minerals

Review

Palladian Gold: Chemical Composition, Minerals in Association, and Physicochemical Conditions of Formation at Different Types of Gold Deposits

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Abstract: This paper reviews and summarizes the available information on the composition of palladian gold with various contents and sets of isomorphic impurities (Ag, Cu, Hg) at 50 deposits and ore occurrences with Au-Pd mineralization. It is revealed that Palladian gold is represented by the systems Au–Pd, Au–Pd–Hg, Au–Pd–Cu, and Au–Pd–Ag–Hg, but more frequently corresponds to Au–Pd–Ag, Au–Pd–Ag–Cu, and Au–Pd–Ag–Cu–Hg. Objects with palladian gold belong to different types of gold deposits and to the deposits at which the main components of ores are PGE, Cr, Cu, Ni, V, and Ti. We propose a classification of the types of deposits with palladian gold: (1) PGE ore deposits related to mafic–ultramafic magmatic complexes (two subtypes—(a) low-sulfide-grade (less than 2%–5% sulfides) Alaskan, and (b) high-sulfide-grade (more than 5% sulfides) Norilsk); (2) orogenic gold deposits (OG); (3) epithermal (porphyry) gold–copper deposits (EPGC); (4) iron oxide copper gold deposits (IOCG); (5) ferruginous quartzite deposits; (6) volcanic exhalation; and (7) gold-PGE placers of five subtypes corresponding to the types of 1–5 primary sources. Physicochemical conditions of the formation of palladian gold at some deposits of type 1 cover two areas—magmatic high-temperature and hydrothermal low-temperature. At the majority of deposits of types 2-4, its formation proceeds with the participation of hydrothermal fluids (300–60 °C) of various salinities (0.2–30 wt.% NaCl eq.). Palladian gold is mainly high-fineness (910‰–990‰), is less frequently medium-fineness, and contains Ag and Cu, but does not contain Hg at the deposits of types 1, 3, and 4. The only exception is the Au-Pd-Hg Itchayvayam ore occurrence (Kamchatka, Russia), for which two varieties of Pd,Hg-bearing native gold (fineness 816‰–960‰ and 580‰–660‰) are determined. Low-fineness palladian gold with the major content of Ag is typical of OG deposits. Medium-fineness palladian gold occurs at ferruginous quartzite deposits and in volcanic exhalations. Hg, Ag, Cu-bearing high-fineness palladian gold is present mainly in placer deposits (type 7). The most common minerals in association with palladian gold are arsenides, stibioarsenides, sulfides, stannides, bismuthides, tellurides, and selenides of Pd and Pt. These are typical of deposit types 1 and 7. The minerals of Au, Ag, and Cu (tetra-auricupride, aurostibite, chalcopyrite, bornite, chalcocite, eucairite, etc.) are in association with palladian gold at OG, EPGC, and IOCG deposits. Hg minerals (cinnabar, tiemannite, coloradoite, potarite) are at some deposits (types 1, 2, 7-1, 7-4). Cu, Fe, and Pd oxides (tenorite, hematite, magnetite, PdO, (Pd,Cu)O) and Fe and Pd hydroxides (goethite, (Fe,Pd)OOH) occur at the deposits of the 3, 4, and 7 groups and indicate the highly oxidizing conditions of ore formation. The most common minerals among host minerals are quartz and muscovite, including fuchsite (Cr-Ms), chlorite, albite, K-feldspar, hornblende, and carbonates (calcite, siderite, etc.). The fineness, content, and set of impurities in palladian gold and minerals in association with it reflect the mineralogy of Au-Pd ores and allow them to be used as indicators for the deposit types.

Citation: Palyanova, G.A.; Zhegunov, P.S.; Beliaeva, T.V.; Murzin, V.V.; Borovikov, A.A.; Goryachev, N.A. Palladian Gold: Chemical Composition, Minerals in Association, and Physicochemical Conditions of Formation at Different Types of Gold Deposits. *Minerals* **2023**, *13*, 1019. https://doi.org/10.3390/min13081019

Academic Editor: Huan Li

Received: 29 June 2023
Revised: 24 July 2023
Accepted: 28 July 2023
Published: 30 July 2023

Keywords: palladian gold; Pd,Cu,Ag,Hg-bearing gold; Au-Pd; Au-Pd-Ag; Au-Pd-Cu; Au-Pd-Hg; Au-Pd-Ag-Cu; Au-Pd-Ag-Hg; Au-Pd-Ag-Cu-Hg systems; fineness; minerals in association; PGE and gold deposits; T,P,X-conditions of ore formation; Au-Pd mineralization types

1. Introduction

Pure native gold without impurities (fineness 1000‰) is rare in nature. It contains some elements in the form of isomorphic (isostructural, i.e., included in the crystal structure without changing it) impurities and mineral microinclusions. Depending on their concentrat
ion, impurity-elements may be classified as major (>10 wt.%), minor (1–10 wt.%), and trace (<1 wt.%). Native gold with only silver impurity (argentian gold or Ag-bearing gold) is most widely spread at gold deposits [1–8]. Some review papers report data on the varieties of native gold with copper (cuprian gold), mercury (gold amalgam or mercury gold), and palladium (palladian gold) impurities [1,2,9–12]. On the basis of the occurrence and concentration, Petrovskaya (1973) [1] referred Pd to rare poorly studied impurities, Hg to third-rate, Cu to secondary, and Ag to major elements. A great number of new data on the content of impurities in native gold appeared over the past five decades. All these four elements, depending on their content, can be referred to as major, minor, and trace impurities.

Native gold often contains microinclusions of ore minerals, silicates, oxides, carbonates, etc. Special attention during recent years has been paid to the study of the impurities and minerals in paragenesis with native gold, since these characteristics are important informative signs of deposits with different types of mineralization [8,13–18]. Effective criteria for forecasting and searching for gold deposits can be provided by a study of the mineralogical–geochemical composition of native gold.

Native gold containing palladium was called «porpecite» after the place where it was first discovered in 1798 in the Porpez region of Brazil in the deposits of itabirites (layered quartzites with magnetite and hematite). The name "porpecite" was not approved by the CNMNC MMA, since the Pd-bearing gold or palladian gold (Au,Pd) is a structural analog and is considered as a Pd-rich chemical variety of native gold (www.mindat.org, accessed on 15 January 2022). Palladian gold was found to contain Ag [19,20], Cu [21,22], and Hg [23–25], whereas Fe, Ni, Pt, Rh, and other impurities are rare [21,26,27].

The purpose of this work is to analyze data on the composition and minerals in the association of palladian gold with impurities (Ag, Cu, and Hg) from different deposits, and to summarize the T,P,X-conditions for the formation of Au-Pd mineralization and to classify the deposits. Analysis of literature data and the results of our research show that the great number of existing deposits with palladian gold require classification. Earlier, reviews were made on the composition of Au-Pd mineralization at endogenous [28] and placer deposits with native gold containing Pd and Ag [20]. Since that time, much data on new deposits with palladian gold have been published ([11], and cited references). New data on the compositions of palladian gold and its minerals in the association have been recently obtained by the authors of this paper for such deposits as Chudnoe [29], Volkovskoe [30], Ozernoe [31] (Urals, Russia), and Bleida Far West (Morocco) [32], and for the placers and ore occurrences of the mafic–ultramafic Itchayvayam massif (Kamchatka, Russia) [33], which differ from other deposits. In this paper, we present a review of the composition of palladian gold of the systems Au–Pd, Au–Pd–Ag, Au–Pd–Hg, and Au–Pd–Cu and the more complex systems Au–Pd–Ag–Cu, Au–Pd–Ag–Hg, Au–Pd–Ag–Cu–Hg, etc.

The study of the composition of native gold is of great scientific and practical importance [14,34–38]. Native gold is a significant indicator mineral for Au-bearing deposits [12,14,39]. The composition of native gold is often used as a predictive tool in the study of the genesis of ore deposits and factors that determine the speciation of mineralization [12,40,41]. Chapman et al. (2021) [12], after analyzing the chemical composition of native gold, concluded that the concentrations of Cu, Hg, and Pd can be important indicators of different types of deposits. The level of concentrations and the ratios of various elements in individual gold particles can be responsible for the geochemical history and "prints" of ore-forming processes. Data on the variations in the concentrations of Pd and other elements (Ag, Cu, Hg) in native gold and specific features of the minerals in association and their occurrence in different types of rocks and ore-forming systems can be used for solving geological tasks that arise when promising gold-bearing areas are under study.

2. Geological Setting and Deposits with Palladian Gold

Palladium gold is present in the deposits of various geneses—magmatic, hydrothermal, and sedimentary-exogenous. The latter are the result of the transformation and differentiation of mineral matter of endogenous origin (magmatic or hydrothermal). Palladian gold often occurs in the placers, the sources for many of which have not been determined.

The deposits and ore occurrences with palladian gold are located in Canada, Brazil, England, Scotland, Poland, Spain, USA, Morocco, Guinea, and other countries [11,20,28]. The mindat.org database contains data on findings of palladian gold in Belgium, Germany, and Venezuela. More than twenty deposits and ore occurrences with palladian gold are known in Russia [11]. The geographical spread and geological–structural location of deposits with palladian gold are shown in Figure 1. They occur in different geological and dynamic settings—terranes, orogenic belts, and shields. According to dating assessments, the processes of formation of Au-Pd mineralization took place in the Archean, Proterozoic, Paleozoic, Mesozoic, and Cenozoic.

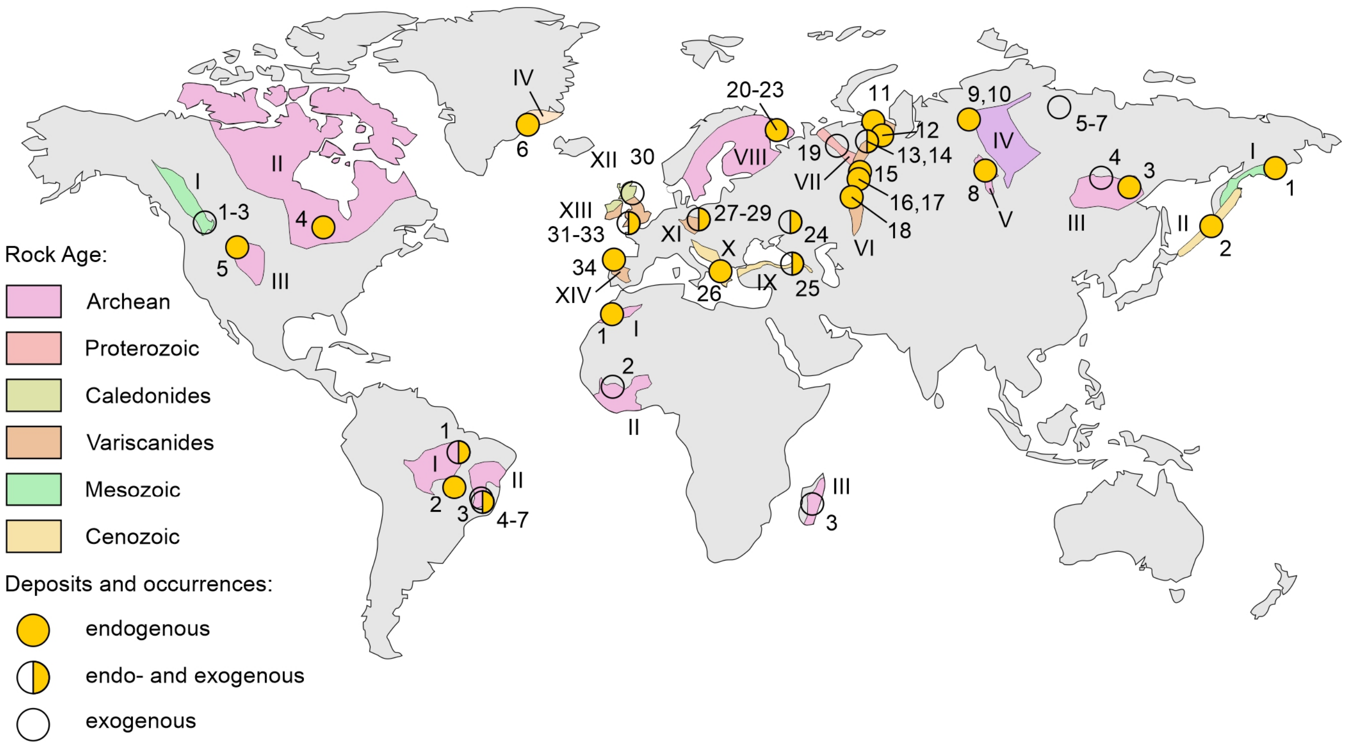

Figure 1. Location of deposits and ore occurrences with palladian gold, and other Au-Pd-Ag-Cu-Hg phases (Arabic numerals indicate deposits, Roman numerals indicate the age of main ore-hosted geological structures; the description is shown below). *Eurasia*: Russia 1–24—1. Itchayvayam complex [33,42]; 2. Ebeko volcano [43]; 3. Konder massif [44,45]; 4. Inagli Pt–Au placer deposit [46]; 5–7. placers of

northern Yakutia [47,48]: 5. Mayat river, 6. Bol'shaya Kuonamka river, 7. Kuoyka river; 8. Uderei [49]; 9,10. Norilsk deposits: 9. Norilsk-1, 10. Talnakh [27,50]; 11. Krutoe, Pay-Khoy Range [51]; 12–19. Ural deposits: 12. Ozernoe [31], 13. Chudnoe and placer Alkes-Voss [29,52,53], 14. Nesterovskoe [53], 15. Serebryansky Kamen [54], 16. Baronskoe [55], 17. Volkovskoe [30], 18. Khamitovskoe [56], 19. Ichet'yu, Timan [57]; 20–23—Fedorovo-Pansky intrusive complex deposits [58]: 20. V. Chuarva, 21. C. Kamennik, 22. Y. Peshempakhk, 23. Fedorova Tundra; 24. Lebedinskoye [59]; 25. Chorokh river, Artvin district, Turkey [60]; 26. Korydallos, Greece [61,62]; 27–29. deposits of the Sudetes Mountains: 27. Zechstein [63], 28. Zimnik Creek [64], 29. Dziwiszów [65]; 30. Lammermuir Hills, Scotland [20]; 31–33. deposits of the south of England: 31. Hope's Nose [66], 32. Dart river [20], 33. Brownstone [20]; 34. Herbeira massif, Spain [67]. Structures: I—Olyutorsky arc terrane, II—Kuril-Kamchatka volcanic belt, III—Aldan shield, IV—Siberian trap province, V—Yenisei ridge, VI—Ural accretionary fold belt (Variscan orogenic belt), VII—Timan folding system, VIII—Baltic Shield, IX—Eastern Pontides-Lesser Caucasus fold-thrust belt, X—Ophiolite belt of Greece, XI—Hercynides of the Sudetes (Variscan orogenic belt), XII—Caledonides of Scotland, XIII—Variscan orogenic belt of Britain, XIV—Central Iberian zone of the Iberian massif (Variscan orogenic belt). *Africa:* 1. Bleida Far West, Morocco [32,68]; 2. Mataganya-Siguiri zone, Guinea [69]; 3. Ambositra District, Madagascar [70]. Structures: I—Anti-Atlas fold belt, II—Kenema-Man shield and Baoule-Mossi domain (West African Craton), III—Precambrian shield of Madagascar. *North America:* 1–3. Deposits of Canada: 1. Friday Creek [71]; 2. Whipsaw Creek [71]; 3. Similkameen river [71]; 4. Marathon [21,72]; 5. Skaergaard massif, Greenland, Denmark [73]; 6. Stillwater, USA [74]. Structures: I—Intermontane terranes of British Columbia (North American Cordilleran orogenic belt), II—Wyoming province, III—Canadian shield, IV—Paleogene platobasalts of eastern Greenland. *South America:* Deposits of Brazil—1. Serra Pelada [25]; 2. Cedrolina Chromitite (Goiás State) [75]; 3. Corrego Bom [76]; 4–7. Itabira deposits: 4. Caue iron mine [26,77], 5. Gongo Soko [25,78], 6. Maquine [28], 7. Conceichao mine [79]. Structures: I—Central Brazilian shield, II—São Francisco craton.

3. Methods

Impurity elements in native gold are determined using chemical, spectral, electron probe microanalyses (EPMA), inductively coupled plasma–mass spectrometry (ICP-MS), and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). The chemical and spectral methods as well as ICP-MS require a considerable amount of native gold and its purification from other minerals. Systematic studies of the typomorphism of native gold from different territories of Russia and the Commonwealth of Independent States, with the application of semi-quantitative ICP-MS analysis carried out in Russia [14,80], showed the presence of 70 chemical elements in it. The drawback of the chemical, spectral, and ICP-MS methods is the inability to separate isomorphic impurities and mineral microinclusions in native gold.

EPMA is used for quantitative analysis of the elemental composition of native gold at a micrometer scale. The detection sensitivity of many elements in the local electron raster microprobe analysis is limited by concentrations no less than 0.1–0.01 wt.%. A more complex composition of native gold can be detected by LA-ICP-MS, the sensitivity of which is considerably higher than that of EPMA. With the appearance of the LA-ICP-MS technique [81] for determining the composition of microelements in solid samples, data on micro- and trace elements in native gold were obtained [35,82–90]. The laser ablation–inductively coupled plasma–mass spectrometer has high sensitivity and low detection levels required for measuring microelements in amounts up to ppb (1 per billion). One of the advantages of this technique is the possibility of cleaning the sample surface. LA-ICP-MS is widely used by foreign scientists to study the composition of gold and has not been used for studying gold in Russia yet. According to Chapman et al. (2023) [91], limits of detection (LODs) for Pd and Cu were typically around 900 ppm and 200 ppm, respectively, whilst the avoidance of spectral interference between the HgM_{α} and AuM_{β} X-rays necessitated using the HgM_{β} X-ray line and the associated higher detection limit of 3000 ppm.

In the majority of studies, the chemical composition of native gold was investigated using EPMA, and less frequently, LA-ICP-MS. The concentration of elements Ag, Cu, Pd, and Hg in native gold is commonly measured using EPMA. The spectrum accumulation time in electron probe microanalysis is 20 or more—60–80 s. Macro-impurities in native gold are determined using SEM/EDS, which allows one to determine Ag, Cu, Pd, and Hg with detection limits of 100–1000 ppm.

