

Simulation of Metamorphism and Fluid Regime in the Mineralized Unit of the Pana Massif in Relation to Its PGE Ore Mineralization

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Abstract—This paper presents materials on one of the units with PGE ore mineralization in the Pana Massif: the results of a detailed petrographic study and microprobe analyses of silicate and sulfide minerals and of the examination of mineral assemblages, typomorphic features of minerals, their crystallization succession and P – T conditions of this crystallization in the mineralized unit and the host mineralized and barren rocks, and the distribution of the fluid phase in them. Metamorphic processes that accompanied the development of the sulfide and PGE mineralization zones are analyzed, and it is established that the metamorphic evolution was associated with changes in the mineralogy of the rock and the composition of fluid in it. This process was of a unidirectional and systematic character and can be realistically reproduced in physicochemical models. The results of our research make it possible to assay the effect of P – T parameters and the fluid regime on the component composition of the solid phases and volatile components during the origin and localization of the PGE ore mineralization.

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INTRODUCTION

The possibility of applying theoretical models of natural systems with a fluid phase to studying homogeneous and heterogeneous natural systems was extensively discussed in the literature. In essence, this approach is underlain by the replacement of a naturally occurring object by a model that corresponds to the subsolidus of this object. The results of the physicochemical simulations are compared with known characteristics (properties) of the object, and their consistency testifies that the model is able to adequately reproduce the object. The complexity and diversity of the factors affecting natural processes that produce ore mineralization make it possible to theoretically analyze them on the basis of justified schemes for the mechanisms of these processes. Techniques of equilibrium thermodynamics that deal with the states of a system find wide application in the development of models for natural processes in papers by Helgeson and his colleagues [1–3], Karpov and his colleagues [4–6], Khodakovskiy [7], Shvarov [8], and many other researchers. The outcome of these studies was the development of several highly efficient computer programs for the direct physicochemical modeling of natural processes.

GEOLOGICAL OVERVIEW

The Fedorovo–Pana Tundra layered mafic intrusion in the central part of the Kola Peninsula belongs to the Early Proterozoic peridotite–pyroxenite–gabbro–gabbro–gabbro association [9]. The Pana Tundra layered massif is part of the Fedorovo–Pana intrusion. The latter is spatially restricted to the junction zone of two structures of different ages and is bounded by the Late Proterozoic Imandra–Varzuga volcano–sedimentary structure of the Kareliides in the south and the Archean Belye Tundra gneisses and alkaline granites in the north. The Fedorovo–Pana intrusion hosts one of the most significant PGE deposits in Russia with low-sulfide PGE ore mineralization [10].

This paper presents an analysis of the character and the role of metamorphic processes, including postmagmatic transformations, in the origin of zones of sulfide and PGE ore mineralization. This analysis is based on the data obtained on the mineral assemblages and typomorphic features of minerals in the ore-bearing unit and its host rocks and materials on the fluid phase and its distribution in one of the layered units.

Our research was focused mainly on the so-called lower layered unit (LLU) and the underlying barren rocks in the western part of the Pana Massif. The ore-bearing (mineralized) unit consists of cyclically alternating leuco- and mesocratic gabbro, gabbro–gabbro, and anorthosites with variable grain sizes and degrees

of alterations. All of these rocks compose layers that are grouped into the lower layered unit. Elevated contents of PGE were detected throughout the whole mineralized zone in bodies of lean Cu–Ni ores [11]. Although the PGE mineralization is distributed unevenly, the PGE contents within a single sulfide body vary insignificantly.

METAMORPHISM AND MINERAL ASSEMBLAGES OF THE MINERALIZED AND BARREN UNITS

The rocks of the lower layered unit are commonly significantly metamorphosed [12]. The evolution of these transformations manifests itself in the amphibolization, biotitization, clinozoisitization, and epidotization. Amphibolization is the most intense in the rocks of the mineralized units and, locally, in the host rocks. The weakly altered rocks occasionally contain well-preserved relics of primary magmatic and autometamorphic minerals and amphibole of the actinolite–tremolite series. The altered rocks commonly bear no primary magmatic minerals but have four amphibole generations. It should be mentioned that the mineralized rocks also contain relict earlier amphibole: cummingtonite (*Cum*).¹ The textural setting of cummingtonite suggests that it crystallized under conditions similar to autometamorphic.

As was mentioned above, the four varieties of colored amphibole occurring in the mineral assemblages are usually zonal and belong (in compliance with the systematics [13]) to Ca-amphibole with $(Ca + Na) > 1.34$ and $Na < 0.68$. According to their optical characteristics and textural relationships with associated minerals, the amphiboles were subdivided into a number of generations (phases). A pale green amphibole-1 (*Amph-1*) develops after pyroxene and is the earliest. The later light-green amphibole-2 (*Amph-2*) replaces the early amphibole-1, is paragenetic with clinozoisite, clinozoisite, and biotite, and occurs in associations typical of the assemblages of metabasites in the greenschist facies. The bluish-green amphibole-3 (*Amph-3*) is the youngest. It composes the outermost parts of zonal amphiboles 1 and 2 and occurs as individual elongated crystals that intersect earlier amphiboles. Amphibole-3 show paragenetic relations with clinozoisite, biotite, and epidote. Amphibole-4 (*Amph-4*) is optically close to amphibole-3, but differs from it in having somewhat richer green or bluish green colors and brighter interference colors. This amphibole occurs in close association with ore sulfides and with clinozoisite, cummingtonite, and epidote. The colorless amphiboles developing after orthopyroxene are cummingtonite or, more rarely, anthophyllite.

¹ Mineral symbols are used according to [14].

