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Formation of Intergrowths of Platinum-Group Minerals and Gold from Magmatogenic Ores in Relation to Phase Changes in Pt-Pd-Fe-Cu-Au System

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Abstract: The article discusses the features of the chemical composition and the formation of intergrowths of platinum-group minerals, gold, gold-bearing phases, and other ore minerals present in placers collected from the Anabar River in the northeast part of the Siberian platform. Based on an analysis of changes in the phase compositions of these intergrowths of noble metals with other ore minerals on (Pt, Pd)-Fe-Au and Pd-Cu-Au phase equilibrium diagrams, potential trends in the crystallization of natural polymineral alloys from multicomponent low-sulfide metallic liquids are discussed. The similarity of the microstructures of natural and metallurgical alloys indicates that the formation of natural multiphase Au-PGE intergrowths occurred in a similar manner to the crystallization of multicomponent synthetic alloys. The authors suggest that magmatic Au-PGE mineralization occurs during the crystallization of a noble-metal-containing, low-sulfide, Cr-rich oxide melt separated from silicate mafic–ultramafic magma. Magmatic gold–platinum deposits are commonly associated with sulfide or oxide disseminated-schlieren ores in layered mafic–ultramafic intrusions. However, due to the high solubility of gold and platinoids in sulfide minerals, PGMs in sulfide ores occur as isomorphic impurities or as microphases and dispersed inclusions that cannot form placers. Therefore, the authors suggest that magmatic Au-PGE mineralization occurs during the crystallization of an immiscible low-sulfide, high-Cr oxide liquid separated from silicate mafic–ultramafic magma. In the northeast part of the Siberian platform, potential sources for these placers are likely alkaline, high-Ti mafic–ultramafic intrusions, as confirmed by the presence of silicate inclusions in ferroan platinum similar in composition to melteigite.

Keywords: platinum-group minerals; gold; phase diagrams; alkaline mafic rocks; Anabar shield; Siberian platform

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1. Introduction

In the northeast part of the Siberian platform, complex diamond-bearing placers have been known to contain significant quantities of associated noble metals, such as gold and platinum-group minerals (PGMs). These placers are recognized over vast territories (Figure 1) of the Lena–Anabar interfluve [1–6]; however, uncertainty remains about their sources. In [7], we examined the typomorphic features of palladium gold (porpezite) and ferroan platinum, which form intergrowths, thus indicating their evident genetic relationship. This approach can be applied to delineate the sources of valuable components of complex placers by their genetic types. It is known that gold–platinum placers are usually associated with large, layered mafic–ultramafic massifs containing chromitite or titanomagnetite oxide ores. At the same time, even unique sulfide deposits with high contents of PGE and gold are devoid of such placers due to the high solubility of noble metals in sulfide minerals, which does not lead to the release of large, placer-forming grains of gold and platinum.