We analyzed the samples of ores and individual gold grains with Pd-bearing gold from the Chudnoe, Volkovskoe, and Ozernoe deposits (Urals, Russia) and from placers and ore occurrences of the mafic–ultramafic Itchayvayam massif (Kamchatka, Russia) and Au-Pd Bleida Far West deposit (Morocco). Chemical analyses of native gold and other minerals were conducted at the Analytical Center for Multi-elemental and Isotope Research in the IGM SB RAS (Novosibirsk, Russia) by electron probe microanalysis (EPMA) using a MIRA 3 LMU scanning electron microscope (Tescan Orsay Holding, Brno, Czech Republic) equipped with an X-ray energy-dispersive spectrometer (EDS) AZtec Energy XMax-50 (Oxford Instruments Nanoanalysis, Oxford, UK) (analysts Dr. N. Karmanov, M. Khlestov). The composition of native gold was studied at the following parameters: accelerating voltage was 20 kV and live spectrum acquisition time was 60 s (total area of spectra ~10^6 counts). The following X-rays were selected: K series for Fe, Cu, and As and L series for Pd, Ag, Sb, Au, and Hg. We used pure metals (Fe, Cu, Pd, Ag, Au) and InAs for As and HgTe for Hg as the standards. The detection limits (in wt.%) were 0.1 Fe, 0.15 Cu, 0.25 Pd, Ag, Sb, 0.3 As, 0.6 Au, and 0.8 Hg. The error in determining the main components with contents higher than 10 wt.% did not exceed 1 relative (rel.) %, and when the content of components ranged from 2 to 10 wt.%, the error was no higher than 6–8 rel. %. Close to the limit of detection, the error was 15–20 rel.%. In some cases, the spectrum acquisition time increased to 120 s, and the lower limits of determined contents and the random error of the analysis decreased about 1.4 times. This review is primarily based on the EPMA results. A significant amount of EPMA data was taken from the published literature.

4. Results

4.1. Composition, Fineness, and Mineral Associations of Palladian Gold

Palladian gold rarely consists of the binary Au-Pd system; it most frequently contains the ternary Au-Pd-Ag, Au-Pd-Cu, and Au-Pd-Hg, and even more complex systems Au-Pd-Ag-Cu, Au-Pd-Ag-Hg, and Au-Pd-Ag-Cu-Hg. Several varieties of palladian gold were found at many deposits. Along with palladian gold, Ag-bearing gold and other varieties of native gold are present at these deposits. Below, we present data on the composition of palladian gold in the binary (Au-Pd), ternary (Au-Pd-Ag, Au-Pd-Cu, Au-Pd-Hg), quaternary (Au-Pd-Ag-Hg, Au–Pd–Ag–Cu), and five-element (Au–Pd–Ag–Cu–Hg) systems, as well as minerals in association and examples of deposits.

According to the “50 mole % rule” for the mineral nomenclature recommended by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA) [92], the formula composition of palladian gold can be represented as $Au_{1-x}Pd_x$, where $x < 0.5$ atomic part, when calculating the formula for 1 atomic unit. Au-Pd solid solutions with Ag, Cu, and Hg impurities can be present as $Au_{1-x-y-z-d}Pd_xAg_yCu_zHg_d$, where $0 < x$ (Pd atomic part in native gold) < 0.5; y, z, d in total $\leq 0.5 - x$ atomic parts; and $1 - x - y - z - d > x, y, z, d$. The fineness of native gold is calculated by the equation (1000*Au/(Au + Pd + Me_1 + Me_2 + and so on), where Au, Pd, and other metals (Ag, Cu, Hg, Pt, Ni, Fe) are expressed as wt.%).

Terms used to characterize the amounts of gold in Au-Ag solid solutions—very high-fineness 999‰–951‰, high-fineness 950‰–900‰, medium-fineness 899‰–800‰, relatively low-fineness 799‰–700‰, and low-fineness gold 699‰–400‰; kustelite 399‰–100‰; silver <100‰—were proposed by Petrovskaya (1973) [1]. We used the same terms to characterize palladian gold. The compositions of solid solutions depend on the amounts of impurities of palladium, copper, mercury, and other metals, and the fineness intervals corresponding to native gold can change, which is determined by the atomic weight and the amount of the impurity element. According to the "50 mole % rule", the fineness of palladian gold can be more than 649‰ ($Au_{0.5}Pd_{0.5}$), cuprian gold > 756‰ ($Au_{0.5}Cu_{0.5}$), argentian gold > 630‰ ($Au_{0.5}Ag_{0.5}$), and gold amalgam > 495‰ ($Au_{0.5}Hg_{0.5}$).

Mineral abbreviations used in the tables are taken from [93] albite (Ab), allanite (Aln), altaite (Alt, PbTe), anilite (Ani, Cu_7S_4), anyuiite (Any, $AuPb_2$), apatite (Ap, $Ca_5(PO_4)_3(F,Cl,OH)$), arsenopyrite (Apy, FeAsS), atheneite (Ah, $(Pd,Hg)_3As$), atokite (Ato, $(Pd,Pt)_3Sn$), auricupride (Auc, Cu_3Au), aurostibite (Ausb, $AuSb_2$), biotite (Bt), bohdanowiczite (Boh, AgBiSe), bornite (Bn, Cu_5FeS_4), braggite (Bg, (Pt,Pd,Ni)S), burangaite (Brg, $(Na,Ca)(Fe^{2+},Mg)Al_5(PO_4)_4(OH,O)_6 \cdot 2H_2O$), calcite (Cal, $CaCO_3$), carbonates (Carb), cerussite (Cer, $PbCO_3$), chalcocite (Cc, Cu_2S), chalcopyrite (Ccp, $CuFeS_2$), chlorargyrite (Cag, AgCl), chlorites (Chl), clinopyroxenes (Cpx), chrisstanleyite (Csl, $Ag_2Pd_3Se_4$), cinnabar (Cin, HgS), clausthalite (Cth, PbSe), coloradoite (Clr, HgTe), cooperite (Cpe, (Pt,Pd,Ni)S), empressite (Eps, AgTe), epidote (Ep), eucairite (Eca, AgCuSe), feldspar (Fsp), fischesserite (Fis, Ag_3AuSe_2), fuchsite (Cr-Ms), galena (Gn, PbS), goethite (Gth), gold (Au), gypsum (Gp), hematite (Hem, Fe_2O_3), hessite (Hes, Ag_2Te), isoferroplatinum (Ifpt, Pt_3Fe), isomertieite (Ism, $Pd_{11}Sb_2As_2$); kaolinite (Kln), keithconnite (Kei, $Pd_{3-x}Te$(x = 0.14 to 0.43)), K-feldspar (Kfs), kotulskite (Ktu, PdTe), magnetite (Mag, Fe_3O_4), merenskyite (Mrk, $(Pd,Pt)(Te,Bi)_2$), mertieite-I (Met-I, $Pd_{11}(Sb,As)_4$), mertieite-II (Met-II, $Pd_8(Sb,As)_3$), monazite (Mnz, $REE(PO_4)$)), moncheite (Mon, $(Pt,Pd)(Te,Bi)_2$), muscovite (Ms), naumannite (Nau, Ag_2Se), oosterboschite (Oos, $(Pd,Cu)_7Se_3$), padmaite (Pdm, PdBiSe), palladium (Pd), palladoarsenide (Pda, Pd_2As), palladseite (Pds, $Pd_{17}Se_{15}$), paolovite (Plv, Pd_2Sn), pentlandite (Pn, $(Fe,Ni)_9S_8$), perite (Pe, $PbBiClO_2$), platinum (Pt), plumbum (Pb), potarite (Ptr, PdHg), pyracmonite (Pyr, $(NH_4)_3Fe(SO_4)_3$), pyrite (Py, FeS_2), pyrrhotite (Pyh, $Fe_{1-x}S$ (x = 0 to 0.17)), quartz (Qz), silver (Ag), skaergaardite (Skg, PdCu), sobolevskite (Sov, Pd(Bi,Te)), sperrylite (Spy, $PtAs_2$), stannopalladinite (Spdn, $(Pd,Cu)_3Sn_2$), stibiopalladinite (Stpdn, Pd_3Sb), sudburyite (Sdb, PdSb), sudovikovite (Svi, $PtSe_2$), sylvanite (Syv, $AgAuTe_4$), telluropalladinite (Tpdn, Pd_9Te_4), temagamite (Tem, Pd_3HgTe_3), tenorite (Tnr, CuO), tetra-auricupride (Taur, AuCu), tetraferroplatinum (Tfpt, PtFe), tiemannite (Tmn, HgSe), tourmaline (Tur), umangite (Um, Cu_3Se_2), vasilseverginite (Vas, $Cu_9O_4(AsO_4)_2(SO_4)_2$), vysokýite (Vys, $U^{4+}[AsO_2(OH)_2]_4 \cdot 4H_2O$), and vysotskite (Vsk, (Pd,Ni)S).

4.1.1. Palladian Gold and Au-Pd System

Palladian gold of composition $Au_{1-x}Pd_x$, where $x \leq 0.5$ is atomic part Pd (<35.1 wt.%) without impurities, was discovered at several deposits and ore occurrences. As an example, Table 1 shows data for four objects: two endogenous—Krutoe ore occurrences in gabbro-dolerites of Pay-Khoy Ridge (Yugor peninsula, Arkhangelsk region, Russia) [51] and Uderei Au-Sb deposit (Yenisei Ridge, Russia) [49], and two placer ore occurrences—Lammermuir Hills (Scotland) [20] and the Chorokh river (Artvin district, Turkey) [60].

Table 1. The composition of palladian gold (in absence of other impurities), its fineness (N_{Au}), and minerals in association at endogenous and exogenous deposits.

Name of Deposit (Location)	N_{Au} ‰/Impurity wt.%	Minerals in Association	Ref.
	Endogenous deposits		
Krutoe ore occurrence (Yugor peninsula, Russia)	949–963/Pd 5.1, 3.7	Qz, Pyh, Ccp, Clr, Alt, Eps, Au-Ag (850–920), Au-Cu-Ag, Au, Taur, Sdb, Spy, Tsp, Hes	[51]
Uderei Au-Sb deposit (Yenisei Ridge, Russia)	970–920/Pd 3.3–7.9	Apy, Py, Au-Ag (760–980), Au, Ausb	[49]
Ebeko volcano (Kuriles, Russia)	787/Pd 21.3 (Au_2Pd)	S	[43]
	Exogenous deposits		
Lammermuir Hills (Scotland)	942/Pd 5.8	Carb, Apy, Gn, Pe, Au_3Cu, Taur, Ausb, Boh, Nau, Um, Tmn, Mrk	[20]
Chorokh river (Artvin district, Turkey)	649–724/Pd 26.5–38.5	Pd, Pd_4S	[60]

Palladian high-fineness gold (Pd content 3.7–5.1 wt.%, fineness 949‰–963‰) with inclusions of argentian gold (Ag content 7.47–15.3 wt.%, fineness 850‰–920‰, sizes from 2 to 100 μm) is intergrown with chalcopyrite in quartz veins and hornblende of gabbro-dolerites in the axial zone of the sill of the Pay-Khoy Ridge (Krutoe ore occurrence, Russia) [51]. Shaibekov et al. (2020) [51] reported that the early (magmatic) association of Au-Pd-Te mineralization is represented by the decomposition products of the ternary Ag—Au—Cu system (tetra-auricupride AuCu and Au-Ag-Cu phases containing Cu from 14.2 to 64.7 wt.% and Ag to 10.2 wt.%), antimonides and stibiotellurides of Pd, and arsenides of Pt (sudburyite, testibiopalladite, and sperrylite), whereas the late (hydrothermal) association, by the minerals of binary Au-Pd and Au-Ag systems, is represented by tellurides of Hg, Pb, and Ag.

Palladian gold from the Uderei deposit contains from 3.3 to 7.9 wt.% Pd and is high-fineness (920‰–970‰) [49]. It occurs in the intergrowth with argentian gold (Ag content from 2.1 to 24.2 wt.%, 760‰–980‰) or pure metal (1000‰). Both varieties of native gold occur in association with arsenopyrite, pyrite, and aurostibite. Gold–antimony ores from this deposit were found to contain grains of zinkenite, chalcostibite, ullmannite, galena, sphalerite, and cinnabar [49].

Native gold from the placers of the Chorokh river (Artvin district, Turkey) contains high concentrations of Pd (26.5–38.5 wt.%, $Au_{0.58}Pd_{0.42}$–$Au_{0.45}Pd_{0.55}$) and, hence, is lower-fineness (649‰–724‰) [60]. In palladian gold, microinclusions of native palladium ($Pd_{0.95}Au_{0.05}$) were detected. The composition of Au-Pd solid solutions with Pd concentrations of more than 35.1 wt.% ($Au_{0.50}Pd_{0.50}$–$Pd_{0.55}Au_{0.45}$) should be attributed to native palladium.

At the ore occurrences of Lammermuir Hills (Scotland) [20], palladian gold contains up to 5.8 wt.% Pd ($Au_{0.9}Pd_{0.1}$, 942‰) and occurs in association with Au-Cu intermetallic compounds—tetra-auricupride and Au_3Cu without Pd impurities, as well as with aurostibite, bohdanowiczite, naumannite, umangite, tiemannite, merenskyite, pyrite, arsenopyrite, galena, and carbonates. Placer gold is heterogeneous and has the characteristics of endogenous and acquired exogenous genesis.

The set of minerals in association with palladian gold from the Uderei deposit (Russia) and placer ore occurrences of Lammermuir Hills (Scotland) are partially similar in that both objects contain aurostibite, arsenopyrite, galena, and argentian gold. Tetra-auricupride is present in paragenesis with palladian gold at the Krutoe ore occurrence (Russia) and the Lammermuir Hills deposit (Scotland), which suggests not only Au-Pd but also Cu-Pd mineralization.

It is worth noting the high concentrations of Pd (21.3 wt.%, Au_2Pd) in gold particles from gray fumaroles and in andesite lavas (Q) of Ebeko volcano (Russia) [43] (Table 1). Au_7Pd (928‰), Au_3Pd (847‰), and Au_2Pd (790‰) phases and Au-bearing palladium are present in the Au-Pd mineralization of the Serra Pelada deposit, Brazil [25]. The Au_3Pd phase as small inclusions was identified in chromite from the Cedrolina Chromitite (Goiás State, Brazil) [75]. Pure gold and Au_3Cu_3Ni alloy were also found at the boundary between chromite and talc or in the silicate matrix of the chromitite ores.

The reported results show that Pd concentrations in gold in the absence of other impurities vary in a wide range from minor (3.3 wt.%, 970‰) up to $Au_{0.50}Pd_{0.50}$ (35.1 wt.%, 649‰). The compositions of this gold are arranged on the Au-Pd side of the ternary diagram of Au-Pd-Ag (Figure 2). This diagram also shows the compositions of palladian gold with and without Ag, which are widespread at other deposits (there are 24 of them; see capture in Figure 2). Summarized literature data on the compositions of palladian gold with the presence of Ag at these deposits are presented in Section 4.1.2.

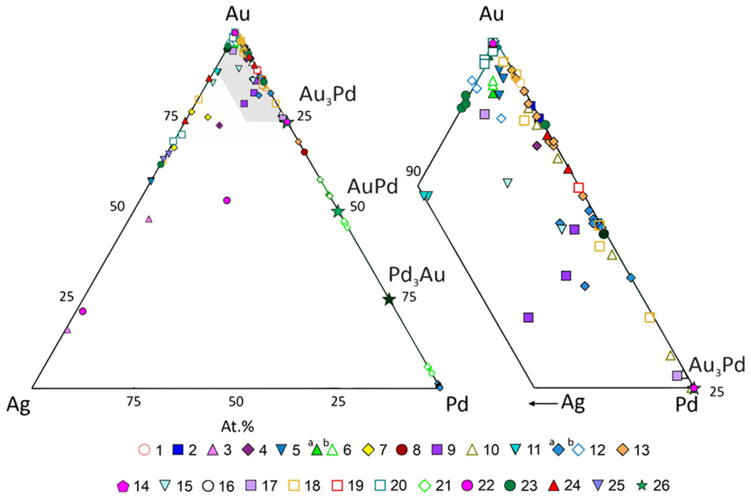

Figure 2. Ag-bearing palladian gold and other phases of Au-Ag-Pd system (in at.%) at the various deposits and ore occurrences: 1. Itchayvayam [33]; Norilsk deposits—2. Norilsk-1, 3. Talnakh, [22]; Ural deposits—4. Baronskoe [55], 5. Chudnoe [53], 6. Nesterovskoe [53]; 7—deposits of the Fedorovo-Pansky intrusive complex [58]; 8—Ebeko Volcano, Kuriles [43]; 9—Stillwater, Montana, USA [74]; 10—Corrego Bom Sucesso, Brazil [76]; 11—Gongo Soco iron mine, Brazil [25]; 12—Serra Pelada, Brazil [25]; 13—Caue iron mine, Brazil [77]; 14—Cedrolina Chromitite (Goiás State, Brazil) [75]; 15—Bleïda Far West, Morocco [68]; 16—Ambositra District, Madagascar [70]; 17—Hope's Nose, Devon, England [66]; 18—Brownstone, Devon, England [20]; 19—Lammermuir Hills, Scotland [20]; 20—placer gold of Zimnik Creek, Poland [64]; 21—Chorokh River, Artvin District, Turkey [60]; 22—Ozernoe [31]; 23—Uderei Au-Sb [49]; 24—Pay-Khoy [51]; 25—KMA (Lebedinskoye) [59]; 26—theoretical compositions of minerals corresponding to their ideal formulas. Shaded markers are endogenous, empty markers are exogenous deposits.

4.1.2. Pd,Ag-Bearing Gold and Au-Pd-Ag System

Palladian gold with Ag impurity (Ag-bearing palladian gold or Pd, Ag-bearing gold) covers the range of solid solutions from Au to $Au_{1-x-y}Pd_xAg_y$, where $y + x \leq 0.5$ atomic fraction, $x \neq 0$, $y \neq 0$, and $1 - x - y > x, y$. As an example, Table 2 contains data on five deposits and occurrences with Ag-bearing palladian gold.

Table 2. The composition of Ag-bearing palladian gold, its fineness (N_{Au}), and minerals in association at endogenous deposits.