CRYSTALLIZATION SUCCESSION OF MINERALS AND THE THERMOBAROMETRY OF SILICATE SYSTEMS OF THE MINERALIZED AND BARREN UNITS

The thermobarometric calculations were conducted by the TWQ method, using the thermodynamic database [15, 16], which was appended with the thermodynamic properties of elementary Pt and Pd and their sulfides [17, 18]. This method is based on the computation of all chemical reactions that occur in a given homogeneous or heterogeneous system depending on the temperature and pressure. The TWQ method is able to identify all reactions that proceed in a system, and if the latter is characterized by an equilibrium, the method makes it possible to evaluate the P – T parameters of these reactions. The equilibrium conditions in the system are determined by the position of the intersection of the lines for the constants of chemical reactions (as functions of pressure and temperature) in a P – T plane. The calculation results are output into the monitor in a graphical form and as a table of calculated chemical reactions. The input data for the calculation of the P – T parameters are the chemical compositions (in the form of oxides) of the mineral phases occurring in a natural rock sample. The TWQ method enables the researcher to reliably determine the P – T parameters, which, in turn, makes it possible to construct the corresponding evolutionary metamorphic P – T paths.

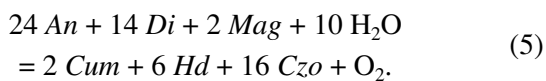
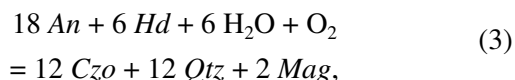
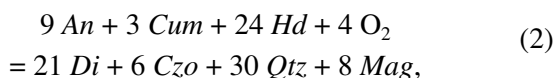
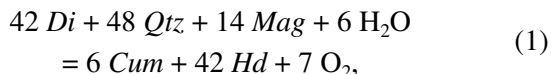
Our samples consisted of the following mineral assemblages: amphibolized leucocratic gabbro from the mineralized unit, $Pl_{69} - (Srp) - Soss - (\pm Cum) - Amph-1_{34} - Amph-2 - Amph-3_{46} - Amph-4_{49} - Bt_{36-38} - Chl_{33} - (Czo_{20}) - Ep_{21-24} - Ap - Qtz - FeS - FeS_2 - CuFeS_2 - Pt - Pd$. Amphibolized mesocratic gabbro from the underlying barren unit: $Pl_{60} - Amph-1_{25} - Amph-2_{33} - Bt_{36} - (Chl_{28}) - Ep_{30} - (Mag)$.

According to all available data (mineral assemblages, compositions of minerals, and the results of mineralogical thermometry), the thermodynamic conditions of metamorphism of the sample from the mineralized unit span a temperature range from the early autometamorphic transformations of the rocks (with Pl – Cum mineral assemblages) to the metamorphic transformations with early (Pl – $Amph-1$) and late (Pl – $Amph-2-4$) assemblages. The calculations conducted for this natural rock sample yielded the following equilibrium P – T parameters. The equilibrium conditions in the system at $T = 504^\circ\text{C}$ and $P = 5650$ bar correspond, in our opinion, to the autometamorphic transformations of the rocks. The postmagmatic processes related to early greenschist metamorphism occurred at $T = 390^\circ\text{C}$ and $P = 2200$ bar, and the later metamorphic transformations corresponding to the epidote-amphibolite facies (low-temperature amphibolite facies) took place at $T = 450^\circ\text{C}$ and $P = 5750$ bar. In a P – T plane, these calculated P – T pairs (Fig. 1) define the P – T path of the metamorphic evolution of the rocks

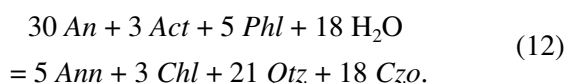
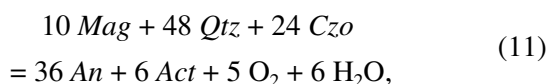
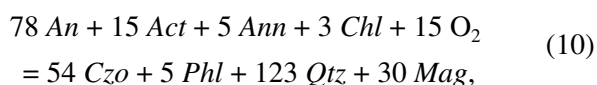
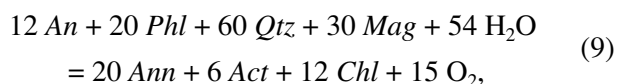
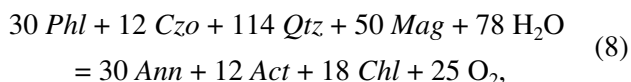
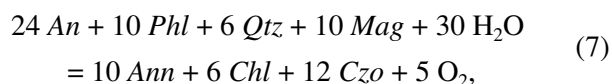
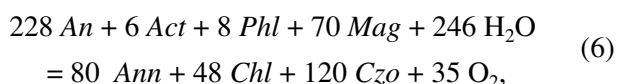
starting with their autometamorphism until the transformations of the epidote-amphibolite facies.

The equilibrium conditions in the systems were determined from the intersection points of the lines of the equilibrium constants of the following chemical reactions:

1. For the autometamorphic transformations:



2. For the conditions of metamorphism to the greenschist facies:



3. For the conditions of metamorphism to the epidote-amphibolite facies:

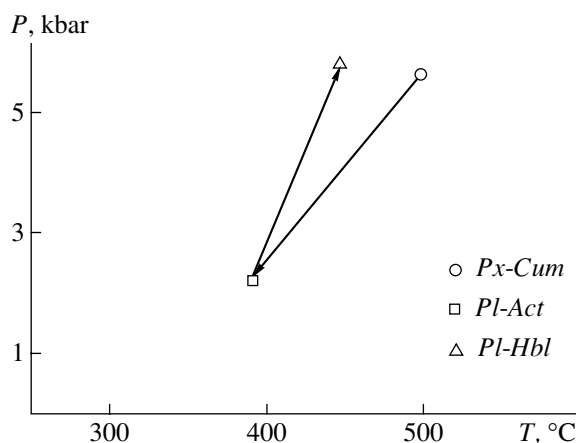
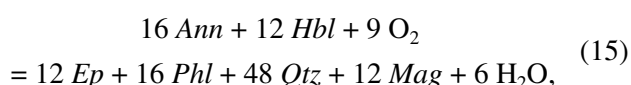
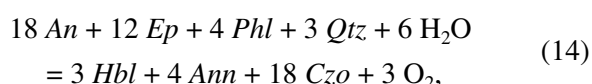
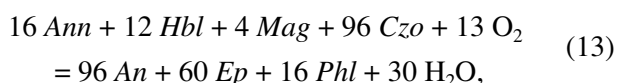
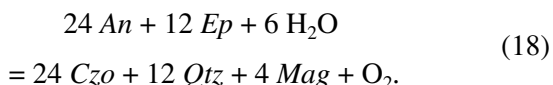
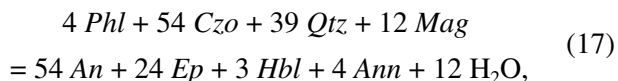
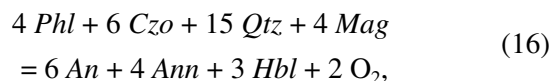


