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GEOCHEMISTRY

Behavior of Pt, Pd, Au, Cu, and Ag during the Burakov Pluton Crystallization, Southern Karelia

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The Lower Proterozoic Burakov (layered mafic–ultramafic) pluton, about 630 km^2 in area, is located in the southeastern Baltic Shield. The massif is divided by submeridional faults into three (northeastern Aganozero, central Shalozero, and southeastern Burakov) blocks. The massif is overlain by a thick cover of Quaternary sediments. The reconstruction of its vertical structure became possible only due to prospecting and mapping drilling carried out by the Karelian Geological Expedition from 1984 [1, 2], and the massif could be assigned to potentially platiniferous ones [3]. The weighted average composition of the intrusive one is close to that of komatiites [2].

The vertical section of the intrusive one is subdivided into the upper and lower near-contact zones (UCZ and LCZ) and the layered series (LS) with five alternating zones distinguished by prevailing cumulative parageneses [2]. The geochemical characteristics of the general vertical section is based on analytical data obtained for rocks from the following zones (from bottom to top): LCZ (Hole 20); ultramafic zone, UZ; (Paragenesis Chr + Ol); holes 20, 14, 72, 71, 15, 16, 68 (Aganozero block); pyroxenite zone, PZ; (Opx + Cpx – Chr – Ol[1] (Hole 68); gabbronorite zone, GNZ; Opx + Cpx + Pl; holes 68, 5 (Aganozero block), Hole 113 (Burakov block); gabbronorite zone with inverted pigeonite, GNZP; Cpx + Pgt + Pl; holes 32, 31 (Shalozero block), Hole 45, (Burakov block); magnetitic gabbronorite–diorite zone, MGNDZ; TiMt + Pgt + Cpx + Pl; holes 47, 46 (Shalozero block), holes 45, 129 (Burakov block). The gabbronorite zone is heterogeneous in composition, and only its lower part (approximately 450 m) is characterized by the contrast alternation of gabbroids, pyroxenites, and peridotites. The zone is divided into several members (from bottom to top): gabbronorite (GN1), peridotite horizon (PH), gabbronorite (GN2), pigeonite-bearing gabbronorite (GN3) (Hole 68), and homogeneous gabbronorites (GN4) (Hole 113). The most abundant sulfide minerals of PZ and GNZ are chalcopyrite, pentlandite, and phyrrotite. Individual grains of pyrite are also present. The sulfide phase of rocks is represented by bornite-bearing chalcopyrite and phyrrotite in rocks from the lower part of MGNDZ and by phyrrotite and pyrite in the upper part.

Analytical data were obtained with the help of atomic absorption spectroscopy [4]. The general vertical section across the pluton made it possible to determine the vertical coordinate for each sample and to qualitatively characterize the evolution of the intrusive rock composition, calculate its weighted average composition, and obtain information on the behavior of chemical elements from the beginning to end of the massif solidification. For large layered massifs (except for Kivakk massif [4]), these data are unavailable in the literature. The weighted average contents of metals in the section are as follows: Cu 110 g/t, Ag 44.0 mg/t, Pt 12.5 mg/t, Pd 4.1 mg/t, Au 4.8 mg/t (Table 1). They are taken as initial compositions of metals (C_0) in the intruded magma. For each sample of the section, the weighted average contents of metals in overlying rocks were calculated and taken as contents in the residual magma (C_i) [4]. The curves of variations in relative metal contents in residual magma (C_i/C_0) versus the fractionation degree H_i/H_0 (H_i is the height of sample in a vertical section, and H_0 is the section thickness) demonstrate the behavior of metals during the whole process of the pluton formation (figure). They reflect the values of bulk coefficients of element distribution, which depend upon coefficients of element distribution between mineral phases and silicate melt and upon mineral proportions in rock.

The analysis of the variation curve in the relative content of Cu, which forms chalcopyrite in the paragenesis of magmatic sulfides, allows us to obtain

[1] Negative sign denotes incongruent solution of mineral from the cumulative paragenesis.

