a member of the pyromorphite–phosphohedyphane solid solution among the ore constituents. As a chlorine-bearing member of the apatite supergroup, its presence in a vein of pyrrhotite, pentlandite, chalcopyrite, pyrite, galena and platinum-group minerals (PGM) raises questions about the role of Cl and other volatiles in mineralized ultrabasic suites. Our aims are to describe the occurrence, documented for the first time in a vein of massive Cu–Ni sulfides bearing platinum-group elements (PGE) at Mount Nittis, in the Monchepluton layered mafic–ultramafic complex of Paleoproterozoic (~2.5 Ga) age [1,2]. We explore what is known about the pyromorphite–phosphohedyphane solid-solution series and document the associated PGM. We believe that this phase is significant not only as a new representative of Cl-bearing minerals associated with ore zones, but also as a monitor of a progressive build-up in levels of oxygen fugacity (fO_2) during ore formation.

Geological Background

The Monchepluton layered complex belongs to an extensive group of Paleoproterozoic layered intrusions in the Fennoscandian Shield, e.g., [2]. It is located at the boundary of the Imandra–Varzuga zone of the Polmak–Pasvik–Pechenga–Imandra–Varzuga rift of

Paleoproterozoic age with the Archean Kola–Norwegian terrane of the Kola Province (Figure 1).

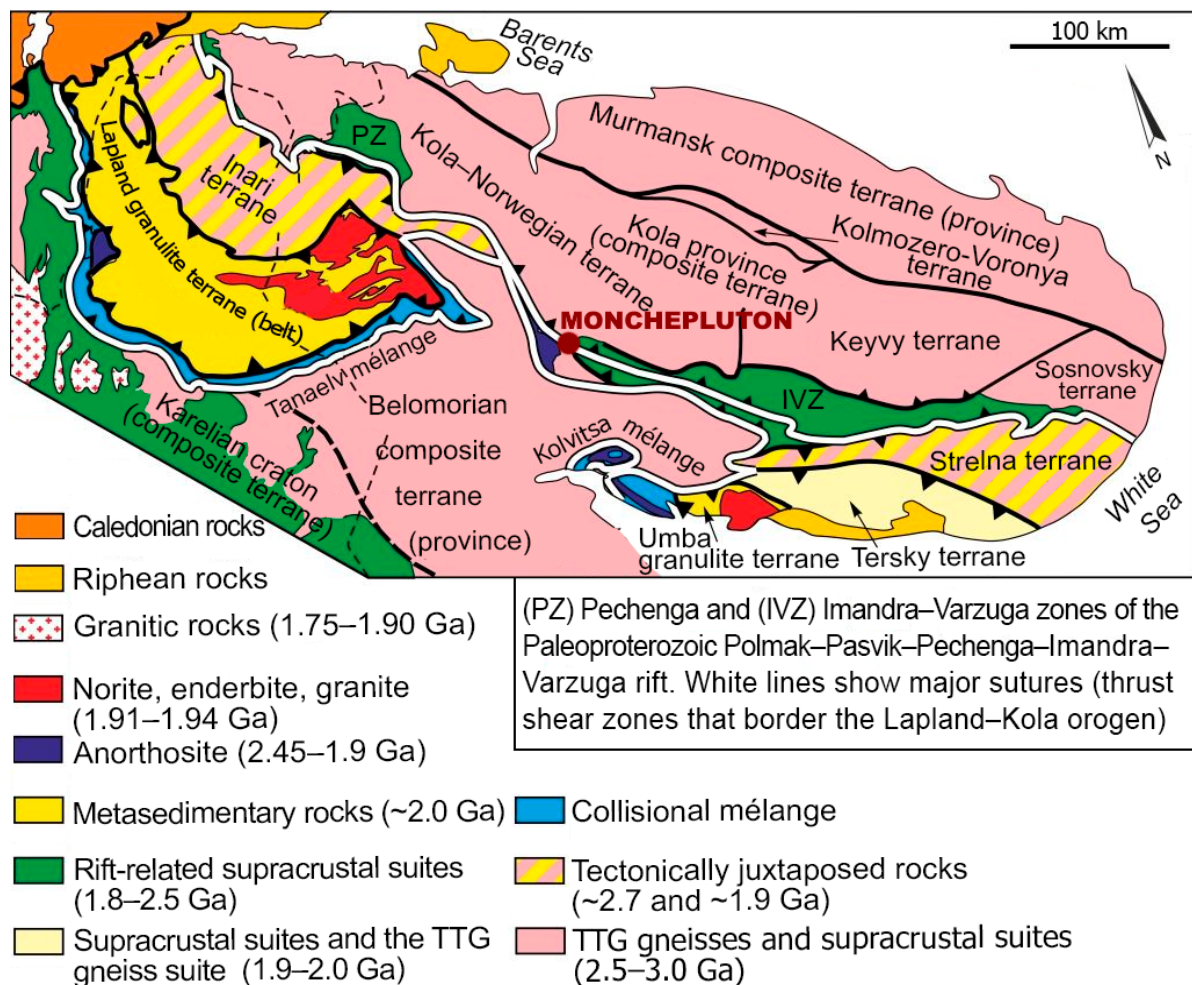


Figure 1. Location of the Monchepluton layered complex shown in the context of tectonic settings in the northeastern part of the Fennoscandian Shield (after [3] and references therein).

The Monchepluton complex consists of sequences of dunite–harzburgite–orthopyroxenite–gabbro–norite [4–7]. Seven divisions are recognized: the Dunite block, mounts Nittis, Kumuzhya, and Travyanaya along a northeasterly trend, and mounts Sopcha, Nyud, and Poaz on an easterly trend (Figure 2). The Dunite block, which hosts the Sopcheozyorskoe chromite deposit [8], may correspond to the location of the magma-feeder channel [5]. This block represents a podiform or core-like zone of olivine and olivine–chromite cumulates formed close to the nexus of the boomerang-shaped structure [5].

