

Communication

A Rare Au-Sb Telluride Pampaloite from the Svetlinsk Gold-Telluride Deposit, South Urals, Russia

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Abstract: Pampaloite AuSbTe, a rare gold-antimony telluride that was first described in 2019 from the Pampalo gold mine, Finland, was found in samples from the large Svetlinsk gold-telluride deposit, South Urals, Russia. Optical microscopy, scanning electron microscopy, electron microprobe analysis, reflectance measurements, electron backscatter diffraction and Raman spectroscopy were used to study eight grains of pampaloite. Pampaloite forms inclusions (5–30 μm) in quartz together with other tellurides (typically petzite), native gold and, less often, sulfides. In reflected light, pampaloite is white or creamy white in color with weak anisotropism and without internal reflections. The empirical formula calculated on the basis of 3 apfu is $\text{Au}_{0.97-1.07}\text{Ag}_{0-0.02}\text{Sb}_{0.96-1.04}\text{Te}_{0.96-1.04}$ ($n = 18$). The holotype pampaloite structure was used as a reference and provided the perfect match for an experimental EBSD pattern (12 bands out of 12, mean angle deviation 0.19°). Raman spectra are reported for the first time for this mineral. All studied pampaloite grains exhibit vibrational modes in the range 60–180 cm^{−1}. Average peak positions are 71, 108, 125, 147 and 159 cm^{−1}. According to experimental data for the Au-Sb-Te system, we estimate the upper temperature range of pampaloite crystallization at the Svetlinsk deposit to be 350–430 °C.

Keywords: pampaloite; AuSbTe; Au-Sb-Te system; EBSD; Raman spectroscopy; Svetlinsk gold deposit; Urals



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1. Introduction

Pampaloite AuSbTe is a new mineral species that was first described at the Pampalo gold mine, Finland [1]. The finds of minerals with similar composition have been repeatedly mentioned in the literature, but due to the small grain size, it was impossible to conduct detailed analyses. An AuSbTe mineral was reported in ores from high-sulfidation epithermal gold deposits in the Enasen deposit, Sweden [2] and the Kairagach deposit, Uzbekistan [3,4]; it was listed twice as an unnamed mineral, as UM1984-41-Te: AuSb and UM2004-/-Te: AuSb [5–7], respectively. The mineral was also reported at the Ward prospect in Eastern Finland (now known as the Pampalo orogenic gold deposit) [8,9]. More detailed studies to fully characterize the mineral led to its approval as the mineral pampaloite by the IMA Commission on New Minerals, Nomenclature and Classification [1]. We reported an unnamed mineral with AuSbTe composition in quartz-sulfide veins of the Svetlinsk (also spelled as Svetlinskoe) gold-telluride deposit, South Urals, Russia [10,11]. The structural identity between our AuSbTe mineral and synthetic AuSbTe [1] based on electron backscatter diffraction confirmed that it was pampaloite. In this paper, optical microscopy, scanning electron microscopy (SEM), electron microprobe analysis (EPMA), reflectance measurements, electron backscatter diffraction (EBSD) and Raman spectroscopy (RS) are applied to study pampaloite from the Svetlinsk deposit. This is the first report

of pampaloite to be made subsequent to the original published description, and it is the first reported occurrence of pampaloite in Russia. New information about pampaloite will be useful for mineralogists studying the mineralogy and genesis of telluride-bearing gold deposits.

2. Geological Setting

Svetlinsk (54°17' N, 60°25' E) is a large gold-telluride deposit (total reserves ~135 t Au), located within the East Uralian megazone at the junction of the Kochkar anticlinorium with the Aramil-Sukhtel synclinorium [12]. Gold mineralization is hosted in Devonian–Carboniferous volcano-sedimentary rocks that have been metamorphosed up to amphibolitic facies. The mineralization is controlled by an NS-trending regional fault. Previous studies have shown the ore to be polygenetic, involving contrasting fluids with multiple sources [12,13]. The gold-sulfide-telluride mineralization is represented by disseminated pyrite-pyrrhotite in the host rocks (C_{Au} up to 1 g/t) and by sulfide-quartz veins and veinlets (C_{Au} = 0.8–2.5 g/t). Native gold in the sulfide-quartz veins is often associated with tellurides and has a fineness of 620–965. Three mineralization stages have been recognized [11,12,14]: (1) the disseminated quartz-pyrite-pyrrhotite stage, with rare chalcopyrite, tetrahedrite, galena and native gold; (2) the quartz-pyrite vein stage, with scheelite; (3) the gold-telluride veinlet stage (main productive), with several mineral assemblages separated by local tectonic events. Tellurides are typical minerals for this deposit. Melonite, frobergite, altaite, montbrayite, calaverite, sylvanite, krennerite, petzite, hessite, empressite, tellurantimony, tsumoite, tetradymite, tellurobismuthite, volynskite and vavřinite, as well as γ -hessite (termed γ -phase [15]) and χ -phase $Ag_{3.23-3.66}Au_{0.20-0.74}Te_{1.85-2.08}$ (termed χ -phase [16]), occur in the ore assemblages [11,17]. Tellurides are usually found in quartz fractures and are rarely associated with pyrite, chalcopyrite and tetrahedrite.

