



Article Au-Ag-Se-Te-S Mineralization in the Maletoyvayam High-Sulfidation Epithermal Deposit, Kamchatka Peninsula

Nadezhda Tolstykh *, Maria Shapovalova 🗈 and Maksim Podlipsky

Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia

* Correspondence: tolst@igm.nsc.ru

Abstract: The Maletoyvayam high-sulfidation (HS) epithermal Au-Ag deposit is one of the numerous hydrothermal deposits of the Kamchatka volcanogenic belt, consisting of two main associations: Au-rich (Ag-free) and Ag-bearing. The first one derived from acidic solutions, whereas the second assemblage crystallized from moderately dilute solutions, with both occurring at high oxygen fugacity. The Au-rich association contains the most atypical gold chalcogenides of the Au-Se-Te-S system, which are characterized by Se-S and Te-Se substitutions, e.g., a complete series from maletoyvayamite to tolstykhite $Au_3(Se_7S)_4Te_6$; a series of auroselenide $Au(Se_{1.00-0.64}S_{0.36-0.00})$; a combined series of gachingite Au(Te,Se) and unnamed Au(Se,Te): Au(Te_{0.80-0.40}Se_{0.20-0.60}). Meanwhile, in the second Ag-bearing assemblage, sulfides of the Au-Ag type prevails, e.g., petrovskaite AuAgS, miargyrite (Ag,Au)(Sb,As)S₂, uytenbogaardtite Ag₃AuS₂, fischesserite Ag₃AuSe₂ with Au-Ag substitution, and tolstykhite. The Se/S ratio, of the second association, decreases while increasing the Ag concentration in the ore-forming system, including Au-Ag substitutions. The Au content in miargyrite (Au,Ag)SbS₃ reaches up to 0.48 apfu, suggesting the existence of a new mineral phase of composition AgAuSb₂S₆. Au oxide complexes, in both associations, are represented by either a mixture of redeposited gold and Fe-Sb oxide or a homogeneous (Au,Sb,Fe)₂O₃ composition. These oxides are formed by replacement of calaverite. The ore mineralization of this HS deposit is considered unique due to the special conditions of the ore-forming environment, such as acidic solutions, high oxygen fugacity, and log fSe_2 above -5.7; all contributed to the formation of AuSe phases.

Keywords: epithermal deposit; high-sulfidation; selenium; selenide; Au-Se-Te system; Kamchatka peninsula; maletoyvayamite; gachingite; tolstykhite; auroselenide

1. Introduction

The epithermal Maletoyvayam Au-Ag deposit, located in the northern part of the Central Kamchatka volcanogenic belt (Figure 1a,b), is the only one in the Kamchatka peninsula corresponding to high sulfidation (HS), according to [1]. This deposit is confined to the Vetrovayam volcano-tectonic structure. The Maletoyvayam ore field comprises volcano-sedimentary succesions of the Vetrovayam suite: andesites, tuffs, and tuffsandstones (Figure 1c). Features, such us vuggy silica and stockwork quartz veining, in the central parts of the ore field are followed outwards by alunite-, sericite-kaolin-quartz, and kaolin-quartz rocks, and then by argillites and propylites at the periphery [2]. The Gaching ore occurrence, belonging to the Maletoyvayam deposit, is located near the head of the Gachingalhovayam River and is represented by quartz stockworks, hosted by vuggy silica and strongly oxidized quartz-alunite rocks, typical of HS type deposits [3]. The regional geology, structural features, and ore-forming processes of the Maletoyvayam deposit have been extensively reported. A collection of these data is given in [4,5], where the approximate conditions for the activity of sulfur, selenium, tellurium, and oxygen were estimated on the basis of mineral paragenesis. This approach revealed that the productive ore association was derived from very acidic solutions under oxidizing conditions, which are indicative of



Citation: Tolstykh, N.; Shapovalova, M.; Podlipsky, M. Au-Ag-Se-Te-S Mineralization in the Maletoyvayam High-Sulfidation Epithermal Deposit, Kamchatka Peninsula. *Minerals* 2023, 13, 420. https://doi.org/10.3390/ min13030420

Academic Editor: Rajesh Kumar Jyothi

Received: 15 February 2023 Revised: 10 March 2023 Accepted: 13 March 2023 Published: 16 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). HS epithermal deposits [6,7]. Additional work about mustard gold and Au oxides in the paragenesis of the Maletoyvayam deposit [8,9], as well as a study on the compositions of fluid inclusions in quartz, have been published [9,10]. Unnamed gold chalcogenides, never described before for other deposits, have been identified in the different ore associations; some of them were synthesized and their experimental analogues studied [11,12], finally leading to the approval, by the International Mineralogical Association (IMA), of four new gold mineral species: maletoyvayamite $Au_3Se_4Te_6$ [13], gachingite $Au(Te_{1-x}Se_x)$ [14], tolstykhite $Au_3S_4Te_6$ [15], and auroselenide AuSe [16]. The presence of four new mineral species among Au-minerals and unnamed Au-compounds at the Maletoyvayam deposit, which have not yet been reported anywhere else, may be related to the special conditions of their forming environment. Acidic ore-forming solutions and high oxygen activity, typical of HS-type epithermal deposits, were accompanied by very high selenium activity: log fSe_2 varying between -12.4 and -5.7 at 250 °C [5]. All of this led to a high Se/S ratio in ore-forming solutions, which triggered the formation of the auroselenide (AuSe) species. Recently obtained mineralogical data also revealed the presence of an Ag-bearing association, in a few samples, in addition to the Au-rich (Ag-free) assemblage. Hence, the aim of this study is to reveal the correlation of Au/Ag and Se/S ratios in mineral parageneses, due to the fact that selenium activity increases when the acidity of solutions is increased [17–19]. Furthermore, a detailed description of the reference mineralogical collection of the Maletoyvayam deposit (Gaching occurrence), characterizing the products of acidic hydrothermal solutions, is also of great scientific importance to understand the ore genesis of epithermal deposits.



Figure 1. Location of the Kamchatka Peninsula in the Russian far east (**a**); geographical position of the Maletoyvayam deposit on the Kamchatka Peninsula (**b**); simplified geological map of the Vetrovayam volcano-tectonic structure, showing the Gaching ore occurence within the Maletoyvayam deposit (**c**).

2. Materials and Methods

Samples of quartz veins and alunite-quartz rocks from the mine trench at the Gaching site (one sample of 20 kg and thirteen of 5 kg each) were provided to the authors for research. Samples of rocks were crushed to a particle size of less than 0.5 mm and were later separated by density, using water and a dense liquid tribromomethane to obtain a heavy mineral concentrate. These concentrates were later prepared as epoxy grain mounts for microprobe analysis, along with polished rock chips, for in situ analysis of paragenetic associations.

The chemical compositions of minerals were analyzed at the Analytical Center for Multi-Elemental and Isotope Research at the VS Sobolev Institute of Geology and Mineralogy SB RAS in Novosibirsk (Russia), using a LEO-413VP scanning electron microscope (SEM) equipped with an INCA Energy 350 X-ray EDS system (Oxford Instruments Ltd., Abingdon, UK) (analysts Dr. N. Karmanov and M. Khlestov), operating at an accelerating voltage of 20 kV, beam current of 0.4 nA, 50 s measuring time, and beam diameter of \sim 1 µm. The following standards were used: pure metals (Ag, Au, Bi, Se, Sb, Fe, Cu), pyrite (S), synthetic HgTe (Te), and sperrylite (As). The detection limit was 0.02%. The following X-ray lines were selected: L α for Ag, Te, As, Sb, and Se; K α for S, Fe, Cu, and O; and M α for Au and Bi. WDS Microprobe analyses of Au-minerals were carried out in the same analytical center, at 20 kV and 50 nA, in a JEOL JXA-8230 microprobe (beam size \sim 1 mm) (analyst V. Korolyuk). The following X-ray lines (and standards) were used: $SeL\alpha$ (Bi₂Se₃), TeL α (AgTe₂), AgL α (Ag), SK α (CuFeS₂), and AuM α (Au). The results were treated using ZAF correction routines in the native JEOL software. The detection limit was <0.05% for all analyzed elements. More than 2000 microanalyzes for mineral compositions were carried out. All data in the tables are listed according to the detection limits of the elements.

3. Results

3.1. Minerals in the Au-Te-Se-S System

3.1.1. Maletoyvayamite-Tolstykhite Solid Solution (Mty—Tls ss)

These two minerals have been previously described as unnamed phases $Au_2Te_4(Se,S)_3$ [5]; however, after performing detailed crystallographic studies, a new chemical formula was assigned for each of the compounds— $Au_3Se_4Te_6$ for maletoyvayamite [13] and $Au_3S_4Te_6$ for tolstykhite [15]—both of which turned out to be isostructural. Maletoyvayamite and tolstykhite are the most common minerals of the ore-bearing association, prevailing over native high-grade gold. As shown in Figure 2a, the composition of these minerals is clustered in a specific area of the ternary diagram, showing limited variations in the ratios between Au and chalcogens, as well as in tellurium and the (S + Se) sum. The Se-S substitution is substantial, forming a complete solid solution between maletoyvayamite and tolstykhite (Figure 2b). The grain morphology of both minerals and intergrowths, with associated phases, are comparable (Figure 3). Individual grains are characterized by anhedral shapes (Figure 3a,b). Both maletoyvayamite and tolstykhite are opaque with metallic luster. Cleavage is well-developed on {010} and {001}. In plane-polarized reflected light, both minerals are bluish gray with high birefringence and strong anisotropy [13,15].