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Table 1. Weighted average contents of metals in the vertical section of the Burakov Pluton

Zone	Members	Thickness, m	Cu	Ag	Pt	Pd	Au
UCZ		87.5	343(2)	145(2)	–	–	–
MGNDZ		597.8	321(19)	139(21)	1.4(17)	0.6(17)	2.5(17)
GNZP		624.8	201(29)	88.3(42)	4.8(29)	1.2(29)	0.76(29)
GNZ	GN4	321.5	185(6)	64.4(7)	3.9(7)	2.2(7)	0.73(7)
	GN3	90.5	385(18)	168(18)	23.7(15)	64.7(15)	8.7(15)
	GN2	202.1	73.3(19)	54.2(19)	14.9(7)	22.8(7)	5.5(7)
	PH	60.1	131(10)	74.4(10)	14.8(5)	12.0(5)	5.6(5)
	GN1	99.3	202(31)	123(31)	18.5(17)	8.9(17)	5.4(17)
	Whole zone	773.5	177(84)	82.1(85)	11.8(51)	16.5(51)	3.9(51)
PZ		182.5	239(9)	129(9)	18.6(9)	7.1(9)	5.0(9)
UZ		3258.7	25(33)	2.3(43)	15.8(22)	1.8(22)	6.2(22)
LCZ		132.3	74(1)	27.7(1)	–	–	–
Average for rocks of the vertical section		5657	110(177)	44.0(203)	12.5(128)	4.1(128)	4.8(128)

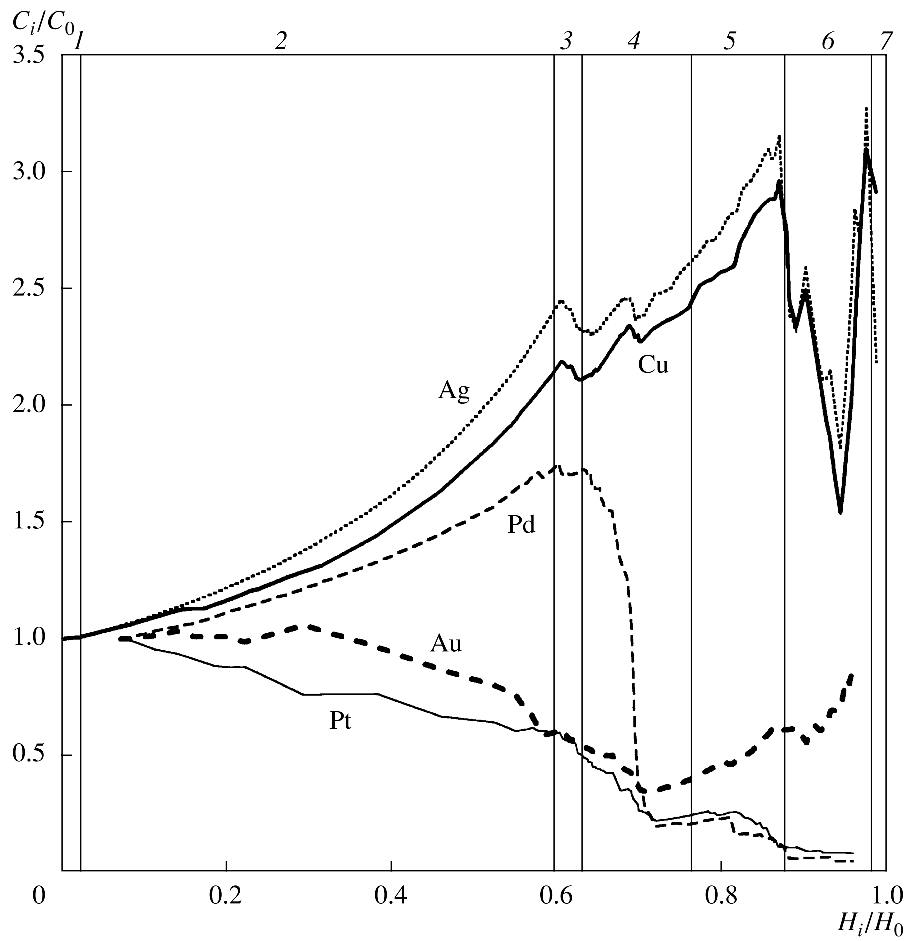
Note: Cu, g/t; the rest elements, mg/t. The number of analyzed samples is given in parentheses.

information on the time of separation of sulfide phase from silicate melt and on its role in concentration of precious metals. It follows from the figure that Cu predominantly accumulated during crystallization in residual magma up to the beginning of the crystallization of MGNDZ rocks. Its content somewhat decreased during the crystallization of PZ, GN1, and GN3 rocks. The Cu content decreased by 1.5 times during the crystallization of the lower part of MGNDZ rocks. The increase in the bulk coefficient of Cu distribution is related to the separation of the sulfide phase. The plot of variation in relative Ag contents in magma is similar to that of Cu, which is testimony to the approximate values of their coefficients of distribution between sulfide phase and silicate melt. Similarly to Cu and Ag, Pd accumulated in the residual magma up to the beginning of the sulfide phase segregation. After the formation of PZ and GNZ (GN4) rocks, which contain over 60% of its quantity in rocks of the vertical section, its content in magma sharply decreased.