3. Methods

Polished samples were studied under a polarizing microscope Olympus BX-51 and a JSM-5610LV scanning electron microscope equipped with an Oxford-INCA-450 EDS at the IGEM RAS.

The chemical composition was determined at the IGEM RAS using JEOL JXA-8200 equipped with five wavelength-dispersive spectrometers (WDS) and operated at 20 kV and 20 nA. Beam diameter was 1 μ m. Calibration standards (X-ray lines, analyzing crystals) included $AuTe_2$ for Au ($M\alpha$, PETH) and Te ($L\alpha$, PETH), Sb_2S_3 for Sb ($L\alpha$, PETH), $AgSbS_2$ for Ag ($L\alpha$, PETH), Bi_2Te_3 for Bi ($M\beta$, PETH), PbS for Pb ($M\alpha$, PETH) and $CdSe$ for Se ($L\alpha$, TAP). Counting times were 10 s on peaks and 5 s on the upper and lower backgrounds for Au, Te, Sb and Ag; 30 and 15 s for Pb and Se; and 60 and 30 s for Bi, respectively. Detection limits (3σ criterion) for the minor elements (wt%) were 0.09 for Ag, 0.06 for Bi, 0.05 for Pb and 0.04 for Se. The ZAF correction was performed using the JEOL software.

Reflectance measurements were performed in air relative to a silicon standard with an MSF-R (LOMO) microscope-spectrophotometer with the HAMAMATSU photoelectronic multiplier (Japan) at the Institute of Mineralogy (Miass, Russia). The lens is 40×0.65 (achromat). The diameter of the measuring area was 0.00675 mm.

Electron backscatter diffraction (EBSD) studies were conducted using a Hitachi S-3400N scanning electron microscope (SEM) equipped with an Oxford X-Max 20 energy dispersive X-ray spectrometer and NordLys Nano EBSD detector (Geomodel Resource Center, Scientific Park, SPbU, Russia). In order to acquire a flat, distortionless surface for further diffraction experiments, the samples were polished with progressively smaller diamond suspensions up to 0.25 μ m. After the mechanical polishing, an Ar^+ plasma etching step was implemented (Oxford Instruments Ionfab300 for 10 min at an incident angle of 45°, accelerating voltage 500 V, current 200 mA, beam diameter 10 cm; Nanophotonics Resource Center, Scientific Park, SPbU, Russia). Pampaloite generates distinct diffraction patterns, which allow the acquisition of single patterns and orientation mapping. Conditions for single pattern acquisition were as follows: 30 kV accelerating voltage, 1 nA beam current,

0.2 s dwell time per image, 20 images averaging. No binning was applied. For mapping, the conditions were the same except 2×2 image binning and 2 images averaging. Image processing was carried in automatic mode using Oxford AzTec software for EBSD image acquisition and matching. The pampaloite structure from [1] was used as a reference.

The Raman spectra were collected with a Horiba XPloRA (Jobin Yvon) Raman spectrometer equipped with a Peltier-cooled (-51°C), Si-based charge-coupled detector (CCD) at the Department of Petrology and Volcanology (Faculty of Geology, Lomonosov Moscow State University) using polarized 532 nm excitation wavelength and a diffraction grating of 1800 lines/mm (spectral resolution of $\sim 1\text{ cm}^{-1}$). The Raman spectra were collected in the range $50\text{--}1200\text{ cm}^{-1}$. Samples were irradiated for 60 s with a $\sim 1\text{ mW}$ laser beam (10% of maximum laser source power) to prevent the mineral destruction that we observed for pampaloite at higher power. After baseline subtraction, peaks positions were obtained by approximation of collected spectra by the sum of five or six Voigt functions. An example of a spectrum fit is shown in Figure A1.

4. Results

4.1. Occurrence and Physical Properties

Eight grains of pampaloite in four samples were found in polished sections from quartz-sulfide veins of the Svetlinsk deposit. In this section and below, the grains of the mineral are indicated in capital letters (from A to H) to match the description in the text, the photos, the chemical compositions and the Raman spectra. Pampaloite grains with a size from about 5 up to $30\text{ }\mu\text{m}$ form inclusions in quartz together with tellurides, native gold and less often with sulfides. The following assemblages were found: pampaloite (grain A, $10\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$) + native gold ($\text{Au}_{0.70}\text{Ag}_{0.26}\text{Cu}_{0.03}\text{Bi}_{0.01}\text{Te}_{0.01}$) + tetrahedrite-(Fe) + chalcopyrite (Figure 1a); pampaloite (grain B, $8\text{ }\mu\text{m} \times 15\text{ }\mu\text{m}$) + petzite + löllingite (Figure 1b); pampaloite (grain C, $5\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$) + native gold ($\text{Au}_{0.83}\text{Ag}_{0.17}$) + petzite + altaite + hessite + tetrahedrite-(Fe) + chalcopyrite (Figure 1c); pampaloite (grain D, $25\text{ }\mu\text{m} \times 5\text{--}12\text{ }\mu\text{m}$) + tellurantimony + petzite + chalcopyrite (Figure 1d); pampaloite (grain E, $7\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$) + tellurantimony + petzite + calaverite + altaite + chalcopyrite + sphalerite (Figure 1e,f); pampaloite (grain F, $30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$) + native gold ($\text{Au}_{0.88}\text{Ag}_{0.12}$) + petzite + altaite (Figure 1g); pampaloite (grain G, $10\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ and $5\text{ }\mu\text{m}$ rim) + hessite $\pm$ aurostibite (Figure 1h); pampaloite (grain H, $8\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$) + petzite + altaite (Figure 1i,j). Pampaloite is typically intergrown with petzite.