There are two types of mineral assemblages: (1) maletoyvayamite and tolstykhite are very often intergrown with Fe-Sb oxides (Figure 3c,d)—FeSbO₄ and FeSb₂O₆, which correspond to tripuhyite compositions, as well as with more oxidized species containing Te, As, Bi, and S as minor elements [8]; (2) intergrowths of maletoyvayamite and tolstykhite with calaverite AuTe₂ and native gold (Figure 3e,f). In this case, the selenium analogue varies all the way up to a S-free composition (Table 1), spectra 83, 84, 98, 100, and 104. However, when associated with tripuhyite or Ag-bearing minerals (fischesserite), the role of S in solid solutions increases significantly.



Figure 2. Compositions of Au-S-Se-Te minerals from the Maletoyvayam deposit in the systems (Se + S)-Au-Te (**a**) and S-Se-Te (**b**).



Figure 3. SEM back-scattered images of individual grains of tolstykhite $Au_3Te_6S_4$ (Tls) (**a**), Tls – Mty solid solutions (**b–d**) and maletoyvayamite $Au_3Te_6Se_4$ (Mty) (**e**,**f**) in intergrowths with Fe-Sb oxides (**e**), with calaverite $AuTe_2$ (Clv) and Au-Sb-Fe oxide (**e**), with native gold (Au) (**f**), and unnamed phase $AuTe_2Se$ (**e**,**f**). Sample reference number is at the lower right corner of the images. Black dots with numbers correspond to analytical points (spectrum) in Table 1.

No.	Sample	Sp.	Au	Te	Se	S	Total	Formulas
1	Mt-4_1-1	132	37.18	51.2	1.08	9.73	99.19	Au _{2,70} (S _{4,35} Se _{0,20}) _{4,55} Te _{5,75}
2	Mt-4_1-1	133	37.09	51.33	0.62	9.3	98.34	Au _{2.76} (S _{4.24} Se _{0.11}) _{4.35} Te _{5.89}
3	Mt-4_1-5	146	37.91	50.35	3.93	7.45	99.64	Au _{2.88} (S _{3.48} Se _{0.74}) _{4.22} Te _{5.90}
4	Mt-4_1-5	147	36.62	50.67	4.54	7.06	98.89	Au _{2.81} (S _{3.33} Se _{0.87}) _{4.20} Te _{6.00}
5	Mt-4_1-6	148	36.19	47.59	9.94	4.05	97.77	Au _{2.95} (S _{2.03} Se _{2.02}) _{4.05} Te _{5.99}
6	Mt-4_1-6	150	37.72	50.96	3.95	7.73	100.36	Au _{2.82} (S _{3.55} Se _{0.74}) _{4.29} Te _{5.89}
7	Mt-4_2-4	162	36.33	47.37	11.65	2.73	98.08	Au _{3.04} (Se _{2.43} S _{1.40}) _{3.83} Te _{6.12}
8	Mt-4_2-4	163	35.98	47.36	12.01	2.57	97.92	Au _{3.02} (Se _{2.52} S _{1.33}) _{3.85} Te _{6.14}
9	G1-f_3-1	82	95.86				97.08 *	$(Au_{0.98}Ag_{0.02})_{1.00}$
10	G1-f_3-1	83	34.72	46.34	17.34		98.4	Au _{3.00} Se _{3.73} Te _{6.17}
11	G1-f_3-1	84	34.54	46.22	19.2		99.96	Au _{2.92} Se _{4.05} Te _{6.03}
12	G1-f_3-1	85	35.52	46.14	15.52		97.18	Au _{0.98} Te _{1.96} Se _{1.06}
13	G1-f_2-1	102	42.43	53.51	1.5		97.44	Au _{0.99} (Te _{1.92} Se _{0.09}) _{2.01}
14	G1-f_2-1	103	42.17	53.72	1.63		97.52	Au _{0.98} (Te _{1.93} Se _{0.09}) _{2.02}
15	G1-f_2-1	98	34.78	46.2	18.24		99.22	Au _{2.98} Se _{3.90} Te _{6.12}
16	G1-f_2-1	100	33.72	45.32	17.68		96.72	Au _{2.97} Se _{3.88} Te _{6.15}
17	G1-f_2-1	104	33.03	45.53	18.02		96.58	Au _{2.90} Se _{3.94} Te _{6.16}
18	G1-f_2-1	96	36.3	46.77	15.8		98.87	Au _{0.98} Te _{1.95} Se _{1.07}

Table 1. Compositions (wt. %) of maletoyvayamite, tolstykhite, and associated minerals shown in Figure 3.

*—Total includes 1.22 wt. % Ag. 1–6—tolstykhite; 7–8, 10–11, 15–17—maletoyvayamite; 9—gold; 12, 18—AuTe₂Se, 13–14—calaverite; Sp.—spectrum number.

A portion of the most Au-rich compositions on the Mty—Tls ss field (Table 1), spectra 85 and 96, lies on the Au/(S + Se + Te) = 1/3 line (Figure 3a) and moves toward the chemical formula Au(Te,Se,S)₃, which can be represented as Au(Se,S)Te₂.

3.1.2. Tellurium-Selenium Solid Solution (Te-Se ss)

Native tellurium, as well as the solid solution it forms with selenium, are representative of the entire ore association. Te-Se ss occur as: (1) individual grains, often intergrown with goldfieldite or selenium goldfieldite (Figure 4a,b,d,e,f); (2) as drop-shaped or rounded inclusions in sulfosalts (tetrahedrite and goldfieldite) (Figure 4c); and (3) as xenomorphic segregations intergrown with Mty—Tls ss (Figure 4d–f). The compositional points of Te-Se ss, confined towards the tellurium region of the diagram (Figure 2a), form an almost continuous series from native tellurium up to Se_{0.58}Te_{0.42}. Minor S, up to 0.65 wt. %, is present in Te-Se solid solutions (Table 2). The main associated minerals are goldfieldite, in which Te predominates over Sb and As, and tetrahedrite (Table 2). All of them include Se within the range 1.00–8.93 wt. %. In some cases, the amount of Se (apfu) prevails over the other chalcogens in the chemical formulae (D_9-1, point 4), which may potentially correspond to a new sulfosalt Cu₁₂Se₄S₁₃ (Table 2). Te-Se solid solutions occur intergrown, in almost the same proportion, with both tolstykhite and maletoyvayamite.

Table 2. Compositions (wt. %) of native tellurium and Te-Se solid solutions, as well as their associated minerals, as shown in Figure 4.

No.	Sample	Sp.	Fe	Cu	Au	Ag	Sb	Te	As	Se	S	Total	Formulas
1	D_4-4	1						53.14		45.77	0.45	99.36	Se _{0.57} Te _{0.41} S _{0.01}
2	D_4-4	2						52.25		45.85	0.36	98.46	Se _{0.58} Te _{0.41} S _{0.01}
3	16h_1-5	1						96.74		1.73		98.47	Te _{0.97} Se _{0.03}
4	16h_1-5	2		42.33			5.28	14.77	6.48	8.93	21.67	99.46	Cu _{11.36} (Te _{1.97} Se _{1.93} As _{1.47} Sb _{0.74}) _{6.11} S _{11.53}
5	16h_2-5	1	0.68	43.15		0.4	10.53	11.75	5.22	4.64	23.32	99.69	$(Cu_{11.39}Fe_{0.20}Ag_{0.06})_{11.65}(Te_{1.54}Sb_{1.45}As_{1.17}Se_{0.99})_{5.15}S_{12.20}$
6	16h_2-5	2						98.42		0.86	0.65	99.93	Te _{0.96} S _{0.03} Se _{0.01}
7	16h_1-2	1			38.56			50.65		4.21	7.06	100.48	Au _{2.94} (S _{3.30} Se _{0.80}) _{4.10} Te _{5.96}
8	16h_1-2	2						89.61		11.06		100.67	Te _{0.83} Se _{0.17}
9	16h_1-2	3	0.45	42.29			9.36	15.66	1.63	5.79	25.49	100.67	$(Cu_{10.94}Fe_{0.13})_{11.07}(Te_{2.02}Sb_{1.26}Se_{1.21}As_{0.36})_{4.85}S_{13.08}$
10	D_6-9	1			36.47			50.39		7.05	5.47	99.38	Au _{2.87} (S _{2.64} Se _{1.38}) _{4.02} Te _{6.11}
11	D_6-9	2						79.96		19.56	0.28	99.8	Te _{0.71} Se _{0.28} S _{0.01}
12	D_6-9	3	0.2	43.36			17.27		6.6	2.77	29.77	99.97	$(Cu_{10.53}Fe_{0.06})_{10.59}(Sb_{2.19}As_{1.36}Se_{0.54})_{4.09}S_{14.33}$
13	D_6-9	4		32.63				43.13		1	22.03	98.79	Cu _{9.60} (Te _{6.32} Se _{0.24}) _{6.56} S _{12.85}
14	D_9-1	1			35.5			47.61		14.76	1.23	99.1	$Au_{3.01}$ (Se _{3.12} S _{0.64}) _{3.76} Te _{6.23}
15	D_9-1	2			35.47			47.08		15.41	1.08	99.04	Au _{3.01} (Se _{3.26} S _{0.56}) _{3.82} Te _{6.17}
16	D_9-1	3						89.43		7.99		97.42	Te _{0.87} Se _{0.13}
17	D_9-1	4	0.35	42.11			6.23	13.7	6.19	8.65	22.49	99.72	$(Cu_{11.17}Fe_{0.11})_{11.28}(Se_{1.85}Te_{1.81}As_{1.39}Sb_{0.86})_{5.91}S_{11.82}$

1–3, 6, 8, 11, 16—Te-Se solid solutions; 4–5, 9, 13—goldfieldite; 7, 10—tolstykhite; 14–15—maletoyvayamite; 12—tetrahedrite; 17—Se-analogue of goldfieldite.



