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Fluid regime of platinum group elements (PGE) and gold-bearing reef formation in the Dovyren mafic–ultramafic layered complex, eastern Siberia, Russia

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Abstract The Dovyren layered dunite–troctolite–gabbro massif (northern Transbaikalia region, Russia) contains precious metal mineralization related to sparsely disseminated sulfides (Stillwater type). The distribution of gases trapped in micro-inclusions and intergranular pores of the Dovyren massif has been investigated. This type of study had previously only been undertaken on the traps or peridotite–pyroxenite–norite intrusions hosting copper–nickel sulfide deposits. A novel method of analyzing trapped gases, involving the grinding of samples under high vacuum at room temperature, was employed. A modified gas-chromatography and mass-spectrometry approach was used to analyze the composition of the extracted gases. The concentrations of reduced gases (CH_4 and H_2) are higher in inclusions trapped by silicate minerals, whereas oxidized gases (H_2O, CO_2) are less common. The content of reduced gases (H_2, CH_4, CO), N_2, He, radiogenic Ar, and C_2H_6 increases upward through the layered series of the massif. The distribution of all gases, especially methane and hydrogen, show peak concentrations coincident with the PGE and gold reef type horizons. A correlation of the gas peaks and noble metal contents appears to be related to their geochemical affinities. This conclusion is supported by the experimental modeling.

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Introduction

The problem of the fluid regime of mafic–ultramafic complexes and its relation to the distribution of copper–nickel sulfides and PGE mineralization has received considerable attention. Investigations devoted to understanding how fluids influenced the deposition of stratabound PGE (Stillwater-type) mineralization related to "reefs" within layered mafic–ultramafic plutons are not abundant. Most presume that halogen gases (Cl, F) were involved in the transfer and localization of precious metals during late-stage magmatic processes (e.g., Boudreau and McCallum 1989; Boudreau and Kruger 1990; Ripley 1990). The role of other fluid components in the origin of stratabound PGE mineralization has escaped the attention of exploration geologists.

Studies of gases participating in rock- and ore-forming processes have been undertaken by some investigators using gas-chromatography and mass-spectrometry (Letnikov et al. 1980; Zimmermann et al. 1987). Recently, these methods were applied to explore the fluid regime at Norilsk (Aplonov 1995; Neruchev and Prasolov 1995). In this paper, we use the same analytical approach to elucidate the fluid regime of the newly discovered Stillwater-type PGE mineralization in the Dovyren dunite–troctolite–gabbro layered massif, eastern Siberia (Distler and Stepin 1993; Kislov 1993). This kind of intrusive series has become an attractive target for economic copper–nickel and noble metal ores, especially after the discovery of the high-grade copper–nickel deposit in the Voisey's Bay troctolite massif in Canada (Lee et al. 1995).