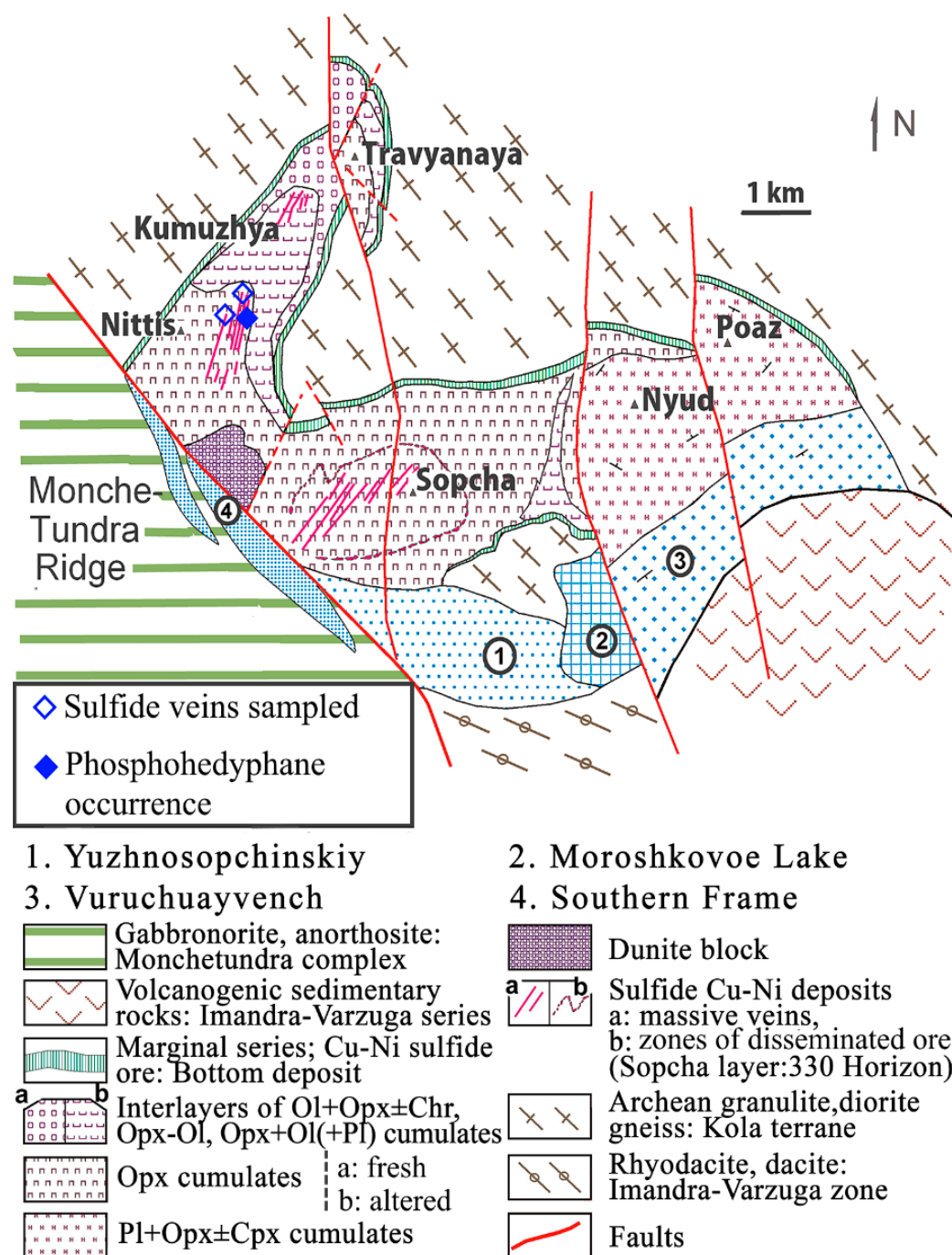


Figure 2. Schematic geological map of the Monchepluton complex ([4], with findings of V.V. Knauf and N.S. Guseva), showing the sampling location in the present investigation.

2. Materials and Methods

Our materials consist of ore samples and heavy-mineral concentrates obtained from three samples (10–15 kg each) of Ni–Cu–PGE ores collected at old mine adits ($67^{\circ}55'18.4''$ N $32^{\circ}46'46.6''$ E; $67^{\circ}55'25.1''$ N $32^{\circ}46'27.3''$ E; $67^{\circ}55'31.7''$ N $32^{\circ}46'44.9''$ E) known historically and built during the years 1933–1936 (Figure 2). The fragments of ore are dense, massive, and coated by an oxidized rind (Figure 3a,b). They consist of pyrrhotite, pentlandite, chalcopyrite and less-abundant pyrite, in varying proportions. The heavy-mineral concentrates studied consist of ~10 to 100 micrometer-sized fractions of galena, grains of platinum-group minerals (PGM), followed by minor amounts of barite, and remnant grains of base-metal

sulfides, mostly pentlandite. By interpolation, the density of our member of the apatite supergroup is approximately 6.5 g/cm^3 .

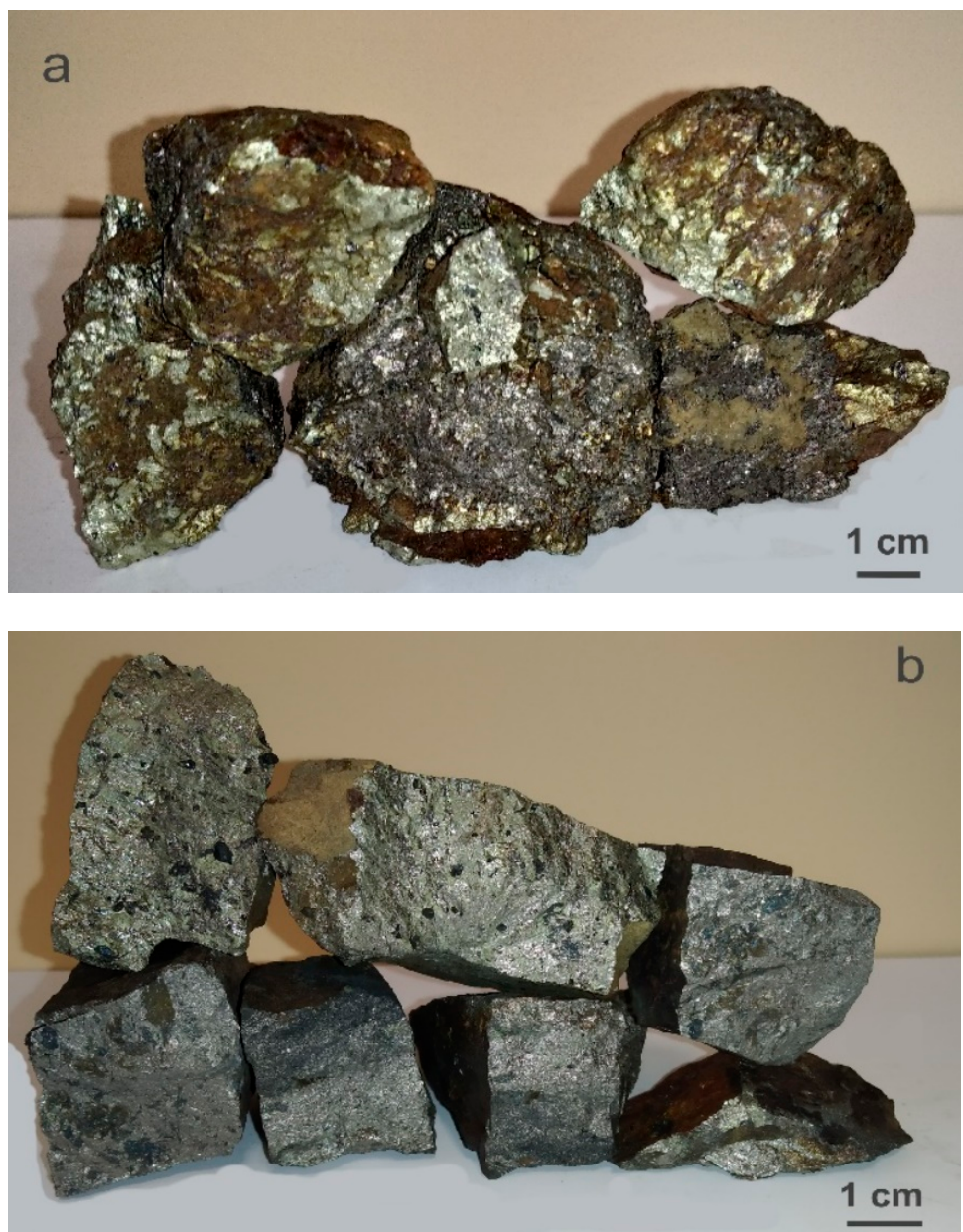


Figure 3. Photographs of fragments of base-metal ores sampled from sulfide veins of the Monchepluton complex. The samples MNP—3 and 4 are shown in (a,b), respectively.

The phosphohedyphane-type phase occurs in a single subhedral grain that is small ($\sim 30 \mu\text{m}$) and cracked due to its brittleness (Figure 4a). It was found in one of the veins sampled (Figure 2). Bismuthotelluride species of Pd and Pt and sperrylite, present in the concentrates, are consistent with the findings of a previous study [9].