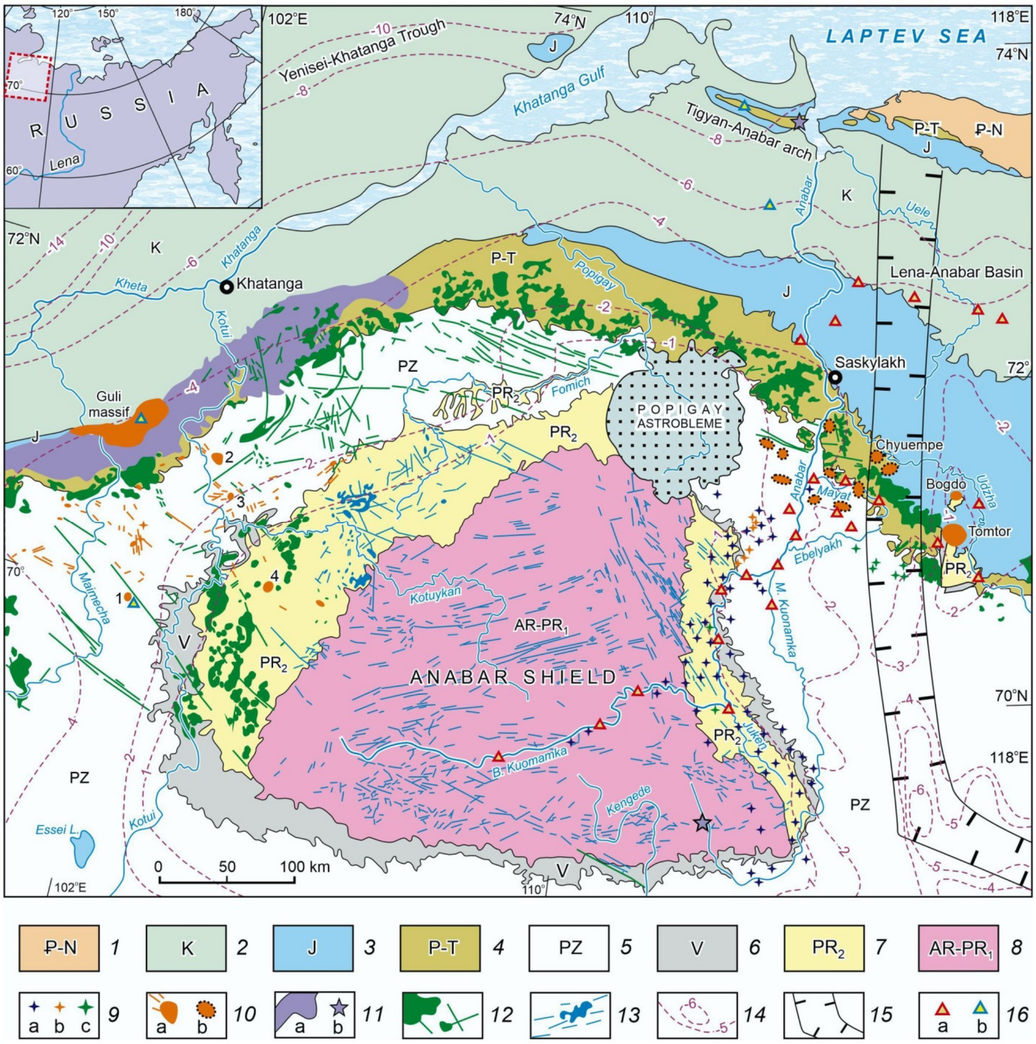

Figure 1. Locations of gold–platinum-bearing placers in the northeastern Siberian platform. 1—Paleogene–Neogene sediments; 2—Cretaceous sands, silts, and gravels; 3—Jurassic conglomerates, sandstones, and siltstones; 4—Permian–Triassic sandstones and siltstones; 5—Paleozoic dolomites, limestones, marlstones, and sandstones; 6—Vendian sandstones, argillite, conglomerates, dolomites, and limestones; 7—Meso-Neoproterozoic (Riphean) conglomerates, sandstones, siltstones, argillite, and dolomites; 8—Archean–Paleoproterozoic metamorphic complexes; 9—kimberlite (a), carbonatite (b), and basite pipes (c); 10—intrusions and dykes of alkaline ultramafic rocks with carbonatites (a—those exposed at the surface (Guli, Tomtor, Bogdo, and Bor-Uryakh (1), Odikhincha (2), Kugda (3), Magan (4), massifs, etc.) and b—those interpreted from geophysical data (Chuempe [8], etc. [9])); 11—effusive basalts and alkaline basaltoids of the Maimecha–Kotui Province (a), and picrite–basalt rocks in the estuary of the Anabar River and meimechite dykes in the upper reaches of the Malaya Kuonamka River (b); 12—Permian–Triassic sills and dykes of the Siberian Trap LIP; 13—Late Precambrian dyke swarms; 14—isolines of the basement surface (-n km); 15—boundaries of paleorift structures; 16—gold–platinum-bearing placers with Fe-Pt (a) and Ir-Os minerals (b). The background map is based on a geological map of the Siberian platform [10] and a geodynamic map of Yakutia [11], with some changes and additions by the authors.

In this article, the authors offer a more detailed assessment of the origin of these placers by studying the features of intergrowths of native alloys of PGM and gold with the use of phase diagrams of multicomponent metal alloys that are applied in materials science and metallurgy. The legitimacy of such a comparative study of the physicochemical conditions for the formation of native, multiphase Au-PGE intergrowths with artificial alloys is proven by the similarity in the microstructures of the natural and metallurgical alloys. This is due to the fact that magmatic Au-PGE mineralization began to develop in the early magmatic stage as a result of the separation of immiscible, low-sulfide metallic liquid from a silicate melt. The further evolution of these immiscible silicate and ore liquids occurs in a high-temperature closed magma chamber, along with the possible genesis of PGE–chromitite mineralization in mafic–ultramafic intrusive rocks, as previously studied [12,13].

In the process of crystallizing magma within the intrusive chamber, the ore components of the magma were concentrated in the residual melt; after the consolidation of the intrusive chamber, some of the most mobile ore elements in the composition of aqueous salt solutions could be separated from the parent rocks and form remote types of hydrothermal ores. This may occur similarly to the mechanism for the formation of gold deposits associated with granitoid intrusions, i.e., intrusion-related gold systems (IRGSs), which form a wide range of deposits from deep IOCG-type deposits with Fe, Cu, Au, U, Ce, and La to near-surface epithermal Au, Ag, Cu, As, Sb, Hg, and Te cross-cutting ores [14].

2. Materials and Methods

The methods of collecting samples containing gold and platinum from placers of the Anabar River basin were described in our previous article [7], with their location shown in Figure 1. Gold and PGMs were studied in concentrates of heavy minerals obtained from dumps during the mining of diamond-bearing placers of the Mayat, Ebelyakh, Khara-Mas, and other rivers, where large (up to 3–8 mm in size) grains of precious metals and their intergrowths are often found. In addition, concentrates of panning samples with a volume of up to 1–2 m^3 from alluvial sediments of watercourses in the basins of the Anabar, Udzha, Bolshaya Kuonamka, and Malaya Kuonamka rivers were studied. Among the more than 500 grains studied, several dozen particles were discovered consisting of intergrowths of PGM with palladium gold and other Au-containing minerals. Such intergrowths undoubtedly carry important information about the physicochemical conditions of their formation, i.e., these minerals are possible indicators for predicting parent ore-magmatic systems. In the northeastern part of the Siberian platform, there are widely developed basites of Precambrian, Middle Paleozoic, and Permian–Triassic ages, Paleozoic and Mesozoic kimberlites and carbonatites, as well as compound complexes of alkaline ultrabasic rocks with carbonatites and occurrences of alkaline picrobasalts [15–23]. Products of Phanerozoic granitoid magmatism have not been found here, so we suggest the relationship of gold and platinum with mantle-derived mafic–ultramafic rocks, potentially belonging to large igneous provinces [24].

When discussing a model for formation of polymineral natural alloys, many researchers turn to the phase-equilibrium diagram of multicomponent systems. The evolution of phase transformations of the multicomponent alloys can be most distinctly demonstrated in the triangular diagrams, some of which were studied earlier [8,9]. The phase diagrams of binary and ternary metallic systems used in this work were taken from handbooks [25–33]. Since intergrowths of Au-bearing minerals and high-Pd ferroan platinum are most common in placers of the Anabar River basin, we consider them in relation to the (Pt, Pd)-Fe-Au and Pd-Cu-Au diagrams. Unfortunately, at the present time, such diagrams have been made only for a limited group of elements involving PGE. Therefore, for the ternary Pt-Fe-Au diagram, the liquidus surface isotherms are schematically drawn by the authors using the method of graphically projecting the liquidus lines of binary systems. To construct ternary phase diagrams based on data from two-component systems, we followed the basic rules according to the works [34–36]. Combined ternary and binary diagrams provide an opportunity to monitor the entire course of crystallization of multicomponent metal systems. Comparison of the chemistry and phase composition of natural polymineral aggregates with metallurgical alloys in these diagrams provides favorable convergence. The microstructures of PGM intergrowths from mafic–ultramafic ores and associated placers correspond to the structures of eutectic, peritectic, and monotectic artificial alloys [34–37].

