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Article

Platiniferous Tetra-Auricupride: A Case Study from the Bolshoy Khailyk Placer Deposit, Western Sayans, Russia

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Abstract: Tetra-auricupride, ideally AuCu, represents the only species showing the coexistence of Au with an elevated level of Pt, as in the case of a detrital grain studied structurally for the first time, from an ophiolite-associated placer at Bolshoy Khailyk, western Sayans, Russia. We infer that tetra-auricupride can incorporate as much as ~30 mol. % of a “PtCu” component, apparently without significant modification of the unit cell. The unit-cell parameters of platiniferous tetra-auricupride are: a 2.790(1) Å, c 3.641(4) Å, with $c/a = 1.305$, which are close to those reported for ordered AuCu(I) in the system Au–Cu, and close also to the cell parameters of tetraferroplatinum (PtFe), which both appear to crystallize in the same space group, $P4/mmm$. These intermetallic compounds and natural alloys are thus isostructural. The closeness of their structures presumably allows Pt to replace Au atoms so readily. The high extent of Cu + Au enrichment is considered to be a reflection of geochemical evolution and buildup in levels of the incompatible Cu and Au with subordinate Pt in a remaining volume of melt at low levels of fO_2 and fS_2 in the system.

Keywords: platiniferous tetra-auricupride; Pt-for-Au substitution; platinum; gold; ophiolite; Bolshoy Khailyk placer; western Sayans; Russia

1. Introduction

1.1. Sample Location and Objective

Tetra-auricupride, AuCu, an intermetallic mineral with a tetragonal symmetry, was first discovered in platiniferous ultrabasic rocks in the Sardala area, Xinjiang Autonomous Region, China [1]. It has since been reported from various localities worldwide (see below). In the majority of cases, the tetra-auricupride is platinum-free, and corresponds closely to the formula AuCu. However, several of them contain elevated levels of Pt; this is the case of the grain described here, originating in the Bolshoy Khailyk placer [2,3], western Sayans, Russia (Figure 1a,b).

The coexistence of Au and Pt is highly uncommon, and has not been observed in other species. Our main objective here was to characterize our specimen of platiniferous tetra-auricupride from Bolshoy Khailyk both compositionally and, for the first time, structurally.

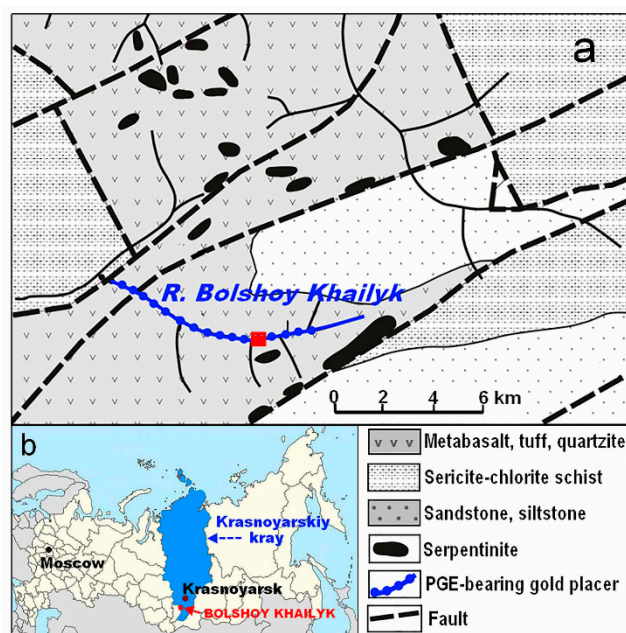


Figure 1. (a) Regional geology of the placer area at Bolshoy Khailyk (Figure 1a: simplified after [4]) and (b) a general map showing the location of the area in the Russian Federation (shown by red square symbol).