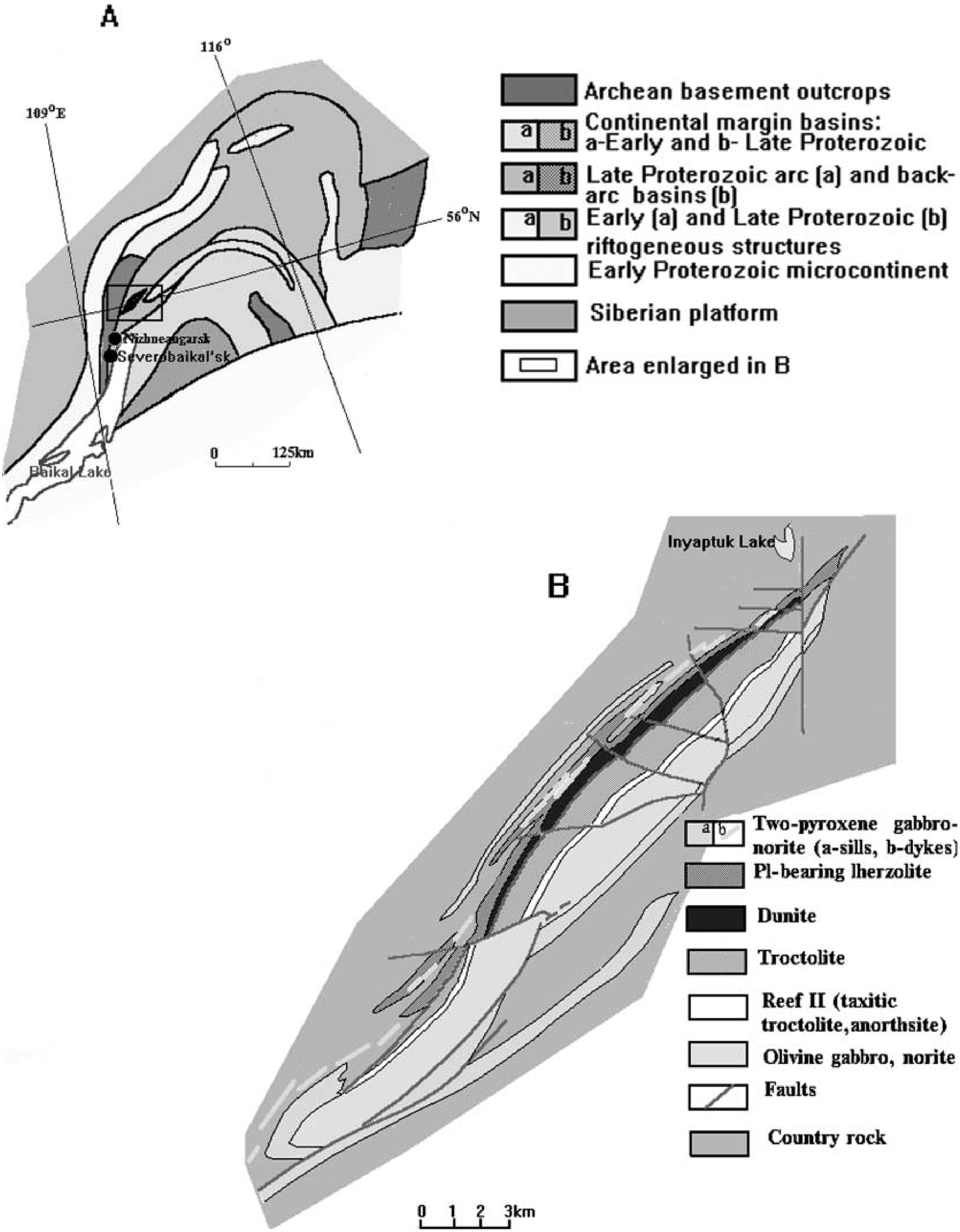

Fig. 1 Geological setting **A** and inner structure **B** of the Dovyren layered massif

Geological setting

The Dovyren layered massif occurs in the Synnir rift basin within the Riphean carbonate–terrigeneous marginal basin at the southern edge of the Siberian platform (Fig. 1). The intrusion was emplaced at about 740 Ma and manifests a distinct genetic affinity to coeval bimodal (basalt–trachydacitic) volcanism (Konnikov et al. 1995). The Dovyren massif is a well-preserved, sill-like body, concordant to its Late Proterozoic country rocks, and has been folded together with them. It extends for nearly 26 km in length, with a maximum thickness of 3.5 km.

The rocks consist of an olivine (Ol) + plagioclase (Pl) + clinopyroxene (Cpx) assemblage. The following zones are delineated in the cross section of the massif (from bottom to top; Fig. 2): (1) Pl-bearing lherzolites form the bottom unit and offset-like apophyses in the country rocks; both the lherzolites and offsets contain disseminated, vein-like, and massive copper–nickel sulfide ores and could be considered as magma channels in the Dovyren massif; (2) a layered dunite–troctolite series; and (3) a moderately layered olivine gabbro–gabbronorite series. The ophitic gabbrononite sills at the bottom and in the roof of the pluton and in the country rocks have resulted from an additional influx of more fractionated melt from a deep intermediate chamber into the contacts of the solidified massif. The parental melt of the Dovyren intrusion was similar to komatiitic or picritic lavas ($SiO_2 = 43$; $TiO_2 = 0.2$; $A1_2O_3 = 10$; $MgO = 24$; $P_2O_5 = 0.04$ wt%), as inferred from comparison of the chemical composition of the Pl-bearing horizon to the weighted average of the layered part of the massif. The massif is characterized by the following cumulate sequence, which is typical for melts solidified under low pressure: Ol $\rightarrow$ Ol + Pl $\rightarrow$ Ol + Pl + Cpx $\rightarrow$ Ol + Pl + Cpx + orthopyroxene(Opx). Copper–nickel sulfide ores occur in the Pl-bearing lherzolites and contain about 2.5 g/t precious metals, with a predominance of Pd over Pt. As has been shown earlier (Konnikov 1986), the quantity of sulfides in these peridotites correlates well with the amount of phlogopite at the same horizon, pointing to fluid saturation at the bottom of the intrusion compared with other zones in which hydroxyl-bearing minerals are rare.