Name of Deposit (Location)	N_{Au} ‰/Impurity wt.%	Minerals in Association	Ref.
Brownstone (England)	970–994 (core)/Pd 0.5–2.4, Ag 0.1–0.5 882–924 (border)/Pd 7.4–11.2, Ag 0.01–0.4	Cth, Tmn, Eca	[20]
Hope's Nose (England)	854–997/Pd 0.2–14.2, Ag 0.2–1.9	Csl, Cth, Fis, Cag, Oos, Cal, Cer	[20,66]
Stillwater (USA)	882–922/Pd 6.6–7.3, Ag 1.1–4.8	Vsk, Bg	[74]
Fedorova Tundra (Russia)	770–870/Ag 10.9–19.7, Pd < 2.76, Fe < 0.19	Plv, Pn	[58]
Lebedinskoye (Russia)	780–790/Ag 21.4–22.6, Pd < 0.15, Pt < 0.4, Ni < 0.05, Fe ≈ 1.2	-	[59]

At the Au-Pd Brownstone deposit (England), native gold is present in a vertical quartz-calcite vein hosted by Devonian slates [20] and is represented by two generations (Ag < 0.5 wt.%): high-fineness gold (970‰–994‰) with low content of Pd < 2.4 wt.% (core) and lower-fineness gold (882‰–924‰) with a higher content of Pd up to 11.2 wt.% (border), in association with clausthalite, tiemannite, and eucairite. The low contents of Ag 1.1–4.8 and 0.2–1.9 and the high contents of Pd ≈ 7 wt.% and up to 14.2 wt.% are typical of native gold at the Au-Pd Stillwater (USA) and Hope's Nose (England) deposits (Table 2), respectively. The trace and low contents of Pd < 0.15 and < 2.76 wt.% and high contents of Ag 21.4–22.6 wt.% and 10.9–19.7 are typical of native gold in ferruginous quartzites, accompanying metasomatites, and in the zones of increased sulfidation at the Au–Pd–Pt Lebedinskoye deposit [59] and in the ores of the Fedorova Tundra Pt-metal deposit (Russia) [58], respectively.

Minerals associated with Ag-bearing palladian gold in small calcite veins at the Cu-Ni-sulfide Hope's Nose (England) are chrisstanleyite, clausthalite, fischesserite, chlorargyrite, oosterboschite, calcite, and cerussite [74]. Vysotskite, braggite, paolovite, and pentlandite are associated with Ag-bearing palladian gold at the Stillwater (USA) and Fedorova Tundra (Russia) deposits, respectively. Minor impurities Pt < 0.4, Ni < 0.05, and Fe 0.2–1.3 wt.% are present in Pd,Ag-bearing gold at the deposits Lebedinskoye [59] and Fedorova Tundra (Russia) [58].

Ag-bearing palladian gold has been found at such deposits as Norilsk-1, Talnakh [22], Baronskoe [55], Chudnoe, Nesterovskoe [53], Ozernoe [31], and Krutoe [51]; deposits of the Fedorovo-Pansky intrusive complex [58] in Russia; Corrego Bom Sucesso, Gongo Soco, Caue, and Serra Pelada in Brazil [25,77]; Bleïda Far West in Morocco [68]; and placers of the Ambositra region, Madagascar [70] and Zimnik Creek, Poland [64]. Native gold from these deposits is heterogenous and is represented by two or more varieties of Ag-bearing palladian gold—with Hg and (or) Cu impurities. Section 4.1.6 is devoted to these deposits.

The Au-Pd-Ag diagram (Figure 2) shows the compositions of Ag-bearing palladian gold, and other minerals and phases of this ternary system found in the ores of some deposits.

Ag-bearing palladian gold of the Au-Pd-Ag system depending on the Pd and Ag contents (Figures 2 and 3) can be divided into three varieties:

(1) Au-Pd solid solution in the absence of impurities (fineness > 649‰, LOD < Pd < 50 at.%). Such gold occurs at the following deposits: Uderei, Norilsk-1, Talnakh, Krutoe, Lebedinskoye, Ebeko volcano (Russia), Corrego Bom Sucesso, Caue iron mines (Brazil), and Serra Pelada, and alluvial placers of Ambositra region (Madagaskar), Chorokh river, Artvin district (Turkey), Lammermuir Hills (Scotland), and Brownstone (England), etc.

(2) Au-Pd-Ag solid solutions with high Pd (10–48 at.%) and low Ag content <10 at.% (fineness > 850‰). Native gold of this composition was found at the deposits Stillwater, Montana (USA), Chudnoe (Russia), Serra Pelada, Corrego Bom Sucesso (Brazil), and Bleida Far West (Morocco).

(3) Au-Ag-Pd solid solutions with a high Ag content (10–48 at.%) and a low Pd content <10 at.% (fineness > 630‰). Ag-rich palladian gold is present at the deposits of Talnakh, Baronskoe, Ozernoe, Fedorovo-Pansky intrusive complex, and Nesterovskoe (Russia); Gongo Soco, Caue (Brazil); Hope's Nose, Brownstone (England); and placer Zimnik Creek (Poland). Native silver with low Pd (fineness < 630‰) is found at some of these deposits (for example, Talnakh and Ozernoe).

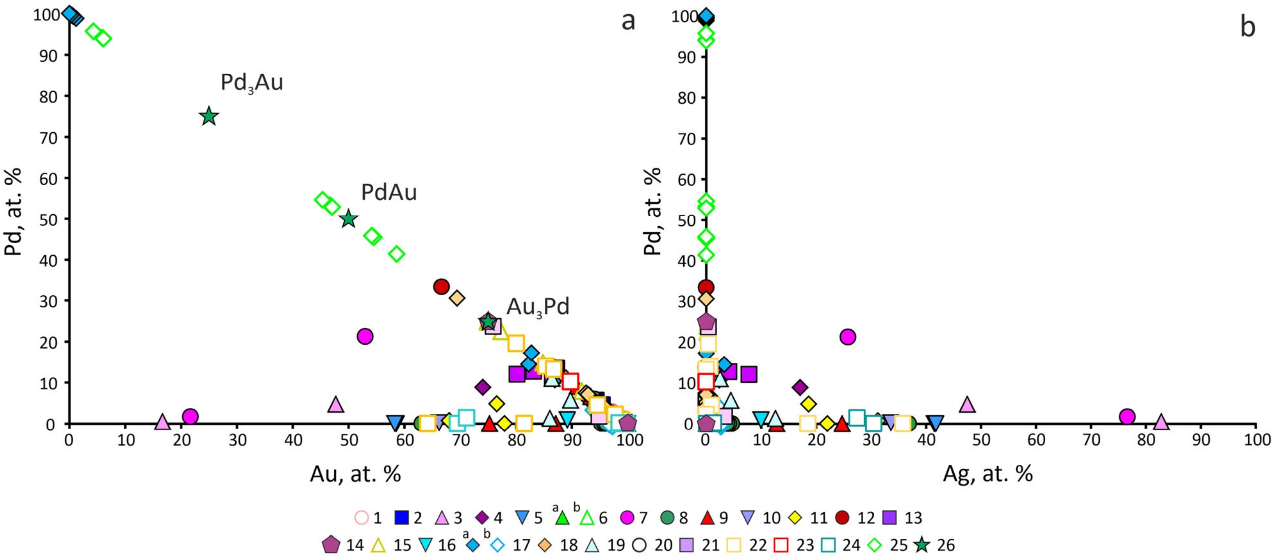

Figure 3. Dependences of the concentrations of Pd on Au (**a**) and Pd on Ag (**b**) in Pd-bearing gold and other Pd-bearing minerals of the Au-Pd-Ag system (in at.%) in various deposits and ore occurrences. Symbols are the same as in Figure 2.

4.1.3. Pd,Cu-Bearing Gold and Au-Pd-Cu System

Palladian gold with Cu impurity (Cu-bearing palladian gold or Pd,Cu-bearing gold) has a composition covering the range of solid solutions from Au to $Au_{1-x-z}Pd_xCu_z$, where $x + z \leq 0.5$ atomic part, $z \neq 0$, $x \neq 0$, and $1 - x - z > x, z$. As an example, Table 3 shows data for two objects with native gold containing Pd and Cu: the Au-Pd-Cu ore occurrence of the Skaergaard massif (Greenland, Denmark) [73] and the placer deposit of the Ambositra region (Madagascar) [70].

Table 3. The composition of Cu-bearing palladian gold, its fineness (N_{Au}), and minerals in association at endogenous and exogenous deposits.

Name of Deposit (Location)	N_{Au} ‰/Impurity wt.%	Minerals in Association	Ref.
Skaergaard massif (Greenland, Denmark)	689–913/Pd 1.3–14.7, Cu 13–19, Pt 0.12–3.6, Fe 0.4–1	Pd-Taur, Pd-Aur, Skg, PdCu, Bn, Cc, Ccp, Ktu, Pda, Vys, Vas	[73]
Ambositra region (Madagascar)	918–978/Pd 1.1–7.9, Cu < 2.8	Taur, Ba-Kfsp, Ca-REE phosphates	[70]

Phases compositionally similar to Pd-Au_3Cu and to Pd-tetra-auricupride in association with skaergaardite, bornite, chalcocite, chalcopyrite, kotulskite, palladoarsenide, vasilseverginite, and vysokýite occur at the Skaergaard layered ultramafic massif (Greenland, Denmark) [73]. In the Au-Cu-Pd-phases, the presence of Pt and Fe was observed (Table 3). Compounds close to stoichiometric $(Au,Pd)_3Cu$ are attributed to the Au_3Cu phase containing on average 24.3 at.% Cu and 15.8 at.% Pd (n = 76). A more numerous (n = 132) group, referred to as (Au,Cu,Pd) alloys containing 31 at.% Cu and 8 at.% Pd, is closely related to the above group. In the grains with the decomposition structure of the solid solution, the matrix contains 32.8 at.% Cu and 8.3 at.% Pd, and lamellas (AuCu phase) contain 44.1 at.% Cu and 8.5 at.% Pd (n = 13) [73].

The Cu content in palladian gold from the placers in the Ambositra region (Madagaskar) is low and varies from 0.6 to 2.8 wt.%, and the Pd content ranges from 1.1 to 7.9 wt.%. Palladium was not detected in tetra-auricupride. In association with tetra-auricupride and Cu-bearing palladian gold, Ba-Kfsp, Ca-REE phosphates were found [70].

Compositions of Pd,Cu-bearing gold and other Au-Cu-Pd phases from different deposits are shown in the diagram of Au-Cu-Pd (Figure 4). Pd,Cu-bearing gold (Pd 3.3–10.3 wt.%, Cu 6.1–25 wt.%) rarely contains Ag up to 1.1 wt.% (900‰–700‰), Au_3Cu, Pd-tetra-auricupride and Pd-auricupride, Pd-bearing gold without Ag, Cu, and Hg (970‰); and Pd sulfides, arsenides, antimonides, bismuthides, tellurides, stannides, plumbides, and germanides were found in chromitites of dunites from the Konder layered massif [44,45]. Cu,Pd-bearing gold and Pd-tetra-auricupride and Pd-auricupride are typical of such deposits as Norilsk-1, Talnakh, Konder, Chudnoe, Nesterovskoe, Ozernoe (Russia), Serra Pelada, Caue (Brazil), and Marathon (Canada) (Figure 4). At these deposits, such phases as Au–Cu with high Pd and, in places, Pt are widespread. Borisov (2005) [53] found that native gold from the Chudnoe deposit contains inclusions of the Au-Cu phases (Au_3Cu, Au_3Cu_2, and Au_2Cu) with minor Pd.

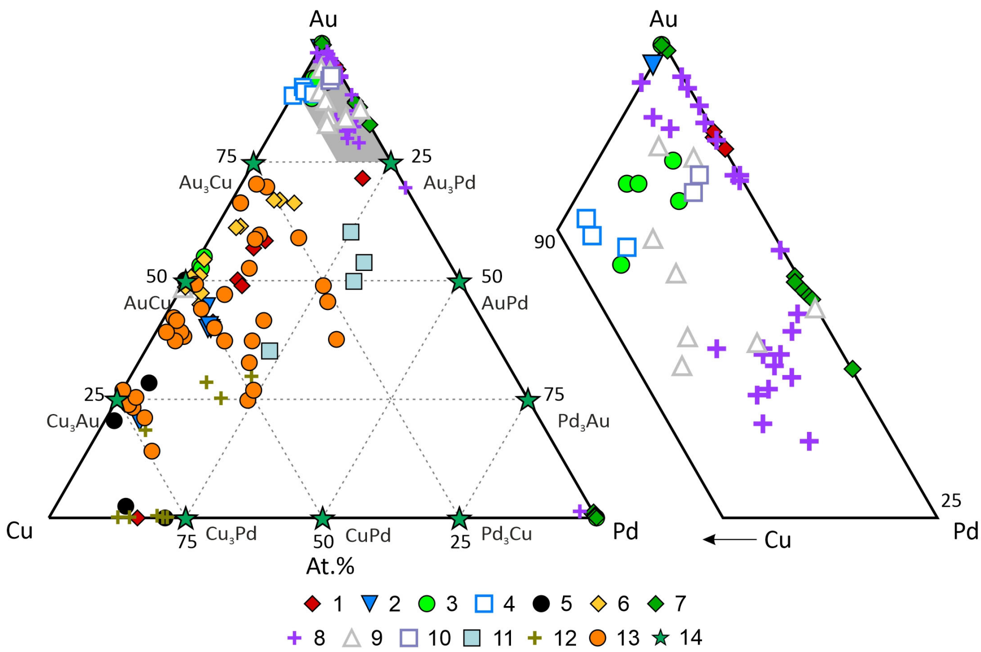

Figure 4. Composition of Pd,Cu-bearing gold and Au-Pd-Cu phases (at.%) from various deposits and ore occurrences. *Russian deposits* (1–6): 1—Norilsk-1 [27]; 2—Talnakh [27]; 3—Chudnoe [53]; 4—Nesterovskoe [53]; 5—Ozernoe [31]; 6—massive Conder [44,45]; *Worldwide deposits* (7–14): 7—Serra Pelada, Brazil [25]; 8—Caue iron mine, Brazil [77]; 9—Ambositra region, Madagascar [70]; 10—Mataganya-Siguiri zone, Guinea [69]; 11—Marathon, Canada [72]; 12—Korydallos Area, Greece [61,62]; 13—Skaergaard intrusion [73]; 14—theoretical composition of minerals in the Cu-Au-Ag system. Shaded markers are endogenous, empty markers are exogenous deposits.

Pd-tetra-auricupride (Au,Pd)Cu and Pd-auricupride $(Au,Pd)Cu_3$ are present in chromitites of the Korydallos Area in the Pindos Ophiolite Complex (NW Greece) [61,62]. The composition of Pd-tetra-auricupride is expressed by the formulae $Cu_{0.53}Au_{0.32}Pd_{0.15}$ and $Cu_{0.56}Au_{0.25}Pd_{0.19}$, and Pd-auricupride is expressed by the formula $Cu_{0.72}Au_{0.18}Pd_{0.10}$.

Cu-bearing palladian gold of the Au-Pd-Cu system depending on the Pd and Cu contents (Figures 4 and 5) can be divided into two varieties:

(1) High- and medium-fineness Cu-bearing palladian gold with low Pd and Cu contents (<10 at.%) (820‰–960‰);

(2) Low-fineness Cu-bearing palladian gold with a high Pd concentration (up to 30 at.%) and 10 at.% < Cu < 50 at.% (580‰–820‰).

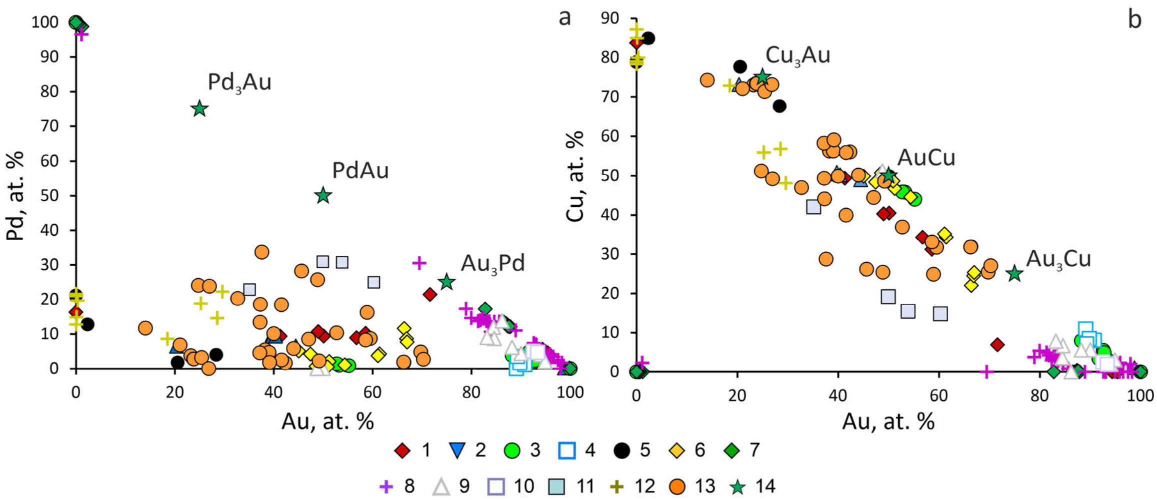

Figure 5. Dependences of the concentrations of Pd (**a**) and Cu (**b**) on Au in Pd,Cu-bearing gold and other minerals of the Au-Pd-Cu system (in at.%) in various deposits and ore occurrence. Symbols are the same as in Figure 4.

The first group includes the Nesterovskoe (Russia), Serra Pelada, and Caue (Brazil) deposits, and placers of the Mataganya-Siguiri zone (Guinea). The second group includes Pd,Cu-bearing gold of the deposits Norilsk-1, Talnakh, Chudnoe, Nesterovskoe, Ozernoe, Konder (Russia), Marathon (Canada), Skaergaard (Denmark), and the placer of Ambositra region (Madagaskar). It is worth noting that the main phases in association with Pd,Cu-bearing gold most commonly are Pd-bearing Au-Cu intermetallic compounds—Pd-tetraauricupride, and Pd-auricupride, as well as Pd sulfides, arsenides, antimonides, bismuthides, and tellurides.

Cu-bearing palladian gold can also contain Ag and (or) Hg. Examples of such deposits are described in Section 4.1.6.