We employed scanning-electron microscopy (SEM) and energy-dispersive analysis (EDS) conducted at an accelerating voltage of 20 kV and a beam current of 1.6 nA, with a beam size of $\sim 1 \mu\text{m}$, using a MIRA 3 LMU (Tescan Orsay Holding, Brno, Czech Republic) SEM with an attached INCA Energy 450 XMax 80 (Oxford Instruments Nanoanalysis, Wycombe, UK) microanalysis EDS system at the Institute of Geology and Mineralogy (the Analytical Center for Multi-Elemental and Isotope Studies), Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia. The standards used were FeS_2 (S), PtAs_2 (As),

PbTe (Pb and Te), wollastonite (Ca), synthetic GaP (P), NaCl (Cl) and pure metals (Fe, Co, Ni, Cu, Rh, Pd, Pt and Bi). For the analytical signal of S, Fe, Ni, Cu, Ca, P and Cl, the *K* family of peaks was used, and for the other elements, the *L* family. The use of the *L* family for Pt and Bi avoids the mutual overlaps of their *M* peaks. Minimum detection-limits (3σ criterion) of the elements (wt.%) were found to be 0.1–0.2 for S, Fe, Co, Ni, Cu, Ca and Cl; 0.2–0.4 for As, Pd and Te; and 0.4–0.7 for Pt and Bi. The analytical error for the main components did not exceed 1–2 relative % and satisfied the requirements for a quantitative analysis.

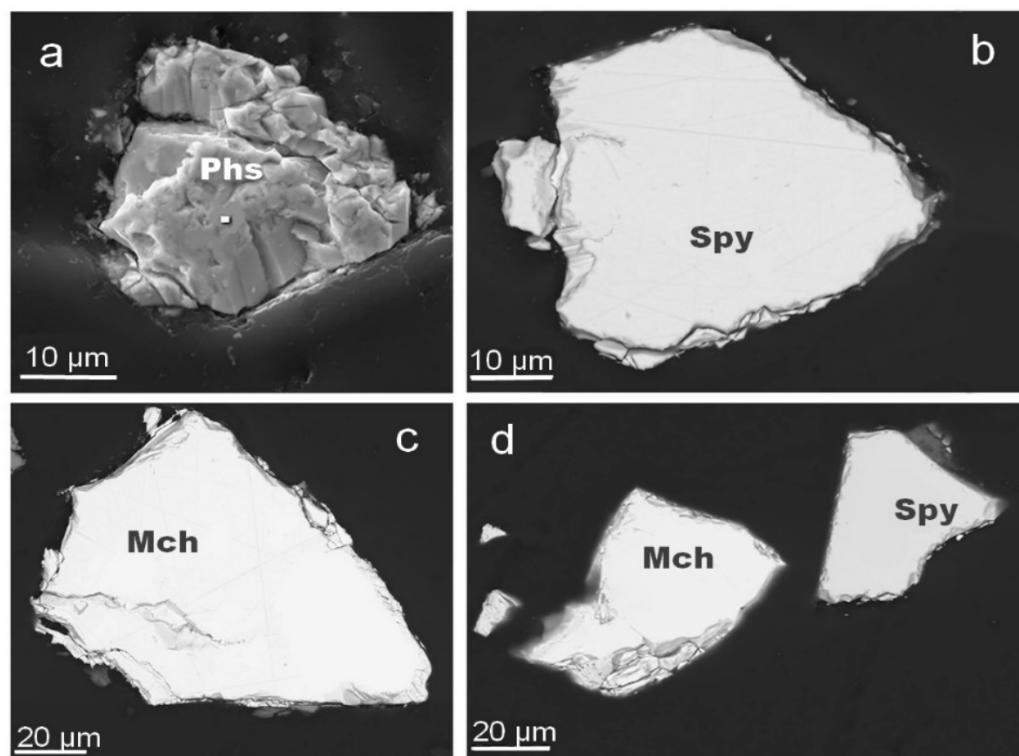


Figure 4. SEM images showing selected grains of phosphohedyphane-like phase labeled Phs (a), sperrylite, Spy (b,d), and michenerite, Mch (c,d), which are present in heavy-mineral concentrates from sulfide veins of the Monchepluton complex.

3. Results

The Pyromorphite–Phosphohedyphane Solid Solution

Phosphohedyphane, ideally $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$, a member of the apatite supergroup [10], was discovered in the Capitana mine, Atacama Province, Chile, where it is commonly encountered in zones of oxidized Pb-bearing ores [11]. Phosphohedyphane and pyromorphite, ideally $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, seem to form a complete solid solution, as demonstrated by a compilation of literature data [11,12]. Values of the ratio $5 \times \text{Ca}/(\text{Ca} + \text{Pb})$ range from 0 to 2 over that interval, and our specimen has a value of 0.78. Values between 2 and 5, i.e., intermediate compositions between phosphohedyphane and chlorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, are not found in nature [11]. Although we do not have supporting structural data, we can assume that our phase, $(\text{Pb}_{4.13}\text{Ca}_{0.76})_{\Sigma 4.90}(\text{PO}_4)_3\text{Cl}_{0.95}$ (Table 1), $(\text{Pb}_{1.13}\text{Ca}_{0.76})_{\Sigma 1.89}\text{Pb}_3(\text{PO}_4)_3\text{Cl}_{0.95}$ or, in general terms, $(\text{Pb,Ca})_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$, is a member of the phosphohedyphane–pyromorphite series, in which Pb^{2+} enters the Ca site in accordance with the formula $(\text{Ca,Pb})_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$. It displays a characteristic EDS spectrum (Figure 5). A complete solid-solution series probably exists between phosphohedyphane and hedyphane, $\text{Pb}_3\text{Ca}_2(\text{AsO}_4)_3\text{Cl}$. Phosphohedyphane is the phosphate analog of hedyphane, i.e., the long-established arsenate [13], and the Cl analog of fluorophosphohedyphane [11]. In an arsenic-bearing system, intermediate members are complex solid solutions involving components of phosphohedyphane,

hedyphane and mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ [14–16]. Members of such a series are developed, for example, in the oxidized zone at the Preguiça mine, Portugal [17]. As in that case, the phase found at Monchepluton is a secondary mineral formed by oxidation of primary Pb-rich precursors.

Table 1. Composition of the phosphohedyphane-type phase from the Monchepluton layered complex, Kola Peninsula.

	Wt. %	apfu	
CaO	3.54	Ca	0.76
PbO	76.74	Pb	4.13
P ₂ O ₅	15.67	Σ	4.90
Cl	2.81		
O≡Cl	0.64	P	2.65
Total	98.12	Cl	0.95

Note: Results of quantitative SEM/EDS analysis are expressed in weight %. Values of atoms per formula unit (apfu) are based on a value of 12 oxygen atoms per formula unit.

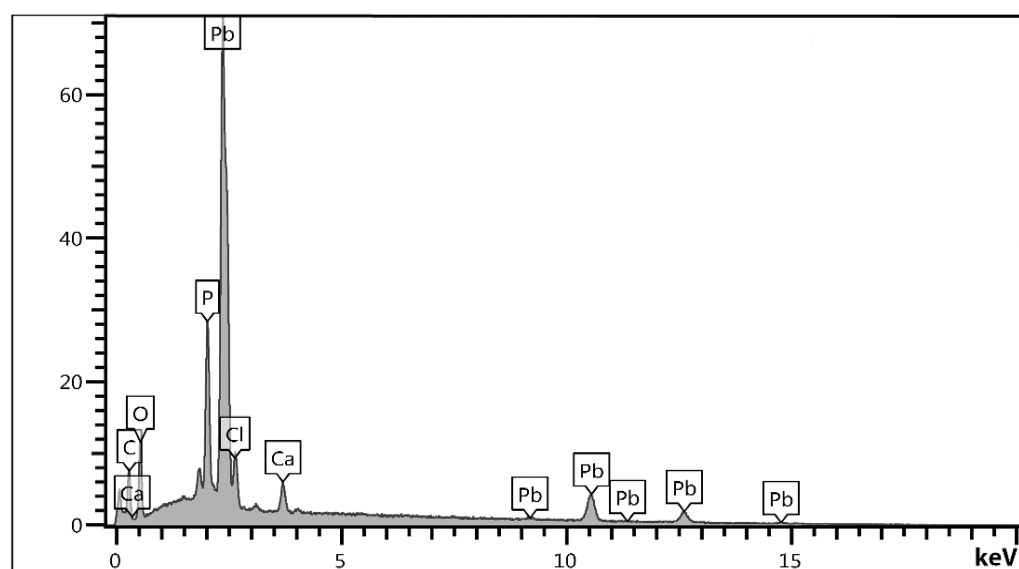


Figure 5. The energy-dispersive (EDS) spectrum of the phosphohedyphane-type phase from the Monchepluton complex.