Fig. 1. Evolutionary trend of the metamorphic thermodynamic parameters.

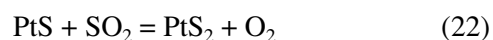
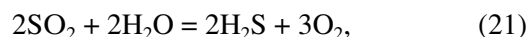
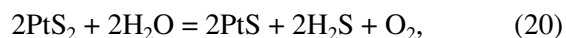


Figures 2a, 2b, and 2c present P - T diagrams for the equilibrium constants, in the form of the intersecting lines of the reactions.

THERMOBAROMETRY OF MODEL SULFIDE MULTISYSTEMS

1. Evaluated P - T Parameters for the Pt - S - H - O and Pd - S - H - O Systems

This study was centered on elucidating the conditions of the origin of the simplest model sulfide systems and the behavior of the components in them. We considered systems with PGE in the form of native elements and sulfides (Pt - S - H - O and Pd - S - H - O). The first model system included Pt , PtS , and PtS_2 (solid), plus gaseous SO_2 , H_2S , S_2 , O_2 , H_2 , and H_2O . The results of our study indicate that the lines of the equilibria of the chemical reactions



intersect at a point having the following coordinates: $T = 330.2^\circ\text{C}$ and $P = 6040$ bar (Fig. 3a). The second model system included Pd , PdS , PdS_2 , and gaseous components analogous to those of the first system. The

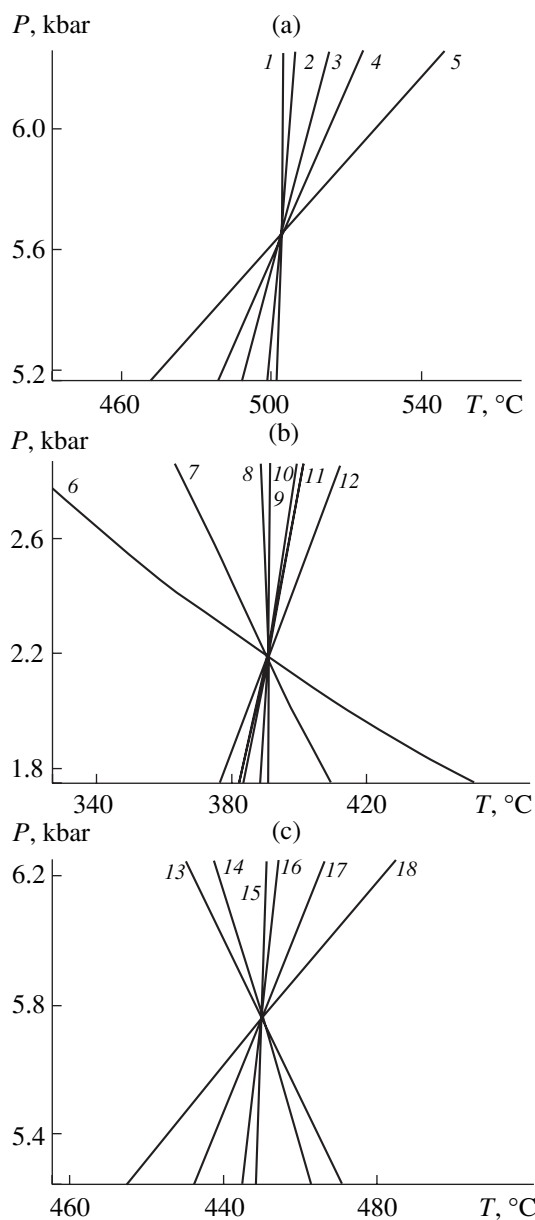
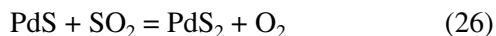
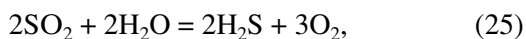
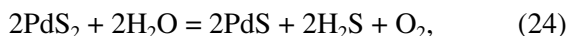
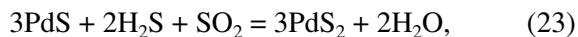


Fig. 2. Intersections of the lines of chemical reaction constants in P - T diagrams for (a) autometamorphism, (b) metamorphism to the greenschist facies, and (c) metamorphism to the epidote-amphibolite facies.

results of our simulations demonstrate that the lines of the equilibria of the chemical reactions



intersect at a point with lower P - T parameters ($T = 301^\circ\text{C}$ and $P = 300$ bar, Fig. 3b) compared to those of the Pt system.