The composition and microstructure of the minerals were studied on a JSM-6480LV (JEOL—Tokyo, Japan) scanning microscope in DPMGI SB RAS; analysts: N. V. Khristoforova, S. A. Karpova. The surveys were conducted under the following conditions: accelerating voltage 20 kV; probe current 1.09 nA; measurement time 25 s; analytical lines: Au—Mα, Ag—Lα, other elements—Kα. Standardized minerals, pure metals, and their alloys were used as standards.

3. Forms of Intergrowths of PGM and Gold, Their Interpretation on Triangular Diagrams of the Phase State

Early in their article [7], the authors provided a mineralogical description of the association of platinum and palladium gold from placers of the Anabar River basin; it was shown that these noble metals develop magmatic paragenesis of minerals associated with complexes of alkaline ultramafic–mafic intrusions. Here, based on the characteristics of the chemical composition, as well as morphological and microstructural forms of intergrowth of PGM and gold, we try to test their interpretation regarding the origin of these minerals at the high-temperature magmatic stage of the formation of mafic intrusions.

In placers of the northeastern Siberian platform, ferroan platinum is major mineral that contains inclusions of other PGMs, gold, and various sulfides, arsenides, tellurides, etc. (Figure 2). In this regard, we will begin the consideration of possible pathways of phase transformations of such multicomponent alloys on a ternary (Pt, Pd)-Fe-Au diagram with expanded binary systems. Due to the large number of system components, elements with similar physicochemical properties are combined into one isomorphous component. For example, platinum and palladium, which form a continuous solid solution with each other and form similar intermediate compounds with iron, are placed together in the ternary diagram of (Pt, Pd)-Fe-Au (Figure 3).

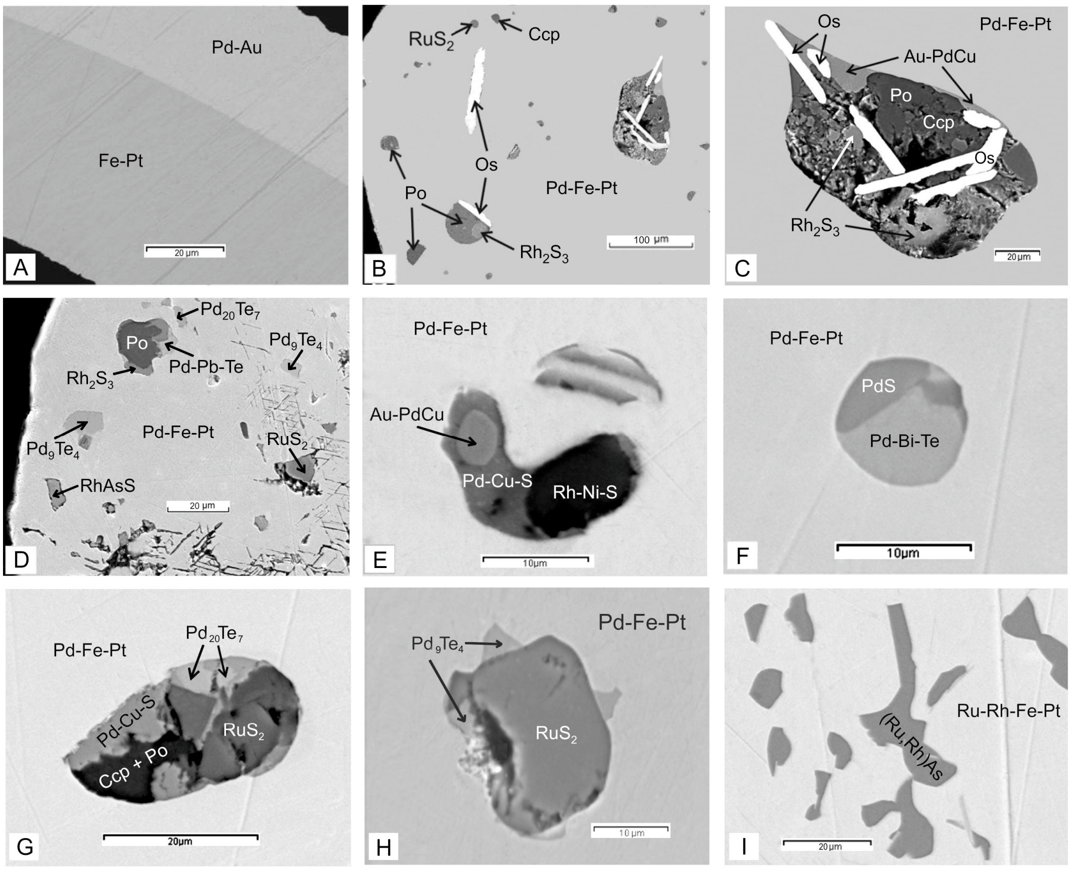

Figure 2. Forms of intergrowths of ferroan platinum and PGM from the Anabar River basin placers: (**A**)—intergrowth of palladium gold (Pd-Au) and ferroan platinum (Fe-Pt), sample VP-1, Bolshaya Kuonamka River; (**B**,**C**)—habit and mineral composition of inclusions in ferroan platinum: sample 18-157, Mayat R. ((**B**)—general view and (**C**)—details of polyphase inclusion); (**D**) sample 7-157, Mayat R.;

(**E**) sample 13-157, Mayat R.; (**F**) sample 23-36, Bolshaya Kuonamka R.; (**G**) sample 23-76, Bolshaya Kuonamka R.; (**H**) sample 12-156, Mayat R. and (**I**) sample 85-157, Mayat R. Minerals: Pd-Fe-Pt and Ru-Rh-Fe-Pt—ferroan platinum with high contents of Pd and Ru-Rh, respectively; Os—osmium; RuS_2—laurite; Rh_2S_3—bowieite; Ccp—chalcopyrite; Po—pyrrhotite; Au-PdCu—Au-bearing skaergaardite; RhAsS—hollingwordite; $Pd_{20}Te_7$—keithoconnite; Pd_9Te_4—telluropalladinite; Pd-Pb-Te—palladium–lead telluride; Pd-Cu-S—basilite; Rh-Ni-S—torryweiserite; PdS—vysotskite; Pd-Bi-Te—palladium–bismuth telluride and (Rh,Ru)As—rhodium–ruthenarsenite.