Figure 4. SEM back-scatter images of Te-Se solid solution members as separate grains (**a**), inclusions and intergrowths with goldfieldite (Gf) (**b**–**f**), and Au chalcogenide: tolstykhite (Tls) (**d**,**e**) and maletoyvayamite (Mty) (**f**). Sample reference number is at the lower right corner of the images. Black dots with numbers correspond to analytical points (spectrum) in Table 2.

3.1.3. Calaverite AuTe₂

Calaverite occurs in subordinate amounts compared to other gold minerals. It is found as discrete grains (Figure 5a) in intergrowth with maletoyvayamite or tolstykhite (Figure 5b), but most often together with Au-Fe-Sb oxides (Figure 5c–e), which instead replace calaverite, forming rims (Figure 5d) or completing pseudomorphs with minor relics (Figure 5f). The Ag concentration in calaverite does not exceed 4 wt. %, and it is usually less than 1 wt. % (Table 3). Calaverite oxidizes when reacting with infiltrating fluids containing Fe, Sb \pm As, Se, S, and Bi, additionally forming Au oxides (Figure 5). Compositions of Au-Fe-Sb(Te,As,Se) complex oxides, associated with calaverite, are shown in Table 3. Minor arsenic is regularly detected in these oxides, with rather rare Ag, Cu, Se content.



Figure 5. SEM back-scatter images of discrete calaverite (Clv) grains (**a**), intergrown with maletoyvayamite (Mty), tolstykhite (Tls), and goldfieldite (Gf) (**b**,**c**); calaverite grains, partially (**d**,**e**) or completely (**f**) replaced by Au-Fe-Sb(As) oxide. The numbers on samples and points with the number of the spectrum correspond to the analyses shown in Table 3.

Table 3. Compositions (wt. %) of calaverite AuTe2 and associated minerals, displayed in Figure 5.

No.	Sample	Sp	Fe	Cu	Au	Ag	Sb	S	0	Total	Formulas
1	D_5-10	1			43.8	1.01		0.36		102.31	$(Au_{0.95}Ag_{0.04})_{0.99}(Te_{1.86}Se_{0.10}S_{0.05})_{2.01}$
2	D_5-10	2			42.06	1.09				98.46	$(Au_{0.96}Ag_{0.05})_{1.01}(Te_{1.89}Se_{0.10})_{1.99}$
3	D_5-10	3			43.15	0.9		0.26		101.15	$(Au_{0.95}Ag_{0.04})_{0.99}(Te_{1.87}As_{0.10}S_{0.04})_{2.01}$
4	16h_1-4	1			38.56	3.94				100.24	$(Au_{0.85}Ag_{0.16})_{1.01}(Te_{1.92}Se_{0.07})_{1.99}$
5	16h_1-4	2			34.7	0		2.56		97.01	$Au_{2.91}(Se_{2.71}S_{1.32})_{4.03}Te_{6.06}(Se_{2.71}S_{1.32})$
6	16h_2-2	1			42.98	0.93				100.85	$(Au_{0.96}Ag_{0.04})_{1.00}(Te_{1.89}Se_{0.11})_{2.00}$
7	16h_2-2	2	7.28	0.64	54.26	1.11	12.55		12.83	84.87	$(Au_{1.00}Fe_{0.47}Sb_{0.37}As_{0.11}Cu_{0.04}Ag_{0.04}Te_{0.04}Se_{0.02})_{2.09}O_{3.00}$
8	16h_2-2	3	7.8	0.76	55.59	1.22	13.44		15.58	90.54	(Au _{0.89} Fe _{0.44} Sb _{0.35} As _{0.11} Cu _{0.04} Ag _{0.04} Te _{0.03} Se _{0.03}) _{1.93} O _{3.07}
9	D_7-6	1			44.27			0.54		101.33	Au _{0.98} (Te _{1.91} S _{0.07} Se _{0.04}) _{2.02}
10	D_7-6	2			45.22			0.54		103.15	Au _{0.98} (Te _{1.88} S _{0.07} Se _{0.06}) _{2.01}
11	D_7-6	3	3.32		61.81	0.75	9.94		13.18	87.79	$(Au_{1.25}Sb_{0.33}Fe_{0.24}As_{0.11}Ag_{0.03})_{1.96}O_{3.04}$
12	D_5-6	1			44.04			0.45		99.29	$Au_{1.00}(Te_{1.89}S_{0.06}Se_{0.05})_{2.00}$
13	D_5-6	2	1.60		58.89	0.77	13.95	0.56	14.08	91.39	$(Au_{1.08}Sb_{0.41}Fe_{0.10}As_{0.08}S_{0.06}Te_{0.04}Ag_{0.03})_{1.80}O_{3.19}$
14	D_5-6	3	1.75		57.98	1.13	13.43	0.87	12.87	88.49	$(Au_{1.13}Sb_{0.42}Fe_{0.12}S_{0.10}As_{0.07}Ag_{0.04}Te_{0.03})_{1.91}O_{3.09}$

3.1.4. Chalcogenides AuX, X—Te,Se,S: Gachingite Au($Te_{1-x}Se_x$), Auroselenide AuSe, and Unnamed Au(Se,Te) Phase

These minerals are considered the rarest of all ore association in the Maletoyvayam deposit and belong to the category of gold chalcogenides with common formula AuX, where X is Se, Te, and S. Auroselenides occur as irregular fragments rimming native gold by replacement (Figure 6a–f). Auroselenides AuSe are also in close association with Mty-Tls ss (Figure 6b,d,e). Gachingite Au(Te_{1-x}Sex), where $0.2 \approx x \leq 0.5$, or more simply (Te_{0.8-0.5}Se_{0.2-0.5}), occurs as individual rounded to drop-shaped inclusions of 10 µm within gold grains (Figure 6f) [14]. Three discrete grains of gachingite, 20–40 µm in size, (Figure 6a–c) intergrown with maletoyvayamite, calaverite, and Au-Sb oxides were recently observed. All Au chalcogenides are difficult to distinguish from each other in reflected light, due to their size and similar optical properties. Auroselenide, gachingite-like, and Mty-Tls ss are

bluish-gray with strong anisotropy, displaying bluish to brownish rotation pleochroism. Nonetheless, gachingite has a lighter blue-gray tone (Figure 6f) and a smoother (polished) mineral surface compared to maletoyvayamite, which possesses a flakier surface (Figure 7a).



Figure 6. Reflected light. Textural features and morphology of grains of auroselenide (AuSe) (**a**–**e**), and gachingite (Gcg) (**f**), in association with minerals of the maletoyvaymite-tolstikhite (Mty) series, mostly replacing native gold (Au), as well as discrete inclusions.

In addition, the composition of both auroselenide and gachingite lies on the same AuSe – AuTe line in the (S + Se) – Au – Te system (Figure 2a). Monoclinic AuSe [16] shows rather limited compositions, with slight variations around Au and (Se + S) end-members and between (Se + S) and Te, as well as an extended Se \rightarrow S substitution series up to Au(Se_{0.64}S_{0.36}) (Figure 2b). The morphology of this phase is comparable to auroselenide, but it differs slightly in lighter shade from other associated minerals (auroselenide, maletoyvayamite, tolstykhite) on SEM images (Figure 8), points 1–3 and 6–11. Compositions of gachingite, as shown in the chemical formula approved by the IMA, also form a limited orthorhombic series from Au_{1.0}Te_{0.5}Se_{0.5} to Au_{1.0}Te_{0.8}Se_{0.2} [14]. The analytical results of auroselenide and gachingite are given in Tables 4 and 5.



Figure 7. SEM images. Individual grains of gachingite (Gcg) (**a**–**c**) intergrown with maletoyvayamite (Mty) and calaverite (Clv) (**a**), and Au,Sb,Se-oxide (**c**). The numbers of the samples and the points with the numbers of the spectrum correspond to the analyses in Table 5.



Figure 8. SEM back-scatter image. An individual grain of native gold, partially replaced by various gold minerals: maletoyvayamite (Mty), tolstykhite (Tls), auroselenide (AuSe), and unnamed phase Au(Se,Te). The reference number of the sample and the white EDS points correspond to the analyses given in Table 6.

Table 4. Composition (wt. %) of auroselenide AuSe, shown in Figure 6.

No.	Sample	Au	Te	Se	S	Total	Formulas
1	d_3-8	69.40	1.95	23.99	1.88	97.22	Au _{0.97} (Se _{0.83} S _{0.16} Te _{0.04}) _{1.03}
2	d_3-9	71.84	3.02	21.83	2.07	99.27	$Au_{0.99}(Se_{0.77}S_{0.18}Te_{0.06})_{1.01}$
3	d_6-12	71.63	1.87	23.47	2.56	99.53	Au _{0.96} (Se _{0.79} S _{0.21} Te _{0.04}) _{1.04}
4	d_2-4	68.03	0.69	23.69	1.85	94.77 *	$(Au_{0.97}Ag_{0.01})_{0.98}(Se_{0.84}S_{0.16}Te_{0.02})_{1.02}$

*—Total includes 0.51 wt. % Ag.