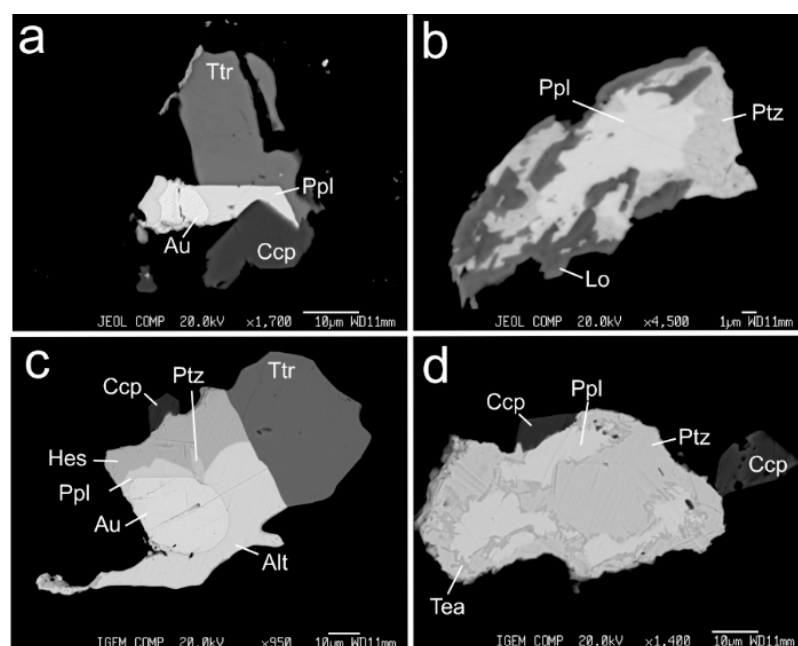


Figure 1. Cont.