1.2. Worldwide Occurrences of Tetra-Auricupride

Tetra-auricupride has been documented in association with concentrically zoned Alaskan-Uralian-(Aldan)-type complexes at Tulameen*, BC, Canada; Nizhniy Tagil, Urals; and Kondyor*, Aldan Shield, Russia [5–7]. It also occurs in layered mafic–ultramafic complexes at Jijal, Pakistan [8]; Yoko-Dovyrenskiy, southern Siberia [9]; Burakovskiy, Karelia, Russia [10]; and Skaergaard, Greenland [11,12]; and in serpentinized ophiolitic rocks on the island of Skyros [13] and the Pindos complex, Greece [14]. It was also found in ore at the Kerr-Addison mine, ON, Canada [15]; in the Itabira district, Minas Gerais, Brazil [16]; the Bleida Far West mine, Morocco [17]; the Sieroszowice mine, Poland [18]; and in association with Cu–Ni sulfide deposits of the Noril’sk complex, Krasnoyarskiy kray, Russia [19,20] and in the alkaline Coldwell gabbro-syenite complex in Ontario, Canada [21]. In addition, tetra-auricupride occurs in various alluvial deposits in the Sotajoki* area, Finland [22]; Durance, France [23,24]; in placers of the rivers Zolotaya* and Bolshoy Khailyk*, western Sayans [2,3,25]; Olkhovaya-1, Kamchatka krai, Russia [26]; and placers of the southeastern Samar island, Philippines [27]. The tetra-auricupride is notably platiniferous in suites indicated by an asterisk.

2. Materials and Methods

Our materials involved data published in the literature sources and the original results of the present investigation obtained on a detrital grain of tetra-auricupride from the western Sayans. This grain hosts a great variety of minute inclusions, some of which were presently studied using single-crystal electron backscatter diffraction (EBSD). We also employed synchrotron micro-Laue diffraction, wavelength-dispersive analysis (WDS), and scanning-electron microscopy (SEM) combined with energy-dispersive analysis (EDS).

2.1. Occurrence and Associated Minerals at Bolshoy Khailyk

As noted, platiniferous tetra-auricupride was found as a detrital and composite grain associated with platinum-group minerals (PGMs) in a placer deposit at the River Bolshoy Khailyk, western Sayans, southern Krasnoyarskiy kray, Russia [2,3]. The river drains the Aktovraskiy ophiolitic complex of dunite, harzburgite, and serpentinite, part of the Kurtushibinskiy belt (Figure 1).

An impressive enrichment in Ru is observed in the associated Os–Ir–Ru alloy minerals [3]. The minerals osmium, iridium, and ruthenium are the main PGMs in the Bolshoy Khailyk deposit. Isoferroplatinum-type alloys of Pt–Fe are subordinate. Alloys of the series (Pt,Ir)(Ni,Fe,Cu)_{3-x}–(Ir,Pt)(Ni,Fe,Cu)_{3-x} are rare. The sulfide species observed in the placer represent members of the laurite–erlichmanite series, cooperite, bowieite (Cu-rich), a monosulfide-type phase (Fe_{0.40}Ni_{0.39}Cu_{0.19})_{Σ0.98}S_{1.02}, a bornite-like phase (Cu_{4.06}Fe_{1.47})_{Σ5.5}S_{4.5}, a godlevskite-like phase Ni_{9.5}S_{7.5}, and a thiospinel-like phase Ni[Ir(Co,Cu,Fe)]₂S₄. Less-common and rare minerals include sperrylite, a zoned oxide Ru₆Fe³⁺₂O₁₅, and an uncommon variety of seleniferous and rhodiferous sperrylite (Pt,Rh)(As,Se,S)₂.

Inclusions of clinopyroxene (diopside: Wo_{48.3–48.6}En_{48.4–48.5}Fs_{2.6}Ae_{0.4–0.7}; Mg# 96.9–97.9), chromian spinel (magnesiocromite: Mg# up to 71), and serpentine are all rich in Mg, consistent with the ultramafic source-rocks. Actinolite, magnesio-hornblende, and barroisite also are present in inclusions.

The placer grain (Figure 2) hosts numerous inclusions: magnetite poor in Cr, Mg, (Rh,Co)-rich pentlandite, members of the tulameenite–ferronickelplatinum series, a tolovkite–irarsite–hollingworthite solid solution, and a Pt(Cu,Sn) phase [3]. In the present study, we reveal the presence of micrometric inclusions of geversite using electron backscatter diffraction (EBSD).