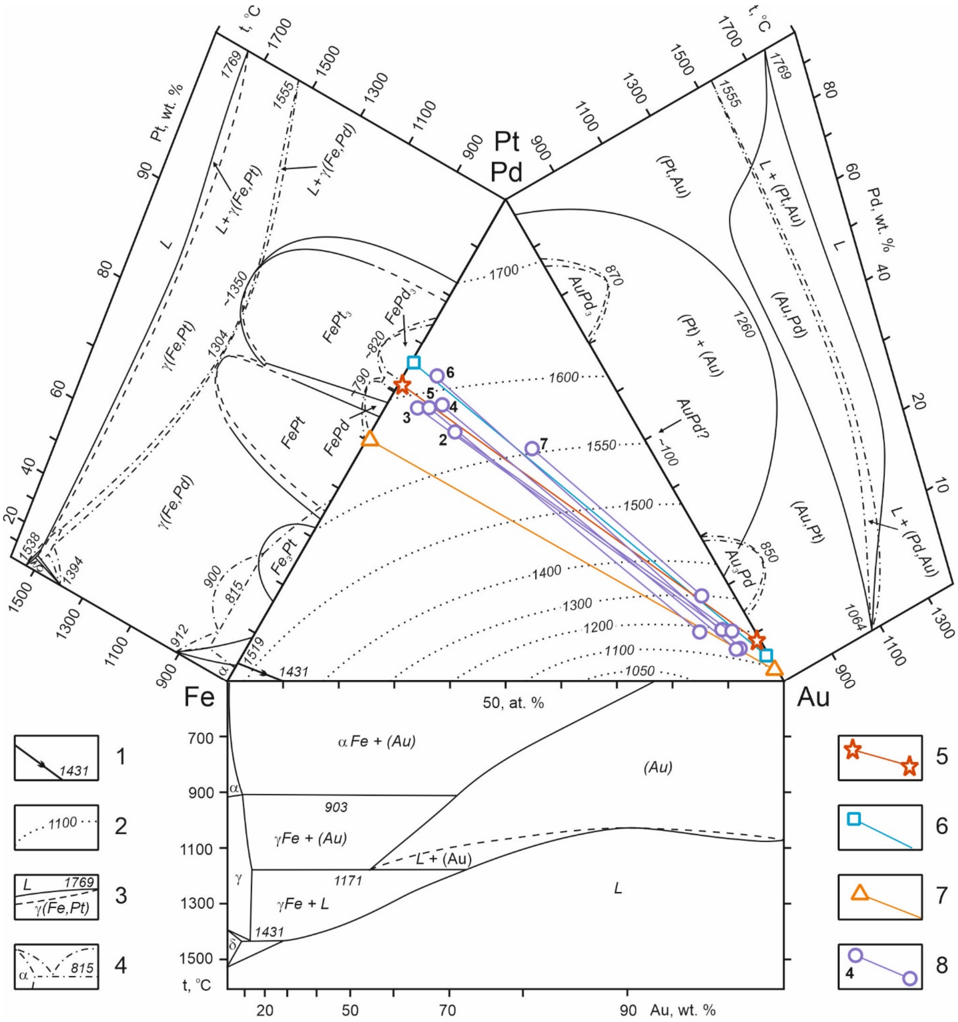

Figure 3. Compositions of coexisting intergrowths of Fe-Pt alloys and palladium gold on the ternary diagram of (Pt,Pd)-Fe-Au with binary systems. 1—cotectic lines; 2—liquidus surface isotherms; 3—phase boundaries; 4—boundaries of solvus changes; 5–8—compositions of coexisting phases from the Bolshaya Kuonamka River placer (5), Konder placer (6) by [38], sulfide ores of the Norilsk deposit (7) by [39], and according to experimental studies (8) on the melting of sulfide–metal alloys (4—fractionation zone number) by [40].

This diagram demonstrates that the coexisting intergrowths of ferroan platinum and palladium gold could be formed during the decomposition of a high-temperature Pt-Au solid solution with impurities of Fe and Pd (Table 1). In the Pt-Au binary system, at high temperatures close to the solidus, platinum and gold form a continuous solid solution; however, with a slight decrease in temperature (1252 °C), a gap in their miscibility is observed. The solubility of Au in platinum at 1000 °C is 18 at. %, at 100 °C it is 5 at. % Au, and the solubility of Pt in gold is 33 at. % and 25 at. % Pt, respectively [28].

Table 1. Representative analyses of mineral intergrowths from placers of the Anabar River basin, wt. %.