The sulfide-poor Stillwater-type PGE mineralization occurs at four levels in the layered part of the Dovyren massif, but, according to the data available so far, economic deposits are found only at the boundary between the banded dunite–troctolite and olivine gabbro–gabbronorite series (reef I). Reef II is located along the contact of the Ol-gabbro and Ol-gabbronorite. The third PGE-bearing level occurs in the lower dunite layer, accompanied by abundant carbonate xenoliths, and the fourth level correlates with a taxitic troctolite band within intercalated olivine gabbro and troctolite.

The PGE mineralization occurs mainly in lens-like sulfide-bearing (as much as 5–7 vol%) masses of anorthosite (maximum 1×40 m^2 in size) that are included in taxitic gabbroic rocks. The anorthositic masses follow layering and form a discontinuous, en echelon horizon with a thickness of 100–150 m and a length of nearly 19 km. The PGE-bearing minerals appear in the copper-rich sulfide assemblages (chalcopyrite, cubanite, bornite, talnakhite, haezlewoodite, godlevskite, pentlandite, pyrrhotite) and are represented by tetraferroplatinum, tulameenite, zvyagintsevite, rustenburgite, and moncheite. The precious-metal contents reach economic values (g/t): Pt = 4.1; Pd = 7.8; Au = 3.2. There is evidence of halogen- and alkali-enriched fluids participating in the genesis of the PGE mineralization. This includes noble metals usually accompanied by biotite, and Na-amphibole and apatite that contain substantial amounts of chlorine and fluorine. Biotite of the Pl-bearing lherzolite, hosting copper–nickel ores, contains 0.18–0.44 wt% F and 0.1–0.16 wt% Cl, while the same minerals from the PGE-bearing horizons (reefs I and II) are enriched in Cl (0.08–0.58 wt%) relative to F (0.04–0.25 wt%).

An enrichment of sulfide- and PGE-bearing rocks in hydroxyl- and halogene-bearing minerals suggests a possible relationship of ore-forming processes in this intrusion with its fluid regime. According to classic viewpoints, PGE distributions in magmatic rocks can be attributed to the geochemical affinity of precious metals for the fluid phase relative to silicate melt (Menyailov et al. 1984; Distler et al. 1988; Gorbachev et al. 1993).