No.	Sample	Sp.	Au	Te	Se	Total	Formulas
1	Mt13_3-4a	19	62.06	27.86	7.85	97.77	Au _{1.00} (Te _{0.69} Se _{0.31}) _{1.00}
2	Mt13_3-4a	20	62.25	28.53	7.29	98.07	$Au_{1.00}(Te_{0.71}Se_{0.29})_{1.00}$
3	Mt13_3-4a	21	62.01	27.95	7.47	97.43	Au _{1.00} (Te _{0.70} Se _{0.30}) _{1.00}
4	Mt13_3-4a	22	61.33	27.94	8.42	97.69	Au _{0.98} (Te _{0.69} Se _{0.33}) _{1.02}
5	Mt13_3-4a	23	43.61	53.63	1.67	98.91	Au _{1.00} (Te _{1.90} Se _{0.10}) _{2.00}
6	Mt13_3-4a	24	35.89	45.27	14.63	97.65 *	Au _{3.04} (Se _{3.09} S _{0.97}) _{4.06} Te _{5.91}
7	Mt13_1-1_2-1	25	62.89	25.52	9.98	98.39	Au _{0.99} (Te _{0.62} Se _{0.39}) _{1.01}
8	Mt13_1-1_2-1	26	62.47	25.54	9.54	97.55	Au _{0.99} (Te _{0.63} Se _{0.38}) _{1.01}
9	Mt13_1-1_2-1	27	62.89	27.91	8.11	98.91	Au _{1.00} (Te _{0.68} Se _{0.32}) _{1.00}
10	Mt13_1-1_2-1	28	62.37	28.94	7.35	98.66	$Au_{0.99}(Te_{0.71}Se_{0.29})_{1.00}$
11	Mt13_1-1_2-1	29	62.32	26.56	9.21	98.09	Au _{0.99} (Te _{0.65} Se _{0.36}) _{1.01}
12	Mt13_1-1_2-1	30	62.87	24.87	9.95	97.69	Au _{1.00} (Te _{0.61} Se _{0.39}) _{1.00}
13	Mt13_3-6	36	62.62	27.9	6.91	97.43	Au _{1.02} (Te _{0.70} Se _{0.28}) _{0.98}
14	Mt13_3-6	37	62.13	27.8	7.76	97.69	Au _{1.00} (Te _{0.69} Se _{0.31}) _{1.00}
15	Mt13_3-6	38	62.45	28.09	7.25	97.79	Au _{1.01} (Te _{0.70} Se _{0.29}) _{0.99}
16	Mt13_3-6	39	62.95	28.13	7.6	98.68	Au _{1.00} (Te _{0.69} Se _{0.30}) _{0.99}

Table 5. Compositions (wt. %) of gachingite Au($Te_{1-x}Se_x$) and related minerals. See Figure 7.

*-Total includes 1.86 wt. % S. 1-4, 7-16-gachingite; 5-calaverite; 6-maletoyvayamite.

Table 6. Compositions (wt. %) of Au(Se,Te) phases and their associated minerals included in native gold in Figure 8.

No.	Sample	Sp.	Au	Te	Se	s	Total	Formulas
1	D_11-3	1	66.26	17.90	16.53		100.69	Au _{0.98} (Se _{0.61} Te _{0.41}) _{1.02}
2	D_11-3	2	67.98	16.30	16.77	0.39	101.44	Au _{0.99} (Se _{0.61} Te _{0.37} S _{0.03}) _{1.01}
3	D_11-3	3	67.10	16.27	15.90	0.56	99.83	Au _{0.99} (Se _{0.59} Te _{0.37} S _{0.05}) _{1.01}
4	D_11-3	4	73.05		25.47	2.05	100.57	$Au_{0.98}(Se_{0.85}S_{0.17})_{1.02}$
5	D_11-3	5	71.99		25.43	1.02	98.44	$Au_{1.02}(Se_{0.90}S_{0.09})_{0.99}$
6	D_11-3	6	65.46	18.04	1.41	0.35	98.26	Au _{1.00} (Se _{0.55} Te _{0.42} S _{0.03}) _{1.00}
7	D_11-3	7	66.65	17.45	14.26	0.40	97.76	Au _{1.01} (Se _{0.54} Te _{0.41} S _{0.04}) _{0.99}
8	D_11-3	8	66.25	16.58	15.55	0.32	98.70	$Au_{1.00}(Se_{0.59}Te_{0.39}S_{0.03})_{1.01}$
9	D_11-3	9	65.64	17.07	14.41	0.48	97.60	$Au_{1.00}(Se_{0.55}Te_{0.40}S_{0.05})_{1.00}$
10	D_11-3	10	65.51	17.25	15.76	0.53	99.05	$Au_{0.97}(Se_{0.58}Te_{0.40}S_{0.05})_{1.03}$
11	D_11-3	11	64.14	17.54	14.89	0.59	97.16	Au _{0.97} (Se _{0.56} Te _{0.41} S _{0.05}) _{1.02}
12	D_11-3	12		6.63	5.34	38.07	100.34	$Au_{2.91}(S_{3.12}Se_{1.02})_{4.14}Te_{5.94}$
13	D_11-3	13		4.96	8.89	36.85	99.86	Au _{2.90} (S _{2.40} Se _{1.74}) _{4.14} Te _{5.96}
14	D_11-3	14		0.84	17.11	36.02	101.56	Au _{2.98} (Se _{3.53} S _{0.43}) _{3.96} Te _{6.07}
15	D_11-3	15		0.93	17.48	36.15	101.78	Au _{2.97} (Se _{3.58} S _{0.47}) _{4.05} Te _{5.98}
16	D_11-3	16		0.79	16.98	3.17	101.64	Au _{2.99} (Se _{3.51} S _{0.40}) _{3.91} Te _{6.10}
17	D_11-3	17				98.51	99.79 *	Au _{0.98} Ag _{0.03}
18	D_11-3	18				96.89	98.31 **	Au _{0.97} Ag _{0.03}

*, **—1.21 and 1.42 wt. % Ag, respectively, included in the total. 1–3, 6–11—unnamed Au(Se,Te); 4–5—auroselenide; 12–13—tolstykhite; 14–15—maletoyvayamite; 17–18—gold.

3.2. Minerals in the Au-Ag-Sb(As)-S System from the Ag-Bearing Association

3.2.1. Miargyrite, Petrovskaite, Uytenbogaardtite, and Fischesserite from the Ag-Bearing Association

In this study, new mineralogical data were obtained; a few Ag-bearing mineral species, such as petrovskaite AuAgS, Au-bearing miargyrite (Ag,Au)(Sb,As)S₂, uytenbogaardtite Ag_3AuS_2 , and fischesserite Ag_3AuSe_2 , were identified in sample MG-63 from the Maletoyvayam deposit. All of them occur in close association with native gold. The first two Ag-bearing species replace gold grains at the margins (Figure 9a,d); uytenbogaardtite is intergrown with gold (Figure 9b,e), whereas fischesserite with maletoyvayamite are grown together. Each of these minerals has its own compositional features, e.g., petrovskaite is characterized by an excess of silver relative to gold (Ag 1.08–1.13 apfu); uytenbogaardtite has Au-Ag variations (Ag 2.87-3.20 apfu) deviated from the ideal Ag₃AuS₂ formula (Figure 10a, Table 7); fischesserite contains minor S (0.18–0.24 apfu); and miargyrite and petrovskaite are closely intergrown, forming a typical rim after gold. At the same time, miargyrite contains a significant amount of Au (0.39–0.48 apfu) (Figure 10b), as well as As \rightarrow Sb substitution, up to 10.2 wt. % or 0.43 apfu (Table 7). In addition, unknown phases, such us (Ag,Au)₉(S,Se)₂Te₃ or (Ag,Au)₉(S,Se)₃Te₅, intergrown with tolstykhite, were found in the Ag-bearing association (sample MG-63). These intergrowths, represented by exsolution textures, are only revealed in reflected light (Figure 9c), but not SEM-BSE image (Figure 9f).



Figure 9. Ag-bearing microparagenesises in reflected light (**a**–**c**) and SEM back-scatter images (**d**–**f**). Miargyrite (May) and petrovskaite (Pvk) occur as rims around gold (Au) grains (**a**,**d**), intergrowths of gold with uytenbogaardtite (Uyt) (**b**,**e**), and tolstykhite (Tls), intermixed with unnamed phases (Ag,Au)₉(S,Se)₂Te₃ and (Ag,Au)₉(S,Se)₃Te₅. The reference number on samples, as well as the marked points, correspond to the analyses in Table 7.



Figure 10. Composition of petrovskaite AuAgS, uytenbogaardtite Ag_3AuS_2 , fischesserite Ag_3AuSe_2 (a), and Au-bearing miargyrite $(Ag_2Au)(Sb_2As)S_2$ (b).