The Platinum-Group Minerals

We have identified five species of PGM in the samples investigated (Table 2). Sperrylite (ideally PtAs_2), both S-bearing (up to 0.63 wt.% S) and essentially devoid of S, is relatively common, as well as michenerite (PdBiTe). Members of the moncheite $\text{Pt}(\text{Te},\text{Bi})_2$ –merenskyite $\text{Pd}(\text{Te},\text{Bi})_2$ series are subordinate, and kotulskite $\text{Pd}(\text{Te},\text{Bi})$ is rare in our samples.

A relative enrichment in Bi is noteworthy; it is observed in compositions of all species of the Pd–Pt bismuthotellurides (Table 2; Figures 6 and 7). Note that Te occupies almost entirely the Te site, and makes up a substantial portion (up to ~20%) of the Bi site (Figure 6).

Table 2. Compositions of platinum-group minerals in sulfide veins of the Monchepluton layered complex.

		Pt	Pd	Te	Bi	As	S	Total	Pt	Pd	Pt + Pd	Te	Bi	Te + Bi	As	S
		Wt. %							apfu							
1	Spy	56.38	bdl	bdl	bdl	44.22	bdl	100.6	0.99	–	0.99	–	–	–	2.01	0.00
2		55.45	bdl	bdl	bdl	43.77	bdl	99.22	0.98	–	0.98	–	–	–	2.02	0.00
3		56.45	bdl	bdl	bdl	44.29	bdl	100.74	0.99	–	0.99	–	–	–	2.01	0.00
4		54.93	bdl	bdl	bdl	43.65	0.53	99.11	0.96	–	0.96	–	–	–	1.98	0.06
5		55.18	bdl	bdl	bdl	42.97	0.36	98.51	0.98	–	0.98	–	–	–	1.98	0.04
6		54.47	bdl	bdl	bdl	43.80	0.48	98.75	0.95	–	0.95	–	–	–	2.00	0.05
7		54.93	bdl	bdl	bdl	42.54	0.53	98.00	0.98	–	0.98	–	–	–	1.97	0.06
8		54.59	bdl	bdl	bdl	42.88	0.63	98.10	0.96	–	0.96	–	–	–	1.97	0.07
9	Ktu	Bdl	38.92	30.25	29.22	bdl	bdl	98.39	–	0.98	0.98	0.64	0.38	1.02	–	–
10	Mch	Bdl	24.56	32.80	41.78	bdl	bdl	99.14	0.00	1.01	1.01	1.12	0.87	1.99	–	–
11		Bdl	24.52	33.66	41.03	bdl	bdl	99.21	0.00	1.00	1.00	1.15	0.85	2.00	–	–
12		Bdl	24.72	33.22	41.53	bdl	bdl	99.47	0.00	1.01	1.01	1.13	0.86	1.99	–	–
13		3.82	22.58	28.29	44.49	bdl	bdl	99.18	0.09	0.96	1.04	1.00	0.96	1.96	–	–
14		4.54	21.31	28.04	45.37	bdl	bdl	99.26	0.11	0.91	1.02	1.00	0.99	1.98	–	–
15		3.09	22.56	28.16	45.24	bdl	bdl	99.05	0.07	0.96	1.03	1.00	0.98	1.97	–	–
16		3.41	22.35	28.42	46.12	bdl	bdl	100.30	0.08	0.94	1.02	1.00	0.99	1.98	–	–
17		1.86	23.99	32.29	40.59	bdl	bdl	98.73	0.04	0.99	1.03	1.11	0.85	1.97	–	–
18	Mon	bdl	24.41	33.53	41.18	bdl	bdl	99.12	0.00	1.00	1.00	1.14	0.86	2.00	–	–
19		bdl	24.05	28.48	45.60	bdl	bdl	98.13	0.00	1.02	1.02	1.00	0.98	1.98	–	–
20		bdl	23.71	28.76	45.85	bdl	bdl	98.32	0.00	1.00	1.00	1.01	0.99	2.00	–	–
21		bdl	24.34	31.82	42.66	bdl	bdl	98.82	0.00	1.01	1.01	1.10	0.90	1.99	–	–
22		5.59	20.50	27.09	45.61	bdl	bdl	98.79	0.13	0.89	1.02	0.98	1.00	1.98	–	–
23		2.06	23.71	29.87	43.39	bdl	bdl	99.03	0.05	0.99	1.04	1.04	0.92	1.96	–	–
24		5.76	20.91	26.83	46.13	bdl	bdl	99.63	0.13	0.90	1.03	0.96	1.01	1.97	–	–
25		31.89	5.50	45.19	16.49	bdl	bdl	99.07	0.76	0.24	1.00	1.64	0.37	2.00	–	–
26	Mrk	36.29	1.76	40.65	19.33	bdl	bdl	98.03	0.91	0.08	0.99	1.56	0.45	2.01	–	–
27		35.47	1.94	41.01	20.01	bdl	bdl	98.43	0.88	0.09	0.97	1.56	0.47	2.03	–	–
28		9.39	21.04	52.96	16.58	bdl	bdl	99.97	0.20	0.80	1.00	1.68	0.32	2.00	–	–
29		6.05	22.64	52.16	17.54	bdl	bdl	98.39	0.13	0.87	0.99	1.67	0.34	2.01	–	–
30		5.36	23.55	52.88	16.52	bdl	bdl	98.31	0.11	0.89	1.01	1.68	0.32	1.99	–	–

Note: Results of quantitative SEM/EDS analyses are listed in weight %. The atomic proportions are based on a total of 3 atoms per formula unit (apfu) for sperrylite (Spy), michenerite (Mch), moncheite (Mon) and merenskyite (Mrk), and on a total of 2 apfu for kotulskite (Ktu). bdl: below detection limit.

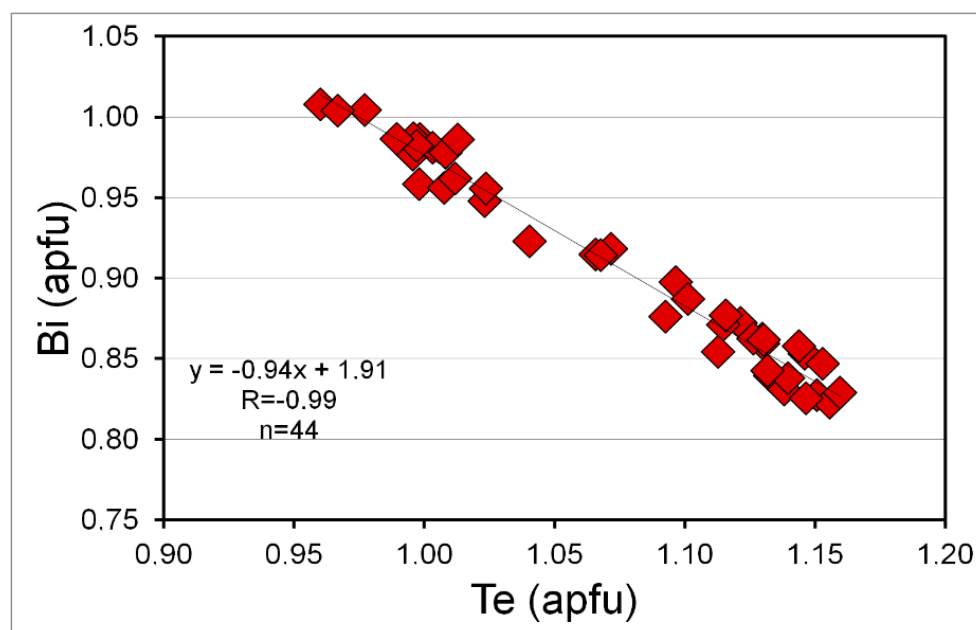


Figure 6. Correlation of Bi vs. Te in compositions of michenerite from sulfide veins of the Monchepluton complex. Results of a total of forty-four data points ($n = 44$) are plotted and expressed in values of atoms per formula unit (apfu). The equation of linear regression and calculated value of correlation coefficient (R) are also shown.