4.1.4. Pd,Hg-Bearing Gold and Au-Pd-Hg System

Palladian gold with Hg impurity (Hg-bearing palladian gold or Pd,Hg-bearing gold) includes palladian gold, covering the range of solid solutions from Au to $Au_{1\text{-}x\text{-}d}Pd_xHg_d$, where $x + d \leq 0.5$ atomic part, $x \neq 0$, $d \neq 0$, and $1 - x - d > x$, $1 - x - d > d$. Several minerals are known in the Au-Pd-Hg system (https://www.mindat.org/min-51827.html, accessed on 15 January 2022): weishanite (Au,Hg(Ag)), aurihydrargyrumite (Au_6Hg_5), potarite (PdHg), gold, palladium, and mercury. The results of studies of Au-Pd-Hg mineralization from some deposits of noble metals showed the presence of binary and ternary phases: Au_2Pd and Au_3Pd [76]; Pd(Hg,Au) to Pd_3Hg_2 and $(Pd,Au)_3Hg_2$ [94]; Pd(Pt)AuHg, Au-rich potarite [95]. At the Herbeira massif (Spain), the Au-Pd-Hg phase contains Pd 53 wt.% [67] and has formula $Pd_{0.7}Au_{0.3}Hg_{0.1}$, which corresponds to Au,Hg-bearing palladium.

Native gold with Pd and Hg impurities in the absence of Ag is quite rare. Table 4 shows data for two objects with Pd,Hg-bearing gold in the absence and presence of Ag in the Itchaivayam mafic–ultramafic massif (Russia) and Mataganya-Siguiri Zone (Guinea). In the weathering crusts of the Mataganya-Siguiri Zone (Guinea), native gold is represented by two varieties: (1) Hg-bearing high-fineness palladian gold with low contents of Pd~2.7 wt.% and Hg~0.1 wt.%, sometimes Pt up to 0.09 wt.%; (2) Ag,Hg-bearing middle-fineness palladian gold with a high content of Ag~5.5–12.5 and low contents of Pd~1.1–1.8 and Hg up to 0.24 wt.% [69].

Table 4. The composition of Pd,Hg and Pd,Hg,Ag-bearing gold, its fineness (N_{Au}), and minerals in association at endogenous and exogenous deposits.

Name of Deposit (Location)	N_{Au} ‰/Impurity wt.%	Minerals in Association	Ref.
	Endogenous deposits		
Itchayvayam (Russia)	816–960/Ag < 6.1, Pd < 5.2, Hg < 8.5 580–660/Pd 13.9–15.9, Hg 19.1–27.8, Ag < 1.7	Ep, Cpy, Ptr, Cpe, Tnr Ep, Cpy, Cu sulfate, Au	[33,42]
	Exogenous deposits		
Mataganya-Siguiri Zone (Guinea)	960–970/Pd 2.6–2.8, Hg 0.07–0.11, Pt < 0.09 860–920/Pd 1.1–1.8, Hg < 0.24, Ag 5.5–12.5	Spy, Bg -	[69]
Zimnik Creek (Poland)	core 980/Pd 0.01–0.95, Hg 0.36–0.96, Ag 0.15–1.93; border 990–1000/Ag < 0.62, Pd < 0.01	Hem, Mag, Ap, Kln, Ms, Qz	[64]
River Dart (England)	630/Pd 22.7, Hg 13.6, Ag 2.2	Au-Ag > 970, Ausb, Ptr, Skg, Stpdn, Carb	[20]

Palladian gold from the placers that occur in the layered Itchayvayam platinum-bearing mafic–ultramafic massif (northern part of the Koryak–Kamchatka platinum-bearing belt, Russia), according to preliminary data, has varying compositions of Pd,Hg-bearing gold [42]. Au-Pd-Cu ore occurrences of this massif were found to contain high-fineness argentian gold and Au-Hg-Pd phases, which form thin veins in bornite and are in paragenesis with platinum group minerals [24,96].

We studied individual gold grains from the heavy concentrates of the Itchayvayam placers and watercourses draining and ore samples from the Barany outcrop of the Itchayvayam mafic–ultramafic complex (Kamchatka) [33]. Gold grains contain substitution structures formed by Pd,Hg-rich low-fineness gold ($Au_{0.59-0.52}Pd_{0.24-0.25}Hg_{0.17-0.23}$, 580‰–660‰) and high-fineness gold with minor contents of Pd and Hg ($Au_{0.94-0.90}Pd_{0.02-0.04}Hg_{0.03}$, 910‰–960‰) (Figure 6). Potarite (PdHg) without and with impurities Au, Cu, and Ag; high-fineness gold with minor contents of Ag ($Au_{0.91}Ag_{0.09}$, 950‰) or also Pd and Hg ($Au_{0.75}Ag_{0.08}Pd_{0.09}Hg_{0.08}$–$Au_{0.88}Ag_{0.09}Pd_{0.02}Hg_{0.01}$, 820‰–930‰); and Pd,Hg-rich low-fineness gold with minor contents of Ag and Cd ($Au_{0.51-0.55}Pd_{0.25-0.22}Hg_{0.21-0.16}Ag_{0.03-0.06}Cd_{0.01}$, fineness 580‰–630‰) were observed in the ore samples.

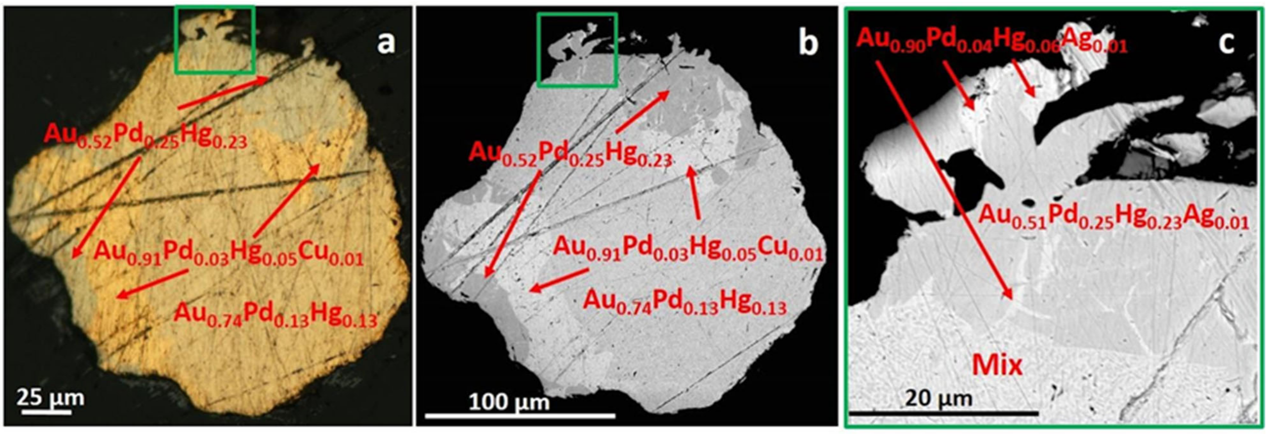

Figure 6. Optical photo (in reflected light) (**a**) and SEM photo (BSE mode) of a gold grain (**b**), as well as SEM photo (BSE mode) of a gold fragment (green box in a,b) (**c**) with low-fineness Pd,Hg-rich gold (580‰–660‰) and high-fineness Pd,Hg-poor gold (910‰–960‰). Ore occurrence of the Itchayvayam mafic–ultramafic complex (Kamchatka, Russia).

Figure 7 shows the composition of Pd,Hg-bearing gold and Au-Pd-Hg phases from the Itchayvayam mafic–ultramafic massif, Chudnoe (Russia) and Herbeira massifs (Spain), and placers of the Mataganya-Siguiri zone (Guinea).

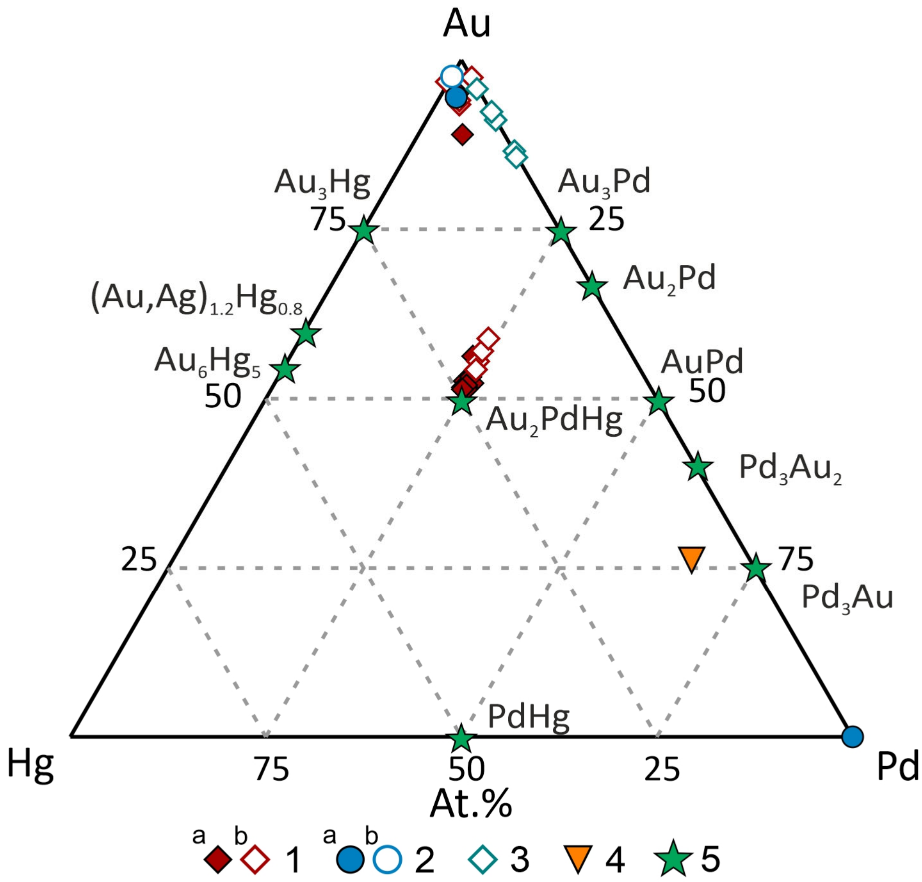

Figure 7. Composition of Pd,Hg-bearing gold and Au-Pd-Hg phases (at.%) from various deposits and ore occurrences. Russian deposits (1, 2): 1—Itchayvayam mafic–ultramafic massif, this study and after Sidorov [42]; 2—Chudnoe [53]; worldwide deposits (3, 4): 3—Mataganya-Siguiri zone, Guinea [69]; 4—Herbeira massif, Spain [67]; 5—theoretical composition of minerals of the Hg-Au-Pd system. Colored markers are endogenous, empty markers are exogenous deposits.

Palladian gold of the Au-Pd-Hg system is represented by two varieties (Figures 7 and 8):

(1) High- and medium-fineness gold with low Hg < 0.02 at.% (<5.2 wt.%) and low Pd contents <0.13 at.% (<8.5 wt.%) (fineness 820‰–960‰);

(2) Low-fineness gold with a high content of Hg 13–27 at.% (13.6–27.8 wt.%) and high Pd ≈25 at.% (13.9–15.9 wt.%) (fineness 580‰–630‰).

Hg-bearing palladian gold of both varieties—low Pd, Hg (1) and high Pd, Hg (2) contents were found at the Itchayvayam deposit. Native gold in the Mataganya-Siguiri Zone (Guinea) placer is an example of ore occurrence with high-fineness Hg-bearing palladian gold (with low Pd and Hg contents) (1).

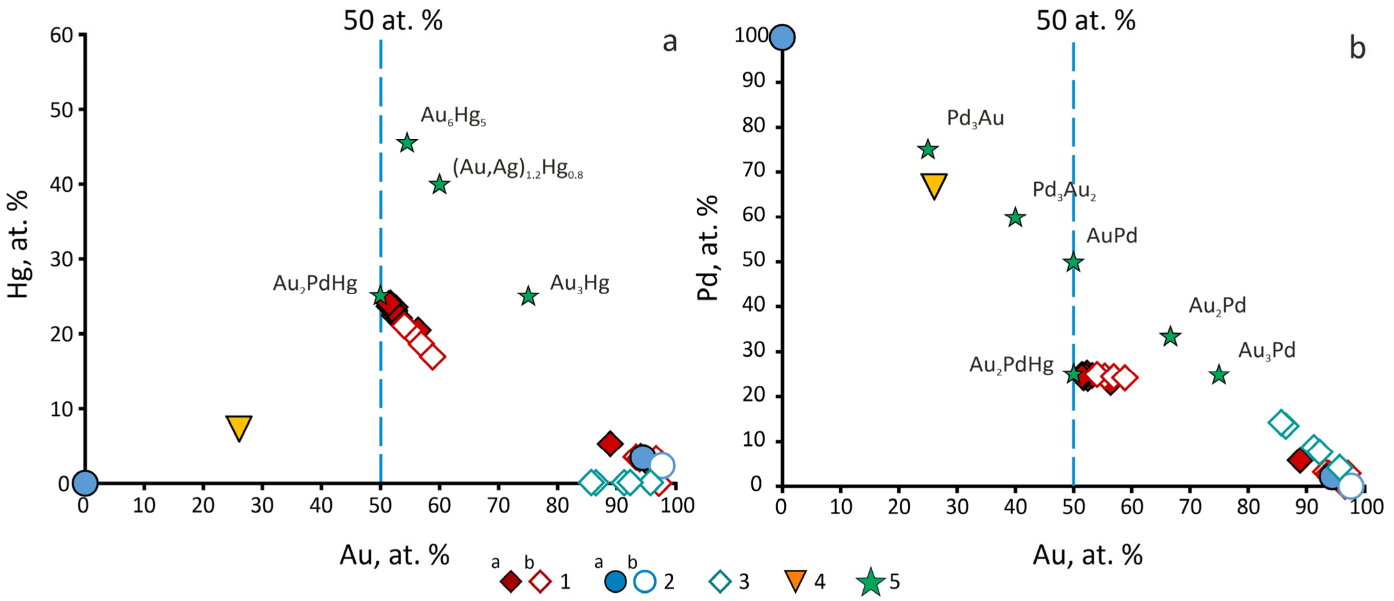

Figure 8. Dependencies of the concentrations of Pd (**a**) and Hg (**b**) on Au in Pd,Hg-bearing gold and other Pd-bearing minerals of the Au-Pd-Ag system (in at.%) in various deposits and ore occurrences. Symbols are the same as in Figure 7.

At some deposits, Pd,Hg-bearing gold has minor contents of Ag. As an example, in Table 4, we provide data on the composition of Pd,Hg,Ag-bearing gold from two alluvial placers related to sediments (conglomerates) and volcanic rocks—Zimnik Creek (Poland) and river Dart (England). The Hg content varies in the range of 0.07 to 13.9 wt.%, and the Ag content is lower at 2.2 wt.%. Native gold with Pd and Hg impurities and higher Ag contents is spread at many other deposits—Serra Pelada (Brazil) [97], Gongo Soco (Brazil) [78,98], Mayat river and Bol'shaya Kuonamka river (Russia) [47], and Dziwiszow (Poland) [65].

The compositions of palladian gold with Hg and Ag impurities cover the range of solid solutions from Au to $Au_{1\text{-}x\text{-}y\text{-}d}Pd_xAg_yHg_d$, where x, y, d in total $\leq$ 0.5 atomic part, $x \neq 0$, $y \neq 0$, $d \neq 0$, and $1 - x - y - d > x, y, d$. Hg,Ag-bearing palladian gold is more widely distributed in nature than Pd,Hg-bearing gold (see Section 4.1.6).

4.1.5. Pd,Cu,Ag-Bearing Gold and Au–Pd–Ag–Cu System

Palladian gold with Cu and Ag impurities (Cu,Ag-bearing palladian gold or Pd,Cu,Ag-bearing gold) covers the range of solid solutions from Au to $Au_{1\text{-}x\text{-}y}Pd_xAg_yCu_z$, where x, y, z in total $\leq$0.5 atomic part, $x \neq 0$, $y \neq 0$, $z \neq 0$, and $1 - x - y - z > x, y, z$. The group of deposits with Cu,Ag-bearing palladian gold is the most numerous group compared to other groups (Tables 1–4) and includes 18 objects among which there is only one placer deposit—Kuoyka river, basin of the Anabar river (Russia) (Table 5).

Au,Pd,Ag,Cu-solid solutions with Au >> Pd, Ag, Cu (>1 vol%), Au,Ag,Pd-solid solutions, argentian gold (Au > Ag), native silver (Ag >> Au), a Pd-bearing tetra-auricupride (Cu,Ag)(Au,Pd), and phase $(Au,Pd,Ag)_3Cu$ occur in the W Horizon mineralization of the Marathon Cu-PGE deposit, which is one of the highest grade PGE repositories in magmatic ore deposits worldwide [21]. The Marathon deposit is located within the Mesoproterozoic Coldwell Alkaline Complex in the Midcontinent rift of North America. The content of impurities in native gold from this deposit is very high and reaches 22.7 wt.% for Pd, Ag < 37.7 wt.% and Cu < 25.8 wt.%, which corresponds to a fineness of 516‰–835‰ (Table 5).

Table 5. The composition of Pd,Cu,Ag-bearing gold, its fineness (N_{Au}), and minerals in association at endogenous and exogenous deposits.