No.	Site	Sp.	Au	Ag	Sb	Te	As	Se	S	Total	Formulas
1	MG-63_10-5	1	98.12							98.12	Au _{1.00}
2	MG-63_10-5	2	100.20							100.2	Au _{1.00}
3	MG-63_10-5	3	28.24	18.17	34.12		0.91		19.29	100.73	$(Ag_{0.56}Au_{0.48})_{1.04}(Sb_{0.93}As_{0.04})_{0.97}S_{2.00}$
4	MG-63_10-5	4	28.42	18.69	25.11		8.22		20.37	100.81	$(Ag_{0.55}Au_{0.45})_{1.00}(Sb_{0.65}As_{0.35})_{1.00}S_{2.00}$
5	MG-63_10-5	5	27.76	20.24	21.37		10.24		20.08	99.69	$(Ag_{0.59}Au_{0.44})_{1.03}(Sb_{0.55}As_{0.43})_{0.98}S_{1.98}$
6	MG-63_10-5	6	27.65	19.03	25.48		8.47		20.28	100.91	(Ag _{0.55} Au _{0.44}) _{0.99} (Sb _{0.66} As _{0.36}) _{1.02} S _{1.99}
7	MG-63_10-5	7	23.18	19.63	33.53		1.85		19.97	98.16	$(Ag_{0.60}Au_{0.39})_{0.99}(Sb_{0.90}As_{0.08})_{0.98}S_{2.04}$
8	MG-63_10-5	8	52.12	36.95					10.35	99.42	Ag _{1.10} Au _{0.85} S _{1.04}
9	MG-63_10-5	9	52.74	38.01					10.13	100.88	Ag _{1.13} Au _{0.86} S _{1.01}
10	MG-63_10-5	10	51.59	36.36				1.45	10.09	99.49	Ag _{1.08} Au _{0.84} (S _{1.01} Se _{0.06}) _{1.07}
11	MG-63_10-7	11	100.51							100.51	Au _{1.00}
12	MG-63_10-7	12	100.52							100.52	$Au_{1.00}$
13	MG-63_10-7	13	36.69	52.25					10.92	99.86	Ag _{2.87} Au _{1.11} S _{2.02}
14	MG-63_10-7	14	31.23	57.05				2.17	9.47	99.92	Ag _{3.14} Au _{0.94} (S _{1.75} Se _{0.16}) _{1.91}
15	MG-63_10-7	15	28.29	57.89				0.73	10.12	97.03	$Ag_{3,20}Au_{0.86}(S_{1.88}Se_{0.06})_{1.94}$
16	MG-63_10-7	16	30.29	56.66					11.48	98.43	Ag _{3.04} Au _{0.89} S _{2.07}
17	MG-63_10-8	44	39.19			50.58		2.61	7.45	99.83	Au _{3.00} (S _{3.51} Se _{0.50}) _{4.01} Te _{5.99}
18	MG-63_10-8	51	38.58			49.46		1.99	7.65	97.68	Au _{3.01} (S _{3.66} Se _{0.39}) _{4.05} Te _{5.95}
19	MG-63_10-8	52	38.91			49.81		2.33	7.48	98.53	Au _{3.02} (S _{3.57} Se _{0.45}) _{4.02} Te _{5.97}
20	MG-63_10-8	49	38.16			50.08		2.55	7.3	98.09	Au _{2.98} (S _{3.50} Se _{0.50}) _{4.00} Te _{6.03}
21	MG-63_10-8	45	30.57	42.24		22.80		1.05	3.62	100.28	(Ag _{6.44} Au _{2.55}) _{8.99} (S _{1.86} Se _{0.22}) _{2.08} Te _{2.94}
22	MG-63_10-8	50	30.43	41.94		23.00		1.09	3.68	100.14	(Ag _{6.39} Au _{2.54}) _{8.93} (S _{1.89} Se _{0.23}) _{2.12} Te _{2.96}
23	MG-63_10-8	46	31.26	29.65		31.21		1.40	4.00	97.52	$(Ag_{5.69}Au_{3.29})_{8.98}(S_{2.58}Se_{0.37})_{2.95}Te_{5.07}$

Table 7. Compositions (wt. %) of Ag-bearing minerals, shown in Figure 9, from the Maletoyvayamdeposit.

1–2, 11–12—gold; 3–7—miargyrite (Ag,Au)(Sb,As)S₂; 8–10—petrovskaite AgAuS; 13–16—uytenbogaardtite Ag₃AuS₂; 17–20—tolstykhite Au₃S₄Te₆; 21–23 13–16—unnamed phases from the Ag-Au-Te-S-Se system: (Ag,Au)₉(S,Se)₂Te₃ and (Ag,Au)₉(S,Se)₃Te₅; 17–20—tolstykhite Au₃S₄Te₆; 21–23—unnamed phases from the Ag-Au-Te-S system: (Ag,Au)₉(S,Se)₂Te₃ and (Ag,Au)₉(S,Se)₃Te₅.

3.2.2. Maletoyvayamite—Tolstykhite Solid Solution in Ag-Bearing Samples

Native tellurium, calaverite, and Mty-Tls ss occur in both Ag-free and Ag-bearing associations (Figure 11a). However, a complete series of solid solution is characteristic of the Ag-free association (Mt-8), whereas, in Ag-bearing samples (MG-63), only the sulfur analogue (tolstykhite) is found; on the other hand, Se is absent in calaverite.



Figure 11. Compositions of maletoyvayamite-tolstykhite solid solution, occurring in the Ag-bearing association (MG-63) in (Se + S) – Au – Te (**a**), and S – Se – Te systems (**b**), compared to those in the Ag-poor association (Mt-8) in the Au – (Se + S) <u>–</u> Te and Se-S-Te systems.

3.2.3. Gold Complex Oxides in the Ag-Bearing Association

Complex compositions of Au-oxides have been reported in the Ag-bearing association, as well as in the previously described Ag-free assemblage [8,9]. They occur, forming rims (Figure 12a), as composites with other chalcogenides and gold (Figure 9f), as well as complete pseudomorphs of primary minerals more likely to be calaverite (Figure 12b,c).



Figure 12. SEM back-scatter images of Au-complex oxides occurring intergrown with gold (**a**,**c**) and as an individual grain (**b**) from Ag-bearing associations. The reference number on samples, as well as the marked points, correspond to the analyses in Table 8.

Table 8. Compositions (wt. %) of Au(Ag)-Fe-Sb oxides, shown in Figure 12, from Ag-bearing associations.

Sample	Sp.	Fe	Au	Ag	Sb	Te	As	0	Total	Formulas
MG-63_10-1	4	8.25	62.89		9.89		1.59	14.95	89.32	(Au _{1.37} Fe _{0.55} Sb _{0.07} As _{0.04} Te _{0.03}) _{2.06} O _{2.95}
MG-63_10-3	6	8.78	77.16		2.51	0.96	0.75	13.48	94.86	(Au _{0.62} Fe _{0.52} Sb _{0.04} As _{0.03} Te _{0.02}) _{1.23} O _{3.76}
MG-63_10-3	8	16.66	69.39		3.00	1.46	1.37	34.29	109.51	(Au _{0.80} Fe _{0.59} Sb _{0.31} As _{0.08}) _{1.78} O _{3.22}
MG-63_10-11	67	11.09	53.47		12.65		2.12	17.44	85.68	$(Au_{0.77}Fe_{0.60}Sb_{0.31}As_{0.09}Ag_{0.03})_{1.80}O_{3.21}$
MG-63_10-11	71	12.00	54.29	1.05	13.74		2.29	18.41	89.78	(Au _{0.85} Fe _{0.57} Sb _{0.29} As _{0.08} Ag _{0.03}) _{1.82} O _{3.19}
MG-63_10-11	72	10.75	57.14	0.91	12.06		1.99	17.37	89.47	$(Au_{1.46}Fe_{0.57}As_{0.07})_{2.10}O_{2.90}$
MG-63_10-11	73	7.98	72.05				1.30	11.64	84.99	(Au _{1.35} Fe _{0.55} As _{0.07} Sb _{0.03}) _{2.00} O _{3.01}
MG-63_10-11	74	8.21	71.76		0.96		1.37	12.97	87.06	(Au _{1.46} Fe _{0.54} As _{0.07} Sb _{0.03}) _{2.10} O _{2.90}
MG-63_10-11	75	7.87	75.31		0.97		1.37	12.14	89.79	$(Au_{1.06}Fe_{0.49}Sb_{0.27}As_{0.07})_{1.89}O_{3.11}$

The composition of oxides vary considerably, trending from fine-grade or slightly oxidized gold to tripuhyite or even hematite (Figure 13). Many compositions move towards the general formula (Au,Fe,Sb,As,Se,Te)₂O₃. For example, the composition of the oxide in Figure 9f is represented by the formula (Au_{1.50}Sb_{0.29}Ag_{0.08}Fe_{0.06}As_{0.03})_{1.96}O_{3.04} or simply (Au,Sb)₂O₃. In some grains, the composition gets closer to the formula (Au,Fe,Sb)₂O₃ or (Au,Fe,As)₂O₃, where iron prevails over antimony and other elements (Table 8).

Typically, the composition of oxides in the Ag-bearing assemblage are more oxidized, with a higher concentration of Fe, Sb, Te, As, and Se than those from Ag-free associations (Figure 13). The clustering of compositional points near the hypothetical Au₃O are usually linked to high-grade "mustard" porous gold. These tiny pores may be filled with iron and antimony hydroxides [8].



Figure 13. Compositional variations of Au, Fe, and Sb complex oxides, with minor Te, As, Se.

4. Discussion

4.1. Possible New Minerals in the Au-Te-Se-S System

The unnamed AuTe₂Se compositions, at the current stage of research, also belong to the maletoyvayamite field Au₃Se₄Te₆, expanding its stability towards gold enrichment. Nonetheless, it should be noted that, in these compounds, the substitution Se by S is limited, up to 0.52 apfu of S (Figure 2b). Thus, it is very likely that compounds with empirical formula Au(Se,S)Te₂ correspond to a theoretically new mineral in the Au-Te-Se-S system, different from maletoyvayamite.

There are also a series of compositions that, according to its empirical formula $AuTe_xSe_{1-x}$, where 0.2> x < 0.5, differ greatly from gachingite, and similarly from auroselenide, mainly owing to its high tellurium content (Table 6). These compositions lie on the range $Au(Se_{0.52}Te_{0.48})$ – $Au(Se_{0.64}Te_{0.36})$ (Figure 2a) and are located next to the gachingite series, more precisely, towards its end-member $Au(Te_{0.5}Se_{0.5})$. This innominate phase is separated from pure auroselenide by an immiscibility region, and it is also distinguished by lower S concentrations (Figure 2b). The morphology of this mineral is comparable to that of auroselenide, although it may be differentiated in back-scatter SEM images due to the lighter shades presented in other associated minerals (e.g., auroselenide, maletoyvayamite, tolstykhite) (Figure 8). Furthermore, it is likely that this solid solution series, of apparent limited compositional range $Au(Se_{0.6-0.5}Te_{0.4-0.5})$, corresponds to a new mineral phase of formula $Au(Se_{1-x}Te_x) 0.4 \approx x \leq 0.5$; however, this requires additional experimental research.