Sample	Mineral	Pt	Ir	Os	Ru	Rh	Pd	Fe	Ni	Cu	Au, Pb, Bi	Te	S	As	Total
18-157	Pd-Fe-Pt	81.23				1.03	4.46	10.32	0.35	1.24					98.63
	Os-Ir-Ru	0.21	10.03	79.55	10.14										99.93
	Os-Ir-Ru		6.29	81.53	11.42										99.24
	RuS_2				61.61								37.99		99.60
	Au-PdCu	4.17					60.62	5.57		25.71	1.35 (Au)			2.37	99.79
	$Fe_{1-x}S$							54.33	3.10	3.23			37.04		97.70
	$CuFeS_2$							31.34		33.42			34.51		99.27
	(Rh,Fe)S					34.73		19.34	9.08	5.50			29.26		97.91
7-157	Pd-Fe-Pt	80.07			0.45	0.37	5.95	11.67	0.45	0.18					99.14
	RuS_2				56.47	3.54							38.62		98.63
	RuS_2		9.40		39.93	10.83							34.4	4.3	98.86
	Rh_2S_3		12.24			38.03		9.77	1.36	6.73			30.54		98.67
	Pd_9Te_4						63.63					34.37			98.00
	Pb-Pd-Te						48.42				10.44 (Pb)	43.26			91.68
	RhAsS		19.39			29.65							15.63	28.45	93.12
	$Fe_{1-x}S$					2.83		56.59	1.09				38.7		99.21
13-157	Pd-Fe-Pt	77.15	0.32		0.29	0.34	8.27	8.78	0.85	1.53	2.16 (Au)				99.69
	Au-PdCu	6.90					54.20	1.45		27.46	4.99 (Au)			3.18	98.18
	Pd-Cu-S	2.34					71.84			13.51		1.33	11.16		100.18
	Rh-Ni-S		3.57			27.73		4.87	21.31	7.64			29.98		95.10
23-36	Pd-Fe-Pt	86.28					5.29	8.64							100.21
	PdBiTe						71.88				14.03 (Bi)	6.12	1.56		93.59
	PdS						83.98		1.44				13.27		98.69
23-76	Pd-Fe-Pt	78.66					7.37	11.03		1.71					98.77
	Pd-Cu-Pt						75.71			10.30			12.73		98.74
	Pd_9Te_4						70.50					27.98			98.48
	RuS_2				60.99								36.52		97.51
12-156	Pd-Fe-Pt	84.16	0.28				4.16	9.76	0.74	0.89					99.99
	Pd_9Te_4						68.82			0.81		30.19			99.82
	RuS_2				60.19								38.83		99.02
85-157	Ru-Rh-Fe-Pt	81.45	0.53		2.00	1.91		10.73	0.88	0.95					98.45
	(Ru,Rh)As	1.23		1.07	22.45	34.20								40.62	99.57
MK-10	Pd-Fe-Pt	76.52					9.57	9.19	0.68	2.90					98.86
	Cu-Pd-Au						37.75			18.63	39.88 (Au)				96.26
	Pd_3Pb						61.24				33.79 (Pb)				95.03
	Pd-Te						68.44				8.35 (Pb)	15.54	1.48	2.56	96.37

Note: The sample numbers and the abbreviation of the minerals correspond to those in Figure 1 of this article and Figure 4 of [7].

In addition to intergrowths of porpezite with ferroan platinum (Figure 2A), inclusions of gold-bearing phases, such as Au-bearing skaergaardite (CuPd) and Cu-Au-Pd alloys, were found in grains of ferroan platinum from placers of the Anabar River basin (Table 1). They form small (10–50 μm) isolated inclusions of rounded or curved teardrop shapes (Figure 2B–G) and are usually found in a matrix of ferroan platinum with a high content of Pd impurity up to 8–9.5 wt. %. In such inclusions of ferroan platinum, skaergaardite, zvyagintsevite, torryweiserite and other sulfides, thiospinelides, arsenides, and tellurides of PGE are also diagnosed. This indicates that such polyphase inclusions were formed as a result of displacement of residual easily fusible elements from the matrix of a crystallizing multicomponent low-sulfide metallic liquid, which consists mainly of platinum and iron. The initial course of phase transformations is determined by the main components of the system—Pt, Pd, Fe, and Au (refractory metals)—although the presence of fusible metals (Pb, Sb, Bi, etc.) in a metallic liquid should significantly reduce the temperatures of phase changes [16].

For example, adding 10 wt. % (~28 at. %) Fe lowers the melting point of platinum (1769 °C) by about 100 °C, but S, As, and Te reduce the melting point of platinum most effectively [31,33]. Thus, the eutectic temperature of platinum–cooperite in the Pt-S system is reached at 1240 °C and 7.5 wt. (~31 at.) % S, platinum–sperrylite eutectic at 600 °C and 14 wt. (~27 at.) % As, and platinum–telluride eutectic at 870 °C and 26 wt. (35 at.) % Te, respectively. During the crystallization of multicomponent melts, a negligible quantity of fusible components can accumulate in the residual melt and concentrate in the interstitial cavities (Figure 2I) of the host metal. These low-melting interstitial liquids of low volume often acquire rounded teardrop shapes (Figure 2E–G) that are affected by the surface tension force [37]. Due to their isolation, such melts evolve autonomously according to the phase transformations set by their composition. The Au-bearing skaergaardite is found in inclusions located in high-Pd ferroan platinum, therefore, the consideration of the chemical composition of these minerals is based on the phase state diagram of the Cu-Au-Pd system (Figure 4).