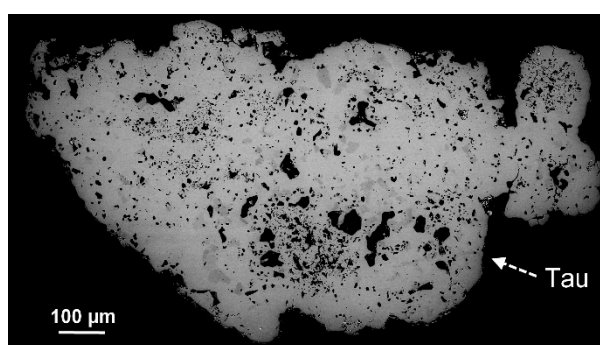


Figure 2. Back-scattered electron image showing the placer grain of platiniferous tetra-auricupride (Tau) from Bolshoy Khailyk. Black inclusions are filled with magnetite; gray phases are Rh–Co-bearing pentlandite and members of the tulameenite–ferronickelplatinum series.

2.2. WDS and SEM/EDS Analyses

Wavelength-dispersive analysis was done using a Camebax-micro electron microprobe at the Sobolev Institute of Geology and Mineralogy, Russian Academy of Sciences, Novosibirsk, Russia. The analytical conditions were 20 kV and 60 nA; the $L\alpha$ line was used for Ir, Rh, Ru, Pt, and Pd; the $M\alpha$ line was used for Os and Au; and the $K\alpha$ line was used for Fe, Ni, Cu, and Co. As standards, we used pure metals (for the platinum-group elements (PGEs) and Au), CuFeS₂, synthetic FeNiCo, and pure metals (for Fe, Cu, Ni, and Co). The minimum detection limit was ≤ 0.1 wt. % for results of the WDS analyses. The SEM/EDS analyses were carried out at 20 kV and 1.2 nA, using a Tescan Vega 3 SBH facility combined with an Oxford X-Act spectrometer at the Siberian Federal University, Krasnoyarsk, Russia. Pure elements (for PGEs, Fe, and Cu) were used as standards. The $L\alpha$ line was used for most of the PGEs except for Pt and Au ($M\alpha$ line); the $K\alpha$ line was used for Fe, Cu, and Ni.

2.3. Synchrotron Micro-Laue Diffraction Study

We have performed synchrotron X-ray scans of the grain of platiniferous tetra-auricupride from the western Sayans (Figure 2) on the basis of Laue microdiffraction measurements at beam line 12.3.2

of the Advanced Light Source (ALS). The Laue diffraction patterns were collected using a PILATUS 1M area detector in reflection geometry. The observed patterns were indexed and analyzed using XMAS (version 6) [28]. A monochromator energy scan was performed to determine the lattice parameters.

2.4. Single-Crystal Electron Backscatter Diffraction (EBSD)

Single-crystal electron backscatter diffraction (EBSD) analyses of micrometer-sized inclusions were performed using an HKL EBSD system on a ZEISS 1550VP Field-Emission SEM (Carl Zeiss Inc., Oberkochen, Germany), operated at 20 kV and 6 nA in focused-beam mode with a 70° tilted stage and in a variable pressure mode (25 Pa). The focused electron beam is several nanometers in diameter. The spatial resolution for diffracted backscatter electrons is ~30 nm in size. The EBSD system was calibrated using a single-crystal silicon standard.

3. Results

3.1. Compositional Variations in Platiniferous Tetra-Auricupride

The formula of the Pt-bearing tetra-auricupride from Bolshoy Khailyk and four other occurrences (Table 1) can be written (Au,Pt)Cu.

Table 1. Compositions of platiniferous tetra-auricupride from Bolshoy Khailyk and other localities.