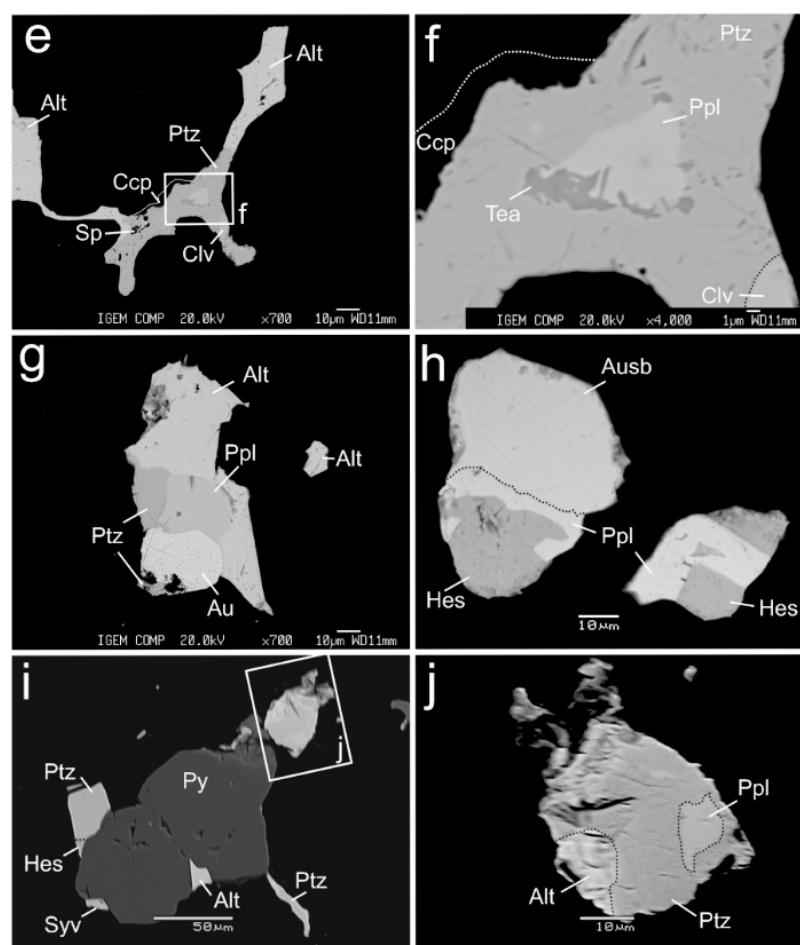


Figure 1. Backscatter electron (BSE) images showing the pampaloite assemblages from the Svetlinsk deposit. (a) Pampaloite (grain A) coexisting with native gold intergrown with tetrahedrite-(Fe) and chalcopyrite. (b) Intergrowth of pampaloite (grain B) with petzite among the crystals of löllingite with rhomb-like sections. (c) Pampaloite (grain C) overgrowing native gold in the complex assemblage of tellurides (altaite, petzite, hessite) and sulfides (tetrahedrite-(Fe) and chalcopyrite). (d) Anhedral pampaloite grain (grain D) in petzite associated with chalcopyrite. Elongate inclusions of tellurantimony at the contact of pampaloite and petzite. (e) Pampaloite (grain E) surrounded by petzite. Petzite along with altaite and calaverite fill a crack in quartz. Chalcopyrite occurs at the contact of petzite and quartz and forms inclusions in petzite, sometimes with sphalerite. (f) Enlarged fragment of Figure 1e with pampaloite. Elongate grains of tellurantimony occur along the contact of pampaloite and petzite. (g) Pampaloite (grain F) inclusion in quartz together with altaite, petzite and native gold. (h) Intergrowth of pampaloite (grain G) with hessite on the right. On the left side, pampaloite forms a border between hessite and aurostibite. (i) Pampaloite (grain H) inclusion in petzite. Au-Ag tellurides (petzite, sylvanite, hessite) and altaite overgrow early pyrite. (j) Enlarged fragment of Figure 1i with pampaloite and altaite inclusions in petzite. The matrix is quartz for all images. Abbreviations: Alt—altaite, Au—native gold, Ausb—aurostibite, Ccp—chalcopyrite, Clv—calaverite, Hes—hessite, Lo—löllingite, Ppl—pampaloite, Ptz—petzite, Py—pyrite, Sp—sphalerite, Syl—sylvanite, Tea—tellurantimony, Ttr—tetrahedrite.

In plane-polarized reflected light, pampaloite is white or creamy white in color. Under crossed polars, the mineral shows weak anisotropism without internal reflections. Reflectance data for pampaloite (grain F) compared with pampaloite and its synthetic analog [1] are shown in Figure 2.

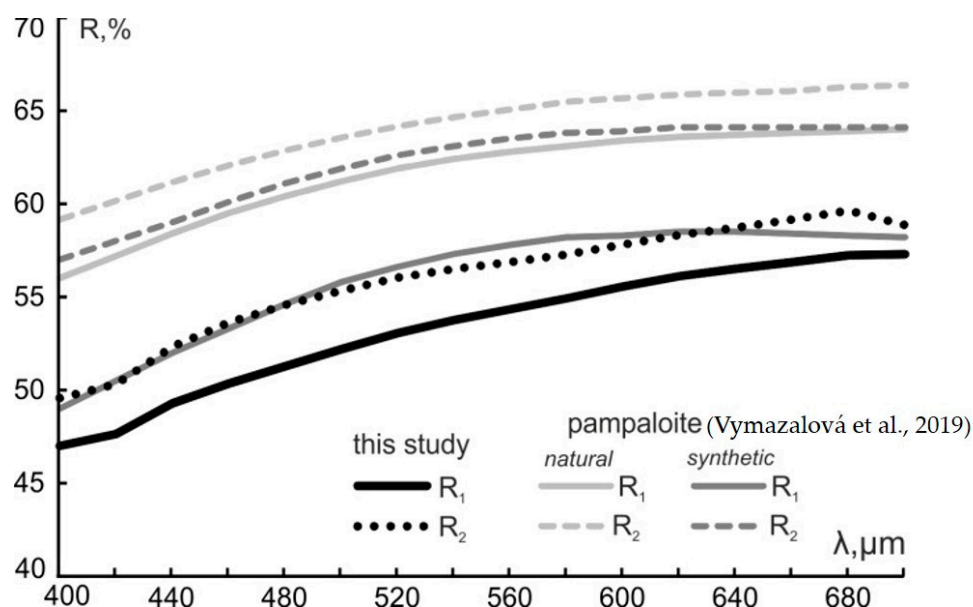


Figure 2. Reflectance spectra for pampaloite (grain F) in comparison with earlier published data [1].

At the Pampalo deposit, pampaloite is intergrown with altaite, frobergite and native gold [1]. The unnamed AuSbTe mineral at the Pampalo deposit occurs in composite grains of other tellurides (altaite, tellurobismuthite, frobergite) in pyrite [9], and at the Enasen deposit coexists with tellurantimony, altaite, $(\text{Sb,Bi})_2\text{Te}_3$ phase and chalcopyrite [2], whereas in the Kairagach deposit it is associated with tellurantimony, altaite, native gold, robinsonite and pyrite [18] or with calaverite [3].