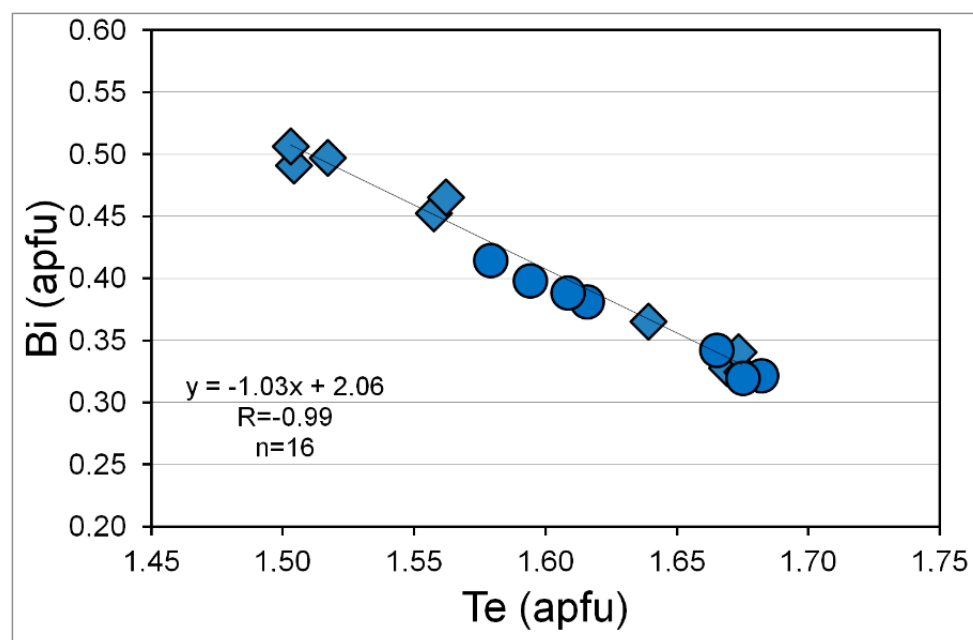


Figure 7. Correlation of Bi vs. Te in compositions of moncheite (shown by diamonds) and merenskyite (circles) from sulfide veins of the Monchepluton complex. Results of a total of sixteen data points ($n = 16$) are plotted (in values of atoms per formula unit, apfu). The equation of linear regression and calculated value of correlation coefficient (R) are shown on the plot.

4. Discussion

The presence of pyromorphite–phosphohedyphane solid solution in association with zones of massive PGE-bearing Cu–Ni sulfide ore provides a direct indication of the role of Cl at the hydrothermal stage in the Monchepluton cumulates. The abundance of galena, Bi-, Te, and As-enriched species of Pd and Pt is consistent with deposition from hydrothermal fluids late in the crystallization history of the complex. The observed assemblages enriched in Bi imply a relative decrease in temperatures of crystallization of the bismuthotelluride species. Experimental results [18] indicate that michenerite is stable below 500 °C, whereas the melting point of the end member of the merenskyite series (740 °C) decreases to 500–525 °C for the Bi-enriched phases having greater extents of Bi-for-Te substitution. Sperrylite is also known to form at a postmagmatic hydrothermal stage in layered intrusions [19]. We therefore presume that the phosphohedyphane-like phase represents a part of the late Pb–S–Te–Bi–As-enriched assemblages deposited hydrothermally during the formation of the sulfide veins.

In Table 3, we review [6,20–45] the occurrences of Cl-rich minerals known in basic–ultrabasic complexes emplaced in different geological settings worldwide. These phases include hydroxylchlorides, such as $(\text{Fe,Mn})(\text{OH})\text{Cl}$ and hibbingite $(\text{Fe}_2(\text{OH})_3\text{Cl})$ from the Sudbury complex, Canada, hibbingite in the Duluth layered complex, USA, members of the hibbingite–kempite $(\text{Mn}_2(\text{OH})_3\text{Cl})$ series, djerfisherite $(\text{K}_6(\text{Fe,Cu,Ni})_{25}\text{S}_{26}\text{Cl})$ and thalfenisite, its thallium analog $(\text{Tl}_6(\text{Fe,Ni})_{25}\text{S}_{26}\text{Cl})$, pyrosomalite-(Fe) in the Noril’sk complex of Russia, djerfisherite in the Guli and Yoko-Dovyren complexes, Russia, a penfieldite-type phase $(\text{Pb}_2\text{Cl}_3(\text{OH}))$ in the Bushveld complex, South Africa, and unnamed Pd–Bi chlorides from Noril’sk and Sudbury.

Table 3. A review of various minerals and phases enriched in Cl from basic–ultrabasic complexes.

Minerals	Complex, Locality	Occurrence	Comment	References
Chlorapatite	Bushveld, South Africa	Lower zone		[20,21]
	Stillwater, Montana, USA			[21]
	Koitelainen, Keivitsa-Satovaara, Finland		Cl-rich Amp	[22]
	Lukkulaivaara, northern Karelia, Russia		Clap in Ol cumulates	[23]
	Klättsjö, Sweden	Gabbro	Clap–PGM	[24]
	Kivakka, northern Karelia, Russia	Lower zones	Clap–PGM	[25,26]
	Monchepluton, Kola Peninsula, Russia	Mounts Nittis, Kumuzh'ya, Travyanaya, Sopcha, Nyud and Poaz	Clap in ultramafic-mafic cumulates	[6]
	Noril'sk, Siberia, Russia	Oktyabr'sky deposit	Pd–Pt, Au–Ag atypical ore	[27]
Cl-bearing Ap	Yoko-Dovyren, Baikal region, Russia	PGM-bearing horizon	≤2.42 wt.% Cl	[28,29]
Cl-bearing mica	Yoko-Dovyren, Baikal region, Russia	PGM-bearing horizon	≤0.58 wt.% Cl	[28,29]
Cl analog of ferrokinoshitalite	Yoko-Dovyren, Baikal region, Russia	Pl-bearing peridotite		[30]
Cl-rich annite	Noril'sk, Siberia, Russia	Oktyabr'sky deposit	≤7.54 wt.% Cl atypical ore	[27]
Cl-rich hastingsite	Noril'sk, Siberia, Russia	Oktyabr'sky deposit	≤4.06 wt.% Cl atypical ore	[27]
“Ferro-chloro-pargasite”	Lukkulaivaara, northern Karelia, Russia	Pegmatitic orthopyroxenite	Fcprg–PGM	[31,32]
	Tudor, Ontario, Canada	Gabbro		[33]
	Monchepluton, Kola Peninsula, Russia	Gabbro, Mount Poaz		[6]
Pd–Bi chlorides	Noril'sk, Siberia, Russia	Ore-bearing zone		[34]
	Sudbury, Ontario, Canada	Strathcona Deep Copper zone		[35]
Hibbingite	Sudbury, Ontario, Canada	Strathcona Deep Copper zone		[36]
	Duluth, Minnesota, USA	Troctolite		[37,38]
	Noril'sk, Siberia, Russia	Ore zone	Solid solution with kempite	[39]
Pyrosmalite-(Fe)	Noril'sk, Siberia, Russia	Oktyabr'sky, massive sulfide	Pys-Fe–Tty	[40]
Penfieldite-type phase	Bushveld, South Africa	Merensky Reef	With PGM in orthocumulate	[41]
Djerfisherite	Noril'sk, Siberia, Russia	Cu–Ni ores		[42]
	Guli complex, Polar Siberia, Russia	Dunitic rocks		[43]
	Yoko-Dovyren, Baikal region, Russia	Magnesian skarn	Included in Spl, Tro	[44]
Thalferisite	Noril'sk, Siberia, Russia	Cu–Ni ores		[45]