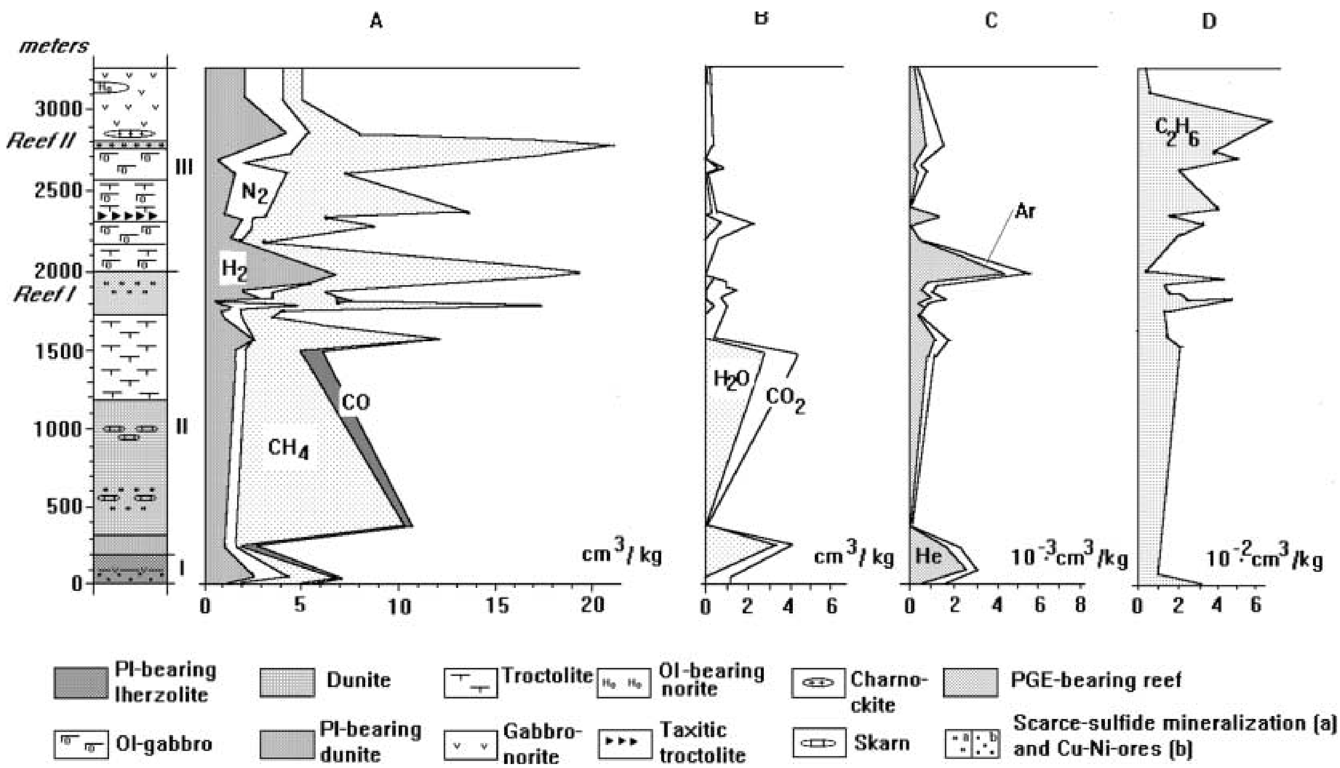

Fig. 2 Trapper gas distributions for a cross section of the Dovyren layered series. Gases: *A* reduced, *B* oxidized, *C* inert. *D* carbohydrates

Analytical methods

To investigate the role of volatile species in the genesis of precious metal deposits in magmatic systems, we have measured the distribution of gases trapped in the micro-inclusions and pores of igneous rocks of the Dovyren intrusion. To this end, 29 samples of rocks were taken across the massif, from its bottom to roof. Thin sections were examined to make sure that all samples were unaltered. The selection of fresh samples for analyses was straightforward because the Dovyren massif has almost no post-magmatic alteration. Olivine, subject to a "loop-liked" serpentinization, is the lithology most affected. All samples have been analyzed by mass-spectrometric methods at the Institute of Oceanology in St. Petersburg.

The gases were extracted from gas–liquid micro-inclusions and closed pores by a mechanical crushing of rock samples and minerals (5–10 g in weight) in a high vacuum (10^{-7} torr) mill. After analysis of the bulk gas volume, a small amount of the sample was separated for chemical analysis using a 180° mass-spectrometer in which the ion trajectory radius equals 5.1 cm. The following compounds were analyzed (vol%): CO_2, CO, N_2, H_2, CH_4, C_2H_6, and (C_3H_8 + C_4H_{10}). Their contents were acquired using splinter-ions contribution data. The relative error (σ) for different compounds is about 3–10% for high concentrations. The minimum abundance of gases necessary for the mass-spectrometric analyses is 10^{-4} cm^3. The compositions of compounds (cm^3/kg) were calculated from the measured results. Water contents were determined in conventional units because it was impossible to account for the losses due to condensation and adsorption in the extraction lines; these water contents were used for comparisons between the samples.

The majority of the extracted gases was used for noble gas analyses and isotopic analyses. Chemically active gases were absorbed by Ti–Zr-getter, whereas noble gases were divided into light fractions (He + Ne) and heavy fractions (Ar + Kr + Xe) by cooling (−196 °C) and collection on activated charcoal. Measurements of gas fractions were made by the volumetric method and gas collections in soldered glass capsules. The error for gases did not exceed 5–10%. Minor noble gas contents (less than 10^{-5} cm^3) were measured from their peak heights on mass-spectrometer diagrams. An isotopic analysis of argon was also carried out on the 180° mass-spectrometer, giving an error for $^{40}Ar/^{36}Ar$ ratio measurements of less than 0.85%. The portions of air and radiogenic argon were calculated from the measurements as follows:

$$(Ar_a/Ar_s) = (^{40}Ar/^{36}Ar)_a/(^{40}Ar/^{36}Ar)_s/(Ar_r/Ar_s) = 1 - (Ar_a/Ar_s)$$

where a is atmospheric argon, r is radiogenic argon, and s is sample argon.