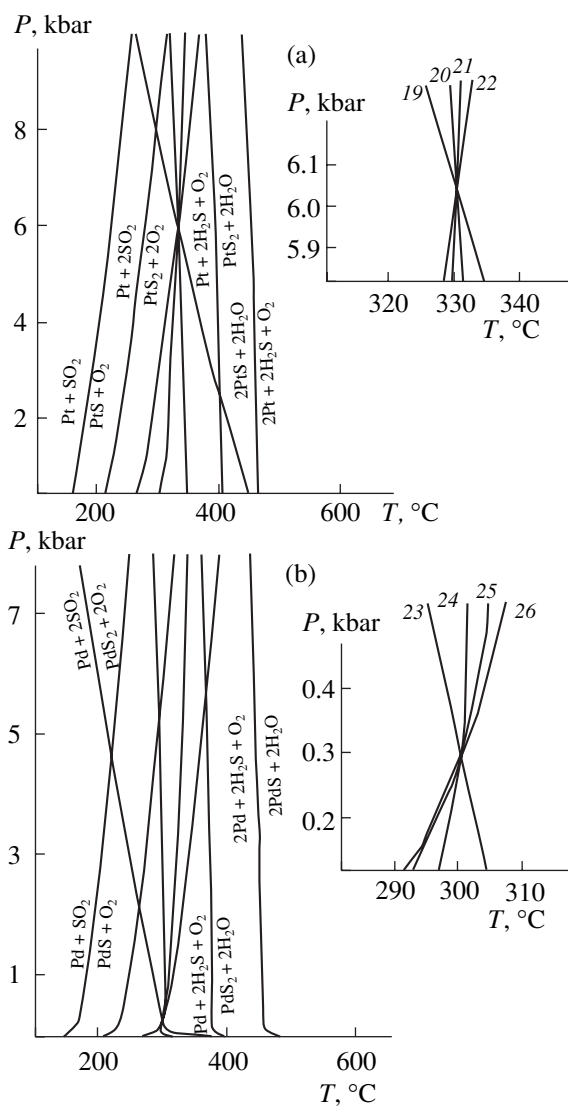


Fig. 3. Evaluated equilibrium parameters for the systems (a) Pt-S-H-O and (b) Pd-S-H-O (fragments) and the position of the P - T plane of chemical reactions occurring in the systems.

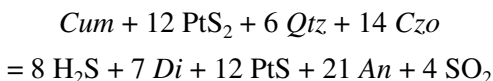
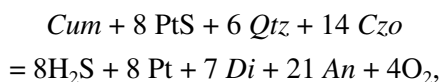
2. Evaluation of the P - T Parameters for More Complicated Model Systems

In order to make the composition of the Pt-S-H-O and Pd-S-H-O close to the composition of the natural objects, we complicated these systems by including corresponding silicate constituents compatible with the facies in question. The thermobarometric results indicate that these complicated systems are characterized by additional chemical reactions. As a result, we obtained additional sets of the intersection points of their equilibrium constants, along with the P - T metamorphic parameters previously determined for autometamorphism ($T = 504^\circ\text{C}$ and $P = 5650$ bar) and metamorphism of the greenschist ($T = 390^\circ\text{C}$ and $P = 2200$ bar) and epidote-amphibolite ($T = 450^\circ\text{C}$ and $P = 5750$ bar) facies. Some of these additional chemical

reactions are characterized by the participation of compounds with Pt and Pd. For example, below we quote some of these reactions.

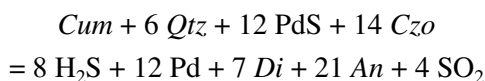
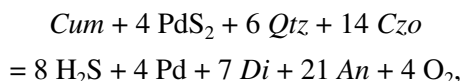
(1) For autometamorphism:

(a) Silicate–Pt system:



with additional P – T parameters of $T = 400^\circ\text{C}$, $P = 2800$ bar; $T = 455^\circ\text{C}$, $P = 4330$ bar; and $T = 523^\circ\text{C}$, $P = 6250$ bar.

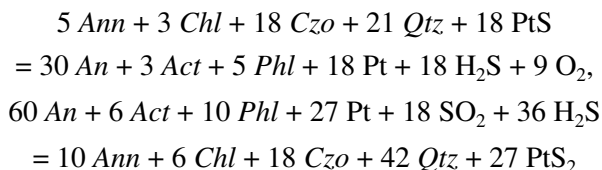
(b) Silicate–Pd system:



with additional P – T parameters of $T = 377^\circ\text{C}$, $P = 2150$ bar; $T = 447^\circ\text{C}$, $P = 4100$ bar; and $T = 470^\circ\text{C}$, $P = 4750$ bar.

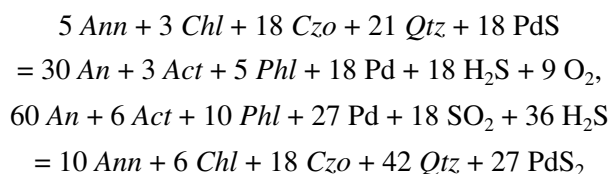
(2) For metamorphism to the greenschist facies

(a) Silicate–Pt system:



with additional P – T parameters of $T = 401^\circ\text{C}$, $P = 2510$ bar and $T = 520^\circ\text{C}$, $P = 6370$ bar.

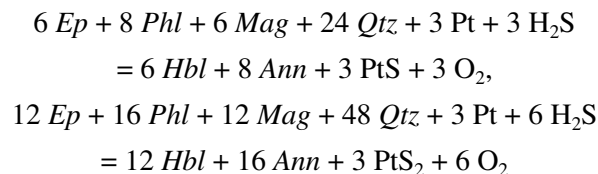
(b) Silicate–Pd system:



with additional P – T parameters of $T = 378^\circ\text{C}$, $P = 1780$ bar; $T = 447^\circ\text{C}$, $P = 3980$ bar; and $T = 470^\circ\text{C}$, $P = 4750$ bar.

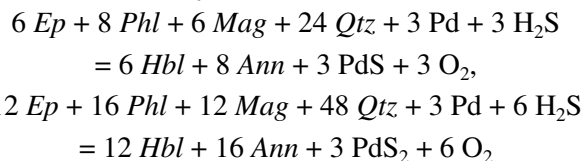
(3) For metamorphism to the epidote-amphibolite facies

(a) Silicate–Pt system:



with additional P – T parameters of $T = 450^\circ\text{C}$, $P = 5660$ bar.

(b) Silicate–Pd system:



with additional P – T parameters of $T = 446^\circ\text{C}$, $P = 4450$ bar.