#	1	2	3	4	5	6	7	8	9
Locality	KHL	KHL	KHL	KHL	TUL	SOT	ZOL	KON	KON
Au	55.49–62.27	59.69	58.46–63.22	60.81	58.45	50.30	54.52	62.54–72.54	66.15
Pt	13.03–21.24	15.23	13.79–18.14	15.67	15.80	20.40	14.69	3.12–11.79	8.41
Pd	bdl	bdl	bdl	bdl	bdl	5.49	1.64	bdl	bdl
Rh	bdl	bdl	bdl	bdl	bdl	bdl	0.51	bdl	bdl
Ir	bdl	bdl	bdl	bdl	bdl	bdl	1.96	bdl	bdl
Cu	23.68–26.07	25.43	24.10–25.25	24.52	23.51	22.00	22.68	23.52–24.69	24.15
Fe	bdl–0.72	bdl	bdl	bdl	bdl	0.66	bdl	bdl	bdl
Ni	Bdl	bdl	bdl	bdl	bdl	0.60	bdl	bdl	bdl
Atoms per formula unit (per a total of 2 apfu)									
Au	0.73–0.80	0.77	0.77–0.83	0.80	0.79	0.66	0.75	0.84–0.96	0.88
Pt	0.17–0.28	0.20	0.18–0.24	0.21	0.22	0.27	0.20	0.04–0.16	0.11
Au + Pt	0.96–1.01	0.98	0.99–1.02	1.00	1.01	0.92	0.95	0.98–1.02	1.00
Pd	0	0	0	0	0	0.13	0.04	0	0
Rh	0	0	0	0	0	0	0.01	0	0
Ir	0	0	0	0	0	0	0.03	0	0
Cu	0.96–1.04	1.02	0.98–1.01	1.00	0.99	0.89	0.97	0.98–1.02	1.00
Fe	0–0.03	0	0	0	0	0.03	0	0	0
Ni	0	0	0	0	0	0.03	0	0	0

Note: These results of EMP analyses expressed in wt. % were obtained using WDS, except for columns 1 and 2, which represent quantitative SEM/EDS data. KHL is Bolshoy Khailyk, western Sayans, Russia (This study); TUL is the Tulameen Alaskan-type complex, BC, Canada [5]; SOT is the Sotajoki area in Finland [22]; ZOL is the Zolotaya River placer, western Sayans, Russia [25]; KON is the Kondyor concentrically zoned complex, northern Khabarovskiy kray, Russia [7]. “bdl” means “not detected” or “not analyzed”. Columns 1, 3, and 8 display the observed ranges, and nos. 2, 4, and 9 pertain to mean results of point analyses, which are based on a total of 22, 10, and 5 individual analyses, respectively.

The proportion of Pt and Au defines a linear correlation. Up to ~0.3 Pt atoms per formula unit (apfu) can substitute for Au in this series (Figure 3a,b). The contents of Fe and Ni are minor; comparatively large quantities of Pd (up to 5.5 wt. %) may also be present in solid solution in some of these examples [22].

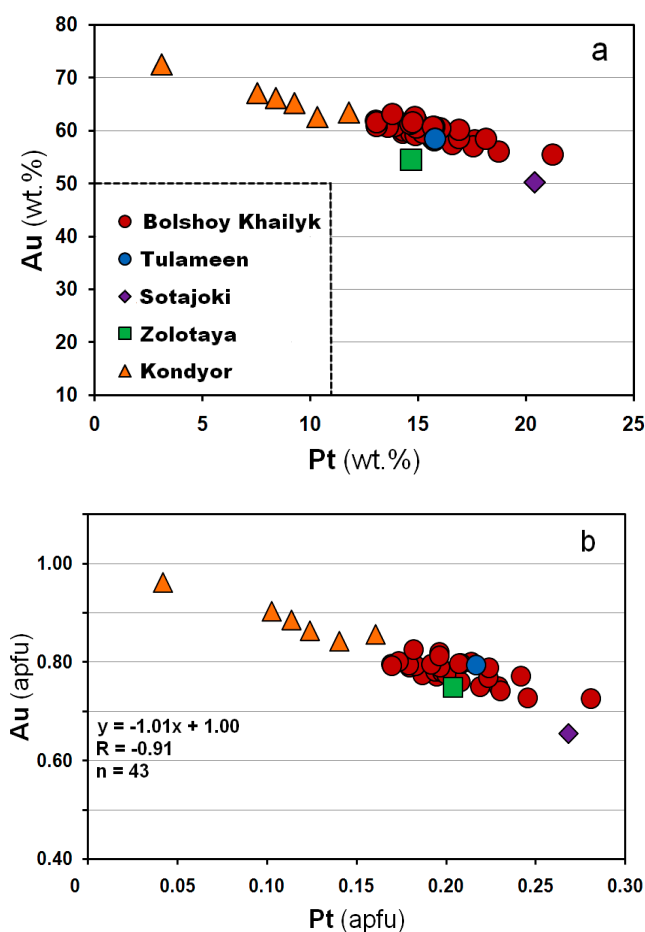


Figure 3. Plots of Pt vs. Au expressed in weight % (a) and values of atoms per formula unit (apfu), on the basis of a total of 2 apfu (b), showing compositional variations in grains of tetra-aurocupride from Bolshoy Khailyk (this study) and various localities reported in the literature.