The unusual composition of goldfieldite is due to selenium in the formula, complementing the tellurium group, although it does not substitute sulfur. In this case, and by assuming an admixture of Se and S, goldfieldite composition would be far from the empirical formula. This problem, however, should be further discussed in future studies.

4.2. Solid Solutions in Natural Gold Chalcogenides

Selenium minerals may be found in sandstones, skarn, uranium deposits, and at epithermal deposits, where Se-rich parageneses occur in association with Te-rich minerals. However, tellurium and selenium do not form mixtures or compounds, due to the fact that the geochemical behavior of tellurium and selenium is different [17]. In nature, tellurides are more common than selenides, with the former tending to produce its own minerals in epithermal deposits, owing to its incompatibility with selenium in the structure of minerals. Therefore, the formation of tellurides is only caused by a Te-rich source, whereas, to form a

selenide mineral, a high $fSe_{2(g)}/fS_{2(g)}$ ratio is not enough, since additional conditions are also required.

They require a highly oxidizing environment with a high pH to form, which is controlled by the H_2Se/H_2S ratio in aqueous fluids [17–19]. A substantial increase of these ratios contributes to the successive substitution of Au–S by Au–Se complexes [20]. Selenium atoms in the structure of sulfides substitute sulfur in sulfides and sulfosalts, even at low H_2Se/H_2S values, as observed in many low sulfidation epithermal deposits. In particular, it is typical for the Rodnikovskoye and, to some extent, the Baranievskoye deposits in Kamchatka [21,22].

Additionally, selenium often plays a significant role in the formation of ores in LS epithermal deposits around the world, e.g., Kremnica ore district and Central Slovakia, where the experimental contents of Se in sulfosalts are the highest ever measured worldwide [23]. Selenide minerals in the Hope's Nose occurrence is part of an epithermal system and is linked to a basic-intermediate igneous rocks, hosted in carbonaceous shale [24], which supports the general idea of a correlation between selenium and organic matter, as well as their general evolution [10]. Furthermore, most of the Au-Ag LS epithermal deposits in Chukotka belong to the Se-bearing type (Korrida, Valunistoye, Dvoynoye, etc.) whose ores contain important amounts of selenium-bearing minerals [25,26]. In the Koch-Bulak deposit in Uzbekistan, the main selenium concentrators are sulfides and sulfosalts [27]. Au-Ag selenide (fischesserite) has been described in the West Tuva ore occurrence [28]. The Se concentration in ores from LS deposits, such us the Baran'evskoe and Rodnikovoe deposits in Kamchatka, is 36 and 25 ppm, respectively. However, selenium reaches the highest concentrations at the Maletoyvayam deposit (92 ppm) [10], which is characterized by Au-selenides and sulfoselenides.

In the Au-Ag-Te-Se-S system for epithermal deposits, as a rule, either tellurides petzite Ag₃AuTe₂, krennerite Au₃AgTe₈, sylvanite AgAuTe₄, muthmannite AuAgTe₂, montbrayite Au₂Te₃ (simplified formula); or selenides—fischesserite Ag₃AuSe₂, naumannite Ag₂Se; or sulfides—acanthite Ag₂S, uytenbogaardtite Ag₃AuS₂, and petrovskaite AuAg are found. All these minerals are characterized by three types of elemental substitutions: (1) between Au and Ag, (2) Se \rightarrow S, and (3) Te \rightarrow Se. In the first case, the existence of a continuous solid solution from naumannite Ag₂Se to α -fischesserite Ag₃AuSe₂ has been experimentally demonstrated; intermediate compositions between monoclinic calaverite AuTe₂ and orthorhombic krennerite Ag₃AuTe₈ have also been demonstrated [29,30]. In addition, significant Au-Ag exchanges have been reported in natural compositions from various deposits in the Au-Ag-S system, including uytenbogaardtite Ag₃AuS₂ and petrovskaite AuAgS substitution [31].

The substitution of S for Se and Se for S is more common and typical for LS deposits: monoclinic acanthite series from Ag₂S to Ag₂S_{0.4}Se_{0.6} and orthorhombic naumannite series from Ag₂S_{0.3}Se_{0.7} to Ag₂Se [32,33]. In the fischesserite—uytenbogaardtite series (Ag₃AuSe₂–Ag₃AuS₂), there are two structurally different solid solutions: cubic Ag₃AuSe₂–Ag₃AuSe₂ and trigonal Ag₃AuSe_{0.75}S_{1.25} – Ag₃AuS₂ [34]. Uytenbogaardtite Ag₃AuS₂ allows the substitution of S for Se up to 0.5 apfu (AgAuS_{0.5}Se_{0.5}), while mineral phases with a higher Se concentration are metastable [35].

The alloys containing up to 10–15 at.% Te consist of a Te-Se solid solution (by substitution) of phase A, whereas those bearing Te between 50–100 at.% are solid solutions of phase B. Alloys with 15 to 50 at. % Te consist of a two-phase mixture (A + B) [36]. Most of the Te-Se ss compositions in this study are native tellurium (phase B), and only a few analyses lie in a two-phase field (Figure 1). It is likely that, among natural Te-Se solid solutions in epithermal deposits, the Maletoyvayam compositions are the most Se-rich (up to 45.9 wt. % Se or Se₃Te₂); meanwhile, in epithermal gold deposits, such as HS Kochbulak and Kairagach, Se does not exceed 10.3 wt. % in native tellurium [37]. Te-Se solid solutions obtained, empirically, the following for silver minerals: $Ag_2Te - Ag(Te_{0.8}Se_{0.2})$ and $Ag(Te_{0.6}Se_{0.4}) - Ag_2TeSe$, with monoclinic and orthorhombic structure, respectively [38].

However, for Au minerals, only a limited substitution of Te for Se is known to occur in calaverite Au(Te_{0.8}Se_{0.2}) [39].

A typomorphic feature of the ore association in the Maletoyvayam deposit, compared to other deposits in the world, is the presence of ternary compounds in the system Au-Te-S-Se (Au sulfoselenotellurides (Figure 2), while Ag plays a very limited role, varying from 0.5 to 1.5 wt. %, never exceeding 3 wt. % (in native alloys and calaverite), whereas, in other minerals, it is usually below the detection limit. In this particular deposit, S-Se solid solutions are widely spread, showing a complete series from maletoyvayamite to tolstykhite, as well as auroselenide, in which the content of S reaches up to 35 apfu—Au(Se_{0.65}S_{0.35}). In addition, there is a Te-Se trend in the recently approved gachingite Au(Te_{0.80-0.50}Se_{0.20-0.50}), and in the unnamed Au(Se,Te) phase, in which Te reaches up to 0.48 apfu Au(Se_{0.52}Te_{0.48}). Thus, it may be assumed that the complete series of solid solutions of gachingite Au(Te,Se) continues into the selenium region of the diagram and mixes with a series of compositions of the unknown Au(Se,Te) phase, forming a single solid solution from (Te_{0.80}Se_{0.20}) to Au(Te_{0.36}Se_{0.64}), with no miscibility break (Figure 2a). Moreover, both of these series are characterized by a single substitution Se-Te trend, which differs from the typical Se-S trend of auroselenide (Figure 2b).

4.3. Calaverite Transformation and the Formation of Au Oxides and Native Tellurium

All compositions of AuTe₂ are intimately linked to calaverite, since Ag concentration in these minerals (up to 3.94 wt. %) is inadequate to form krenerite, and it is required that Ag exceeds 6 wt. % in the formula Au₃AgTe₈. Furthermore, krennerite is always metastable at low temperatures and will not form below 270 °C [40]. On the other hand, calaverite is presumably the main, primary mineral of the ores studied in the Maletoyvayam epithermal deposit, although it occurs no more frequently than other minerals. This is due to the fact that calaverite is weakly stable and, under oxidizing conditions, is replaced by Au-Fe-Sb oxides (Figure 4), which are also very common at the Maletoyvayam deposit. Such replacements, from partial to almost complete pseudomorphs, are observed in different ore associations (Figure 5d–f). In earlier publications, including [8], the initial stage of calaverite replacement was revealed in the shape of worm-like veinlets of secondary products, comprising a mixture of fine particles of native gold and Fe-Sb oxides. One of the mechanisms for primary calaverite replacement is AuTe₂ + Fe, Sb, Bi, As, Se, and S-containing solutions + $O_2 \rightarrow Au$ + Te,Se solid solution + Te O_2 + Fe(Sb,As) O_3 . The reaction products correspond to high grade (spongy) gold with Sb–Fe oxide \pm admixtures and native Se-rich tellurium [8]. All the textural observations considered, in these replacements, suggests that tellurium, which is released from calaverite during detellurization processes, is not redeposited at the place of substitution. Rather, this one migrates as transferable units and bonds with mobile selenium, all of which are later recombined in the form of Te-Se solid solutions, in association with Te-bearing sulfosalts (goldfieldite) (Figure 4). Moreover, the replacement of calaverite by gold oxide only occurs in hydrothermal solutions [41], but not under near-surface conditions. The porosity of mustard gold is deemed as textural evidence for reactions that lead to a negative volume [42]. Thus, the influx of Fe, Sb, As, Se, Bi-atoms, and the removal of oxidized Te takes place in the reaction, contributing to a local decrease in oxygen activity, and hence, favoring the deposition of Au(I) gold [41]. Depending on the degree of oxidation and the rate of Te removal, the final products can be either (1) a fine mixture of spongy gold (redeposited), along with Fe-Sb oxide (tripuhyite), or (2) homogeneous complex Au oxides. These oxides tend toward a stable state when the amount of oxygen reaches 60 at. %, which corresponds to the formula $(Au+Fe+Sb+As,Te,Se)_2O_3$ (Table 4). Micron-sized gold particles are the building blocks in the formation of secondary mustard gold aggregates. At the same time, tripulyite is oxidized to limonite [8], and high-grade gold either clumps, forming coarse-grained gold due to the accretion of smaller particles, or crumbles into dust-like particles, enriching the dusty fraction of ores as a result.