When these values are analyzed, it should be mentioned that PGE typically affect the P – T parameters of the systems. The P – T parameters obtained for the PGE-bearing silicate systems (with both Pt and Pd) under autometamorphism and metamorphism to the greenschist facies are quite close. At the same time, we did not note an influence of PGE on the P – T parameters of metamorphism to the epidote-amphibolite facies. Evidently, the equilibrium conditions in the system containing, for example, compounds with Pt do not correspond to the equilibrium in the analogous system with Pd and vice versa, which should be reflected in their compositions. The results of the calculations (the formation of PGE sulfides) are in good agreement with the literature data for standard conditions [19].

EFFECT OF SULFUR CONCENTRATIONS AND THE P – T PARAMETERS ON THE COMPOSITION OF Pd, Pt, AND THEIR SULFIDES

The input data for the model calculations included the chemical composition of the rock that makes up the ore-bearing unit with PGE mineralization. The vector composition of the independent components of the multisystem was calculated by recalculating chemical analyses into mole concentrations in 1 kg of the rock. The model multisystem contained the following components (elements) Si–Al–Fe–Mg–Ca–Na–K–Cu–Ni–Pt–Pd–H–C–O–S. The calculated matrix of the multisystem consisted of 23 independent components (silicate, sulfide minerals, and chemical compounds) and a fluid phase, which included nine gaseous components: H_2O , H_2 , O_2 , CO , CO_2 , H_2S , SO_2 , S_2 , and CH_4 . The numerical simulations of the models were conducted by minimizing the free energies, using thermodynamic databases [4, 5], which were appended with thermodynamic characteristics for native Pt and Pd, their sulfides, and some amphiboles [17, 18, 20]. During the first stage, we evaluated the compositions of the solid phases and fluid in the course of the metamorphic evolution of the rocks from their autometamorphism to metamorphism to the epidote-amphibolite facies. The starting temperature and pressure assumed in the calculations were equal to the P – T parameters calculated by the TWQ method: $T = 504^\circ\text{C}$ and $P = 5650$ bar for autometamorphism, $T = 390^\circ\text{C}$ and $P = 2200$ bar for metamorphism to the greenschist facies, and $T = 450^\circ\text{C}$ and $P = 5750$ bar for metamorphism to the epidote-amphibolite facies (under the assumption of $P_{\text{tot}} = P_{\text{fl}}$).

The ore mineralization of the Panskie Tundry intrusion is low-sulfide. According to chemical analyses, the sulfur concentrations in our rock sample was 2.066 wt % (6.455×10^{-2} mol/kg), with this value showing local variations throughout the intrusion. Additionally, the Pd concentration in the sample assumed as original for our research was almost tenfold higher than the Pt concentration (the usual proportions of these elements are the opposite: Pt dominates over Pd). Because of this, we developed a series of models for multisystems in which the S concentrations were varied from 0.48 wt % (1.5×10^{-2} mol/kg) to 2.41 wt % (7.5×10^{-2} mol/kg). The models were examined in two variants: (i) the Pd concentration was higher than the Pt concentration (as in the original sample), and (ii) the Pt concentrations was tenfold higher than the Pd concentration. This enabled us to assay the effect of the S concentration on the crystallization succession and stability conditions for native Pd and Pt and their sulfides (for both of the variants) and for minerals with Ni, Cu, and Fe.

It is interesting to examine the changes in the concentrations of Pd, Pt, and their sulfides with increasing S concentration in the system. The behavior of these elements can be considered as a function of the metamorphic grade (at $T = 504^\circ\text{C}$, $P = 5650$ bar for autometamorphism; $T = 390^\circ\text{C}$, $P = 2200$ bar for metamorphism to the greenschist facies; and $T = 450^\circ\text{C}$, $P = 5750$ bar for metamorphism to the epidote-amphibolite facies). The results of the calculations are presented in (Figs. 4a–4f). The diagrams demonstrate typical successive transformation of native Pd and Pt into their sulfides with increasing S concentration in the system. Regardless of Pd and Pt concentrations, equilibria like $\text{Pd} \longleftrightarrow \text{PdS}$ and $\text{Pd} \longleftrightarrow \text{PdS}_2$, $\text{Pt} \longleftrightarrow \text{PtS}$ and $\text{Pt} \longleftrightarrow \text{PtS}_2$ correspond to certain S concentrations. Equilibria between native Pd and Pt and their sulfides significantly differ depending on the aforementioned metamorphic process. For example, the equilibria $\text{Pd} \longleftrightarrow \text{PdS}$ and $\text{Pt} \longleftrightarrow \text{PtS}$ occur at $[\text{S}] \approx 3.2 \times 10^{-2}$ mol/kg at autometamorphism, $[\text{S}] \approx 6.2 \times 10^{-2}$ mol/kg at metamorphism to the greenschist facies, and $[\text{S}] \approx 1.8 \times 10^{-2}$ mol/kg at metamorphism to the epidote-amphibolite facies. The equilibria $\text{Pd} \longleftrightarrow \text{PdS}_2$ and $\text{Pt} \longleftrightarrow \text{PtS}_2$ in the system differ depending on both the metamorphic grade and the S concentration. The reactions $\text{Pd} \longleftrightarrow \text{PdS}_2$ and $\text{Pt} \longleftrightarrow \text{PtS}_2$ occur at $[\text{S}] \approx 4.4 \times 10^{-2}$ and $[\text{S}] \approx 3.8 \times 10^{-2}$ mol/kg, respectively, at autometamorphism; $[\text{S}] \approx 7.4 \times 10^{-2}$ and 6.5×10^{-2} mol/kg at metamorphism to the greenschist facies; and $[\text{S}] \approx 3.0 \times 10^{-2}$ and 2.4×10^{-2} mol/kg at metamorphism to the epidote-amphibolite facies. Such equilibria as $\text{PdS} \longleftrightarrow \text{PdS}_2$ and $\text{PtS} \longleftrightarrow \text{PtS}_2$ were detected only at the metamorphism to the epidote-amphibolite facies at $[\text{S}] \approx 7.4 \times 10^{-2}$ and $\approx 3.3 \times 10^{-2}$ mol/kg, respectively.