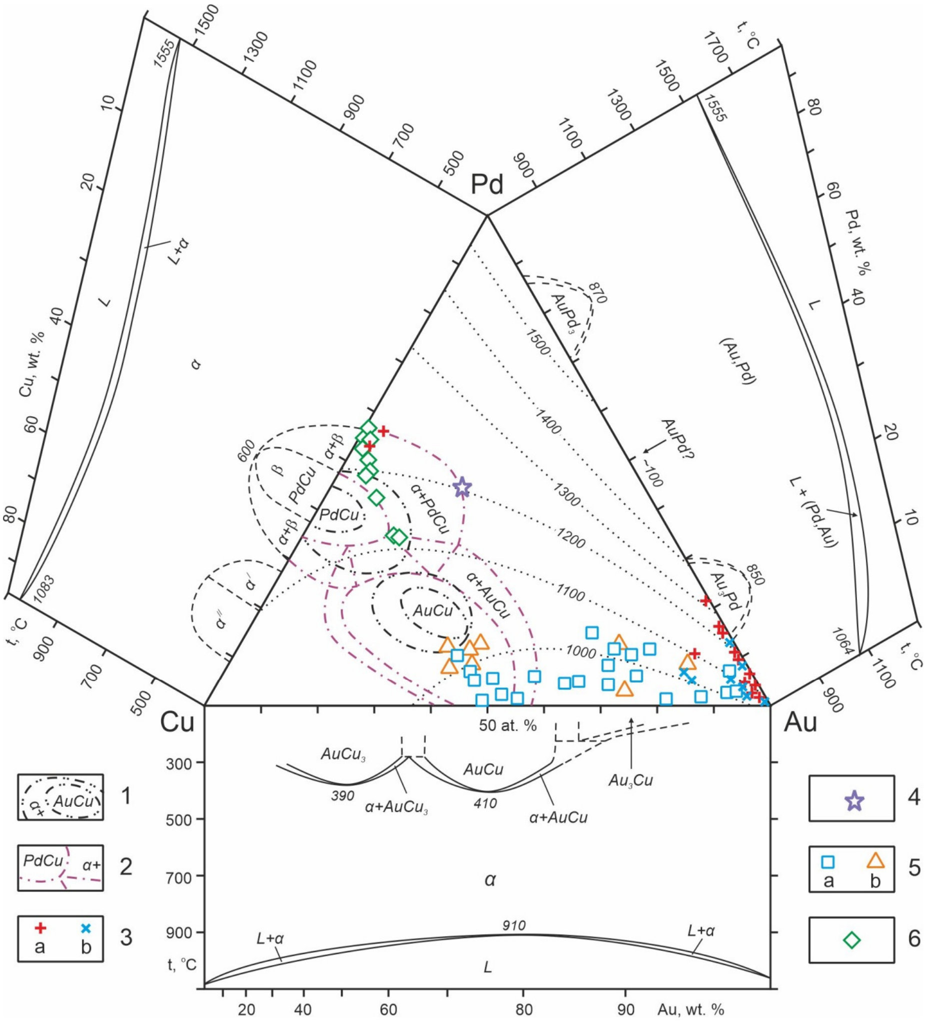

Figure 4. Compositions of Cu-Pd-Au alloys on the diagram of Cu-Pd-Au with binary systems. 1—isotherms of two-phase coexistence fields surrounding the ordered phases PdCu and AuCu at 550 °C; 2—the same at 350 °C and liquidus surface isotherms (thin dotted lines) of the system Cu-Pd-Au by [26]. For other symbols, see Figure 3; 3–6—mineral compositions: from the placers of the Mayat River (3a), Bolshaya Kuonamka River (3b), Malaya Kuonamka River (4), placer of Konder massif (5a) by [38,41], sulfide ores of the Norilsk deposits (5b) by [42] and ores of the Skaergaard massif by [43].

Thus, judging by the set of mineral associations in such inclusions (see Figure 2) Cu, Pd, and Au are mainly concentrated in the interstitial residual melt along with Rh, Ru, Pb, Bi, As, S, Te, and other elements. Therefore, the presence of gold impurities should be expected in ferroan platinum and, in fact, the matrix of ferroan platinum, which contains gold-bearing skaergaardites, often possesses areas with an increased gold content ranging from less than 1 to 1–2 wt. %. As seen from the binary Pt-Au system (see Figure 3), during crystallization under high-temperature conditions, intensive removal of gold from platinum into the residual melt occurs, since there is an extremely large temperature gap (up to 300 °C) between the Pt-Au liquidus and solidus curves. In this setting, continuous miscibility is observed between Pd and Au, both in solid and liquid states. The solubility of

Au in other PGEs (Os, Ru, Ir, Rh), as well as in Fe, is very limited and at low temperatures, usually amounting to only a few percent. Thus, during crystallization of a multicomponent liquid based on platinum with high contents of Fe, Rh, Ru, Os, and Ir, gold will be displaced into the residual melt. Crystallization of such a system leads to a strong enrichment of the residual melt in Pd due to a sufficiently large gap between the Pt-Pd liquidus and solidus. Such a combination of simultaneous accumulation of Pd and Au will lead to the final separation of the residual Pd-Au liquid, since the area of immiscibility in the solid state sharply expands between Pt and Au at low temperatures.

On the Cu-Pd-Au diagram (Figure 4), compositions of Cu-Pd-Au alloys from placers of the Bolshaya Kuonamka and Malaya Kuonamka rivers fall into the field of a two-phase area (α + β) surrounding an ordered compound of β-PdCu with a volume-centered lattice. They are generally found in the composition field of skaergaardite [43], i.e., they are an Au-bearing variety of skaergaardite. In addition to the β-PdCu phase in the Cu-Pd-Au system, the presence of an ordered ternary compound based on AuCu with a face-centered tetragonal lattice has been established. This compound with the highest melting point is composed of 19 wt. % Pd, 30% Cu, 51% Au, and corresponds to the $Au_3Pd_2Cu_5$ formula. The Cu-Pd-Au diagram also shows two-phase areas at 350 and 550 °C surrounding the ordered phases of PdCu and AuCu, which according to [26] are in contact at 545 °C. Palladium alloying of gold–copper alloys increases the formation temperature of the AuCu compound. The article [44] describes in detail the associations of minerals of the Cu-Pd-Au system, their compositions, and conditions of formation in various types of gold deposits.

The smallest teardrop inclusions of Au-bearing skaergaardite and nielsenite occur in sulfide and magnetite–ilmenite mineral aggregates of the Skaergaard layered gabbroid massif, which is consistent with the formation of Pd-Cu alloys from a sulfide–metallic melt [43]. The inclusions studied by the authors occur in ferroan platinum, i.e., gold and platinum from placers of the Anabar River, in contrast to the Cu-Pd-Au alloys from the Au-Pd ores of the "Platinum Reef" Skaergaard massif, which presumably belong to a different type of PGE-Au mineralization.

4. Discussion

To explain the origin of the paragenetic association of gold and platinum in placers with unidentified primary sources, it is essential to review the current literature on the joint formation of complex gold–platinum ores under various conditions.