4.4. Comparison of Typomorphic Features in Ag-Free (Au-Rich) and Ag-Bearing Associations

Ag-bearing association of the Maletoyvayam deposit is typical for one sample out of many studied. Within this silvery assemblage, sulfur prevails over Se in chalcogenides. Au-Ag sulfides are rather common and are represented by petrovskaite AuAgS and uytenbogaardtiteAg₃AuS₂, which have typical Au-Ag variations [31] and sporadic Se. Only S-rich tolstykhite associates with these minerals (Figure 10b). In the case of miargyrite, the significant range of Se-S substitution is characteristic in other deposits as well: up to 0.75 apfu of Se in the Kremnica ore district, Central Slovakia [23], and up to 0.62 apfu from Kutná Hora, Czech Republic [43]. However, in the Ag-bearing association of the Maletoyvayam deposit, no S-Se substitutions have been observed. On the other hand, miargyrite includes As, which is not typical for Au-rich associations, constituting a solid solution with proustite AgSbS₃-AgAsS₃, up to 0.43 apfu of As. A particular feature of this mineral is defined by its high Au content (up to 0.48 apfu of Au) (Table 7). Furthermore, we suggest the possibility of this compound representing a potential new mineral whose approximate formula may correspond to AuAgSb₂S₆. Finally, the presence of mineral compounds, including all five elements of the Au-Ag-S-Se-Te system, such as maletoyvayamite, tolstykhite, gachingite, and auroselenide, within the Ag-bearing association, had not yet been reported in natural samples. All this, once again, is evidence of the uniqueness of this geological body and the ore-forming environment.

Au–Ag LS-type epithermal deposits, which are characterized by Ag-rich and S-rich associations (acantite-augilarite), were derived from neutral pH solutions under conditions of $fSe_2/fS_2 < 1$ [19]. At low H₂Se/H₂S values in aqueous fluids, selenium enters sulfides as solid solutions [17] and does not form Au-selenides. The formation of selenides is aided by a significant increase in the activity of selenium, which is only possible in acidic solutions at elevated fO_2 , when Au–S complexes are successively replaced by Au–Se. Accordingly, the concentration of Ag in ores is positively correlated with the S/Se ratios in such ore-forming systems. At the same time, S/Se ratios in maletoyvayamite-tolstykhite solid solutions are good indicators of the physicochemical conditions of the ore-forming environment. Since LS-type deposits, where silver mineralization dominates, were derived from neutral pH solutions under conditions of $fSe_2/fS_2 < 1$ [19], it means that a must-have condition during the formation of the Ag-bearing (and S-rich) association of Maletoyvayam deposit has to do with a decrease in the acidity of solutions. This could have been achieved by diluting acidic magmatic solutions with meteoric water.

5. Conclusions

Two ore associations are typical of the Maletoyvayam deposit: Au rich (Ag-free) and Ag-bearing. The former crystallized from acidic solutions, whereas the latter formed from more diluted ones.

- 1. In the Au-rich type, in addition to the usual calaverite $AuTe_2$, triple gold chalcogenides, i.e., compounds of the Au-Se-Te-S system, are typical. This association is characterized by Se-S and Te-Se substitution in minerals. The Se-S trend is confirmed by a complete solid solution between maletoyvayamite and tolstykhite $Au_3Se_4Te_6 Au_3S_4Te_6$, as well as by a limited solid solution of auroselenide, from AuSe up to $Au(Se_{0.64}S_{0.36})$. Te-Se substitution is quite evident in native Te-Se alloys up to 0.58 Se apfu, and in two combined series of solid solutions of gachingite Au(Te,Se) and an unnamed Au(Se,Te) phase with common variations of selenium $Se_{0.20-0.60}$, as well as in calaverite $Au(Te,Se)_2$, with Se content up to 0.2 apfu.
- 2. In the Ag-bearing association, an increased role of silver and sulfur is observed. Au-Ag sulfides dominate: petrovskaite AuAgS, miargyrite (Ag,Au)(Sb,As)S₂, uytenbogaardtite Ag₃AuS₂, and fischesserite Ag₃AuSe₂. Among the Mty-Tls ss, only S-rich tolstykhite is present. Au-Ag sulfides are characterized by Au-Ag substitution. Moreover, miargyrite (Au,Ag)SbS₃ contains significant Au, the amount of which is sufficient to form a new unnamed mineral AgAuSb₂S₆. Additionally, a rare compound (Ag,Au)₉(S,Se)₂Te3 within the same association has been revealed.

3. Complex Au oxides are rather common in both associations, ranging from a finely dispersed mixture of redeposited gold and tripuhyite to homogeneous compounds of (Au,Sb,Fe)₂O₃ composition. These oxides are mostly the result of calaverite replacement: the removal of oxidized Te and the addition of Fe,Sb into hydrothermal solutions.

Author Contributions: Conceptualization, writing, review, and funding management: N.T.; field work, laboratory research, and editing: M.S. and M.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the RSF, grant number 23-27-00258.

Data Availability Statement: Not applicable.

Acknowledgments: We thank analysts Karmanov N., Khlestov M., Chubarov V., and Korolyk V. for analytical assessment EDS and WDS of gold minerals; Belkina N. for technical support, Petrova E. and Bobrova O. for providing the ore samples.

Conflicts of Interest: The authors declare no conflict of interest. The Sponsors played no role in the design of the study; collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

- 1. Hedenquist, J.W.; Arribas, A.; Gonzalez-Urien, E. Exploration for epithermal gold deposits. SEG Rev. *Econ. Geol.* 2000, 13, 245–277.
- Melkomukov, B.H.; Razumny, A.V.; Lopatin, W.B. The new highly promising gold objects of Koryakiya. *Min. Bull. Kamchatka* 2010, 14, 70–74. (In Russian)
- Berger, B.R.; Henley, R.W. Advances in the understanding of epithermal gold-silver deposits, with special reference to the western United States. In *The Geology of Gold Deposits: The Perspective in 1988*; Keays, R.R., Ramsay, W.R.H., Groves, D.I., Eds.; Economic Geology Monograph 6; Society of Economic Geologists: Yale, America, 1989; pp. 405–423.
- Tolstykh, N.D.; Vymazalova, A.; Petrova, E.A.; Stenin, N. The Gaching Au mineralization in the Maletoyvayam ore field, Kamchatka, Russia. In *Geological Survey of Canada, Open File 8317, Proceedings of the 14th Biennial SGA Meeting, Quebéc, QC, Canada,* 20–23 August 2017; Mercier-Langevin, P., Goutier, J., Dubé, B., Eds.; Society for Geology Applied to Mineral Deposits: Quebec, Canada, 2017; Volume 1, pp. 195–198. ISBN 978-2-9816898-0-1.
- 5. Tolstykh, N.; Vymazalova, A.; Tuhy, M.; Shapovalova, M. Conditions of formation of Au-Se-Te mineralization in the Gaching ore occurrence (Maletoyvayam ore field), Kamchatka, Russia. *Mineral. Mag.* **2018**, *82*, 649–674. [CrossRef]
- White, N.C.; Hedenquist, J.W. Epithermal gold deposits: Styles, characteristics and exploration. *Publ. SEG Newsl.* 1995, 23, 9–13. [CrossRef]
- Hedenquist, J.W.; Arribas, R.A. Epithermal ore deposits: First-order features relevant to exploration and assessment. In Proceedings of the 14th SGA Biennial Meeting, Quebec City, QC, Canada, 20–23 August 2017; Volume 1, pp. 47–50.
- 8. Tolstykh, N.; Palyanova, G.; Bobrova, O.; Sidorov, E. Mustard gold of the Gaching ore occurrence (Maletoyvayam deposit, Kamchatka, Russia). *Minerals* **2019**, *9*, 489. [CrossRef]
- Sidorov, E.G.; Borovikov, A.A.; Tolstykh, N.D.; Bukhanova, D.S.; Palyanova, G.A.; Chubarov, V.M. Gold mineralization at the Maletoyvayam Deposit (Koryak Highland, Russia) and physicochemical conditions of its formation. *Minerals* 2020, 10, 1093. [CrossRef]
- 10. Tolstykh, N.D.; Bortnikov, N.S.; Shapovalova, M.O.; Shaparenko, E.O. The Role of Hydrocarbons in the Formation of Epithermal Gold–Silver Deposits in Kamchatka, Russia. *Dokl. Earth Sci.* 2022, 507, 994–1000. [CrossRef]
- 11. Tuhý, M.; Vymazalová, A.; Tolstykh, N.; Plášil, J.; Laufek, F. Gold chalcogenides natural occurrence in Maletoyvayam (Kamchatka, Russia)—An experimental approach. In Proceedings of the 15th Biennial Meeting of SGA, Glasgow, UK, 27–30 August 2019.
- Palyanova, G.; Beliaeva, T.; Kokh, K.; Seryotkin, Y.; Moroz, T.; Tolstykh, N. Characterization of synthetic and natural gold chalcogenides by electron microprobe analysis, X-ray powder diffraction and Raman spectroscopic methods. *J. Raman Spectrosc. Methods* 2022, 53, 1012–1022. [CrossRef]
- 13. Tolstykh, N.D.; Tuhý, M.; Vymazalová, A.; Plášil, J.; Laufek, F.; Kasatkin, A.V.; Nestola, F.; Bobrova, O.V. Maletoyvayamite, Au₃Se₄Te₆, a new mineral from Maletoyvayam deposit, Kamchatka peninsula, Russia. *Mineral. Mag.* **2020**, *84*, 117–123. [CrossRef]
- 14. Tolstykh, N.D.; Tuhỳ, M.; Vymazalova, A.; Laufek, F.; Plášil, F. Gachingite, Au($Te_{1-x}Se_x$) 0.2 $\approx x \le 0.5$, a new mineral from Maletoyvayam deposit, Kamchatka peninsula, Russia. *Mineral. Mag.* **2022**, *86*, 205–231. [CrossRef]