The results of our theoretical research indicate that various metamorphic facies are characterized by the redistribution of native Pt and Pd and their sulfides. Proceeding from the S concentration in the natural sample (2.066 wt %), we obtained the following changes: PdS, PdS₂, PtS₂, and PtS (listed in order of decreasing amounts) for autometamorphism; PdS, Pd, PtS, and Pt for metamorphism to the greenschist facies; and PdS, PdS₂, PtS₂, and PtS for metamorphism to the epidote-amphibolite facies. The results obtained for the second variant (with Pt dominating over Pd) were somewhat different: PtS₂, PtS, PdS, and PdS₂ for autometamorphism; PtS, Pt, PdS, and Pd for metamorphism to the greenschist facies; and PtS₂, PtS, PdS, and PdS₂ for metamorphism to the epidote-amphibolite facies. It should be mentioned that the fluid composition and silicate components of both variants turned out to be practically identical (Tables 1, 2).

The results described above indicate that PGE typically occur in low-temperature greenschist facies (at a constant S concentration) as native Pt and Pd and their sulfides, but not disulfides, whose origin under these conditions requires higher S concentrations.

Cu, Ni, AND Fe SULFIDES OF ROCKS WITH PGE MINERALIZATION AND FLUID REGIME

Physicochemical (thermodynamic) simulations of equilibria in natural systems make it possible to study mineral assemblages depending on temperature and pressure and to determine the composition of the fluid phase in equilibrium with the silicate and sulfide phases. This approach enabled us to assay the effects of external factors and the fluid phase on the mineral assemblages. A fluid phase always participates in natural metamorphic processes, and its composition depends on the composition of the system and its equilibrium conditions. This phase plays a determining role in mineral-forming processes, affects the mineral assemblages, and the processes of forming rocks and ores. During this research, we used some possibilities offered by theoretical studies in analyzing our models for metamorphic processes. A mathematical model for such a system can be regarded as accurate enough for a quantitative and qualitative assessment of the gases in equilibria with minerals during metamorphism.

Variations in the P – T parameters in a natural system and the crystallization of minerals in it affect the composition of the fluid. The analysis of the quantitative and qualitative composition of fluid components in the system at temperatures corresponding to the early and late metamorphic episodes yield the composition of the fluid during the onset of postmagmatic alterations. The metamorphic process was responsible for the changes in the concentrations of fluid components (H_2O , H_2S , SO_2 , H_2 , CH_4 , and others). The results of our calcula-