It also follows from the figure that Pt was fractionated from the very beginning of the crystallization of UZ rocks. After the formation of PZ rocks and the lower part of GNZ, its content in residual magma was sharply decreased due to an increase in the bulk coefficient of Pt distribution as a result of its concentration in the sulfide phase of low-sulfide horizons. During the crystallization of the lower part of UZ rocks, the bulk coefficient of Au distribution remained close to 1, then its content in magma began to diminish, and its bulk coefficient of distribution increased during the formation of rocks in the upper part of UZ, PZ, and GNZ, up to the crystallization of GN4, and then Au was slightly accumulated in residual magma. About 75% of the total amount of Pt and Au in the section is concentrated in the UZ. Isoferroplatinum and native gold were detected in chromitite horizons in the upper part of the UZ [5]. The low contents of Cu, Ag, and Pd in UZ rocks do not allow us to relate the concentration of Pt and Au with the sulfide phase.

The Cu and Ag plots show that a very small amount of sulfides separated from the silicate melt during the formation of PZ and GNZ. However, due to high values of the coefficient of Pd, Pt, and Au distribution between sulfide phase and silicate melt [6], sulfides concentrated noble metals, and magma turned out to be depleted in noble metals after the crystallization of GN3. In separate low-sulfide horizons, we detected the following tellurides and bismuthides of Pt and Pd: moncheite, merenskite, sobolevskite, and kotulskite [5]. The greatest sulfide content should be expected in rocks of the lower part of MGNDZ, but these sulfides should not be enriched in Pt and Pd, because the content of these metals in magma was minimal.

Analysis of pair ratios for weighted average contents of metals in the vertical section (Table 2) demonstrates that Pt dominated over Pd (Pt/Pd = 3) in the source magma. During the evolution of magma, the Pt/Pd value decreased from UZ to PZ. In the GNZ, it regularly decreased from the bottom to top. Platinum dominates over Pd in lower rocks of (GN1 and PH) rocks, whereas Pd dominates over Pt in rocks of GN2 and GN3. The ratio of weighted average contents of Cu and Ag in rocks of the vertical section (except for UZ) are close to the value in the source magma. This testifies to the similarity of their coefficients of distribution in sulfide and silicate melts. At the same time, beginning from the upper part of GNZ, ratios of Cu and Ag to precious metals sharply increase after the formation of rocks hosting low-sulfide horizons. This observation testifies the following: since the values of coefficients of the distribution between sulfide and silicate melt are



Variation in relative contents of Cu, Ag, Au, Pt and Pd in residual magma of the Burakov Pluton. (*1*) LCZ, (*2*) UZ, (*3*) PZ, (*4*) GNZ, (*5*) GNZP; (*6*) MGNDZ; (*7*) UCZ.

higher for noble metals than for Cu and Ag, magma turned out to be depleted in noble metals after the concentration of Pt and Pd in sulfide phase of the lower part of GNZ. Consequently, ratios of Cu/Pt, Cu/Pd, Cu/Au and Ag/Pt, Ag/Pd, Ag/Au increased. We established a similar tendency for the Kivakk intrusive [4]. Later, Barns *et al.* did it for the Bushveld massif [7]. A regular increase in the ratios of chalcophile elements to noble

Table 2. Ratios of Cu/Ag, Cu/Pt, Cu/Pd, Cu/Au, Ag/Pt, Ag/Pd, Ag/Au, Pt/Pd in the vertical section of the Burakov Pluton

Zone	Members	(Cu/Ag) $\times 10^3$	(Cu/Pt) $\times 10^3$	(Cu/Pd) $\times 10^3$	(Cu/Au) $\times 10^3$	Ag/Pt	Ag/Pd	Ag/Au	Pt/Pd
MGNDZ		2.3	229	553	128	99.3	240	55.6	2.4
GNPZ		2.3	41.9	168	264	18.4	73.6	116	4
GNZ	GN4	2.9	47.4	84.1	253	16.5	29.3	88.2	1.8
	GN3	2.3	16.2	6	44.2	7.1	2.6	19.3	0.37
	GN2	1.4	4.9	3.2	13.3	3.6	2.4	9.8	0.65
	PH	1.8	8.8	10.9	23.4	5	6.2	13.3	1.2
	GN1	1.6	10.9	22.7	37.4	6.6	13.8	22.8	2.1
	Whole zone	2.2	15	10.7	45.4	7	5	21	0.72
PZ		1.8	12.8	33.7	47.8	6.9	18.2	25.8	2.6
UZ		10.9	1.6	13.9	4	0.15	1.3	0.37	8.8
Average for rocks of the vertical section		2.5	8.8	26.8	22.9	3.5	10.7	10.7	3

elements can be regarded as a geochemical criterion for PGE-bearing rocks within the intrusive sequence.

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