Note: Symbols used: Amp: amphibole, Clap: chlorapatite, Fcprg: ferro-chloro-pargasite, Ol: olivine, Pl: plagioclase, PGM: platinum-group minerals, Spl: spinel, Tty: tatyanaite, Tro: troilite.

On the basis of findings in the reviewed occurrences (Table 3), we infer that Cl-rich compounds typically form at relatively low temperatures as a consequence of build-up in levels of Cl attained locally during late or final stages of formation, or during stages of post-magmatic alteration of the complexes. Chlorapatite, which is the most abundant expression of Cl buildup, crystallized from pockets of intercumulus melts [6,21,25] or is a result of phase transformations involving fluorapatite as a precursor phase [46]. In addition, Cl was important in PGE remobilization in the Duluth complex, Minnesota, USA [47]. The amphibole “ferro-chloro-pargasite” likely precipitated from a late phase of hydrous Cl-bearing fluids (e.g., micro-inclusions hosted by PGM), or formed as a result of transformation reactions, which involved a primary plagioclase during deuteric (autometasomatic) events of alteration [6,31,32]. Many of the uncommon compounds rich in Cl likely formed from residual droplets of highly fractionated melts or crystallized from remaining microvolumes of aqueous hydrochloric solutions [41].

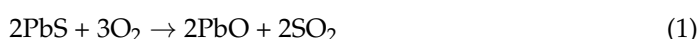
The Behavior of Cl during Crystallization of the Monchepluton Complex and the Origin of Calcian Pyromorphite

A recent evaluation of geochemical trends and their link to compositions of rock-forming silicate and oxide minerals at Monchepluton indicates that variations in apatite differ from trends reported for other layered intrusions [6]. Chlorapatite (>6 wt.% Cl) is

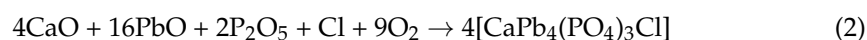
invariably abundant, and compositional variations in apatite are generally similar in all of the geological divisions of the complex (i.e., the Mounts Nittis, Kumuzhya, Travyanaya, Sopcha, Nyud and Poaz). No relationship exists between the Cl content of apatite and the degree of magnesium enrichment in the coexisting magmatic silicates. Two fields of apatite compositions are recognized: ≤ 3 wt.% and >6 wt.% Cl, which overlap extensively, consistent with two generations of apatite. The first nucleated early during crystallization of pockets of H₂O-bearing intercumulus melts. An inferred stage of degassing of the crystallizing melt likely caused a decoupling of Cl and F. Fluorine at Monchepluton essentially remained in the melt, whereas Cl was partitioned efficiently to an H₂O-bearing fluid phase. As a result, at the early stage, the apatite incorporated combinations of the components hydroxylapatite and fluorapatite, with a low content of Cl. At a late stage, chlorapatite precipitated from a Cl-rich fluid. Consequently, “ferro-chloro-pargasite” (4.1 wt.% Cl) formed via reactions of that fluid with plagioclase and pyroxene during an event of autometasomatic alteration occurring in relatively evolved cumulates of gabbro-noritic sequences of the Poaz massif (Figure 2) [6].

Features of the geochemical behavior of Cl [6] are useful in recognizing a mode of formation of the phosphohedyphane-like phase occurring in a sulfide vein of the Monchepluton complex. The investigated veins occur close to the nexus (Figure 2); they are representative examples that belong to the entire system of steeply dipping veins of massive sulfide ores (0.1 to 1.4 km long and up to 0.5 m in thickness, locally up to 2–3 m thick). These veins presumably formed by remobilization of early occurrences of magmatic sulfide melts, accumulating and filling the space along the system of early brittle faults developed in the nexus region of the complex: [6] and references therein. In accordance with previous observations at Monchepluton [6], we presume that Cl was locally abundant in a late fluid during the formation of the sulfide Cu–Ni–PGE mineralization of the veins. We propose a secondary origin, related to a low-temperature oxidation of a Pb-bearing precursor, presumably galena, to account for the presence of a pyromorphite–phosphohedyphane solid solution at Monchepluton. This mechanism and mode of formation are consistent with findings on related Cl-rich phosphates of Pb and Ca from other localities [11,17].

We believe that the lead-bearing phosphate likely formed at elevated levels of fO_2 via two-stage reactions of precursor grains of galena with components of the residual fluid saturated with respect to an apatite-super group mineral and containing Ca (and minor Ba) as incompatible components during crystallization of the sulfide ore:



and



Grains of barite, also present in the heavy-mineral concentrate of the veins, could well form according to the following reaction: $Ba + SO_2 + O_2 \rightarrow BaSO_4$.

The inferred regime of progressive increase in fO_2 is further corroborated by the common occurrence of highly oxidized varieties of ochreous and porous ores, which commonly accompany the primary sulfide ores in the veins at Monchepluton. A progressive rise in intrinsic fO_2 is also inferred for some other ultrabasic complexes in the Serpentine belt of the Kola Peninsula [48–50].

5. Conclusions

- (1) We describe the occurrence of a pyromorphite–phosphohedyphane solid solution in zones of massive PGE-bearing Cu–Ni sulfide mineralization in the Monchepluton complex. An elevated level of Cl developed in the cumulates at the hydrothermal stage and migrated along the system of early brittle faults.
- (2) The phosphohedyphane-like phase is a member of the late Pb–S–Te–Bi–As-enriched assemblages, which include Pd–Pt bismuthotellurides and sperrylite, all deposited hydrothermally, from ~750 to below 500 °C, during the formation of the sulfide veins.

- (3) A secondary origin is inferred, involving a low-temperature oxidation of a Pb-bearing precursor, presumably galena, to form grains of the phosphohedyphane-like phase. This mechanism and mode of formation are consistent with findings on related Cl-rich phosphates of Pb and Ca from other localities, which are reviewed.
- (4) There was a progressive increase in fO_2 , in agreement with the abundance of oxidized varieties of ores in association with primary ores in the veins at Monchepluton and at other ultrabasic complexes of the Kola Peninsula.

Author Contributions: The authors wrote the article together. A.Y.B.: investigations, writing; A.A.N.: writing, discussions; L.P.B.: interpretations, writing; R.F.M.: conclusions, writing. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Russian Science Foundation (grant #22-27-00419).

Data Availability Statement: The data are available upon a reasonable request (from A.Y.B.).