- 15. Kasatkin, A.V.; Nestola, F.; Plášil, J.; Sejkora, J.; Vymazalová, A.; Škoda, R. Tolstykhite, Au₃S₄Te₆, a new mineral from Maletoyvayam deposit, Kamchatka peninsula, Russia. *Mineral. Mag.* **2022**, *87*, 34–39. [CrossRef]
- Tolstykh, N.; Kasatkin, A.; Nestola, F.; Vymazalová, A.; Agakhanov, A.; Palyanova, G.; Korolyuk, V. Auroselenide, AuSe, a new mineral from Maletoyvayam deposit, Kamchatka peninsula, Russia. *Mineral. Mag.* 2022, 1–20. [CrossRef]
- 17. Yuningsih, E.T.; Matsueda, H.; Rosana, M.F. Diagnostic Genesis Features of Au-Ag Selenide-Telluride Mineralization of Western Java Deposits. *Indones. J. Geosci.* 2016, *3*, 67–76. [CrossRef]
- 18. Hustor, D.L.; Sieb, S.H.; Suterb, G.F. Selenium theoretical and its importance to the study of ore genesis: The basis and its application to volcanic-hosted massive sulfide deposits using pixeprobe analysis. *Nucl. Instrum. Methods Phys. Res.* **1995**, 104, 476–480. [CrossRef]
- Simon, G.; Kesler, S.E.; Essene, E.J. Phase Relations among Selenides, Sulfides, Tellurides, and Oxides: II. Applications to Selenide-Bearing Ore Deposits. *Econ. Geol.* 1997, 92, 468–484. [CrossRef]
- 20. Slobodskoy, R.M. Organoelement Compounds in Magmatic and Ore-Forming Processes; Nauka: Novosibirsk, Russia, 1981. (In Russian)
- Tolstykh, N.; Bukhanova, D.; Shapovalova, M.; Borovokov, A.; Podlipsky, M. The gold mineralization of the Baranyevskoe Au-Ag epithermal deposit in Central Kamchatka. *Minerals* 2021, 11, 1225. [CrossRef]
- Tolstykh, N.D.; Shapovalova, M.O.; Shaparenko, E.O.; Bukhanova, D.S. The Role of Selenium and Hydrocarbons in Au-Ag Ore formation in the Rodnikovoe Low-Sulfidation (LS) Epithermal Deposit, Kamchatka Peninsula, Russia. *Minerals* 2022, 12, 1418. [CrossRef]
- Števko, M.; Sejkora, J.; Dolnícek, Z.; Škácha, P. Selenium-Rich Ag–Au Mineralization at the Kremnica Au–Ag Epithermal Deposit, Slovak Republic. *Minerals* 2018, 8, 572. [CrossRef]
- 24. Stanley, C.J.; Criddle, A.J.; Lloyd, D. Precious and base metals selenide mineralization at Hope's Nose, Torquay, Devon. *Mineral. Mag.* **1990**, *54*, 485–493. [CrossRef]
- 25. Kolova, E.; Savva, N.; Zhuravkova, T.; Glukhov, A.; Palyanova, G. Au-Ag-S-Se-Cl-Br Mineralization at the Corrida Deposit (Russia) and Physicochemical Conditions of Ore Formation. *Minerals* **2021**, *11*, 144. [CrossRef]
- Bortnikov, N.S.; Savva, N.E.; Prokofiev, V.Y.; Kolova, E.E.; Dolomanova-Topol', A.A.; Galyamov, A.L.; Murashov, K.Y. Epithermal Au-Ag-Se-Te deposits of the Chukchi Peninsula (Arctic Zone of Russia): Metallogeny, mineral assemblages, and fluid regime. *Russ. Geol. Geophys.* 2022, 63, 435–457. [CrossRef]
- 27. Kirezidi, S.V. Geochemistry of selenium and tellurium in the ores of the Kochbulak deposit. *Geol. Miner. Probl. Geoecol. Bashkortostan Ural. Adjac. Areas.* **2018**, *12*, 249–255. (In Russian)
- Kuzhuget, R.V.; Zaykov, V.V.; Ankusheva, N.N. Au-Se-Te Mineralization of the Aldan-Maadyr Gold-Ore Cluster (Western Tuva). Geosph. Res. 2021, 1, 18–32. (In Russian) [CrossRef]
- 29. Wiegers, G.A. Electronic and Ionic Conduction of Solid Solutions $Ag_{2-x}Au_xSe$ ($0 \le x \le 0.5$). *J. Less-Common Met.* **1976**, 48, 269–283. [CrossRef]
- Echmaeva, E.A.; Osadchii, E.G. Determination of the Thermodynamic Properties of Compounds in the Ag–Au–Se and Ag–Au–Te Systems by the EMF Method. *Geol. Ore Depos.* 2009, *51*, 247–258. [CrossRef]
- Savva, N.E.; Pal'yanova, G.A. Genesis of gold and silver sulfides at the Ulakhan deposit (northeastern Russia). *Russ. Geol. Geophys.* 2007, 48, 799–810. [CrossRef]
- 32. Bindi, L.; Pingitore, N.E. On the symmetry and crystal structure of aguilarite, Ag4SeS. Mineral. Mag. 2013, 77, 21–31. [CrossRef]
- Pal'yanova, G.A.; Chudnenko, K.V.; Zhuravkova, T.V. Thermodynamic properties of solid solutions in the system Ag₂S–Ag₂Se. *Thermochim. Acta* 2014, 575, 90–96. [CrossRef]
- 34. Seryotkin, Y.V.; Pal'yanova, G.A.; Savva, N.E. Sulfur-selenium isomorphous substitution and morphotropic transition in the Ag₃Au(SeS)₂. *Russ. Geol. Geophys.* **2013**, *54*, 841–848. [CrossRef]
- Palyanova, G.A.; Seryotkin, Y.V.; Bakakin, V.V.; Kokh, K.A. Sulfureselenium isomorphous substitution in the AgAu(S,Se) series. J. Alloys Compd. 2016, 664, 385–391. [CrossRef]
- 36. Ghosh, G.; Sharma, R.C.; Li, D.T.; Chang, Y. The Se-Te (Selenium-Tellurium) system. J. Phase Equilibria 1994, 15, 213–224. [CrossRef]
- Plotinskaya, O.Y.; Kovalenker, V.A.; Seltmann, R.; Stanley, C.J. Te and Se mineralogy of the high-sulfidation Kochbulak and Kairagach epithermal gold telluride deposits (Kurama Ridge, Middle Tien Shan, Uzbekistan). *Mineral. Petrol.* 2006, 87, 187–207. [CrossRef]
- Zhu, T.; Su, X.; Zhang, Q.; Tang, X. Structural transformation and thermoelectric performance in Ag₂Te_{1-x}Se_x solid solution. *J. Alloys Compd.* 2021, 871, 159507. [CrossRef]
- Palyanova, G.A.; Tolstykh, N.D.; Zinina, V.Y.; Kokh, K.A.; Seryotkin, Y.V.; Bortnikov, N.S. Synthetic Gold Chalcogenides in the Au–Te–Se–S System and Their Natural Analogs. *Dokl. Earth Sci.* 2019, 487, 929–934. [CrossRef]
- 40. Cabri, L.J. Phase relations in the Au-Ag-Te system and their mineralogical significance. Econ. Geol. 1965, 60, 1569–1605. [CrossRef]

- 41. Xu, W.; Zhao, J.; Brugger, J.; Chen, G.; Pring, A. Mechanism of mineral transformations in krennerite, Au3AgTe8, under hydrothermal conditions. *Am. Mineral.* 2013, *98*, 2086–2095. [CrossRef]
- Xia, F.; Brugger, J.; Chen, G.; Ngothai, Y.; O'Neill, B.; Putnis, A.; Pring, A. Mechanism and kinetics of pseudomorphic mineral replacement reactions: A case study of the replacement of pentlandite by violarite. *Geochim. Cosmochim. Acta* 2009, 73, 1945–1969. [CrossRef]
- Pažout, R.; Srein, V.; Korbelova, Z. An unusual Ni-Sb-Ag-Au association of ullmannite, allargentum, Au-rich silver and Aubearing dyscrasite from Oselske pasmo 'silver' Loge of Kutna Hora Pb-Zn-Ag ore district (Czech Republic). J. Geosci. 2018, 62, 247–252. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.