Deposit Name (Location)	N_{Au} ‰/Impurity wt.%	Minerals in Association	Ref.
	Endogenous deposits		
Caue (Itabira region, Brazil)	800–918/Pd 0.9–19.2, Ag 0.1–1.1, Cu 0.04–4.1	Qz, Fsp, Hem, Gth, Ms, Tur, Ap, Mnz, Carb, Pd-Cu-oxides, Pd	[26,77]
Conceichao mine, - « -	930–940/Pd 0.8–3.2, Ag 0.4–1, Cu 0.7–1, Fe 0.3–6.1 980/Pd 0.9, Ag 0.6	Hem, Mag, Py, Qz, Ms, Met-II, Au-Ag, Kln	[79]
Maquine, - « -	900–948/Ag 3.5–8.2, Pd 1.5–2.75, Cu 0.1–0.8, Pt ≈ 0.03	Hem, Gth, Qz, Spy, Stpdn, Ism	[28]
Marathon (Canada)	516–835/Pd 0.5–22.7, Ag < 37.7, Cu 0.8–25.8	Cpy, Bn, Brg, Ifp, Vas, Vys, Au, Ag, Taur	[21]
Ozernoe (Ural, Russia)	690–700/Cu, Ag > Pd < 3.8	Chl, Cpx, Met-I, Stpdn, Py, Cpy, Bn, Mrk, Taur, Auc, Ag-Cu-Au	[31]
Nesterovskoe (- « -)	970/Pd 0.06–0.91, Ag 0.87–0.96, Cu < 2.01	Qz, Ab, Cr-Ms, Aln, Met, Ah, Mon, Au_3Cu	[53]
Volkovskoe (- « -)	1000	Ti-Mag	[30,55]
	810–914/Ag 8.4–16.2, Pd ≤ 0.3, Cu 0.2–0.4	Mrk, Kei, Syv, Hes, Spy	
Baronskoe (- « -)	840–940/Pd 3.5–9, Ag 1–10.6, Cu 0.6–1.9	Brn, Ccp, Py, Cc, Dg, Vsk, Pd tellurides and arsenides	[55]
	916/Pd 4.3, Ag 1.6, Cu 2.5/$Au_{0.90}Pd_{0.06}Cu_{0.03}$	Pds	
Serebryansky Kamen (-«-)	783/Pd 12.1, Cu 7.5, Ag 2.1	Bn, Vsk, Pd tellurides, Au-Ag (760–970)	[54]
Khamitovskoe (- « -)	880–920/Ag 7.6, 8.1, Cu 1.1, Pd 0.5, 0.9	-	[56]
Bleida Far West (Morocco)	912–993/Pd 0.04–6.29, Ag 0.67–8.34, Cu < 3.1	Pdm, Mrk, Met, Oos, Spy, Pds, Ktu, Taur, Hem, Cc, Ani, Mag, Gth, Kfs, Bt, Chl, Cal, Au-Ag (770–870)	[32,68]
Konder Massif (Aldan, Russia)	974/Pd 2.58	Au_3Cu, Pd-Taur, Pd-Aur, Pd sulfides, arsenides, antimonides, bismuthides, tellurides, stannides, plumbides, germanides	[44,45]
	700–900/Pd 3.3–10.3, Cu 6.1–25, Ag < 1.1		
Norilsk-1 (Russia)	570–880/Ag 6.8–42.1, Pd < 6.2, Cu < 1.5, Pt < 3.9	Pd-Taur, Tfpt, Pyr, Pn	[27]
	950–975/Pd 2.22–2.89, Ag < 3.59, Cu < 0.15, Pt < 1.6	-	
Talnakh (- « -)	160–210/Ag 70.1–82.9, Pd < 3, Cu < 1.5	Pt-Ato, Spdn, Pd-Taur, Pb-Pol, Zvy, Ccp	[27]
	>980/Pd < 1.25, Cu < 0.54, Ag < 0.38		
Deposit Name (Location)	**N_{Au} ‰/Impurity wt.%**	**Minerals in Association**	**Ref.**
Yu. Peshempakhk (1), V. Chuarvy (2), S. Kamennik (3) (- « -)	(1) 960/Pd 1.90, Ag 0.46, Cu 1.25	-	[58]
	(2) 830–970/Pd 1.44–3.48, Ag 0.78–1.69, Cu 0.23–0.25, Fe 0.2–0.36, Ni < 0.03	-	
	(3) 833–920/Ag 1.5–16.2, Pd < 6.5, Cu < 0.6, Fe < 0.2	Ktu, Pda, Met, Spy	
	Exogenous deposits		
Kuoyka river (Anabar river basin, Russia)	(20) 960/Pd 3.43, Ag 0.39, Cu 0.07	-	[47,48]

The Cauê iron mine, in the ltabira District of Brazil, contains a unique precious-metal-bearing mineral assemblage that includes palladian gold, pure gold, native palladium, palladseite, arsenopalladinite, and Pd-Cu oxide minerals. Palladian gold grains contain up to 19.2 wt.% Pd, while Cu is typically below 4.1 wt.% and rarely reaches 8.3 wt.%, and Ag does not exceed 1.1 wt.% (fineness 808‰–993‰) [77] (Table 5). Palladian gold from the Conceichao deposit in the same region of Brazil has lower concentrations of Pd (<3.2 wt.%) and minor contents of Ag, Cu (fineness 930‰–940‰) or Ag (fineness 980‰) (Table 5) in association with hematite, magnetite, pyrite, quartz, muscovite, mertieite-II, argentian gold (940‰–950‰), and kaolinite. Palladian gold from the Maquine deposit (Brazil) is characterized by lower contents of Pd, Cu, and also trace Pt, whereas the concentrations of Ag amount to 3.5–8.2 wt.% (fineness 900‰–948‰), and minerals in the association are hematite, goethite, quartz, sperrylite, stannopalladinite, and isomertieite.

Palladian gold from some Uralian deposits also has low contents Pd (in wt.%): Volkovskoe < 0.3, Khamitovskoe 0.5–0.9, Nesterovskoe < 2.8, Ozernoe < 3.8. Higher contents of Pd to 9 wt.% were detected in palladian gold from the Baronskoe, and to 12.1 wt.%—from the Serebryansky Kamen deposits (Table 5).

Noble metal mineralization at the Volkovskoe Cu-Fe-Ti-V deposit is concentrated in meso- and melanocratic taxite gabbro containing a dissemination of V-bearing titanomagnetite, chalcopyrite, and bornite. Palladian gold has low concentrations of Cu~0.3 wt.% and high concentrations of Ag from 8.4 to 16.2 wt.% (fineness 800‰–914‰) (Table 5) [30]. Among the minerals of noble metals in copper-sulfide (chalcopyrite, bornite, digenite) ores, there are also tellurides—merenskyite, hessite, and sylvanite, and platinum arsenide—sperrylite [55,99–103].

At the Baronskoe deposit, native gold is composed of Au-Ag, Au-Ag-Pd, Au-Pd-Cu, and Au-Pd-Ag-Cu solid solutions [55,104–106]. Au-Ag-Pd solid solutions (3.5–9 wt.% Pd, to 10 wt.% Ag) form inclusions in chalcopyrite, vysotskite, bornite, Pd tellurides, and arsenides. The Au-Pd-Cu solid solution ($Au_{0.90}Pd_{0.06}Cu_{0.03}$) was found in the intergrowth with palladseite in olivine-magnetite gabbro. Ag,Cu-bearing palladian gold contains Pd 3.4–5.7 wt.%, Ag up to 10.6 wt.%, and Cu 0.6–1.9 wt.% (fineness 840‰–916‰) (Table 5) [55]. Au-Ag solid solutions occur in secondary silicates (serpentine, amphibole, chlorite) and do not contain Pd.

The Ozernoe deposit is known for Au-Ag-Cu solid solutions (to 6.5 wt.% Cu, 7–69 wt.% Ag) and Au-Cu intermetallic compounds (tetra-auricupride, auricupride), in which palladium up to 16.9 wt.% occurs sporadically [31,107,108]. Palladian gold with Cu and Ag impurities has a low fineness (690‰–700‰) (Table 5), and the majority of compositions of Au-Pd-Ag-Cu phases are similar to tetra-auricupride, auricupride, native copper, or silver. Olivine clinopyroxenites from this deposit contain impregnations of sulfides in an amount of no less than 0.5% (in separate zones to 1–3). Palladian gold is present in the cubanite–pentlandite–pyrrhotite–chalcopyrite (1) and bornite–chalcopyrite (2) mineral associations. The first association was found to contain minerals of Pt (native platinum, ferruginous platinum, braggite, sperrylite, and moncheite) and Pd (palladian copper, vysotskite, arsenopalladinite, mayakite, atheneite, isomertieite, stibiopalladinite, michenerite, merenskite, froodite, and palladian silver). In the second association, minerals of Pt (sperrylite), Pd (atheneite, mertieite, stibiopallandinite, kotulskite, tarkianite, sobolevskite, and froodite) and Ag (native silver and hessite) were found. According to Murzin et al. (2022) [31], the Pd content increases from <1.5 wt.% Pd in Au-Ag solid solution to 6 wt.% Pd in Au-Cu intermetallic compounds and to 16.2–16.9 wt.% Pd in Cu-Au-Ag-Pd solid solutions.

Native gold in copper-sulfide ores of the Serebryansky Kamen from gabbro of the Serebryansky massif is heterogeneous and corresponds to Au-Ag (fineness 760‰–970‰) and Au-Cu-Pd-Ag solid solutions with high Pd and lower contents of Cu and Ag (fineness 780‰) (Table 5) [54]. It forms inclusions in bornite and chalcopyrite and frequently occurs in association with Pd sulfides, arsenides, and tellurides.

The ore samples from the Central and Intermediate zones of the Au-Cu epithermal (porphyry) Bleida Far West deposit (Anti-Atlas, Morocco) contain high-fineness palladian gold with low concentrations of Pd and Ag in the absence of Cu, or with minor Cu 0.3–0.8 wt.% (912‰–993‰) [32,68]. Au-Pd-mineralization at this deposit contains no sulfides, and palladian gold occurs in association with mertieite, isomertieite, keitconnite, palladseite, merenskyite, kotulskite, sperrylite, hematite, calcite, quartz, barite, and chlorite (Table 5).

Various alloys of the Au–Ag, Au-Ag-Cu, and Au-Ag-Cu-Pd systems have been found in Cu–Ni–PGE ores from Norilsk and Talnakh deposits (Russia) [27,109]. The Au-Cu-Ag-Pd (Pt) phase is characterized by wide variations in Cu content from LOI up to 42 wt.% and Ag from LOI up to 37 wt.%, Pd from LOI to 14 wt.%, and occasionally Pt < 5 wt.%, which corresponds to Cu,Ag,Pd-bearing gold, $(Au,Pd)_3Cu$, Pd-tetra-auricupride, Pd-auricupride, and Cu,Au,Pd-silver. They are in association with mertieite/isomertieite, keitconnite, palladseite, kotulskite, merenskyite, isoferroplatinum, vysotskite, hematite, calcite, quartz, barite, epidote, chlorite, etc. The fineness of Cu,Ag,Pd-bearing gold changes from 570 to 880 and from 950 to 975‰ for Norilsk-1 and is higher (980‰) for Talnakh (Table 5).

Au–Cu alloys with significant amounts of Pt, Pd, and Ag impurities were reported from platinum placers associated with the Konder alkaline–ultramafic complex, where abundant Au–Cu alloys intergrow with PGM (particularly Pt–Fe alloy) and show a range of compositions close to Au_3Cu and AuCu along with a single Cu_3Au grain [44,45,110]. The Pt and Pd concentrations in these alloys reach 11.8 and 10.3 wt.%.

The contents of Pd in Cu,Ag-bearing palladian gold at Pt-metal deposits of the Fedorovo-Pansky intrusive complex (Russia) change from 0.03 to 6.5 wt.%, Cu < 1.2 wt.%, Ag up to 16.2 wt.%, and the fineness increases from 830 to 970‰ [58]. In places, the presence of impurities of Fe and Ni was observed (Table 5). Native gold from the Kuoyka river (basin of the Anabar river, Russia) contains 3.43 wt.% Pd, whereas Ag and Cu concentrations are low at 0.4 wt.% (fineness 960‰) [47,48].

Figure 9 shows that Ag,Cu-bearing palladian gold of the Au-Pd-Ag-Cu system depending on the Pd, Ag, and Cu contents can be divided into several varieties:

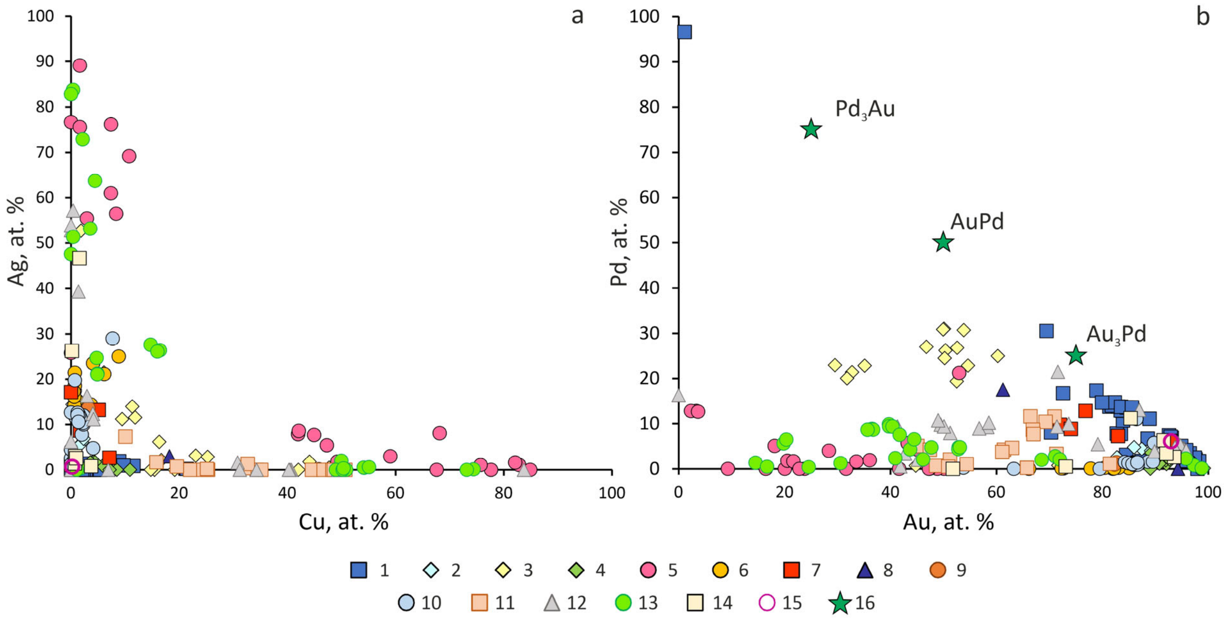

Figure 9. Dependences of the concentrations of Ag on Cu (**a**) and Pd on Au (**b**) in Pd,Ag-Cu-bearing gold and other Pd-bearing minerals of the Au–Pd–Ag–Cu system (in at.%) in various deposits and ore occurrences (Table 5) (filled marker—endogenous, empty—exogenous): 1—Caue iron mine (Itabira, Minas Gerais, Brazil) [26,77]; 2—Maquine (Brazil) [28]; 3—Marathon (Canada) [21]; 4—Nesterovskoe (Polar Urals, Russia) [53]; 5—Ozernoe (Subpolar Ural, Russia) [31]; 6—Volkovskoe (Middle Urals, Russia) [30,55]; 7—Baronskoe (Middle Urals, Russia) [55]; 8—Serebryansky Kamen (Northern Urals, Russia) [54]; 9—Khamitovskoe (Yu.Ural, Russia) [56]; 10—Bleida Far West (Morocco) [32,68]; 11—Konder massif (Aldan, Russia) [44,45]; 12—Norilsk-1, 13—Talnakh (Russia) [27]; 14—Y. Peshempakhk (1), V. Chuarvy (2), S. Kamennik (3) (Russia) [58]; 15—Kuoyka River (Anabar river basin, Russia) [47,48]; 16—theoretical compositions of Au-Pd intermetallic compounds.

(1) High-fineness gold with low contents of Pd, Ag, and Cu < 10 at.% (900‰–970‰). The palladian gold of this composition was found in Conceichao and Maquine mines (Brazil), Nesterovskoe, Khamitovskoe, Kuoyka River (Russia), and Bleida Far West (Morocco).
(2) Middle- and low-fineness gold with a high content of Ag 10–48 at.% and low contents of Pd and Cu < 10 at.%. Volkovskoe and Norilsk (Russia) are examples of deposits with such native gold.
(3) Middle- and low-fineness with high contents of Pd 10–30 at.%, Cu 10–48 at.%, and Ag < 10 at.%. Marathon (Canada), Konder (Russia), and Caue iron mine (Brazil) are examples of deposits with native gold containing high concentrations of Pd and Cu, and low Ag.

4.1.6. Palladian Gold with Ag, Cu, Hg, and Other Metals

Palladian gold commonly contains impurities of all three elements—Ag, Cu, and Hg (Cu,Ag,Hg-bearing palladian gold or Pd,Cu,Ag,Hg-bearing gold) and has a heterogeneous structure and a variable composition of $Au_{1-x-y-z-d}Pd_xAg_yCu_zHg_d$. The Au-Pd-REE Chudnoe (Russia), Fe-oxide-Cu-Au Gongo Soco, Au–Pd–Pt Serra Pelada (Brazil), and Zechstein (Poland) deposits are examples of deposits with such palladian gold (Table 6). Pd,Cu,Ag,Hg-bearing gold is typical of some alluvial deposits: placers of the Mayat and Bol'shaya Kuonamka river basins (Anabar massif, northeast of the Siberian Platform, Russia), Dziwiszow (Poland), Whipsaw Creek, and Similkameen river (Canada) (Table 6).

Table 6. The composition of Pd,Cu,Ag,Hg-bearing gold, its fineness (N_{Au}), and minerals in association at endogenous and exogenous deposits.