Acknowledgments: We sincerely thank the Editors and the three anonymous reviewers for their comments on a previous version of our manuscript. We are grateful to the late Sergey S. Kramzaev (ChSU, Cherepovets) for his assistance and efforts during the field investigations. A.Y.B. gratefully acknowledges additional support for this investigation by Cherepovets State University.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Amelin, Y.; Heaman, L.; Semenov, V. U–Pb geochronology of layered mafic intrusions in the eastern Baltic Shield: Implications for the timing and duration of Paleoproterozoic continental rifting. *Precambrian Res.* **1995**, *75*, 31–46. [\[CrossRef\]](#)
2. Alapieti, T.T.; Lahtinen, J.J.; Lavrov, M.M.; Smolkin, V.F.; Voitsekhovskiy, S.N. Early Proterozoic layered intrusions in the northeastern part of the Fennoscandian Shield. *Mineral. Petrol.* **1990**, *42*, 1–22. [\[CrossRef\]](#)
3. Balagansky, V.V.; Gorbunov, I.A.; Mudruk, S.V. Palaeoproterozoic Lapland-Kola and Svecofennian orogens (Baltic Shield). *Her. (Vestn.) Kola Sci. Cent. RAS* **2016**, *3*, 5–11. (In Russian)
4. Sharkov, E.V.; Chistyakov, A.V. The Early Paleoproterozoic Monchegorsk layered mafite-ultramafite massif in the Kola Peninsula: Geology, petrology, and ore potential. *Petrology* **2012**, *20*, 607–639. [\[CrossRef\]](#)
5. Barkov, A.; Martin, R.; Izokh, A.; Nikiforov, A.; Korolyuk, V. Ultramagnesian Olivine in the Monchepluton (Fo₉₆) and Pados-Tundra (Fo₉₃) Layered Intrusions (Kola Peninsula). *Russ. Geol. Geophys.* **2021**, *62*, 324–338. [\[CrossRef\]](#)
6. Barkov, A.; Sharkov, E.; Nikiforov, A.; Korolyuk, V.; Silyanov, S.; Lobastov, B. Compositional Variations of Apatite and REE-Bearing Minerals in Relation to Crystallization Trends in the Monchepluton Layered Complex (Kola Peninsula). *Russ. Geol. Geophys.* **2021**, *62*, 427–444. [\[CrossRef\]](#)
7. Barkov, A.; Nikiforov, A.; Martin, R. A novel mechanism of spheroidal weathering: A case study from the Monchepluton layered complex, Kola Peninsula, Russia. *Bull. Geol. Soc. Finl.* **2015**, *87*, 79–85. [\[CrossRef\]](#)
8. Chashchin, V.V.; Galkin, A.S.; Ozeryanskii, V.V.; Dedyukhin, A.N. Sopcha Lake chromite deposit and its platinum potential, Monchegorsk pluton, Kola Peninsula (Russia). *Geol. Ore Deposits* **1999**, *41*, 460–468.
9. Dedeev, A.V.; Khashkovskaya, T.N.; Galkin, A.S. PGE Mineralization of the Monchegorsk layered mafic-ultramafic intrusion of the Kola Peninsula. In *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements, Canadian Institute of Mining, Metallurgy and Petroleum*; Cabri, L.J., Ed.; Canadian Institute of Mining, Metallurgy and Petroleum: Montreal, QC, Canada, 2002; Volume 54, pp. 569–577.
10. Pasero, M.; Kampf, A.R.; Ferraris, C.; Pekov, I.V.; Rakovan, J.; White, T. Nomenclature of the apatite supergroup minerals. *Eur. J. Mineral.* **2010**, *22*, 163–179. [\[CrossRef\]](#)
11. Kampf, A.R.; Steele, I.M.; Jenkins, R.A. Phosphohedyphane, Ca₂Pb₃(PO₄)₃Cl, the phosphate analog of hedyphane: Description and crystal structure. *Am. Mineral.* **2006**, *91*, 1909–1917. [\[CrossRef\]](#)
12. Kampf, A.R.; Housley, R.M. Fluorophosphohedyphane, Ca₂Pb₃(PO₄)₃F, the first apatite supergroup mineral with essential Pb and F. *Am. Mineral.* **2011**, *96*, 423–429. [\[CrossRef\]](#)
13. Breithaupt, A. Bestimmung neuer Mineral-Specien, 2. Hedyphan. *J. Chem. Phys.* **1830**, *60*, 308–316.
14. Hochleitner, R.; Kaliwoda, M.; Rewitzer, C. Natural members of the phosphohedyphane-hedyphane-mimetite series. In *Proceedings of the 2nd European Mineralogical Conference Minerals, Rocks and Fluids: Alphabet and Words of Planet Earth*, Rimini, Italy, 1–15 September 2016; p. 569.
15. Calos, N.J.; Kennard, C.H.L.; Davis, R.L. Crystal structure of mimetite, Pb₅(AsO₄)₃Cl. *Z. Krist.* **1990**, *191*, 125–129. [\[CrossRef\]](#)
16. Dai, Y.; Hughes, J.M.; Moore, P.B. The crystal structures of mimetite and clinomimetite, Pb₅(AsO₄)₃Cl. *Can. Mineral.* **1991**, *29*, 369–376.