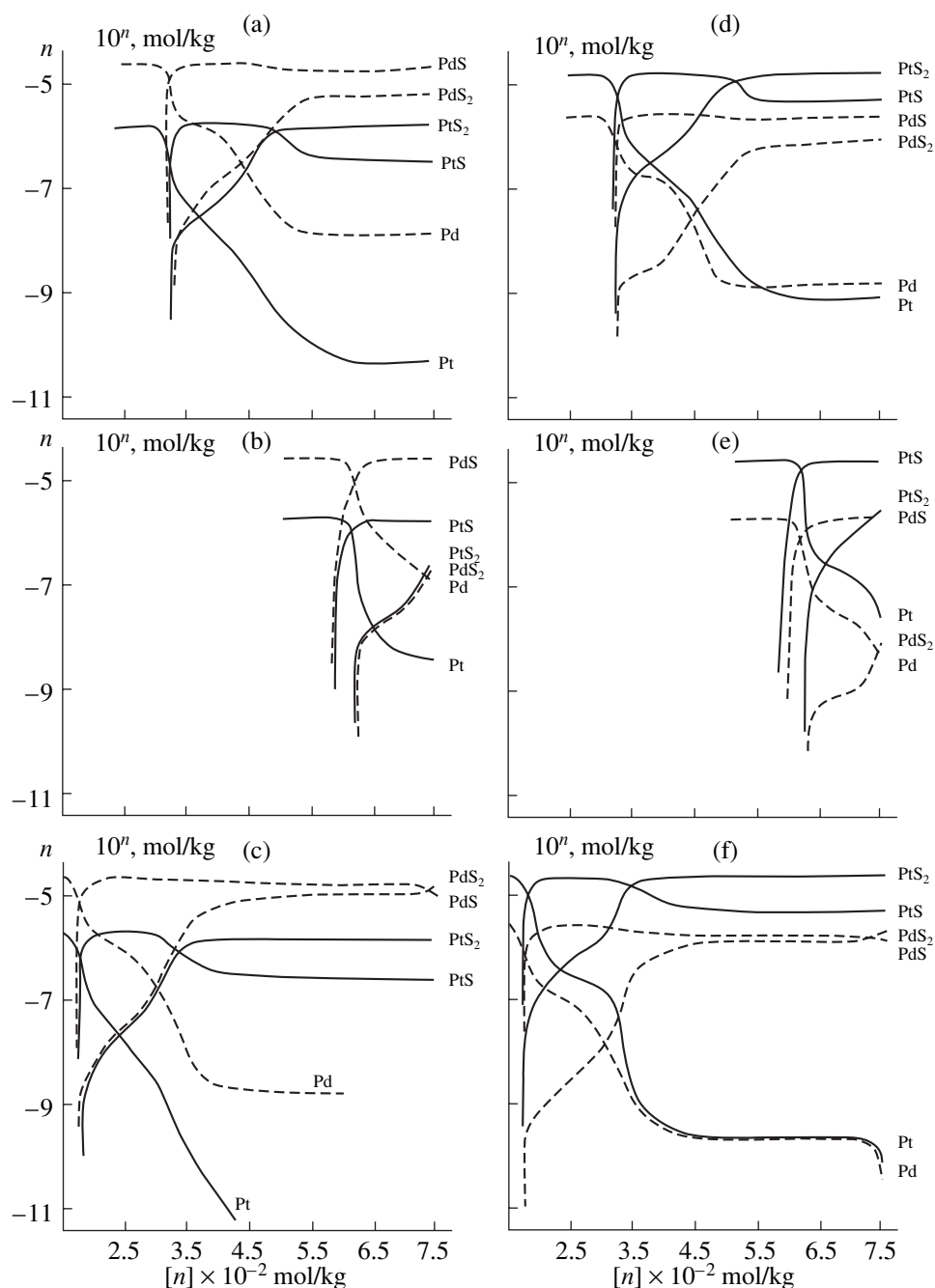


Fig. 4. Variations in the composition of native Pt and Pd and their sulfides depending on S concentration at Pd > Pt for (a) autometamorphism, (b) metamorphism to the greenschist facies, and (c) metamorphism to the epidote-amphibolite facies; and at Pd < Pt for (d) autometamorphism, (e) metamorphism to the greenschist facies, and (f) metamorphism to the epidote-amphibolite facies.

tions indicate that the concentrations of these components reached maxima during autometamorphism. The subsequent transition to the early and late metamorphic stages was associated with changes in the P - T conditions and the composition of the fluid and with insignificant changes in the redox conditions (Table 2). The calculation results suggest that the fluid composition was in equilibrium with the chemical and mineralogical compositions of the rocks within the temperature range

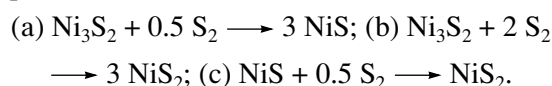
of 390–504°C. This temperature range is believed to correspond to the onset of metamorphic alterations (the appearance of actinolite and hornblende).

The results obtained for the behavior of S-bearing fluid components and Cu, Ni, and Fe sulfides, depending on the S concentration in the multisystem, are presented in Fig. 5. The lines in the diagram clearly illustrate the characteristic variations in the concentrations of S-bearing components in the system. Chalcosine

Table 1. Calculated compositions (wt %) of minerals in various metamorphic facies

Mineral	Metamorphic facies		
	autometamorphism	greenschist facies	epidote-amphibole facies
Ab	21.76	22.15	21.39
An	51.43	32.58	25.93
Di	12.07	–	–
Hd	6.09	–	–
Cum	0.26	–	–
Act	–	18.41	–
Ann	–	tr.	tr.
Phl	–	3.76	3.63
Hbl	–	–	6.02
Ep	–	–	37.1
Chl	–	3.79	–
Czo	–	17.06	–
Qtz	0.16	0.10	1.87
Mag	4.76	–	0.20
Cu ₅ FeS ₄	1.41	–	1.39
CuFeS ₂	tr.	–	–
FeS	–	–	–
FeS ₂	0.75	–	1.10
NiS	0.01	0.30	tr.
NiS ₂	1.36	0.17	1.34
Ni ₃ S ₂	tr.	0.53	tr.
Cu ₂ S	–	1.14	–

(Cu₂S), heazlewoodite (Ni₃S₂), and millerite (NiS) are the first minerals to appear in the system. The S-bearing fluid contains SO₂, H₂S, and S₂. As can be seen in the diagram, the conditions under which they are formed variously depend on the S concentration in the system and on the metamorphic grade. At the same time, variations in their concentrations in the system depending on the S concentration are virtually identical. These S-bearing components start to appear in the system during metamorphism (greenschist facies) at a higher S concentration in the system. As the S concentration in the system increases, Cu₂S, Ni₃S₂, and NiS gradually disappear from the system and give way to vaesite (NiS₂), bornite (Cu₅FeS₄), and pyrite (FeS₂), with a subsequent transformation of bornite into covellite (CuS) and pyrite. The transformation succession of S-bearing N compounds is as follows:



These transformations of Ni sulfides are thermodynamically justified by the chemical reactions. Comparing the sulfides occurring in the facies in question, one should note the following transformations that take place by increasing S concentration in the system:

(1) Cu-bearing components: Cu₂S → Cu₅FeS₄ (autometamorphism); Cu₂S (greenschist facies); Cu₂S → Cu₅FeS₄ → CuS (epidote-amphibolite facies);

(2) Fe-bearing components: Fe₃O₄ ↔ FeS₂ (autometamorphism); Cu₅FeS₄, FeS₂ (epidote-amphibolite facies);

Table 2. Calculated concentrations of Pt and Pd and the composition of fluid in various metamorphic facies

Mineral	Metamorphic facies		
	autometamorphism	greenschist facies	epidote-amphibole facies
<i>Concentration, mol/kg</i>			
Pt	7.4×10^{-11}	2.8×10^{-8}	1.67×10^{-11}
PtS	5.6×10^{-7}	2.2×10^{-6}	3.84×10^{-7}
PtS ₂	1.7×10^{-6}	1.6×10^{-8}	1.9×10^{-6}
Pd	8.7×10^{-9}	1.4×10^{-6}	3.0×10^{-9}
PdS	3.1×10^{-5}	3.9×10^{-5}	2.9×10^{-5}
PdS ₂	8.8×10^{-6}	1.3×10^{-8}	1.1×10^{-5}
<i>Partial pressure (fugacity) of components (atm)</i>			
H ₂	8.49×10^{-4} (3.27×10^{-3})	1.46×10^{-7} (2.81×10^{-7})	1.42×10^{-4} (6.28×10^{-4})
H ₂ O	4.21×10^3 (1.92×10^3)	1.83×10^2 (3.38×10^1)	3.36×10^3 (1.21×10^3)
H ₂ S	6.01×10^{-1} (3.76×10^0)	3.83×10^{-7} (5.04×10^{-7})	2.18×10^{-1} (1.52×10^0)
O ₂	1.61×10^{-17} (9.91×10^{-17})	4.11×10^{-18} (8.85×10^{-18})	5.01×10^{-19} (3.67×10^{-18})
SO ₂	1.25×10^3 (1.32×10^4)	1.92×10^3 (2.63×10^3)	1.96×10^3 (2.42×10^4)
CO	3.80×10^{-5} (3.80×10^{-4})	4.16×10^{-8} (1.14×10^{-7})	2.00×10^{-5} (2.48×10^{-4})
CO ₂	1.36×10^2 (1.07×10^3)	1.01×10^2 (1.79×10^2)	3.84×10^2 (3.54×10^3)
CH ₄	5.29×10^{-14} (5.95×10^{-13})	8.52×10^{-25} (2.30×10^{-24})	4.05×10^{-15} (5.61×10^{-14})
S ₂	4.00×10^{-2} (1.90×10^{-1})	2.22×10^{-9} (4.02×10^{-9})	2.00×10^{-2} (1.07×10^{-1})