Large deposits of platinum group elements (PGEs) are associated with magmatic sulfide and chromite ores localized in mafic–ultramafic intrusions [45–48]. Many researchers do not reject the potential for high concentrations in sulfide and chromitite ores of PGEs and Au, as these elements possess a very high degree of distribution in sulfide [49–51] and oxide liquids [13], which can be separated from the host silicate magma early in the development of mafic–ultramafic ore-magmatic systems. Due to the high content of low-melting metals and volatile components in ore melts, they can be preserved for a long time in closed magmatic chambers in an autonomous mode, therefore sulfide and chromitite segregations often form injection schlieren, veins, and layers of various shapes. Numerous studies of different deposits show that the distributions of PGEs and Au in chromitite and sulfide ores localized in stratified massifs differ significantly [52], which indicates the complex mechanisms of metal concentration in these ores. However, in sulfide deposits PGEs and Au are mainly found as isomorphic impurities (from a few tenths to several %) in sulfide minerals [39] and only part of them forms individual metal microphases, which explains the absence of platinum–gold placer deposits around large PGE-Cu-Ni deposits in the Norilsk region.

It is known that large platinum-bearing placers are associated with mafic–ultramafic massifs of the Ural–Alaskan and Aldan types. In the work [13], a schematic ternary chromite–osmium–platinum diagram showed a possible mechanism for the formation of large placer-forming platinum nuggets, which sometimes weigh up to several kilograms and contain abundant inclusions of chromespinel. This is due to the lower solubility of PGEs in crystalline chromite than in chromitite liquid, which, during crystallization of the ore liquid, leads to the displacement of platinum into the interstitial cavities and cementation of earlier chromite crystals. Thus, we suggest that the paragenetic association of gold and platinum in placers of the Anabar River basin is related to undersaturated sulfur ore of layered mafic–ultramafic intrusions. This is confirmed by the insignificant sulfide inclusions in PGMs, as well as high concentrations (up to 8–12 wt. %) in ferroan platinum, of admixtures of Ru, Rh, and Pd, the most chalcophile platinoids.

On the Siberian platform, intergrowths of palladium gold and Au-Cu-Pd minerals with Fe-Pt alloys and other PGMs were described in the composition of Cu-Ni sulfide ores of the Norilsk region [39,42,46,47] and in minerals from the platinum-bearing placer of the alkaline ultramafic Kondyor massif [38,41,53,54]. Palladium gold is also found in Au-PGM placers derived from the Guli ultramafic massif [55], therefore, in the northeast of the Siberian platform we have all the prerequisites for the existence of complex mafic ultrabasic complexes promising for gold–platinum mineralization. One grain of ferroan platinum from the Mayat River placer contained a silicate inclusion consisting of diopside, nepheline, phlogopite, titanomagnetite, and amphibole, the bulk composition of which corresponds to the rocks of the ijolite–melteigite series [24]. An unusual series from chromite to ulvospinel has been identified [56] in the alkaline picritic basalts, alkaline ultramafic rocks, and kimberlites of this area, indicating a paragenetic relationship between these rocks. Such Cr-Ti-Fe spinels are constant companions of gold and platinum in the studied placers. Using the method of the olivine–chromespinel oxythermobarometer [57], it was shown that for the studied alkaline mafic–ultramafic rocks the oxygen fugacity $lgfO_2$ is 2–4 orders of magnitude higher than that specified by the fayalite–magnetite–quartz (FMQ) buffer and corresponds to the oxidation state of platinum-bearing dunite–clinopyroxenite rock associations Ural–Alaskan and Aldan types [56].

Finds of high-Pd gold are known in gabbros of the Platinum Belt of the Urals [58,59], i.e., palladium gold is a permanent indicator satellite mineral of PGMs in mafic–ultramafic igneous rocks. The origin of these PGMs and gold intergrowths has been defined differently by various authors, as, for example, many researchers recognize the high-temperature early magmatic nature of PGMs [60–62], etc.; however, post-magmatic deposition from mineralized fluids is also accepted in relation to gold (e.g., [38,41]). Several researchers believe that the formation of complex mineralization of precious metals in igneous rocks occurred throughout the evolution of ore-magmatic systems, starting from the early magmatic stage to the separation of post-magmatic hydrothermal ore-bearing fluids. As mentioned above, formations of PGE-Au-containing sulfide ores as a result of the separation of immiscible sulfide liquid from mafic magma do not raise questions among researchers, however, many questions appear regarding the explanation of chromitite or titanomagnetite massive segregations. This issue is based on the fact of potential separation from silicate mafic–ultramafic magma of an immiscible oxide liquid enriched with chromium and other metals, including noble ones, and was discussed in the works of one of the authors [5,12,13]. It is now generally agreed that PGMs cannot directly precipitate from a magma owing to the high melting temperatures of platinum-group metals, the so-called "nuggets problem" effect. However, following the rule of a two-component eutectic system, the temperature of coexistence of two immiscible liquids is lower than the melting point of the metal, and that of the eutectic metal–silicate is, correspondingly, lower than the melting temperature of magma, which suggests the segregation of PGMs from magma both as crystals and as a metallic liquid [9].

Experimental work on the fractional crystallization of Cu-Fe-Ni sulfide melts with noble metals and Te impurity (0.2 mol. % each) showed [40] that microphases of noble metals and their intergrowths crystallize simultaneously with the main sulfide minerals. In this case, $Pt_{3-x}Fe$ and RuS_2 form crystals up to 100–200 microns in size, and Au and Ag are found in the form of microinclusions or rims around $Pt_{3-x}Fe$ crystals. It should be noted that Au contains significant impurities of Cu and Pd (up to 7–8 wt. % each), and Fe-Pt alloys contain Au up to 10 wt. %. At the final stage of crystallization, Te is concentrated in the residual sulfide melt, forming drop-shaped inclusions of palladium tellurides up to

10 μm in size. Thus, we can assume that during the crystallization of multicomponent low-sulfide metal melts, larger intergrowths of Fe-Pt alloys with palladium gold, skaergaardite, palladium tellurides, and other PGE-containing minerals can form. The explanation of some researchers that the overlay of a gold film on platinum crystals from the Konder placer is due to hydrothermal fluids coming from outside seems unlikely to us.