17. Will, P.; Friedrich, F.; Hochleitner, R.; Gilg, H.A. Fraipontite in the hydrothermally overprinted oxidation zone of the Preguiça mine, Southern Portugal. In Proceedings of the 7th Mid-European Clay Conference, Dresden, Germany, 16–19 September 2014; p. 133.
18. Hoffman, E.L.; MacLean, W.H. Phase relations of michenerite and merenskyite in the Pd-Bi-Te system. *Econ. Geol.* **1976**, *71*, 1461–1468. [\[CrossRef\]](#)
19. Barkov, A.Y.; Fleet, M.E. An unusual association of hydrothermal platinum-group minerals from the Imandra layered complex, Kola Peninsula, northwestern Russia. *Can. Mineral.* **2004**, *42*, 455–467. [\[CrossRef\]](#)
20. Boudreau, A.E.; Mathez, E.A.; McAllum, I.S. Halogen Geochemistry of the Stillwater and Bushveld Complexes: Evidence for Transport of the Platinum-Group Elements by Cl-Rich Fluids. *J. Pet.* **1986**, *27*, 967–986. [\[CrossRef\]](#)
21. Boudreau, A.E.; McCallum, I.S. Investigations of the Stillwater Complex: Part V. Apatites as indicators of evolving fluid composition. *Contrib. Mineral. Pet.* **1989**, *102*, 138–153. [\[CrossRef\]](#)
22. Mutanen, T.; Törnroos, R.; Johanson, B. The Significance of Cumulus Chlorapatite and High-temperature Dashkesanite to the Genesis of PGE Mineralization in the Koitelainen and Keivitsa-Satovaara Complexes, Northern Finland. *Geo-Platinum* **1988**, 159–160. [\[CrossRef\]](#)
23. Barkov, A.Y.; Savchenko, E.E.; Menshikov, Y.P. Chlorapatite as indicator of platinum-group elements fluid mobilization in the Lukkulaivaara intrusion, northern Karelia. *Dokl. Akad. Nauk* **1993**, *328*, 84–89. (In Russian)
24. Meurer, W.P.; Hellström, F.A.; Claeson, D.T. The relationship between chlorapatite and PGE-rich cumulates in layered intrusions: The Kläppsjö gabbro, north-central Sweden, as a case study. *Can. Mineral.* **2004**, *42*, 279–289. [\[CrossRef\]](#)
25. Barkov, A.Y.; Nikiforov, A.A. Compositional Variations of Apatite, Fractionation Trends, and a PGE-Bearing Zone in the Kivakka Layered Intrusion, Northern Karelia, Russia. *Can. Mineral.* **2016**, *54*, 475–490. [\[CrossRef\]](#)
26. Barkov, A.Y.; Nikiforov, A.A. A new criterion for searching zones of PGE mineralization of the “Kivakka Reef” type. *Vestn. VGU. Geol.* **2015**, *4*, 75–83. (In Russian)
27. Barkov, A.Y.; Nikulin, I.I.; Nikiforov, A.A.; Lobastov, B.M.; Silyanov, S.A.; Martin, R.F. Atypical Mineralization Involving Pd-Pt, Au-Ag, REE, Y, Zr, Th, U, and Cl-F in the Oktyabrsky Deposit, Norilsk Complex, Russia. *Minerals* **2021**, *11*, 1193. [\[CrossRef\]](#)
28. Kislov, E.V.; Konnikov, E.G.; Orsoev, D.A.; Pushkarev, E.V.; Voronina, L.K. The chlorine role in platinum-bearing horizons formation in the Ioko-Dovyren layered massif by the results of fluid-bearing minerals investigations. *Dokl. Akad. Nauk* **1995**, *340*, 805–808. (In Russian)
29. Kislov, E.V.; Konnikov, E.G.; Orsoev, D.A.; Pushkarev, E.V.; Voronina, L.K. Chlorine in the genesis of the low-sulfide PGE mineralization in the Ioko-Dovyrenskii layered massif. *Geokhimiya* **1997**, *5*, 521–528. (In Russian)
30. Spiridonov, E.M. Barium Minerals Barite and Chlorine dominant Ferrokinoshitalite $\text{BaFe}_3^{2+}[\text{Cl}_2/\text{Al}_2\text{Si}_2\text{O}_{10}]$ in plagioperidotites of the Yoko-Dovyren intrusion, northern Baikal area: Products of epigenetic low-grade metamorphism. *Geochem. Int.* **2019**, *57*, 1221–1229. [\[CrossRef\]](#)
31. Barkov, A.Y.; Martin, R.F.; Tarkian, M.; Poirier, G.; Thibault, Y. Pd-Ag Tellurides from a Cl-Rich Environment in The Lukkulaivaara Layered Intrusion, Northern Russian Karelia. *Can. Mineral.* **2001**, *39*, 639–653. [\[CrossRef\]](#)
32. Barkov, A.Y.; Martin, R.F.; Laajoki, K.V.O.; Alapieti, T.T.; Iljina, M.J. Paragenesis and origin of staurolite from a palladium-rich gabbro-norite: An unusual occurrence from the Lukkulaivaara layered intrusion, Russian Karelia. *Neues Jahrb. für Mineral.-Abh.* **1999**, *175*, 191–222. [\[CrossRef\]](#)
33. Duesterhoeft, E.; Raase, P.; Gremier, P. A new occurrence of extremely rare Ferro-Chloro-Pargasite in Tudor, Ontario. *Geol. Rundsch.* **2017**, *106*, 2815–2816. [\[CrossRef\]](#)
34. Karpenkov, A.M.; Rudashevsky, N.S.; Shumskaya, N.I. Natural palladium bismuth chloride–phase of $\text{Pd}_4\text{Bi}_5\text{Cl}_3$ composition. *Zap. Vses. Mineral. Obshch.* **1981**, *110*, 86–91. (In Russian) [\[CrossRef\]](#)
35. Li, C.; Naldrett, A.J. Platinum-group minerals from the Deep Copper Zone of the Strathcona deposit, Sudbury, Ontario. *Can. Mineral.* **1993**, *31*, 31–44. [\[CrossRef\]](#)
36. Springer, G. Chlorine-bearing and other uncommon minerals in the Strathcona Deep Copper zone, Sudbury district, Ontario. *Can. Mineral.* **1989**, *27*, 311–313.
37. Dahlberg, E.H.; Saini-Eidukat, B. A chlorine-bearing phase in drill core of serpentinized troctolitic rocks of the Duluth Complex, Minnesota. *Can. Mineral.* **1991**, *29*, 239–244.
38. Saini-Eidukat, B.; Kucha, H.; Keppler, H. Hibbingite, $\gamma\text{-Fe}_2(\text{OH})_3\text{Cl}$, a new mineral from the Duluth complex, Minnesota, with implications for the oxidation of Fe-bearing compounds and the transport of metals. *Am. Mineral.* **1994**, *79*, 555–561.
39. Saini-Eidukat, B.; Rudashevsky, N.S.; Polozov, A.G. Evidence for hibbingite–kempite solid solution. *Mineral. Mag.* **1998**, *62*, 251–255. [\[CrossRef\]](#)
40. Barkov, A.Y.; Martin, R.F.; Poirier, G.; Tarkian, M.; Pakhomovskii, Y.A.; Men’shikov, Y.P. Tatyanaite, a new platinum-group mineral, the Pt analogue of taimyrite, from the Noril’sk complex (northern Siberia, Russia). *Eur. J. Mineral.* **2000**, *12*, 391–396. [\[CrossRef\]](#)
41. Barkov, A.Y.; Martin, R.F.; Kaukonen, R.J.; Alapieti, T.T. The occurrence of Pb-Cl-(OH) and Pt-Sn-S compounds in the Merensky reef, Bushveld layered complex, South Africa. *Can. Mineral.* **2001**, *39*, 1397–1403. [\[CrossRef\]](#)
42. Genkin, A.D.; Troneva, N.V.; Zhuravlev, N.N. The first find in ores of a potassium, iron and copper sulfide–djerfisherite. *Geol. Rudn. Mestorozhd.* **1969**, *5*, 57–64. (In Russian)

43. Zaccarini, F.; Thalhhammer, O.A.; Princivalle, F.; Lenaz, D.; Stanley, C.; Garuti, G. Djerfisherite in the Guli dunite complex, Polar Siberia: A primary or metasomatic phase? *Can. Mineral.* **2007**, *45*, 1201–1211. [[CrossRef](#)]
44. Kislov, E.V.; Orsoev, D.A.; Pushkarev, E.V. Halogens in djerfisherite from a magnesian skarn of the platinum-bearing Yoko-Dovyren massif. *Geol. Geophys.* **1994**, *11*, 54–57. (In Russian)
45. Rudashevskii, N.S.; Karpenkov, A.M.; Shipova, G.S.; Shishkin, N.N.; Ryabkin, V.A. Thalfenisite, the thallium analogue of djerfisherite. *Zap. Vsesoyuzn. Mineral. Obshch.* **1979**, *108*, 696–701. (In Russian)
46. Cawthorn, R.G. Formation of chlor- and fluor-apatite in layered intrusions. *Mineral. Mag.* **1994**, *58*, 299–306. [[CrossRef](#)]
47. Raič, S.; Mogessie, A.; Krenn, K.; Hauzenberger, C.A.; Tropper, P. Deciphering Magmatic and Metasomatic Processes Recorded by Fluid Inclusions and Apatite within the Cu–Ni ± PGE–Sulfide Mineralized Bathtub Intrusion of the Duluth Complex, NE Minnesota, USA. *J. Petrol.* **2018**, *59*, 1167–1192. [[CrossRef](#)]
48. Barkov, A.Y.; Korolyuk, V.N.; Barkova, L.P.; Martin, R.F. Double-Front Crystallization in the Chapesvara Ultramafic Subvolcanic Complex, Serpentinite Belt, Kola Peninsula, Russia. *Minerals* **2019**, *10*, 14. [[CrossRef](#)]
49. Barkov, A.Y.; Nikiforov, A.A.; Korolyuk, V.N.; Barkova, L.P.; Martin, R.F. Anomalous chromite–ilmenite parageneses in the Chapesvara and Lyavaraka ultramafic complexes, Kola Peninsula, Russia. *Period Di Mineral.* **2020**, *89*, 299–317.
50. Barkov, A.Y.; Nikiforov, A.A.; Korolyuk, V.N.; Barkova, L.P.; Martin, R.F. The chromian spinels of the Lyavaraka ultrabasic complex, Serpentinite Belt, Kola Peninsula, Russia: Patterns of zoning, hypermagnesian compositions, and early oxidation. *Can. Mineral.* **2021**, *59*, 1693–1709. [[CrossRef](#)]