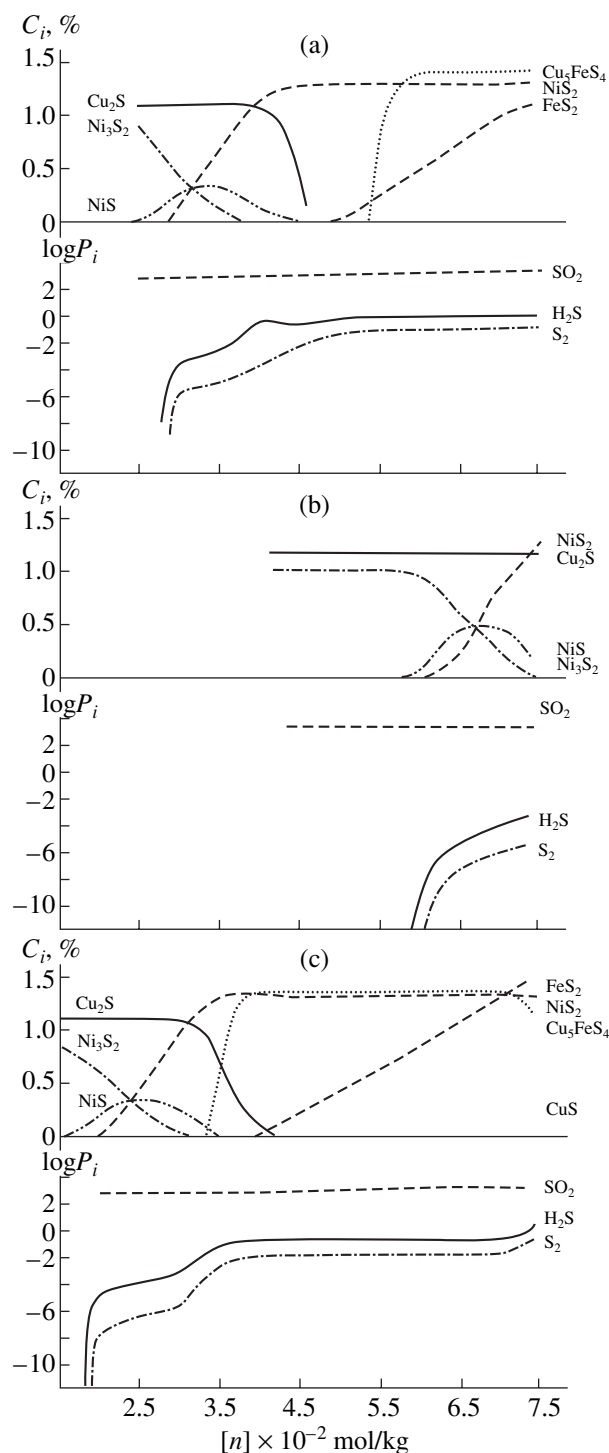


Fig. 5. behavior of Cu, Ni, and Fe sulfides and S-bearing fluid components depending on S concentration for (a) autometamorphism, (b) metamorphism to the greenschist facies, and (c) metamorphism to the epidote-amphibolite facies.

(3) Ni-bearing components: $\text{Ni}_3\text{S}_2 \rightarrow \text{NiS}$ (greenschist facies); $\text{Ni}_3\text{S}_2 \rightarrow \text{NiS} \rightarrow \text{NiS}_2$ (autometamorphism and epidote-amphibolite facies).

There are good reasons to believe that the compositions (associations) of Cu, Ni, and Fe sulfides play a determining role in controlling the main modes of PGE occurrence.

The variations in the redox conditions during metamorphism also affected the composition of the fluid phase during the crystallization of the barren rock. The fluid phase was also subject to quantitative and qualitative changes. The high-temperature fluid had reduced characteristics and became more oxidized with decreasing temperature.

CONCLUSIONS

The rocks of the lower layered unit are metamorphosed to the epidote-amphibolite facies. These rocks display traces of older autometamorphic transformations of rocks with pyroxene-cummingtonite mineral assemblages and their metamorphism to the greenschist metamorphic facies with plagioclase-actinolite mineral assemblages.

The analysis and comparison of the results of the theoretical calculations and the data of petrographic observations are used to test the accuracy and adequacy of the selected scheme and, thus, enables us to identify the major factors controlling the characteristics of the object. The determined character of the evolution of the silicate mineral assemblages in the multisystems is consistent with the observations. The fluid regime of the postmagmatic transformations was controlled by the temperature: the fluid was more oxidized during autometamorphism than during lower temperature alterations (regional metamorphism).

The mineral-forming processes in the mineralized units proceeded with the participation of predominantly $\text{H}_2\text{O}-\text{CO}_2$ fluid, with significant SO_2 concentrations. The composition of the fluid was a determining factor of the transformations of the PGE-bearing sulfide ores. The S concentration in the natural system controlled the origin of S-bearing compounds with Pt, Pd, Ni, Cu, and Fe during metamorphism, and the compositions of these compounds could be crucial for identifying the modes in which PGE occur in the rocks.

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