Name of Deposit (Location)	N_{Au} ‰/Impurity wt.%	Minerals in Association	Ref.
	Endogenous deposits		
Chudnoe (Ural, Russia)	829–886/Ag 7.7–13.4, Pd 0.5–1.1, Cu 1.1–7.6	Qz, Ab, Kfs, Cr-Ms, Ah, Taur, Au_{950}	[29,53,111–113]
	839–866/Ag 11.9–12.5, Pd 0.5–0.8, Cu 1.7–2.5, Hg 0.6–1	Qz, Ab, Kfs, Cr-Ms, U-Met, Taur, Au_{930}	
	932–986/Ag < 5.64, Pd < 2.78, Cu < 2.78	$Au_{840-860}$	
Serra Pelada (Brazil)	920–930/Pd 6.9–7.8, Ag < 0.2, Cu < 0.1, Hg < 0.02, Fe < 0.05	Pd, Pd-Au-Pt-As phase, Svi, Pds, Pd_3As, Pd-oxide, Gth, $Au_{990-996}$	[97]
	880–940/Pd 3.2–9.8, Ag < 0.3, Cu ≈ 0.7, Hg 0.3–1.5, Fe < 0.05	Ah, Pd–Hg–Se and Pd–Bi–Se phases	
	965–975/Pd 1.6–2.4, Ag 0.4, Cu ≈ 0.6, Hg < 0.02, Fe < 0.1	Ism, Mn–Ba oxide	
	993–997/Ag ≈ 0.3, Pd 0.04–0.1, Cu < 0.07, Fe 0.05–0.3	Au_7Pd, Gth	
Gongo Soco (Brazil)	880–890/Pd 5.9–6.1, Hg 0.9, Ag ≈ 2, Cu 0.1–2.7	Hem, Gp, Ism, Met, Au-Ptr, (Pd,Cu)O, (Fe,Pd)OOH	[25,78]
Zechstein (Poland)	576–795/Ag 12.5–34, Pd 3–6.9, Cu 0.1–0.4, Hg 0.7–6.0, Pt 0.46–1.6, Ir < 0.8	Cat, kerogen, Sov, Pb, Cth, Any, Pd	[63]
	Exogenous deposits		
r.Mayat (1), r. Bol'shaya Kuonamka (2) (Anabar river basin, Russia)	(1) 860–960/Pd 0.8–12.8, Hg < 0.3, Ag 0.9–2.8, Cu < 0.4	Tpdn, Ktu	[47,114]
	(2) 910–970/Pd 0.7–7.5, Hg < 1.7, Ag 0.6–2.2, Cu 0.1–1.5	Pt	
Dziwiszow (Poland)	centre 960–990/Pd < 0.5, Hg < 2.5, Ag 1.1–3, Cu < 0.1, Pt < 0.04	Hem, Gth, Kln	[65]
	core 975–997/Pd < 1.4, Hg < 1.9, Ag 0.2–1.8, Cu < 0.1, Pt < 0.03		
Whipsaw Creek (Canada)	910–940/Pd ≈ 2.5, Hg 0.20–2.28, Ag 0.7–3, Cu 1.1–3.1	Stpdn, Cc, Spy	[71]
Similkameen river (- « -)	970/Pd < 2.1, Hg 0.1–0.7, Cu 0.06–1.8, Ag 0.7	Tem, Bn, Cc, Ccp, Cin, Pd-telluride, Pd-arsenoantimonide	[71]
Friday Creek (- « -)	930/Ag 3.97, Pd 1.94, Cu 0.55, Hg 0.32	Bn, Cc	[71]

Au-Pd-REE ores from the Chudnoe deposit contain palladian gold with various sets of impurity elements: (1) all 4 elements—Ag, Cu, Hg, and Pd; (2) 3 elements—Ag, Cu, Pd or Cu, Hg, and Pd [29]; (3) 2 elements—Hg (3.4–3.5 wt.%) and Pd (1.2–1.6 wt.%) [53]. The presence of Au-Ag (fineness 720‰–730‰) and Au-Ag-Cu-solid solutions (Ag 11.4–14.8 wt.%, Cu 1.4–4.6 wt.%, fineness 836‰–869‰) was also detected in these ores. The content of Ag in palladian gold varies in a wide range, but is no more than 13.4 wt.%, Cu < 7.6 wt.%, Hg < 3.5 wt.% [53], Pd < 2.8 wt.%, and fineness 829‰–986‰ (Table 6). High concentrations of Hg (36 wt.%) and Pd (15.2 wt.%), and low Cu in the absence of Ag were found in the ore samples collected from the surface in weathered material at the Chudnoe deposit [53]—in the composition, this is the Au-Hg phase with Pd and Cu impurities ($Au_{0.41}Hg_{0.31}Pd_{0.25}Cu_{0.03}$). The specific features of this deposit are an unusual association of Cu,Ag,Pd,Hg-bearing gold and palladium minerals (mertieite, isomertieite, atheneite, stillwaterite, and stibiopalladinite) with Cr-bearing muscovite (fuchsite) and REE mineral (allanite) in the absence of sulfides [29,112,113], and the low content of Hg in Cu,Ag,Pd-bearing gold is normally less than 1 wt.% (Table 6).

The Chudnoe deposit is the recharge source for the placer of the Al'kes-Vozh creek and, partly, for other placers downstream of the Balaban-Yu river. The presence of native gold with impurities of Pd (to 2 wt.%), Cu (to 5 wt.%), and Hg (to 0.6 wt.%) in the Al'kes-Vozh placer, as well as the presence of Pd minerals (mertieite, atheneite, stibiopalladinite) in gold grains, served as the basis for identifying a placer-forming type of gold mineralization in the Urals prior to the discovery of its endogenous source [52]. The occurrence of palladian gold in the Al'kes-Vozh placer is 81% and it gradually decreases to 13% in the Balban-Yu placers located below [115].

Ores from the Au–Pd–Pt Serra Pelada deposit (Brazil) contain up to 1 cm coarse-grained gold aggregates that occur in powdery, earthy weathered material [25]. They exhibit a delicate arborescent fabric and are coated by goethite. Four compositional types of palladian gold are recognized at this deposit: (1) "Au_7Pd", the most abundant Au–Pd alloy, hosts Pd arsenides ("guanglinite" and Sb-bearing "guanglinite"), Pd–Pt–Se and Pd–Se phases, sudovikovite, and palladseite; (2) Au–Pd–Hg alloy, characteristically with atheneite and rarely observed Pb-bearing Pd–Hg–Se and Pd–Bi–Se phases; (3) Pd-poor gold—isomertieite—Mn–Ba oxide assemblage; and (4) pure gold with trace Pd (>993‰) in goethite assemblage (Table 6). The Ag content in these types of palladian gold is lower than 0.4 wt.%. The Pd,Ag-poor gold assemblage possibly formed later than the Au–Pd–Hg–Ag alloy. In the ores of the Fe-oxide-Cu-Au Gongo Soco deposit (Brazil), palladian gold with Ag, Cu, and Hg impurities occurs in the form of nuggets, grains, and their aggregates in association with hematite. Gold grains have dark-color coatings composed of Pd–O particles and iron hydroxide. The palladian gold is characterized by a variable Pd content reaching up to 6 wt.% and sporadically observed Hg content up to 1 wt.% [97]. Pd,Hg-bearing gold at these deposits can also contain Cu and Ag impurities to 3 and more wt.% [78]. Palladian gold contains inclusions of platinum group minerals (PGMs): isomertieite, mertieite-II, chrisstanleyite, selenides $Pd_5(Hg,Sb,Ag)_2Se_6$, and $(Pd,Sb,Ag,Hg)_5Se_4$.

Palladian gold (with minor content of Hg, Cu, Ag) in association with Pt minerals is found in the placers of the Mayat and Bol'shaya Kuonamka river basins (Anabar massif, northeast of the Siberian Platform) [116].

Figure 10 shows the dependences of the concentrations of elements in Pd-bearing gold and other Pd-bearing minerals of the Au-Pd-Ag-Cu-Hg system (in at.%) at various deposits and ore occurrences (Table 6). Variations in the concentrations of impurities in native gold range from LOI up to 26 for Pd, <50 Ag, <18 Cu, and <6 Hg (in wt.%). According to Figure 10, the Ag,Cu,Hg-bearing palladian gold depending on the Pd, Ag, and Cu contents can be divided into several varieties:

(1) High-fineness gold with low contents of Pd, Ag, Cu < 10 at.% and Hg < 5.7 at.% (900‰–970‰). The palladian gold of this composition is typical of the deposits Chudnoe (Russia), Serra Pelada and Gongo Soco (Brazil); and alluvial placers Dziwiszow (Poland), Whipsaw Creek, Similkameen River, and Friday Creek (Canada); and Mayat and Bol'shaya Kuonamka river basins (Russia).
(2) Medium- and low-fineness gold with high Ag 10–48 at.% and low contents of Pd, Cu < 10 at.%, and Hg < 5.7 at.%. Chudnoe (Russia) and Zechstein (Poland) are examples of deposits with such Ag,Cu,Hg-bearing palladian gold.
(3) Medium- and low-fineness gold with a high content of Pd 10–28 at.%, and low Cu and Ag < 10 at.% and Hg < 5.7 at.%. Serra Pelada (Brazil), Mayat river basin, and Chudnoe (Russia) are examples of deposits with native gold containing high concentrations of Pd and low Cu, Ag, and Hg.

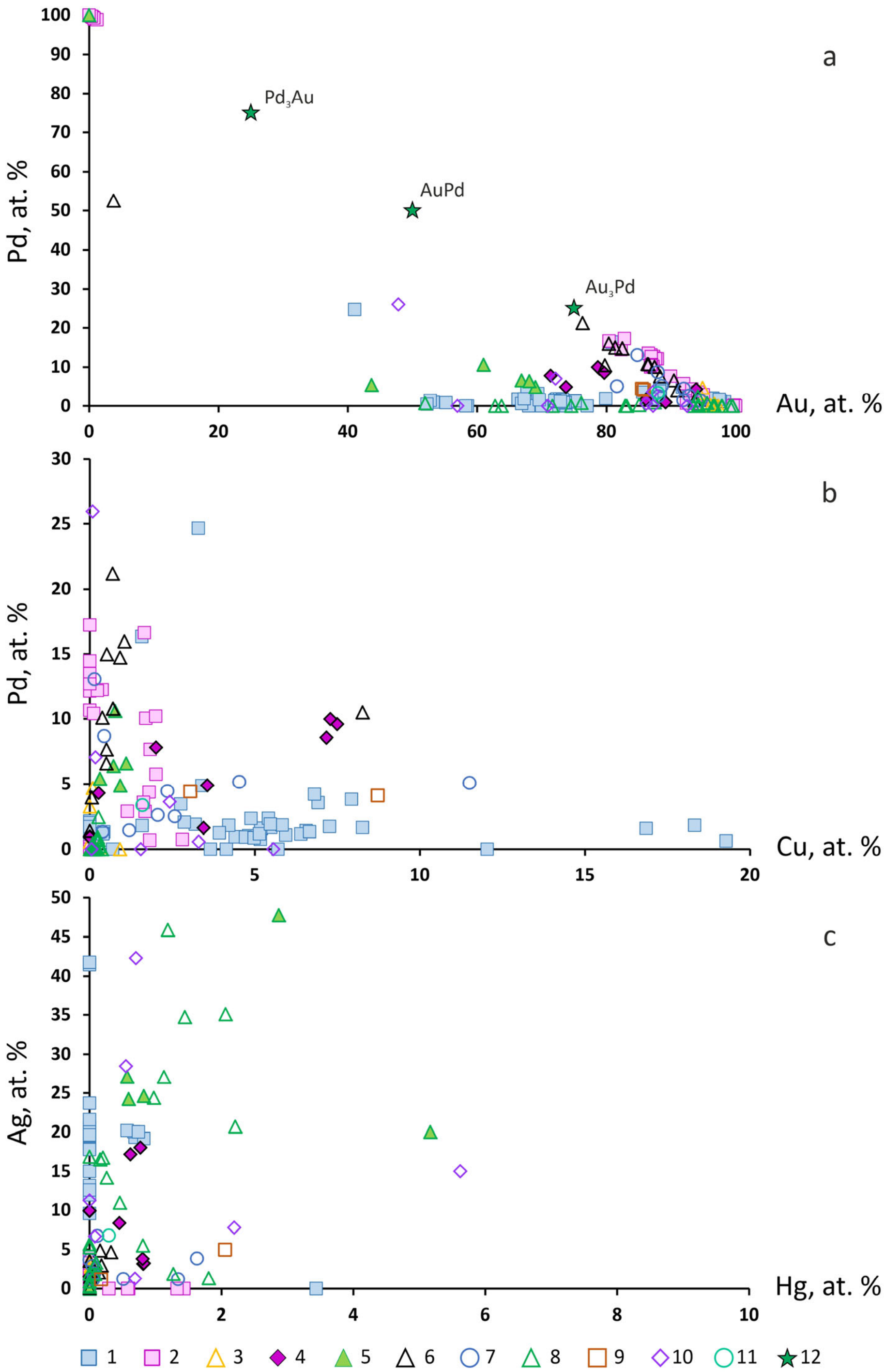

Figure 10. Dependencies of the concentrations of Pd on Au (**a**), Pd on Cu (**b**), and Ag on Hg (**c**) in Pd-bearing gold and other Pd-bearing minerals of the Au–Pd–Ag–Cu–Hg system (in at.%) in various deposits and ore occurrences (Table 6) (filled marker—endogenous, empty—exogenous): 1—Chudnoe (Subpolar Urals, Russia) [29,53,112–114]; 2, 3—Serra Pelada (Brazil) [97]; 4—Gongo Soco (Brazil) [25,78]; 5—Zechstein (Poland) [63]; 6, 7—r.Mayat and r. Bol'shaya Kuonamka, Anabar river basin (Russia) [47,116]; 8—Dziwiszow (Poland) [65]; 9—Whipsaw Creek (Canada) [71]; 10—Similkameen river (Canada) [71]; 11—Friday Creek (Canada) [71]; 12—theoretical compositions of Au-Pd intermetallic compounds.

5. Discussion

5.1. Types of Deposits with Palladian Gold

Native gold occurs in a wide range of gold deposit types and settings [1,2,5–8]. Impurity elements in native gold and minerals in association are indicators of geochemical and mineral types of deposits and regional geochemical conditions [13]. Petrovskaya (1973) [1] reported that the number and concentrations of impurity metals in native gold tend to increase at the deposits with a multistage formation of mineralization or with features of hybridism, and local and uneven changes in the composition of ore bodies with superimposed hydrothermal transformations.

The mechanism of formation of native gold is complex and depends on many factors. A wide range of impurity elements is associated with different geochemical environments in which the mobilization, transportation, and deposition of gold ore mineralization take place. The content of elements in native gold depends on their amounts in hydrothermal solutions, which are controlled by temperature, the presence of ligand elements—Cl, S, and Se and Te to a lesser degree—and also the pH of solutions and oxidation–reduction conditions [20,117]. Metals are largely derived from the mantle or crust by partial melting and fluid-related leaching. Ligands can be provided from the same sources, or from the atmosphere, hydrosphere, and biosphere. Gold and impurity elements can be transported not only by hydrothermal solutions and supercritical fluids, but also by gas mixtures, as well as by sulfide, silicate, and carbonate melts. The spectrum of element impurities and mineral microinclusions often depends on the formational affiliation of the gold deposit, on its connection with any magmatic complex and post-ore processes, and also on the metallogenic features of the gold-bearing provinces.

In this review, based on the literature data and our own studies of the composition of palladian gold from numerous deposits with Au-Pd mineralization, we suggest the following classification of types (Table 7). The studied objects with palladian gold belong not only to gold deposits of different types but to deposits at which the main ore components are PGE, Cr, Cu, Ni, V, and Ti. In the proposed systematization, we do not claim innovations but report them based on materials from various authors for the convenience of presenting results. It includes the main types of PGE-deposits in mafic–ultramafic magmatic complexes [118] within one type with two subtypes—low-sulfide-grade (less than 2%–5% sulfides) Alaskan (1a) and high-sulfide-grade (more than 5% sulfides) Norilsk (1b) (base on Naldrett, 2010 [119]), and gold deposits of 2–4 types: orogenic gold (OG) (type 2a,b), epithermal (porphyry) gold–copper (EPGC) (type 3), and iron oxide–copper–gold (IOCG) (type 4) [119–123] (Table 7). To these types, we added ferruginous quartzites (type 5), which were identified by Dill (2010) [118] within the frames of an independent type of PGE-deposits, and a new non-industrial type of volcanic exhalations (Kamchatka) (type 6), in which gold with Pd impurity was found (Table 1). An important role in the studied objects belongs to gold from placer alluvial deposits and occurrences, which we subdivided into four subtypes (7-1 . . . 7-4) in accordance with the profile of their primary sources and a special subtype of placers associated with horizons of conglomerates and weathering crusts in the cover of large cratons (7-5).

Table 7. Types and subtypes of deposits with palladian gold, its fineness, and impurities.

Type	Subtype (Numbers)	Deposits (Country)	Fineness (Impurities)
1. PGE ore deposits related to mafic–ultramafic magmatic complexes	1a Low-grade sulfide mineralization (includes chromitite and low-grade Cu, Ni)	Skaergaard (Denmark) Stillwater (USA) Konder (Russia) Baronskoe (- “ -) Serebryansky Kamen (- “ -) Volkovskoe (- “ -) Ozernoe (- “ -) Khamitovskoe (- “ -) 1 V. Chuarvy (- “ -), 2 S. Kamennik (- “ -), 3 Yu. Peshempakhk(- “ -), 4 Fedorova tundra (- “ -) Itchayvayam (- “ -)	689–913 (Pd,Cu,Ag,Pt,Fe) 882–922 (Pd,Ag) 974 (Pd), 700–900 (Pd,Ag,Cu) 840–940 (Pd,Ag > Cu) 783 (Pd > Cu > Ag) 810–914 (Pd,Ag,Cu) 690–700 (Cu,Ag > Pd) 880–920 (Pd,Ag,Cu) (1) 960 (Pd,Ag,Cu), (2) 830–970 (Pd,Ag,Cu,Fe,Ni), (3) 833–920 (Ag,Pd,Cu,Fe), (4) 770–870 (Ag > Pd > Fe) 816–960, 580–660 (Pd,Hg)
	1b High-grade sulfide mineralization (includes high-grade Cu-Ni)	Norilsk-1 (Russia) Talnakh (- “ -) Krutoe (- “ -) Marathon (Canada) Cedrolina (Brazil)	570–880, 950–975 (Pd,Ag,Cu,Pt) 980–990, 160–210 (Pd,Ag,Cu) 949–963 (Pd) 663–835 (Cu,Ag > Pd or Cu > Pd) 847 (Au > Pd)
2. Orogenic gold deposits	2a—OGD (Pd,Ag or Pd,Ag,Cu) (5)	Uderei (Russia) Chudnoe (- “ -) Nesterovskoe (- “ -) Hope’s Nose (England) Brownstone (- “ -)	920–970 (Pd) 840–990 (Pd,Ag or Pd,Ag,Cu) 955–970 (Pd,Ag,Cu) 854–997 (Pd > >Ag) 970–994, 882–924 (Pd > Ag)
	2b Cu with Organic	Zechstein (Poland)	576–795 (Ag > Pd,Cu,Hg)
3. Epithermal (porphyry) gold–copper deposits	alkaline rocks areas	Bleida Far West (Morocco)	912–993 (Pd,Ag,Cu)
4. Iron Oxide Copper Gold deposits	(5)	Serra Pelada (Brazil) Gongo Soco (- “ -) Caue (- “ -) Conceichao (- “ -) Maquine (- “ -)	880–975 (Pd > Ag,Hg,Cu,Fe) 821–967 (Pd,Ag,Cu,Hg) 885–918 (Pd > Ag,Cu) 930–940 (Pd > Ag,Cu) 899–941 (Pd,Ag,Cu)
5. Ferruginous quartzite deposits	(1)	Lebedinskoye (Russia)	780–790 (Ag,Pd,Pt,Ni,Fe)
6. Volcanic exhalation	fumaroles	Ebeko Volcano (- “ -)	790 (Pd)
7. Gold-PGE placers	1Pl type 1 areas (2)	Chorokh river (Turkey) river Dart (England)	649–724 (Pd) 630 (Pd > Hg >> Ag)
	2Pl type 2 areas (4)	Ambositra reg. (Madagascar) Lammermuir Hills (Scotland) Zimnik Creek (Poland) Dziwiszow (- “ -)	918–978 (Pd > Cu) 942 (Pd) 980–990 (Ag,Pd,Hg) 960–997 (Pd,Ag,Hg,Cu,Pt)
	3Pl type 3 alkaline rocks areas (3)	Friday Creek (Canada) Whipsaw Creek (- “ -) Similkameen river (- “ -)	930 (Ag > Pd,Hg,Cu) 910–940 (Pd,Ag,Cu,Hg) 970 (Pd,Ag,Cu,Hg)
	4Pl type 4 areas (1)	Corrego Bom Sucesso (Brazil)	770–975 (Pd > Ag,Hg,Cu,Pt)
	5Pl type 5 craton placer areas (4)	Mayat river (Russia) Bol’shaya Kuonamka river (- “ -) Kuoyka river (- “ -) Mataganya-Siguiri (Guinea)	860–960 (Pd,Ag,Cu,Hg) 910–970 (Pd,Ag,Cu,Hg) 960 (Pd > Ag,Cu) 920–970 (Pd > Hg,Ag,Pt)

According to Figure 1, deposits with palladian gold occur in different geological and dynamic settings—terranes and orogenic belts and shields. Table 8 illustrates that palladian gold is found in the deposits related to different types of magmatism (but mainly with mafic–ultramafic) and in different periods. It is worth noting that the lacuna is more than a billion years old, coinciding with the so-called “dead billion” in the history of the Earth (1.7–0.7 Gya), when the stability conditions existed throughout the planet and a limited number of deposits formed, among which there were virtually no ore-bearing deposits (except IOCG type) [124].