Based on the nature of the intergrowths of the mineral phases outlined above, the following sequence of formation of PGM intergrowths with other minerals can be described (Figure 5). In the early magmatic stage, the first protocrystals are chromite and olivine that occur as inclusions in the PGMs from placers. At this time, a long-term autonomous solidification process begins from a multicomponent low-sulfide metal liquid based on PGEs separated from the silicate mass. The low fugacity of sulfur in the system leads primarily to the crystallization of high-temperature minerals, which obviously include Os-Ir-Ru alloys (Figure 2B,C). They usually form idiomorphic crystals similar to porphyry minerals of igneous rocks. Idiomorphic polygonal inclusions of laurite in ferroan platinum can also be attributed to this process (Figure 2H). Numerous teardrop-shaped inclusions, often consisting of polymineral intergrowths of sulfides, arsenides, tellurides, PGEs, and other elements, are similar to inclusions in metallurgical alloys [34]. These admixtures considerably reduce the crystallization temperatures of PGE alloys; during eutectic or peritectic crystallization of the main component, they are also displaced into interstitial cavities, forming teardrop-shaped or amoeboid separations. During rapid cooling, some part of the impurity component remains in the main α-phase, which is then released in the form of parallel-oriented exsolution lamella, similar to the Widmanstätten structure (Figure 2I).

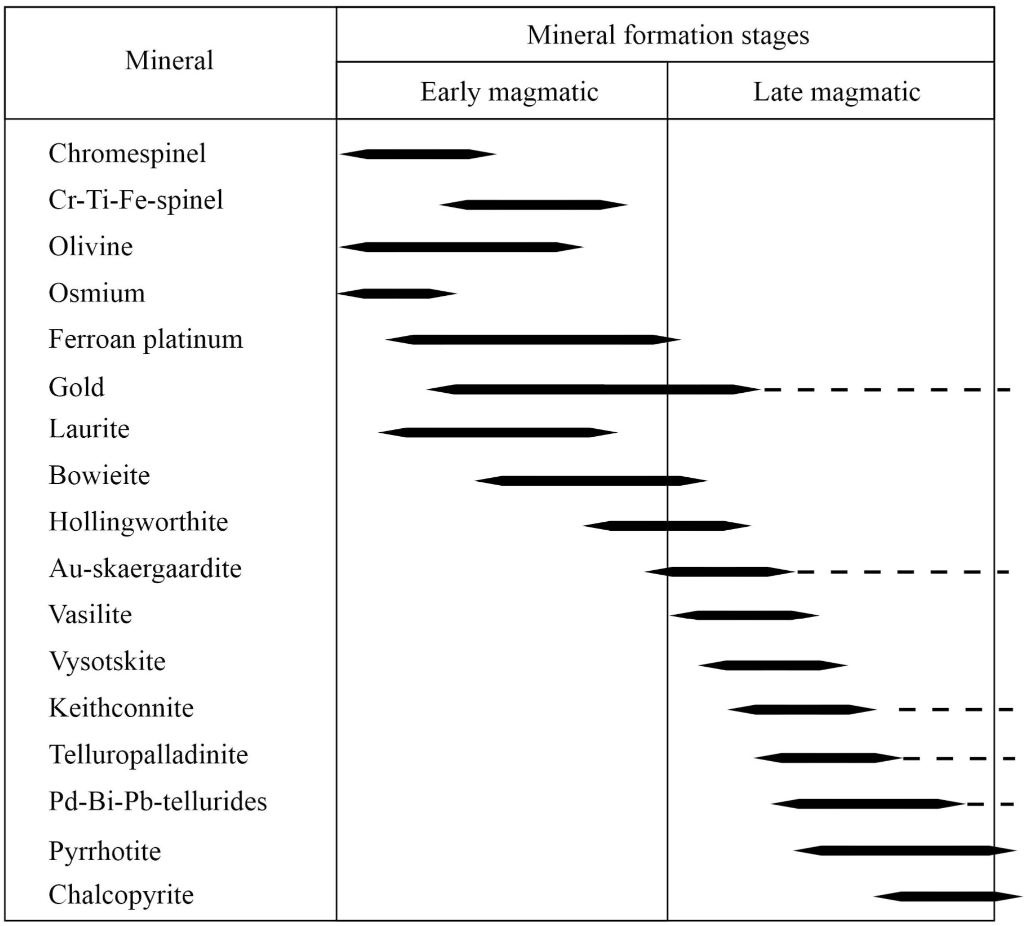

Figure 5. Scheme of the magmatic paragenetic sequence of crystallization of minerals in association with ferroan platinum and gold from placers in the Anabar River basin.

5. Conclusions

Polymineral intergrowths of PGMs, palladium gold, Au-Cu-Pd alloys, and other minerals comprising sulfides, arsenides, and PGE tellurides have been found in the placers of the Anabar River basin. Based on the presence of most of these minerals in the form of rounded isolated microinclusions in the matrix of ferroan platinum, the authors suggest that the formation of such intergrowths occurred as a result of crystallization of a multicomponent low-sulfide metallic liquid, which was separated from the host mafic–ultramafic magmatic melt. Immiscible metal liquids, containing PGEs, Fe, Cu, and Au, contained S, As, and Te in sufficiently large quantities of up to 20–30 wt. %, which significantly reduced the crystallization temperature of refractory platinum group metals.

The high stability of PGEs protects such isolated inclusions of sulfide and other minerals from further destruction. During the crystallization of magma, the most mobile ore components, for example, Pd, Au, and Ag in the composition of water–salt solutions, can leave the magma chamber and form remobilized skarn, metasomatic and hydrothermal types of ores around the intrusive body. Such ore-magmatic systems associated with mafic–ultramafic volcanic–plutonic complexes can be sources of gold–platinum placers that occupy vast areas of the northeast of the Siberian platform.

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