Results

The gas compositions and distributions between rock types are shown in Table 1 and Fig. 2. As shown, reduced gases predominate over oxidized gases in the fluid phase of the Dovyren intrusion. This result agrees with the well-known data on the fluid regime of basaltic magmas obtained by the study of gases preserved in the nickel-bearing intrusions of the Siberian traps (Neruchev 1988) and high-temperature exhalations of the Tolbachik volcano at Kamchatka (Menyailov et al. 1984). Among the reduced gases in the Dovyren massif, methane and hydrogen dominate, with methane much more abundant than hydrogen. The amounts of the other reduced gases (CO) and N_2 are considerably lower. Based on the relationship between CH_4 and H_2, the Dovyren intrusion is very similar to the Norilsk I deposit (Neruchev and Prasolov 1995, Fig. 2), which also has a high methane abundance.

From the gas-distribution diagrams (Fig. 2), bulk gas concentrations increase upwards across the Dovyren massif, as do the contents of H_2, N_2, and CH_4. No conclusions can be drawn from carbon monoxide because of its very low abundance. The upper portions of this massif are enriched in inert gases, especially He, and carbohydrates (Fig. 2). A very irregular distribution of all gases occurs throughout the cross section of the layered series of the intrusion.

Local maxima occur for most gases; the first major peak of the reduced gases correlates with the low-plagioclase-bearing peridotite-hosted disseminated and massive sulfide ores containing PGE. The second maximum, the largest in concentrations of H_2, He, and carbohydrates, is distinctly associated with Reef I and its upper levels where an economically interesting noble metal mineralization is found. The third most intensive peak (in H_2, N_2, but more so in CH_4) coincides with reef II. High CH_4 contents in the middle of the dunite zone correlate with numerous xenoliths of monticellite–spinel–forsterite skarn and sparse accumulation of

Table 1 Average gas content of micro-inclusions in the Dovyren magmatic rocks

Rock name (# of samples)	H_2	N_2	CH_4	CO	H_2O	CO_2	He	Ar	C_2H_6	C_3–C_5
	cm^3/kg						$10^{-3} \cdot cm^3$/kg			
Dolerite (chilled margin) (1)	1.3	0.2	2.8	0.3	0.2	0.4	0.6	0.4	3.9	3.4
Plagioclase-bearing lherzolite (1)	2.5	1.7	2.4	0.3	–	1.0	2.9	0.4	1.2	1.6
Plagioclase-bearing dunite (2)	1.2	0.4	1.7	0.9	3.3	1.0	1.3	0.3	1.5	1.8
Dunite (1)	1.0	0.5	8.9	0.3	0.2	0.2	–	–	1.1	0.2
Troctolite (1)	2.7	–	9.1	–	–	0.5	1.2	0.7	1.2	7.4
Poikilitic wherlite (1)	0.7	1.0	0.8	–	0.02	0.8	0.3	–	1.0	0.5
Plagioclase-bearing dunite (4)	1.1	0.5	6.4	0.6	0.4	0.5	0.9	0.4	1.9	1.1
Olivine gabbro (3)	1.8	1.6	6.1	0.4	0.4	0.5	0.6	0.5	2.3	1.7
Taxitic troctolite (3)	1.4	1.7	9.2	0.7	0.6	0.6	–	–	3.6	1.5
Anorthosite veins (4)	3.8	1.0	7.2	0.2	0.3	1.2	1.8	0.6	2.1	2.1
Olivine gabbro (5)	1.0	1.1	6.1	0.3	0.4	0.1	0.7	0.4	2.7	0.8
Olivine norite (1)	2.6	2.1	18.0	1.0	–	0.4	6.4	1.4	4.8	2.4
Charnockite (1)	4.3	1.0	2.5	0.2	0.08	0.1	1.8	1.2	6.6	2.5
Sills of gabbronorite (1)	2.1	2.0	0.8	–	–	0.1	1.0	0.5	0.5	0.5

troilite–pentlandite. Anomalous PGE contents have been detected by sampling at this level (in ppb): Pt = 48, Pd = 370, and Au = 440. Nevertheless, some peaks of the gas distribution diagram (Fig. 2) do not relate to definitely anomalous PGE contents across the intrusion, e.g., small peaks in CH_4 and N_2 occur in the middle of the intercalated troctolite and olivine gabbro, and maxima in H_2, CH_4, and inert gases occur in the upper half of the troctolite zone, beneath reef I. While the former might be associated with a layer of taxitic troctolite similar to the analogous rocks in the PGE-bearing reef I, there is no comparable correlation of sparse sulfide mineralization with the latter. Given the distinct correspondence of gas peaks to the PGE-bearing horizons of the Dovyren massif, further research should be focused on a more careful sampling of these levels.