Table 8. Structure, host rock, and mineralization age (Ma) of some endogenous deposits with palladian gold.

Type	Name	Structure (Craton)	Host Rock	Ma	Ref.
1a Low-grade sulfide mineralization (includes chromitite and low-grade Cu, Ni)	Skaergaard, Denmark	East Greenland volcanic province	Mafic	55	[73,125]
	Stillwater, USA	Wyoming Province (N. American)	Mafic–ultramafic	2700–2713	[74,126]
	Itchayvayam	Olyutorsky arc terrane	Mafic–ultramafic	60–74	[42,127]
	Konder	Aldan Shield (Siberian)	Alkaline–ultramafic	130–140	[128,129]
	Baronskoe	Uralian Orogenic belt	Mafic	445–430	[55,125]
	Serebryansky Kamen	- “-	Mafic	415–430	[54,130]
	Volkovskoe	- “-	Mafic	445–430	[30,131]
	Ozernoe	- “-	Mafic–ultramafic	445–455	[31,132]
	Khamitovskoe	- “-	Mafic–ultramafic	587–215	[56,133]
1b High-grade sulfide mineralization (includes high-grade Cu-Ni)	Norilsk-1, Talnakh	Siberian LIP (-“-)	Mafic–ultramafic	250	[27,50]
	Krutoe	Pay-Khoy Fold Belt	Mafic	330–370	[51,134]
	Fedorov-Pana	Baltic Shield (East European)	Mafic–ultramafic	2501–2446	[58,135,136]
	Marathon, Canada	Superior Province (-“-)	Alkaline–mafic–ultramafic	1100	[21]
2 OG	Uderei	Yenisey Fold Belt	Metamorphic	640–710	[49,137]
	Chudnoe, Nesterovskoe	Ural Orogenic belt	Contact metasediments and felsic–mafic volcanites	250–260	[29,53,138]
3 EPGC	Bleida Far West, Morocco	Anti Atlas orogen	Mafic (ophiolite association), felsic, metamorphic	600–550 or 300–330	[32,68]
4 IOCG	Gongo Soco, Caue, Maquine	Atlantic shield (South American)	Metasedimentary, metavolcanic	2600–2400	[25,26,28,77,78]
5 Ferruginous quartzite	Lebedinskoye	(East European)	Metamorphic	2612–2050	[59]

Thus, the above-mentioned facts suggest that Au-Pd mineralization formed in different conditions and from different sources, from mantle riftogenic (oceanic), active margins, and island arcs (subduction) to orogenic accretion-collision and post orogenic (riftogenic).

5.2. Physicochemical Conditions for the Formation of Palladian Gold at Deposits of Different Types

Scarce data are available on the physicochemical conditions of the formation of palladian gold. We summarize the published information on the T,P,X-parameters of the formation of Au-Pd mineralization known for some types of deposits in Table 9.

Table 9. T,P,X-conditions for the formation of Au-Pd mineralization with Pd-bearing gold according to the results of the study of fluid inclusions (FIs) (reference data).

Type of Deposit	Deposit (Country)	T°C; P kbar; wt.% eq. NaCl; FI Composition	Ref.
PGE ore deposits related to mafic–ultramafic magmatic complexes	Au-Pd ores of the Skaergaard massif; Norilsk-1,-2, Volkovskoe, Baronskoe (Russia)	1200–1000; 600–140; -; 23.3–13.6; NaCl	[27,55,106,139]
Orogenic gold deposits	Chudnoe (Russia); Au-Pd deposits in the Permian-Triassic basins (SW England); Zechstein (Poland)	186–60; 0.5–1.15; 0.2–30; Na, Ca, Cl	[29,63,140–142]
Epithermal (porphyry) gold–copper deposits	Bleida Far West (Morocco)	132–80; 0.5–0.04; 1.7–33; Na, Ca, Cl, CO_2	[32,68,143]
Iron oxide copper gold deposits	Serra Pelada, Carajas, Corrego Bom Susesso, Gongo Soco, Conceichao (Brazil)	500–115; 1.2–1.7; 3–30; Na, K, Ca, Mg, Cl, CO_2	[25,78,79,144–147]

Type 1—PGE-deposits in mafic–ultramafic magmatic complexes. In Au-Pd ores at the Skaergaard massif, the formation of Au-Cu-Pd melts and Pd-tetra-auricupride is due to the decomposition of Au-Cu-Pd solid solutions at temperatures of 1200–1000 °C [73]. Au-Pd mineralization of the Volkovskoe and Baronskoe deposits has a hydrothermal-metasomatic genesis, was formed in the range of temperatures of 600–400 °C [55,106,139], and is related to superimposed metamorphic and metasomatic processes (occurrence of amphibole, serpentine, and chlorite) on olivine clinopyroxenites [107,108].

Data on fluid inclusion studies show that the crystallization of palladian gold in Cu-Ni-PGE ores of the Norilsk deposit proceeds with the participation of reduced hydrothermal fluids ($CH_4 \pm C_2H_6$, C_2H_2, and C_3H_8) at temperatures of 270–140 °C and salinities of 23.3–13.6 wt.% eq. NaCl [27].

Type 2—orogenic gold deposits. Au-Pd mineralization at the Chudnoe deposit (Russia) could have been formed by chloride fluids of low and medium salinity at temperatures from 105 to 230 °C and pressures from 0.05 to 1.15 kbar. The salinity of fluids varies from 20.1 to 0.2 wt.% NaCl eq. [29] (Table 9). Au-Pd and Au deposits of the Permian-Triassic basins in SW England (Thorverton) formed in the temperature range from 60 to 155 °C, and the salinity of fluids varied from 2 to 30 wt.% NaCl eq. [140,141]. In the ores from the Au-Pd Zechstein deposit (Poland), an association of palladian gold with chalcosine, digenite, and djurleite was detected, which limits its formation temperature to a range of 93 to 103 °C [63,142,148] (Table 9).

Type 3—epithermal (porphyry) gold–copper deposits. Hematite-quartz veins of the Au-Pd Bleida Far West deposit (Anti-Atlas, Morocco) formed at temperatures from 145 to 325 °C and fluid salinities from 6 to 33 wt.% NaCl eq. The gas phase of fluids included CO_2, CH_4, and N_2 [68,143]. The Au-Pd mineralization at this deposit was formed in the temperature range from 80 to 132 °C with the participation of fluids with high salinity ranging from 18.8 to 29.6 wt.% eq. NaCl. The composition of fluids is dominated by NaCl and $CaCl_2$. Quartz-hematite veins were formed at pressures from 0.76 to 31 kbar; during the formation of quartz veins with Cu-mineralization, the pressure changed from 0.63 to 0.51 kbar. EPMA analysis showed that the mineral-forming fluids contained Cl, Na, Ca, K, Mn, Ba, Sr, Fe, Cr, and S [32].

Type 4—iron oxide copper gold deposits. Hematite-quartz veins from the Au-Pd Gongo Soco mine (Brazil) formed at temperatures of 365–74 °C from fluids with salinities of 10–30 wt.% eq. NaCl. The composition of fluids is dominated by NaCl with $MgCl_2$ impurities [78,146]. Au-Pd mineralization was formed later in the temperature range of 148–229 °C with the participation of medium-salinity fluids of 7.2 to 11.7 wt.% NaCl eq. (Table 9). Iron ores of the Conceichao mine (Brazil) formed at temperatures of 660–600 °C (according to $\Delta\, \delta^{18}O$ hematite/quartz). The deposition of Au-Pd mineralization took place later at lower temperatures (351–115 °C) with the participation of fluids of salinities from 3 to 20 wt.% NaCl eq. [79,147]. Hematite-quartz veins of the Serra Pelada deposit (Brazil) formed in the temperature range from 140 to 185 °C and fluid salinity range from 2.6 to 23.5 wt.% NaCl eq. The fluids contained chlorides Na > K > Ca ≥ Mg. The trapping temperature and salinity of fluid inclusions without and containing gold (50–500 ppb) in hematite are 155–185 °C and 4–6.5 wt.%, and 165–175 °C and 4.5–6 wt.%, respectively [144].

The physicochemical formation conditions of Pd-bearing gold in the ores of deposits of type 1 include two temperature ranges—magmatic high-temperature and hydrothermal low-temperature. In the former case, the formation of Pd-bearing gold takes place as a result of the decomposition of Au-Cu-Pd solid solutions at 1200–1000 °C. In the latter, Au-Pd alloys form with the participation of low-temperature hydrothermal fluids (270–140 °C) of medium salinity (13.6–23.3 wt.% NaCl eq.) (Figure 11A).

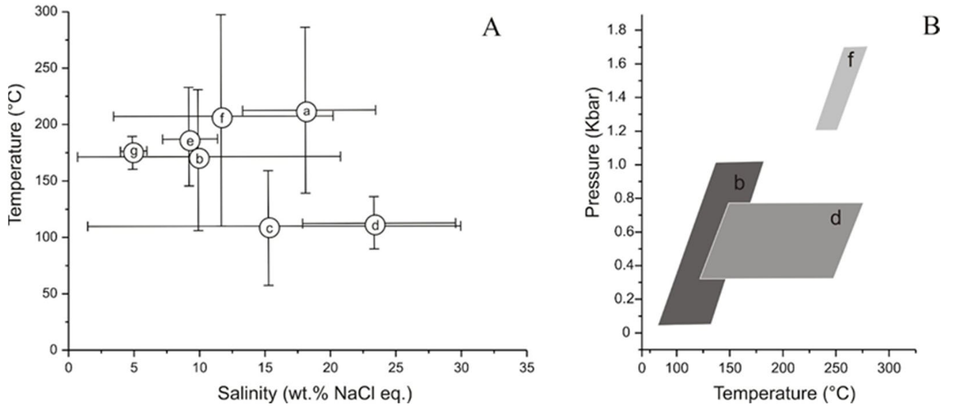

Figure 11. Homogenization temperature and salinity of fluid inclusions in quartz and calcite in association with palladian gold in ores from deposits of different types (**A**): 1c—Norilsk (a); 2—Chudnoe (Russia) (b) and Hope's Nose, Thorverton (England) (c); 3—Bleida Far West (Morocco) (d); 4—Gongo Soko (e), Conceichao (f), and Serra Pelada (Brazil) (g). Probable P-T formation conditions (**B**) for the Au-Pd deposits of Chudnoe (b), Bleida Far West (d), and Serra Pelada (f).

The physicochemical conditions of formation of palladian gold in the ores of deposits of types 2–4 are similar and correspond to the conditions of low-temperature hydrothermal ore formation (Figure 11B). At these deposits, Pd-bearing gold formed in the temperature interval of 300–60 °C, and the salinity of hydrothermal fluids ranges widely from 30 to 0.2 wt.% NaCl eq. (Figure 11A). Estimation of the ore formation pressure at Au-Pd deposits of types 2–4 is based on the results of studies of fluid inclusions in the minerals of early stages that preceded the formation of Pd-bearing gold, and the pressure varies from 1.7 to 0.05 kbar (Figure 11B).

5.3. Impurities, Fineness of Palladian Gold, and Minerals in the Association as Indicators of Deposit Types

The content of Ag, Cu, and Hg in palladian gold and minerals in association with it from deposits of various types has been studied by many researchers. Each of the deposits (Figure 1, Tables 1–7) for which the information was collected and analyzed is unique and has a specific composition of palladian gold and a set of minerals in the association. The heterogeneity of palladian gold forms either during primary crystallization or results from further modification under the effect of chemical and physical factors during subsequent residence in hypogene or surficial environments.

Figure 12a shows data on the palladian gold with various sets of impurities and other co-occurring phases of the Au–Pd–Ag–Cu–Hg system. The Ag impurity was found in palladian gold at 36, Cu—at 32, and Hg—at 20 deposits. The palladian gold is represented by the systems Au–Pd, Au–Pd–Hg, Au–Pd–Cu, and Au–Pd–Ag–Hg, but more frequently corresponds to the Au–Pd–Ag, Au–Pd–Ag–Cu, and Au–Pd–Ag–Cu–Hg. The variations in Ag content in Au–Pd–Ag–Cu solid solutions are considerable and cover the widest range of fineness from 160 to 993. At some deposits, the Pd content exceeds that of Ag and Cu, whereas at others, Cu dominates over Pd and Ag or Ag dominates over Pd and Cu. Low-fineness palladian gold is related to elevated contents of Pd, Ag, Cu, and Hg. At the Marathon deposit (Canada), the fineness of palladian gold is 663–835, and the content of Cu (and Ag) is higher than that of Pd (Table 6). At the Zechstein deposit (Poland), the fineness of palladian gold is low (576‰–795‰) and the content of Ag is higher than that of Pd, Cu, and Hg. The content of Pd is higher than those of Hg and Ag in native gold from the placers of the Dart river (England) (630‰–972‰). Talnakh ores contain palladian silver (160‰–210‰) (Table 5). Wide variations in the concentrations of all four elements and fineness (556‰–931‰) were revealed for palladian gold from placers of the Similkameen river (Canada) (Pd,Ag,Cu,Hg) (Tables 6 and 7). The low fineness of palladian gold is due to the high concentrations of Pd (Chorokh river, Turkey); or Pd and Hg (Itchayvayam (Russia); River Dart (England)); or Pd, Ag, and Cu (Norilsk-1, Talnakh, Ozernoe (Russia); Marathon (Canada); Skaergaard (Denmark)); or Pd, Ag, Cu, and Hg (Zechstein (Poland); Similkameen river (Canada)).

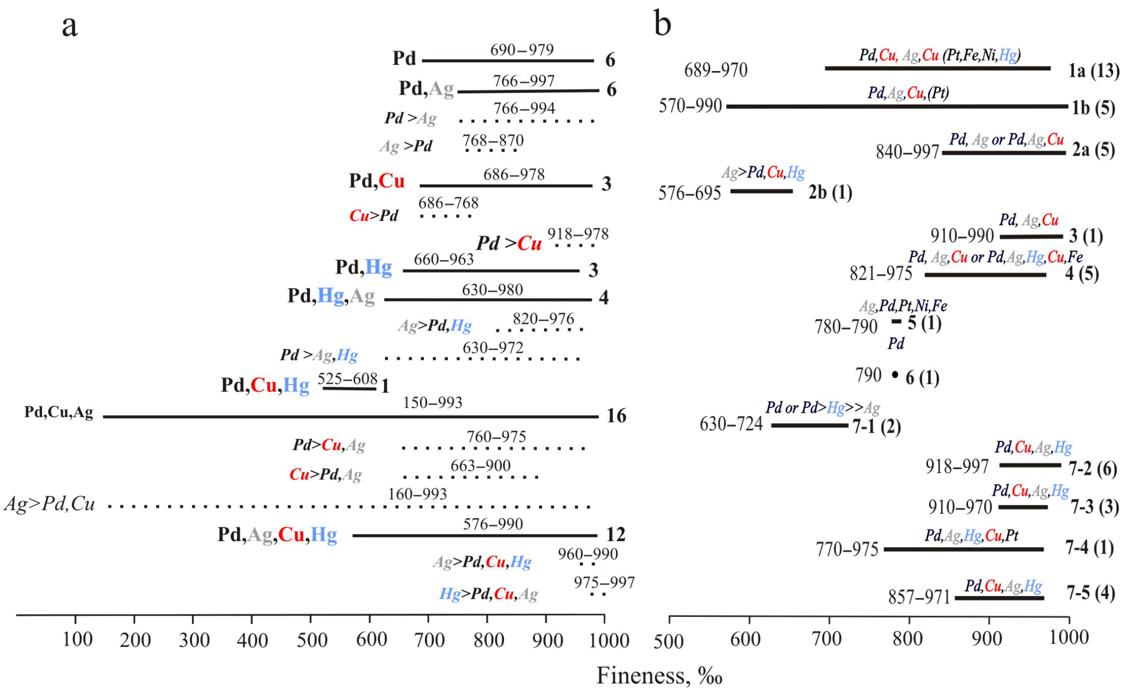

Figure 12. Fineness intervals of palladian gold for deposits with Au-Pd mineralization (**a**) depending on the set and concentrations of impurities (Pd, Ag, Cu, Hg, . . .) in native gold (numerals on the right are the number of deposits) (**b**) for different types and subtypes of deposits.