4.2. Chemical Composition

Electron microprobe analyses of pampaloite from the Svetlinsk deposit are given in Table 1. The empirical formula calculated on the basis of the sum of all atoms being 3 *pfu* is $\text{Au}_{0.97-1.07}\text{Ag}_{0-0.02}\text{Sb}_{0.96-1.04}\text{Te}_{0.96-1.04}$, which closely corresponds to stoichiometric AuSbTe. Some pampaloite grains contain trace bismuth (up to 0.08 wt% for grains A–C and E–F) and lead (up to 0.09 wt% only for grain F) in addition to silver (up to 0.5 wt%). Variations in the chemical composition of pampaloite are shown in Figure 3 together with that from [1], as well as results for both natural and synthetic AuSbTe from the literature. The AuSbTe mineral from the Enasen deposit contains 1.2–1.4 wt% Bi [2] and that from the Kairagach deposit — 0.1–0.4 wt% Se [3,18].

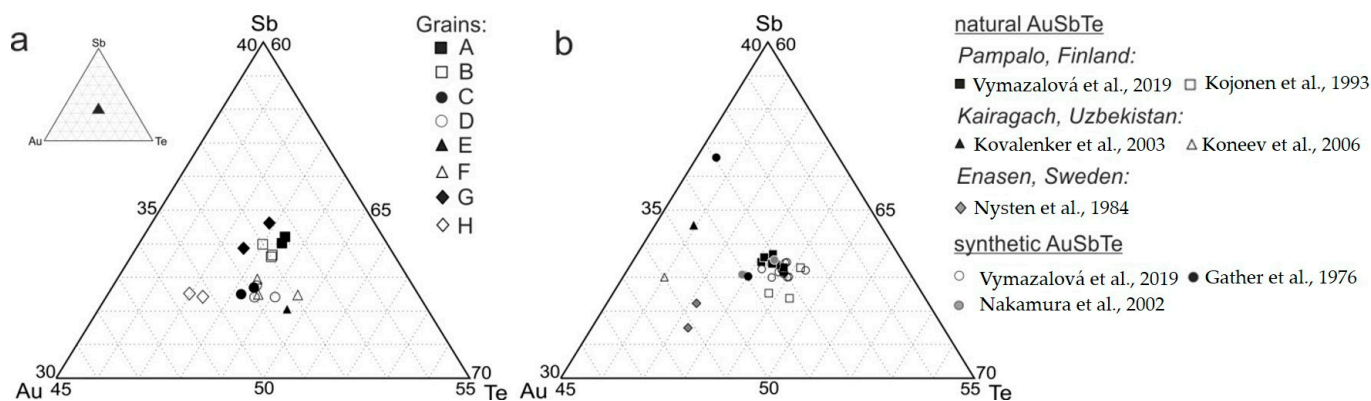


Figure 3. Ratios of major constituents in pampaloite from the Svetlinsk deposit (a) and from the other localities and in synthetic AuSbTe (b) (literature data [1–3,8,18–20]). The black triangular area has been enlarged.

Table 1. Electron microprobe analyses of pampaloite from the Svetlinsk deposit.

No	wt%							Formula Calculated on the Basis of 3 Atoms					
	Ag	Au	Pb	Sb	Bi	Te	Total	Ag	Au	Pb	Sb	Bi	Te
1	–	42.69	–	27.84	–	28.50	99.03	0	0.97	0	1.03	0	1.00
2	–	43.71	–	28.21	–	29.06	100.98	0	0.98	0	1.02	0	1.00
3	0.17	43.12	–	27.31	–	28.42	99.02	0.01	0.98	0	1.01	0	1.00
4	–	44.36	–	28.21	–	28.70	101.27	0	0.99	0	1.02	0	0.99
5	0.23	43.33	–	27.59	–	28.67	99.82	0.01	0.98	0	1.01	0	1.00
6	0.50	43.93	–	26.26	–	28.12	98.80	0.02	1.01	0	0.97	0	1.00
7	0.40	43.97	–	26.65	–	28.54	99.56	0.02	1.00	0	0.98	0	1.00
8	0.12	43.82	–	26.35	–	28.20	98.49	0	1.01	0	0.98	0	1.00
9	0.15	44.15	–	26.13	–	28.38	98.81	0.01	1.01	0	0.97	0	1.01
10	0.14	43.45	–	26.10	–	28.74	98.43	0.01	1.00	0	0.97	0	1.02
11	0.25	44.28	–	26.53	0.07	29.95	101.08	0.01	0.99	0	0.96	0.001	1.04
12	–	43.75	0.09	26.73	0.08	29.82	100.48	0	0.99	0.002	0.97	0.002	1.04
13	–	45.10	0.05	26.74	–	28.99	100.87	0	1.02	0.001	0.97	0	1.01
14	–	44.47	–	27.00	0.07	28.66	100.19	0	1.01	0	0.99	0.002	1.00
15 *		43.32		28.41		28.26	99.99		0.98		1.04		0.98
16 *		44.50		27.72		27.97	100.19		1.01		1.02		0.98
17 *		46.57		26.31		27.12	100.00		1.07		0.97		0.96
18 *		45.70		25.94		27.13	98.77		1.06		0.97		0.97

Notes: dash—below detection limit, blank—not analyzed, *—SEM analyses, all others by EMPA. Analyses 1–2 are for grain A, 3–5 for B, 6–7 for C, 8–10 for D, 11 for E, 12–14 for F, 15–16 for G and 17–18 for H. The Se content is below detection limit in all analyses.