A last observation on the gas distribution diagram is that low contents of oxidized gases (H_2O, CO_2) characterize the Dovyren intrusions. Figure 2 shows that water concentrations increase downward over the cross section of the layered series (i.e., opposite in direction to the trends for the reduced gases), attaining maxima at the dunite and troctolite levels. The most probable explanation of this regularity is that the abundance of olivine, a major serpentine-bearing mineral, increases in the same direction.

Discussion

We suggest that the reduced gas peaks coincide with the bands of PGE-bearing mineralization in the Dovyren massif. Some authors (Neruchev and Prasolov 1995) pointed out that PGE tend to be concentrated in the fluids dominated by reduced species and subsequently deposited at discrete horizons within the intrusion. As emphasized above, the rocks hosting noble metal mineralization in this intrusion have crystallized from a fluid-saturated silicate liquid. That is confirmed by the occurrence of volatile-bearing minerals (phlogopite, pargasite, biotite, apatite, etc.) within the PGE-bearing horizons. Usually these minerals are not present in the other parts of the layered massif. The correlation between the PGE mineralization setting and fluid distribution within the Dovyren layered series can be interpreted in two ways: (1) a result of the replenishment of the intrusion by more new fluid- and precious-metal-saturated melt as per the hypothesis of Campbell et al. (1983) or (2) the outcome of the discrete distribution of the PGE-bearing post-magmatic fluid within the layered series, as recently proposed by Meurer and Boudreau (1996).

The first hypothesis is not supported by the background and economic distributions of PGE in the Dovyren massif, i.e., there is no correlation between the fractionation of the silicate liquid and noble metal concentrations. This point is made by high concentrations (reef) in the upper part of the intrusion compared with only background contents of Pt, Pd, and Au in the lower part of the layered series (Fig. 3).

Analyzing the distribution of PGE mineralization of the "sparse sulfide type" over the cross section of the Dovyren massif, we notice the following trend: all reefs containing economic concentrations of PGE occur near an abrupt change in the cumulus assemblage. Thus, the main reef, reef I, is located between the ultramafic portion of the massif and the more gabbroic portion, and reef II occurs near the contact of the olivine gabbro and gabbronorite zones. Even the taxitic troctolite, which lacks PGE mineralization, is located at the transition from massive olivine gabbro to intercalated gabbros and leucotroctolites.

In our opinion, the most appropriate explanation of the regular association of the rocks with PGE mineralization of the "sparse sulfide type" and the positions of lithologic change in the cumulus assemblage is the "compaction hypothesis" (Meurer and Boudreau 1996). According to this hypothesis, the horizons where the cumulus assemblage changes during crystallization and differentiation of basaltic magmas, especially the transition from ultramafic to mafic assemblages, are marked by horizons of high residual porosity or liquid fractions. These "porosity waves" can be formed as a dynamic response to changes in the density of the accumulating solid assemblage or in the rate of accumulation. The "porosity waves" represent zones of dilation of the crystal pile accumulated under lower permeability caps and are enriched in intercumulus minerals. Anorthositic and taxitic veins, typical of reefs containing PGE mineralization, are identical to the intercumulus paragenesis of the dunite–troctolite portion of the Dovyren massif, as shown by Kislov (1993), and represent dilational features. The noble metals are thought to have been concentrated in exsolved fluids, based on their fluid–basaltic liquid distribution coefficients (Gorbachev et al. 1993). These fluids subsequently redissolved in the undersaturated liquid in "porosity waves" associated with lithologic changes in the cumulus assemblage so as to yield discrete stratigraphic enrichments in the noble metals.

Conclusions

Based on the above discussion, we conclude that:

1. The gas distribution in the Dovyren layered pluton is dominated by methane and hydrogen, which are preserved within pores and micro-inclusions of the igneous rocks.
2. Gas distribution patterns in the Dovyren massif cross section clearly relate to the location of the PGE-bearing layers (reefs), suggesting the participation of reduced fluids (CH_4, H_2, CO, etc.) in the deposition of PGE.