Figure 12b shows the variations in the fineness and impurity elements of palladian gold from deposits of various types (and subtypes) summarized in Table 7. Palladian gold most commonly occurs in the PGE ore deposits related to mafic–ultramafic magmatic complexes (Table 7, type 1) and contains Ag and Cu impurities; occasionally minor Pt, Fe, and Ni; and does not contain Hg. This is mostly high-fineness gold, is less often medium-, and is rarely low-fineness. The only exception is the Au-Pd-Hg Itchayvayam ore occurrence (Kamchatka, Russia), for which two varieties of Pd,Hg-bearing gold—high- (low content of Pd and Hg) and low-fineness (high content of Pd and Hg) gold—were determined [33,42]. This type is most likely typical of territories with elevated background levels of Hg. It is in the northern part of Kamchatka that a great number of deposits and ore occurrences of the argillisite formation were discovered [149,150]. Ore objects are related to island arc terrigenous and volcanic-siliceous deposits of the Early and Late Cretaceous (terranes of the Olyutorskaya island arc in Figure 1). The Itchayvayam ore occurrence occurs in the deep fault zones and frequently accompanies the massifs of mafic–ultramafic magmatic complexes. The elevated background levels of Hg seem to be because oceanic sediments contain high Hg concentrations compared to clarke. Enrichment of oceanic sediments with Hg could be a result of volcanic activity [150].

For orogenic gold (subtype 2a), epithermal (porphyry) gold–copper (type 3), and iron oxide copper gold (type 4) deposits, palladian gold is mainly high-fineness and contains Ag impurities or Cu too. Low-fineness palladian gold with a major content of Ag is typical of the Zechstein deposit (Poland) (subtype 2b). Palladian gold of medium fineness (780‰–790‰) with Ag, Pd, Pt, Ni, and Fe impurities occurs at the Au–Pd–Pt Lebedinskoye deposit (Russia) (type 5), and was also found in volcanic fumaroles of Ebeko volcano (Russia) (only Pd impurity) (type 6). High-fineness gold (910‰–970‰) with low contents of Pd, Ag, Cu, and Hg is spread over a great part of gold-PGE placers (type 7). Pd,Hg-rich low-fineness gold (630‰–770‰) has been found in some placers of the Chorokh river (Turkey) [60], the Dart river (England) [20], and weathering crusts at the Corrego Bom Sucesso (Brazil) [76].

Tables 1–6 show the minerals that occur in association with palladian gold at the deposits with various types of Au-Pd mineralization. The number of minerals is about 90, apart from unnamed phases. Table 10 contains data on minerals in association with palladian gold from deposits of different types. Minerals (bold) are the most frequent phases. Mineral groups are presented by native metals and intermetallic compounds, oxides, hydroxides, and chalcogenides. Pd, Ag, Cu, and Hg metals that occur in native gold frequently form their minerals and are present in association with palladian gold. In Table 10, these minerals are listed separately by group.

Table 10. Minerals in association with palladian gold from deposits of different types.

Mineral Groups	Minerals	Types of Deposits
Elements and intermetallics	**Pd**, **Pt**, **Cu**, Ag, S, **Taur**, Auc, Skg, Tfpt, Ifpt	Types 1, 2a, 3, 7-2, 6
Pd minerals	Ah, **Met-I/II**, **Ism**, Stpdn, Ktu, Tpdn, Tem, Pds, Ato, Spdn, Plv, **Vsk**, Mrk, Kei, Cpe, Mon, Csl, Oos, Sov, Pdm, **Ptr**	Type 1
Minerals of Au and Ag	Ausb, Any, **Syv**, Fis, **Hes**, Cag, Boh, **Nau**, **Eca**, **Taur**, **Auc**	Types 2, 4, 7-1
Cu minerals	**Ccp**, **Bn**, Cc, Ani, Eca, Um, **Taur**, **Auc**	Types 1, 7-1
Hg minerals	Cin, Tmn, Clr, **Ptr**	Types 1b,d, 7-1, 7-4
Pt minerals	**Spy**, **Bg**, Svi, Pda, Ifpt, Tfpt	Type 1
Oxides, hydroxides	**Hem**, **Mgt**, Tnr, (Pd,Cu)O, PdO, **Gth**, (Fe,Pd)OOH	Types 3, 4, 5, 7-2
Fe, Ni, Pb chalcogenides	**Pn**, **Pyh**, **Gn**, Cth, Alt	Type 1
Host minerals	**Qz**, **Ms** (including fuchsite Cr-Ms), **Chl**, **Ab**, **K-fs**, **Hbl**, Tur, **Carb** (including Cat, Sid and other), S, Kln	Types 1–7

Note: The most common minerals are in bold.

Palladium minerals make up the largest group. Most common among them are arsenides, stibioarsenides, sulfides, stannides, bismuthides, tellurides, selenides, etc. (Table 10). In association with them, Pt minerals—sperrylite, braggite, sudovikovite, palladoarsenide, isoferroplatinum and tetraferroplatinum—are present. Pd and Pt minerals are typical of the deposits of types 1 and 7 (Table 7), which indicates their paragenetic relationship.

Gold and silver minerals frequently occur in association with palladian gold—these are Au-Ag-Cu solid solutions and Ag-Cu intermetallic compounds (tetra-auricupride, auricupride)—and more rare minerals are aurostibite, anyuiite, sylvanite, fischesserite, hessite, chlorargyrite, bohdanowiczite, naumannite, and eucairite. Au-Cu intermetallic compounds were found at more than ten deposits. Tetra-auricupride is spread at the deposits belonging to groups 1 and 7. Aurostibite is in association with palladian gold in the ores of the Uderei deposit (Russia) (type 2a) [49] and placer ore occurrences of Lammermuir Hills (Scotland) and River Dart (England) (type 7a,b) [20].

Copper minerals are represented by sulfides (chalcopyrite, bornite, chalcocite, anilite) and selenides (eucairite, umangite)—these are typical minerals at some deposits of mafic–ultramafic magmatic complexes (type 1). Cu oxides (tenorite, (Pd,Cu)O) were found in exogenous deposits (type 7). The most widespread mercury mineral is potarite, whereas cinnabar, tiemannite, and coloradoite are rare. They were detected at some deposits of types 1, 2b, 7-1, and 7-4.

Fe oxides (hematite, magnetite) and Fe and Pd hydroxides (FeOOH, (Fe,Pd)OOH) are spread at the deposits of 3,4,7 groups and characterize highly oxidizing conditions of ore formation. Chalcogenides of Fe, Ni, and Pb (pentlandite, pyrrhotite, galena, clausthalite, altaite) occasionally occur in association with palladian gold at the deposits of type 1. Arsenopyrite in association with palladian gold was found only at the Uderei (Russia) [49] and Lammermuir Hills (Scotland) deposits [20]. Arsenic often occurs in arsenides and arsenoantimonides of Pd and Pt. Among host minerals containing palladian gold, the most common are quartz, muscovite, including fuchsite (Cr-Ms), chlorite, albite, K-feldspar, kaolinite, hornblende, and carbonates (calcite, siderite).

The above-listed minerals of Au, Pd, Cu, Ag, Hg, Pt, Fe, and Pb are formed together with palladian gold and influence its composition and redistribution of metals between fluids and solid phases. On the whole, minerals in association with palladian gold reflect the mineralogy of ores, which points out their use as indicators of the type of mineralization. PGE at elevated temperatures are typical chalcophiles, and have a high affinity with S, As, Te, Sb, and Bi. After post-magmatic fluid processing, a significant part of the native metals leave the high-temperature solid solutions, and various minerals of PGE, Au, and Ag are formed: native, sulfides, arsenides, tellurides, antimonides, bismuthides, etc.

An important area of research is works focused on studying the mechanism of the mobilization, transfer, and deposition of noble metals. It was proved that during crystallization, hot water fluids are generated, which migrate in the crust [151]. Metals can be transported by brines, altered meteoric water, and metamorphic and magmatogenic fluids. Their deposition from hydrothermal solutions takes place at temperatures from 500 to 100 °C. They can form their own minerals or occur in other minerals as isomorphic impurities. The ability of particular metals to occur in gold depends on their amount in the ore-forming system and the content of other elements with which they can form stable minerals in ore-forming conditions.

The question of the influence of the activity of elements (S, Te, Sb, As, Bi, etc.) that bind palladium into its own minerals on its ability to occur in native gold has not been resolved so far. The solution to this problem is complicated by the fact that hydrothermal fluids that formed Au-Pd mineralization simultaneously contain several of these elements, and native gold is found in parageneses with many minerals of Pd. The Baronskoe in the Middle Urals is an example of deposits at which palladian gold is in paragenesis with Pd sulfides, tellurides, sulfotellurides, arsenides, stibnides, and bismuthides. For this type of deposit, we managed to trace the variations in the contents of Pd in Ag-bearing gold with sulfides (vysotskite), tellurides (kotulskite, telluropalladinite), arsenides Pd and Pt, arsenotellurides (keitconite, As-keitconite), and As-Sb-Te minerals (Te-arsenopalladinite, Te-guanglinite, isomertieite). It was revealed that the occurrence of Pd, as well as Ag, is controlled mainly by the activity of S and Te, and the effect of the activity of As and Sb is negligible (Figure 13).

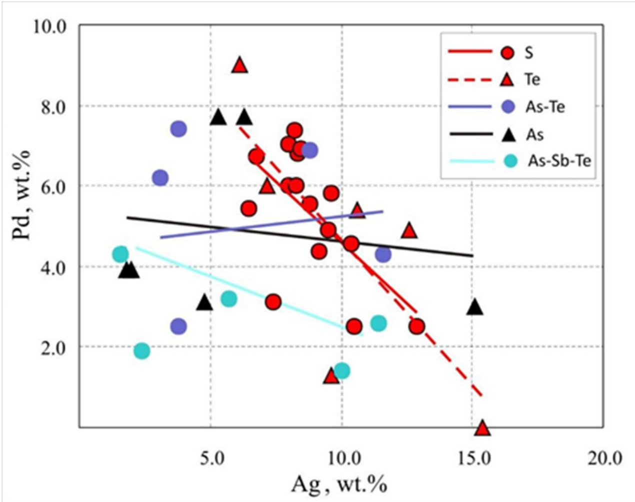

Figure 13. Ratios of Ag and Pd impurities in native gold in parageneses with Pd sulfides (S), tellurides (Te), arsenotellurides (As-Te), arsenides (As), and arseno-stibiotellurides (As-Sb-Te) at the Baronskoe deposit. Ag–Pd linear correlation trends are shown.

What do the Pd impurity and level of its concentrations in native gold indicate? What other isomorphic impurities along with Pd can be present in native gold? Which minerals occur in the intergrowth with palladian gold? At what deposits are Pd-bearing gold spread? What is the source of Pd and other accompanying impurities in native gold? What are the mechanisms and processes of mobilization, transfer, and joint deposition of these noble metals? In what physicochemical conditions and environments does Pd-bearing gold form? We tried to answer these and other questions in this paper. We will make attempts to answer many questions in the future. Impurities are a kind of fingerprint for minerals that make it possible to determine the composition and conditions of ore-forming medium. The composition of native gold is an important typomorphic characteristic of this indicator mineral, bearing fingerprints of formation conditions specific to each deposit. The knowledge of impurity elements in native gold and their content is important for identifying the ore formation to which gold mineralization belongs, for determining the source of placer ore occurrences, developing efficient criteria for forecasting, and searching gold and gold-bearing deposits. The minerals in association with native gold and the sequence of their formation reflecting the specific features of ore formations are the basis for ore-formational analysis [152]. The distribution of these associations determines the contours of deposits. Analysis of data on the deposits with palladian gold showed specific compositional features of the productive mineral associations from various types of deposits located on different continents and in different countries.

Construction of the quantitative genetic models of ore-forming processes at deposits with palladian gold requires thermodynamic data for solid solutions of various compositions. Estimation of the thermodynamic characteristics was performed only for some binary and ternary systems with gold [6,153–156], which makes it impossible to carry out this kind of work at this stage. Model calculations were made for the systems containing Au-Ag [4,6,7], Au-Ag-Hg [155], Au-Ag-Pd [156], Au-Ag-Cu [157], and Au-Ag-Cu-Hg [158]. The composition and set of impurities in palladian gold were found to be more diverse than it was thought to be. Most likely, very soon, it will be possible to confidently determine any region from which its samples were obtained from the composition of impurities in native gold.

6. Conclusions

(1) Depending on the set of impurities, the following varieties of palladian gold are distinguished: Ag-, Cu-, Hg-, Ag,Cu-, Ag,Hg-, Cu,Hg-, and Ag,Cu,Hg-bearing palladian gold. Palladian gold may contain Pt, Fe, Ni, and Cd (in minor quantity).

(2) A classification of types of deposits with palladian gold has been proposed: (1) PGE ore deposits related to mafic–ultramafic magmatic complexes (two subtypes—(a) low-sulfide-grade (less than 2%–5% sulfides) Alaskan and (b) high-sulfide-grade (more than 5% sulfides) Norilsk); (2) orogenic gold deposits; (3) epithermal (porphyry) gold–copper deposits; (4) iron oxide copper gold deposit type; (5) ferruginous quartzite deposits; (6) volcanic exhalation; and (7) gold-PGE placers with five subtypes corresponding to the types of 1–5 primary sources.

(3) Ag,Cu-bearing palladian gold is mainly high-fineness (910‰–990‰), is less frequently medium-fineness, and is rarely low-fineness and does not contain Hg at the deposits of PGE ore deposits related to mafic–ultramafic magmatic complexes, epithermal (porphyry) gold–copper deposits, and iron oxide copper gold deposits (types 1, 3, 4). The only exception is the Au-Pd-Hg Itchayvayam ore occurrence (Kamchatka, Russia) (type 1d) with two varieties of Pd,Hg-bearing gold (high-fineness 816‰–960‰ and low-fineness 580‰–660‰). Low-fineness palladian gold with the major content of Ag is typical for OGD deposit Zechstein (Poland) (type 2), whereas that with the major content of Pd is typical of the placers of the Chorokh river (Artvin district, Turkey) (type 7). Medium-fineness palladian gold with a high content of Pd occurs at deposits and in volcanic exhalations (types 5, 6). Hg,Ag,Cu-bearing high-fineness palladian gold is mainly present in placer deposits (type 7).

(4) The most common minerals in association with palladian gold are Pd and Pt arsenides, stibioarsenides, sulfides, stannides, bismuthides, tellurides, and selenides. They are typical of deposits related to mafic–ultramafic magmatic complexes (types 1, 7). Au, Ag, and Cu minerals (tetra-auricupride, auricupride, aurostibite, chalcopyrite, bornite, sylvanite, hessite, naumannite, eucairite, etc.) occur in association with palladian gold at gold–copper deposits (types 2–4). Cu and Fe oxides (tenorite, hematite, magnetite, (Pd,Cu)O) and Fe and Pd hydroxides (goethite, (Fe,Pd)OOH) are spread at the deposits of 3,4,7 groups and indicate highly oxidizing conditions of ore formation. The most common of Hg minerals is potarite. The main host minerals of palladian gold are quartz, muscovite, including fuchsite (Cr-Ms), chlorite, albite, K-feldspar, kaolinite, hornblende, and carbonates (calcite, siderite).

(5) Palladian gold from many deposits has a heterogeneous composition and occurs in two or more varieties, which suggests unstable deposition conditions, subsequent recrystallization processes, and a long history of formation. Physicochemical conditions of the formation of Pd-bearing gold at some deposits of one type cover two areas—magmatic high-temperature and hydrothermal low-temperature. At the majority of deposits of types 2 and 4, the formation of Pd-bearing gold proceeds with the participation of hydrothermal fluids (300–60 °C) of various salinities (0.2–30 wt.% NaCl eq.).

(6) The fineness, impurity metals, and minerals in association with palladian gold reflect the mineralogy of Au-Pd ores and allow them to be used as indicators for types and subtypes of gold deposits.

7. Future Directions

In the studies of new objects, it is necessary to more thoroughly analyze the chemical composition of palladian gold and minerals in association with it. An important characteristic of palladian gold is the data on the composition of microinclusions obtained by LA-ICP-MS. However, the heterogeneity of its composition and the presence of mineral microinclusions must be taken into account for interpreting the obtained results.

A database of the deposits with palladian gold, as well as argentian, cuprian, and mercury gold must be created. Scarce data are known on the P,T,X-parameters of the formation of native gold of various compositions and sources of both gold and impurity elements (major, minor, and trace). Possible and important directions of further works are a study of different forms of transfer of Au, Pd, Ag, Cu, Hg, and other elements at different P,T,X-parameters of ore-forming conditions, obtaining thermodynamic characteristics of Au-

Pd-Ag-Cu-Hg solid solutions and minerals of these elements and minerals in association with the aim to construct the genesis models of palladian gold and other varieties of native gold.

Author Contributions: Conceptualization, G.A.P.; methodology, G.A.P.; formal analysis, T.V.B., P.S.Z., G.A.P. and V.V.M.; investigation, G.A.P. and V.V.M.; data curation, T.V.B. and P.S.Z.; writing—original draft preparation, G.A.P., V.V.M., A.A.B. and N.A.G.; writing—review and editing, G.A.P., V.V.M. and N.A.G.; visualization, G.A.P., P.S.Z., T.V.B. and V.V.M.; supervision, G.A.P.; project administration, G.A.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the Russian Foundation for Basic Research (project No. 20-05-00393) and within the framework of the state assignment of Institutes: Sobolev Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk, Russia) (No. 122041400237-8); Zavaritsky Institute of Geology and Geochemistry, Ural Branch of Russian Academy of Sciences (No. 123011800011-2); Institute of Volcanology and Seismology of the Far East Branch of Russian Academy of Sciences (No. AAAA-A20-120121090011); and North-East Interdisciplinary Scientific Research Institute, Far East Branch of the Russian Academy of Sciences (No. 121031700301-5).

Data Availability Statement: Not applicable.

Acknowledgments: We are grateful to the anonymous reviewers for polishing the English and the constructive and helpful corrections and comments that improved the manuscript.

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

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