4.3. EBSD Study

The EBSD study shows a perfect agreement (12 bands out of 12, mean angle deviation 0.19°) of the studied grains (E and F) with the pampaloite structure type (Figure 4). Together with the chemical composition, this directly confirms the identification of the mineral from Svetlinsk as pampaloite. EBSD mapping of these grains of pampaloite can provide additional information about the mineral association, crystallite sizes and spatial characteristics. Orientation maps show that the pampaloite is represented by a single crystal grain with no signs of recrystallization or multi-stage growth. Total misorientation of the pampaloite does not exceed first degrees, does not show any twinning and is shown as a compact area on inverse pole figures (Figure 5).

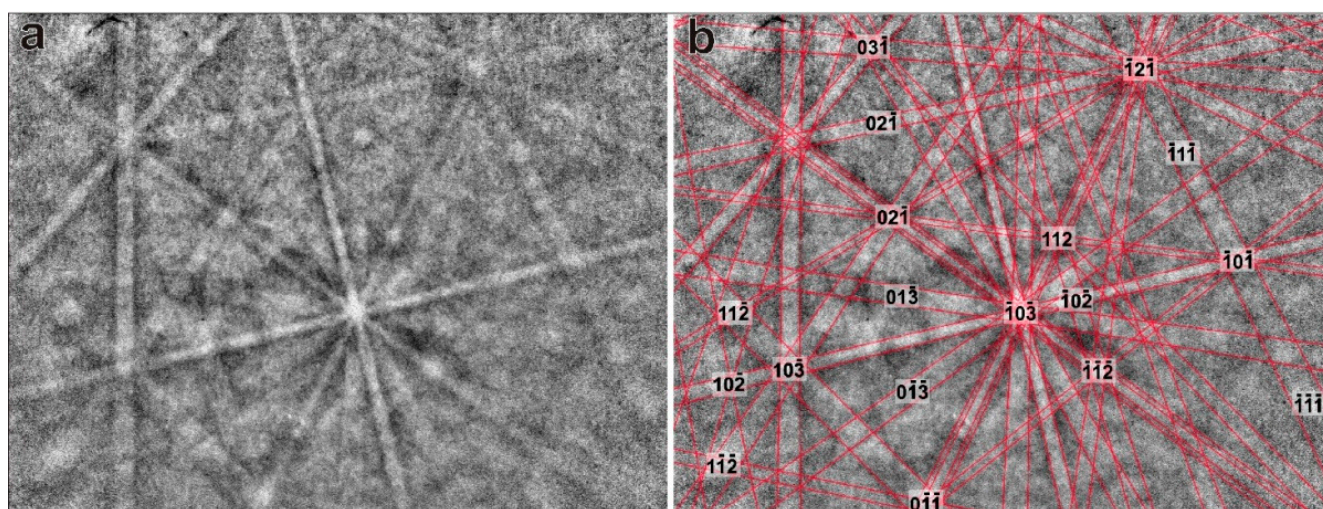


Figure 4. EBSD pattern of pampaloite (a) and its indexing (b) (grain F).