3.2. Synchrotron Micro-Laue Diffraction Study

The Laue microdiffraction patterns of the studied specimen of platiniferous tetra-aurocupride from the western Sayans are shown in Figure 4a,b and Figure 5, and listed in Table 2. The inferred unit-cell parameters of this phase are: a 2.790(1) Å, c 3.641(4) Å, with $c/a = 1.305$; its space group is $P4/mmm$.

Table 2. X-ray diffraction pattern of platiniferous tetra-aurocupride from Bolshoy Khailyk.

h	k	l	d(obs.)	I(rel.)
0	0	1	3.63819	9.5
1	0	0	2.79045	16.1
1	0	1	2.21541	100
1	1	0	1.97535	34.1
1	1	1	1.73554	28.8
1	0	2	1.52408	20.1
2	0	0	1.39583	16.1
1	1	2	1.33812	56.9
2	0	1	1.30304	32.1
2	1	0	1.24814	12.5
2	1	1	1.1808	46.5

Note: The powder-diffraction data were obtained by scans over a large area of the platiniferous tetra-aurocupride phase (Figures 2 and 4a,b), d(obs.)—observed values; I(rel.)—intensity (I) is given in relative (rel.) units.

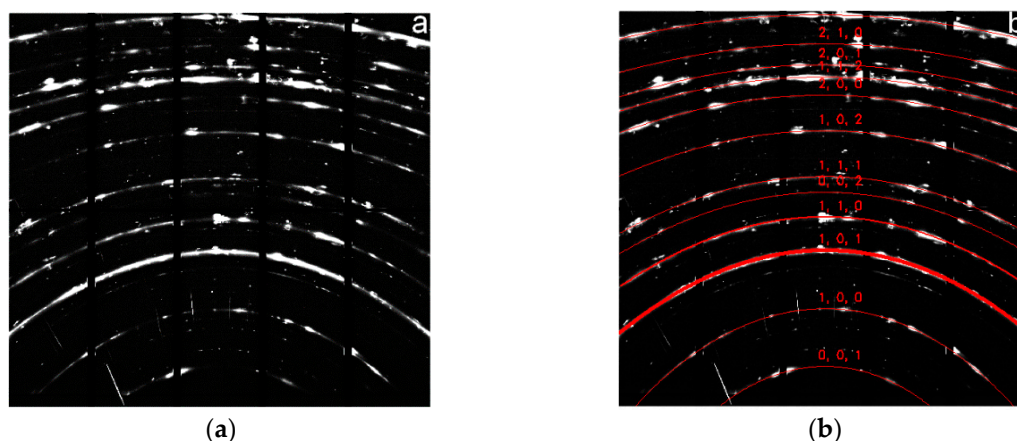


Figure 4. The observed and indexed powder-diffraction patterns (a and b, respectively) of a specimen of platiniferous tetra-auricupride at Bolshoy Khailyk, which were obtained by summing scans over a large area of the matrix phase in the detrital grain shown in Figure 2.

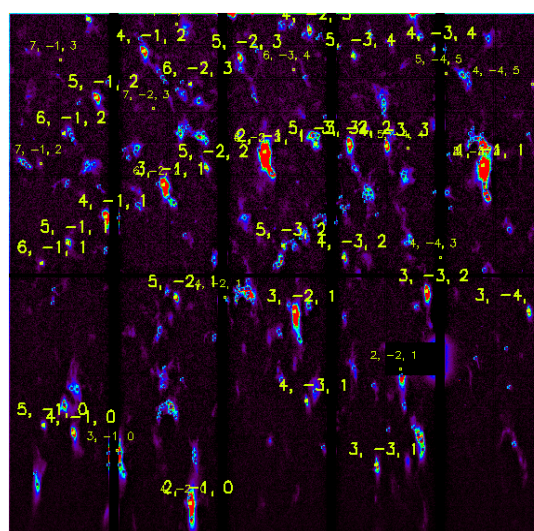


Figure 5. Indexed micro-Laue pattern of platiniferous tetra-auricupride from the western Sayans.