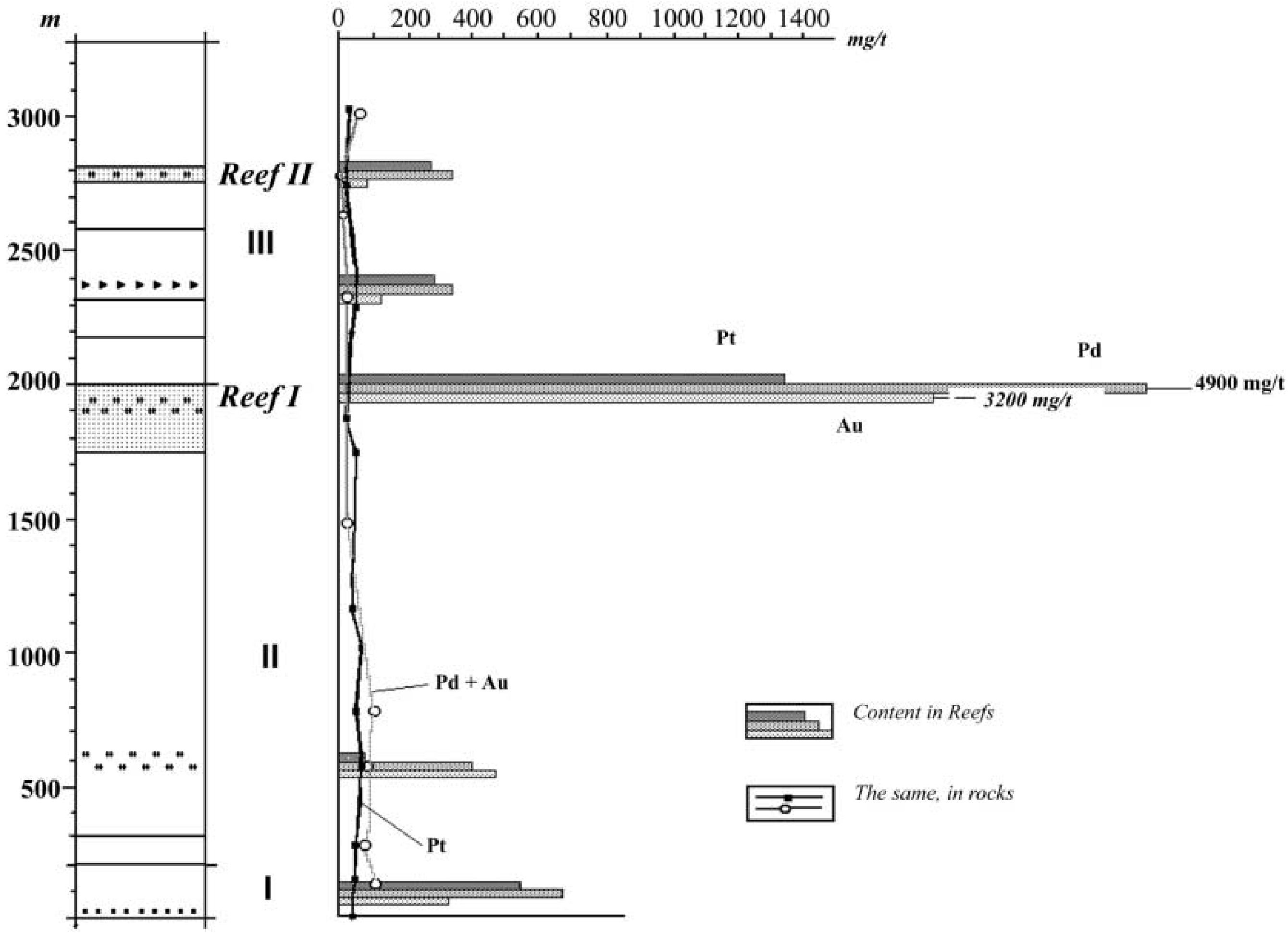

Fig. 3 Pt, Pd, and Au concentrations for a cross section of the Dovyren massif. I plagioclase-bearing lherzolite, II layered dunite–troctolite series, III layered olivine gabbro–gabbronorite series

3. We suggest the compaction mechanism for PGE concentration in layered mafic–ultramafic intrusions, as proposed by Meurer and Boudreu (1996), quite satisfactorily explains all the peculiarities in the distribution of the ''sparse sulfide type'' noble metal mineralization in the Dovyren massif.

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