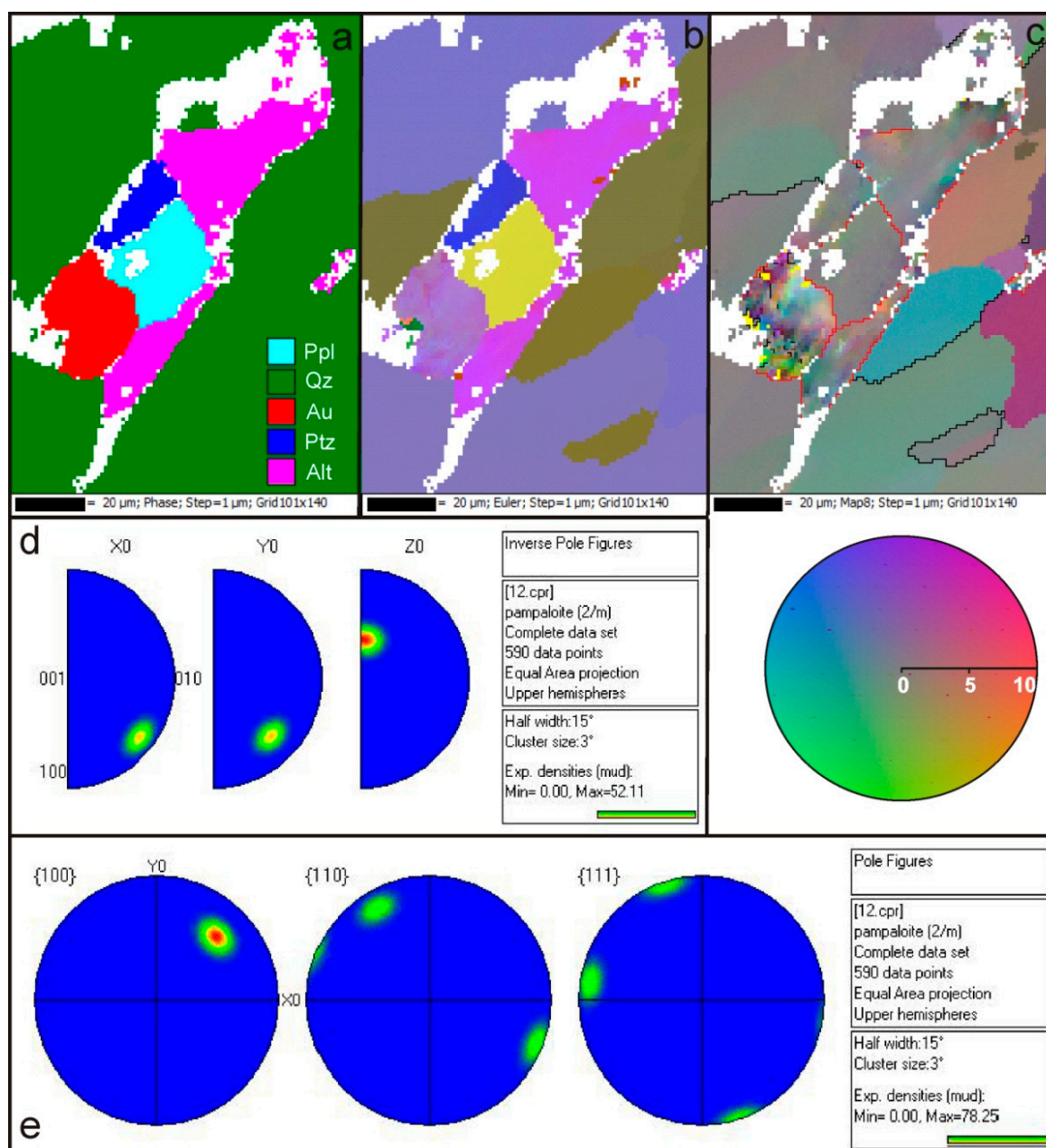


Figure 5. EBSD mapping of a pampaloite-containing assemblage: (a) phase map; (b) Euler map; (c) misorientation map with color coding of misorientation; (d) inverse pole figures for pampaloite; (e) pole figures for pampaloite. Abbreviations: Alt—altaite, Au—native gold, Ppl—pampaloite, Ptz—petzite, Qz—quartz.

4.4. Raman Spectroscopy

All studied pampaloite grains exhibit vibrational modes in the range 60–180 cm^{-1} (Figure 6). Average peak positions are 71, 108, 125, 147 and 159 cm^{-1} . A low-intensity band with a center at 80 cm^{-1} is observed for some grains. Variation of peak positions among spectra is within 3 cm^{-1} and can be attributed to instrument drift. The observed relative intensities of bands vary and are likely dependent on crystal orientation. Careful assignment of the observed Raman bands to specific vibrations in the crystal structure generally requires modeling of spectra based on crystallographic data or observation of natural spectra in grains with a specific orientation. Based on the published data on other compounds of Au, Sb and Te, we attempted to relate the observed Raman peaks and chemical bonds as follows: peaks at 71, 108 and 159 cm^{-1} likely correspond to Sb–Te [21,22]

and Sb–Sb bonds [21,23]; peaks at 125 and 147 cm^{-1} likely correspond to Au–Te [24], Te–Te [22] or Au–Sb bonds [25]. This assignment may be speculative and requires further research.