Our results are consistent with those obtained for the ordered AuCu(I) phase known in the Au–Cu system, which has the following parameters: a 2.785–2.810 Å, c 3.671–3.712 Å, space group $P4/mmm$ [29]. Furthermore, they agree with the suggested revision [30]. Tetra-auricupride is quoted with a 2.800 Å, c 3.670 Å, space group $P4/mmm$, that is close to the parameters of tetraferroplatinum, PtFe: a 2.724 Å, c 3.720 Å, which were also revised by this author. We can conclude that the incorporation of up to 30 mol. % of a “PtCu” component does not notably change the unit cell of tetra-auricupride. Note that hongshiite, PtCu, is not an end member in this series. Hongshiite is trigonal, space group: $R32$, $R3m$, or $R\bar{3}m$, with the unit-cell parameters: a 10.713 Å, c 13.192 Å, $Z = 48$ [31,32]; synthetic PtCu also adopts the trigonal structure [33].

Note that the holotype tetra-auricupride, of composition $Au_{1.01}Cu_{0.99}$, is different. Chen et al. (1982) [1] reported it to have the cell parameters a 3.98 Å, c 3.72 Å, $Z = 2$, with $C4/mmm$ as the probable space group. These values agree with those reported for the AuCu(II) phase documented in the system Au–Cu: a 3.96 Å, b 3.97 Å, c 3.68 Å, space group $Imma$ [29].

The results of the EBSD analysis (Figure 6a,b) indicate that micrometric inclusions in the tetra-auricupride matrix consist of geversite, $PtSb_2$.

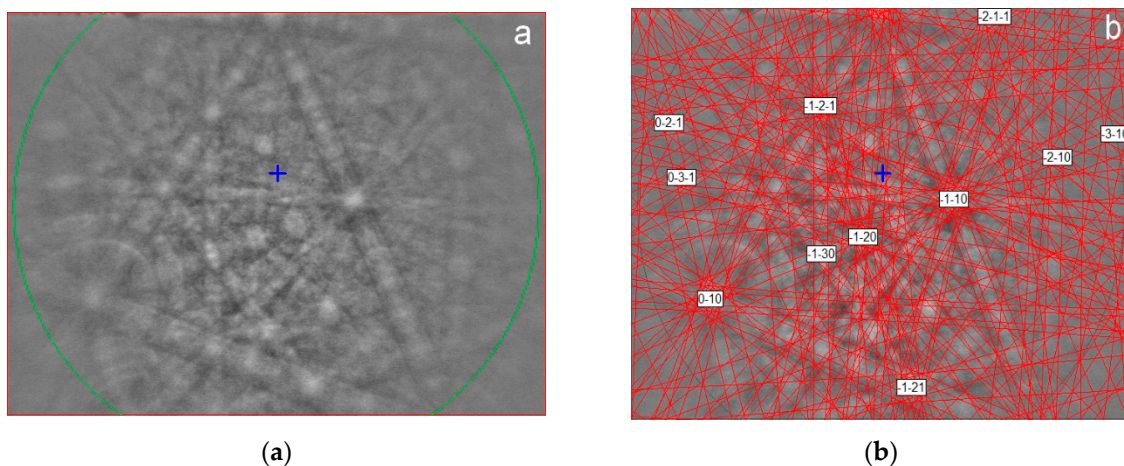


Figure 6. The observed and indexed EBSD patterns (a and b, respectively) obtained for micrometer-sized inclusion of geversite hosted by the placer grain of platiniferous tetra-auricupride at Bolshoy Khailyk.