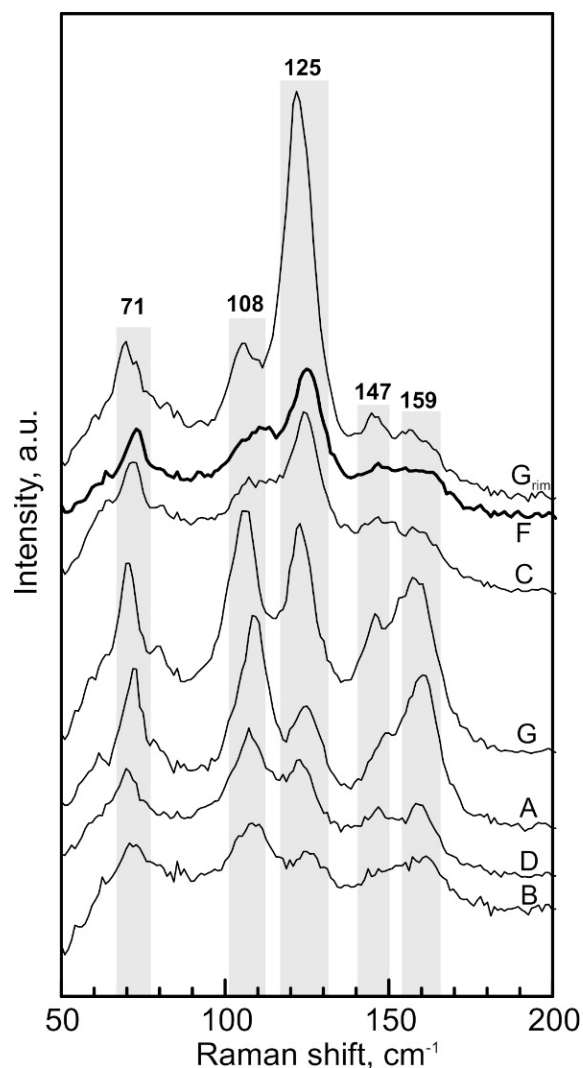


Figure 6. Raman spectra of pampaloite. The bold line depicts the spectrum for the grain where EBSD patterns were obtained. Main vibrational modes and their average position are shown with gray bands with numbers on top. The capital letters correspond to pampaloite grains.

5. Discussion

Pampaloite is a relatively new mineral in the Au–Sb–Te system. The synthesis of the compound AuSbTe was first reported by Gather and Blachnik [20] who investigated the ternary Au–Sb–Te system by using thermoanalytical, X-ray diffraction and metallographic measurements and found a new ternary compound of the approximate composition AuSbTe. The eutectic assemblage AuSbTe + Au + AuSb₂ crystallized at 356 °C [20], and the peritectic temperature was 424 °C (AuSbTe – Sb₂Te₃ + L; [26]). Later, Nakamura and Ikeda [19] studied the ternary phase relations in the Au–Sb–Te system at 350 °C and also found the AuSbTe phase. The authors determined that AuSbTe stably coexists with Au, AuSb₂ and Sb₂Te₃, producing three univariant assemblages: AuSbTe + Au + AuSb₂, AuSbTe + AuSb₂ + Sb₂Te₃ and AuSbTe + Sb₂Te₃ + Au. Vymazalová et al. [1] prepared synthetic AuSbTe for crystallographic and structural investigations and obtained intergrowths of Sb₂Te₃ and AuSbTe with Au symplectites at 350 °C and a homogeneous AuSbTe phase at 400 °C. Considering the mentioned experimental data and reactions from [20], we estimate the upper temperature range of the pampaloite crystallization to be 350–430 °C. These data

are consistent with the data from fluid inclusion thermometry (200–400 °C; [13]) and from the mineral geothermometers (350–385 °C; Vikent'eva, unpublished data).

Since this is the second well-studied finding of pampaloite, our new data on the chemical composition and mineral associations as well as the first Raman study of the mineral extend the general characterization of a rare mineral. We believe that the obtained results will be of interest both for specialists studying telluride-bearing gold deposits and occurrence modes of gold and for mineralogists who are studying the Au-Sb-Te system and are interested in additional information about pampaloite.

Author Contributions: Methodology and investigation, O.V.V., V.V.S. and V.D.S.; field work, I.V.V. and O.V.V.; writing—original draft preparation, O.V.V.; reviewing and editing of the draft, O.V.V., I.V.V., V.D.S. and N.S.B.; project administration, N.S.B. All authors have read and agreed to the published version of the manuscript.

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

Appendix A

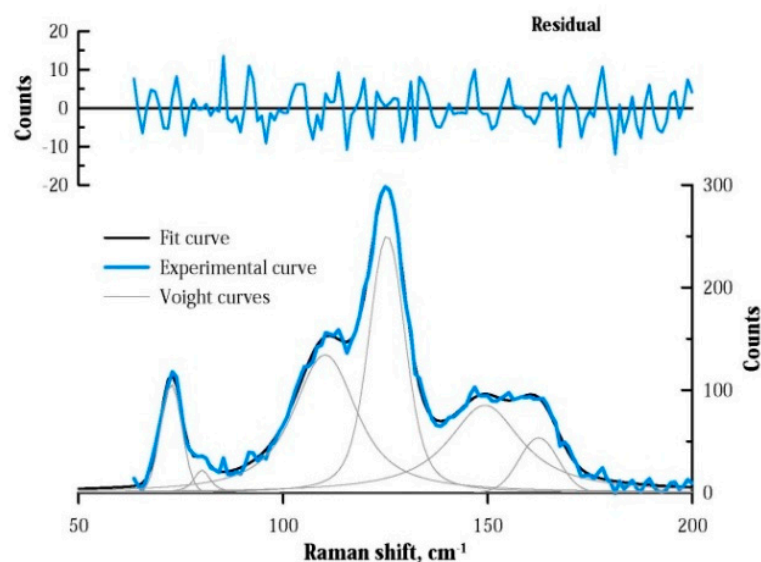


Figure A1. Deconvolution of Raman spectrum of pampaloite using six Voigt functions.

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