4. Discussion and Concluding Comments

The strong dominance of Os–Ir–Ru alloy minerals, their patterns of Ru enrichment, and the regional association of detrital grains of PGMs and Pt-rich tetra-auricupride with exposed bodies of the Aktovraskiy complex (Figure 1a) provide clear indications of an ophiolite origin of the PGE + Au mineralization at Bolshoy Khailyk. The platiniferous tetra-auricupride in the Zolotaya River placers is also spatially associated with serpentinites of this complex [25]. The high extent of Cu + Au enrichment expressed by the presence of tetra-auricupride is considered to be a reflection of geochemical evolution and the buildup in levels of the incompatible Cu and Au with subordinate Pt in a remaining volume of melt during the bulk crystallization of Os–Ir–Ru alloy phases, after the early crystallization of chromian spinel and olivine [3]. Low levels of O_2 and S_2 fugacities are inferred to have existed in the system.

The suggested crystallization of the Pt-rich tetra-auricupride from a fractionated melt at a moderately low temperature is consistent with compositions of magnetite inclusions, which are poor in Mg and Cr, in contrast to magnesiochromite inclusions in the associated grains of Os–Ir–Ru-rich PGM at Bolshoy Khailyk. It is known that tetra-auricupride (Pt-free) is a late phase deposited during serpentinization of ophiolitic rocks of Skyros Island, Greece [13]. Hydrothermal processes related to serpentinization are recognized to concentrate efficiently elevated levels of gold (1–10 ppm) in sulfide-rich varieties of serpentinites, or in carbonatized (listwaenite) varieties, or in silicified serpentinites associated with ophiolites [34,35].

We establish that in such a low-temperature environment, tetra-auricupride can incorporate as much as ~30 mol. % of a “PtCu” component, apparently without significant modification of the unit cell. This surprising level of incorporation of Pt for Au has not been documented in any other mineral. The unit-cell parameters of such platiniferous auricupride are close to those reported for ordered AuCu(I) in the Au–Cu system, and are also close to the cell parameters of tetraferroplatinum (PtFe). In addition, both seem to crystallize in the same space group, $P4/mmm$ [30]. These intermetallic compounds and natural alloys are thus isostructural. The closeness of the two structures presumably allows platinum to displace gold atoms so readily, possibly at conditions of disequilibrium growth.

As noted, the tetra-auricupride grain enriched in Pt at Bolshoy Khailyk hosts a variety of inclusions: Cr–Mg–Mn-bearing magnetite, Co–(Rh)-rich pentlandite and various platinum-group minerals: the tulameenite–ferronickelplatinum series (Pt_2FeCu – Pt_2FeNi), a tolovkite (IrSbS)–irarsite (IrAsS)–hollingworthite (RhAsS) solid solution, geversite $PtSb_2$ (this study), and unnamed (Pt,Pd)(Cu,Sn), among others. On the basis of our experience, we note that EBSD analysis can be a useful tool to recognize micrometric inclusions of PGMs or other phases.

The ore-forming system thus involved at least 17 elements: Cu, Au, Pt, Rh, Pd, Ir, Fe, Co, Ni, S, Sb, As, Sn, Cr, Mn, Mg, and O, present as major or minor constituents in the mineral assemblage in

association with platiniferous tetra-auricupride. The observed diversity—the presence of compositions rich in Cu, Au, and Sn, along with PGE species having lower melting points (Rh and Pd) and metalloids (Sb and As)—is consistent with crystallization from a highly fractionated melt remaining after the deposition of primary phases such as highly magnesian olivine, magnesiochromite, and alloys of Os–Ir–Ru and (Pt,Ir)₃Fe. The upper limit of stability of a synthetic variant of ordered AuCu(II) is 410 °C, whereas the temperature of the phase transition of AuCu(II) to AuCu(I) varies under different conditions of synthesis and is generally close to 385 °C [29,36]. The observed incorporation of high amounts of Pt is expected to somewhat increase the crystallization temperature of the platiniferous AuCu(I) phase at Bolshoy Khailyk. Nevertheless, this phase presumably crystallized at a relatively low temperature, which is unlikely to have exceeded ~600–800 °C. This temperature is consistent with deposition from a droplet of residual melt.

Author Contributions: Authors wrote the article together. A.Y.B., R.F.M. and B.W. provided the interpretation of data and conclusions of the research, including results of synthesis of AuCu(I)-type compounds (B.W.). N.T., C.V.S. and C.M. contributed results of the micro-Laue and EBSD studies. G.I.S. collected placer samples and completed a field work on the Bolshoy Khailyk placer deposit.

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Conflicts of Interest: There is no conflict of interests.

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