

Article

Ore Formation and Mineralogy of the Alattu–Päskylä Gold Occurrence, Ladoga Karelia, Russia

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Abstract: The Alattu–Päskylä gold occurrence is located in the Northern Lake Ladoga area, in the Raaha-Ladoga suprasubduction zone, at the Karelian Craton (AR)—Svecofennian foldbelt (PR₁) boundary. Its gold ore mineral associations are of two types of mineralization: (1) copper-molybdenum-porphyry with arsenopyrite and gold (intrusion-related) and (2) gold–arsenopyrite–sulfide in shear zones. Optical and scanning electron microscopy, X-ray fluorescence spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA) and fire analysis with AAS finishing were used to study them. Type 1 was provoked by shallow-depth tonalite intrusion (~1.89 Ga) and type 2 by two stages of Svecofennian metamorphism (1.89–1.86 and 1.83–1.79 Ga) with the possible influence of the impactogenesis of the Janisjärvi astrobleme (age ~1 Ga). Intrusive and host rocks were subjected to shearing accompanied by the formation of ore-bearing metasomatic rocks of the propylite-beresite series (depending on substrate) and quartz–sericite, quartz and sericite–tourmaline veins and streaks. Ore mineralization is present as several consecutive mineral associations: pyritic–molybdenite with arsenopyrite and gold; gold–arsenopyrite; quartz–arsenopyrite with antimony sulfosalts of lead; gold–polysulfide with tetrahedrite–argentotetrahedrite series minerals and gold–antimony with Pb–Sb–S system minerals and native antimony. Arsenopyrite contains invisible (up to 234 ppm) and visible gold. Metamorphosed domains in arsenopyrite and rims with visible gold around it are usually enriched in As, indicating higher (up to >500 °C) temperatures of formations than original arsenopyrite with invisible gold (<500 °C). A paragenetic sequence associated with the deposition of invisible and visible gold established at the Alattu–Päskylä ore occurrence: pyrrhotite + unaltered arsenopyrite (with invisible gold) → altered arsenopyrite (As-enriched) + pyrite ± pyrrhotite + visible gold. Gold, associated with gudmundite, sphalerite and native antimony, seems to be due to cainotypic rhyodacitic porphyry cutting tonalite intrusion or with a retrograde stage in post-Svecofennian metamorphism. The isotopic composition of Pb and ²³⁸U/²⁰⁴Pb (9.4–9.75) for the feldspar of the tonalite intrusion and the pyrite of gold mineralization, εNd (–4 up to –5) for tonalites and δ³⁴S values of –2.10–+4.99 for arsenopyrite, indicate the formation of gold occurrence provoked by Svecofennian magmatic and tectono-thermal processes with the involvement of matter from a mantle-lower crustal reservoir into magma formation and mineralization.



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1. Introduction

Gold is usually associated with sulfides and sulfoarsenides in many hypogene deposits, including epithermal, intrusion-related and orogenic [1]. The concentration and distribution of gold in these minerals varies markedly from several ppb to >1% [2–5]. Gold is present there as visible or invisible phases produced (remobilized?) by multi-stage hydrothermal or metamorphic processes [6–8]. Invisible gold may occur as a solid solution in the crystalline lattice of a host mineral or as micron-sized (<1 μm) inclusions [3,7,9,10]. Gold in orogenic deposits typically exhibits a bimodal distribution, where initially invisible gold within pyrite and arsenopyrite is later overprinted by visible gold [6,7,11]. In

polygenetic deposits with signs of intrusion-related and orogenic origin, the formation and correlation of invisible and visible gold are poorly understood [12,13]. In this project, the polygenetic Alattu–Päskylä gold occurrence was studied, and the ore mineralogy and distribution pattern of visible and invisible gold were described in detail.

The Alattu–Päskylä gold occurrence is located in the Northern Lake Ladoga region, 1.5 south of Lake Janisjärvi (Figure 1). Gold mineralization was first found here in 1986 during a 1:50,000 geological survey and prospecting conducted by the Karelian Geological Survey and the All-Union Geological Institute and was entitled the Alattu ore occurrence in the crumple zones of terrigenous rocks. Prospecting of economic gold mineralization of this type was recommended. No work at the ore occurrence and in the adjacent area was done for about 10 years due for various reasons.

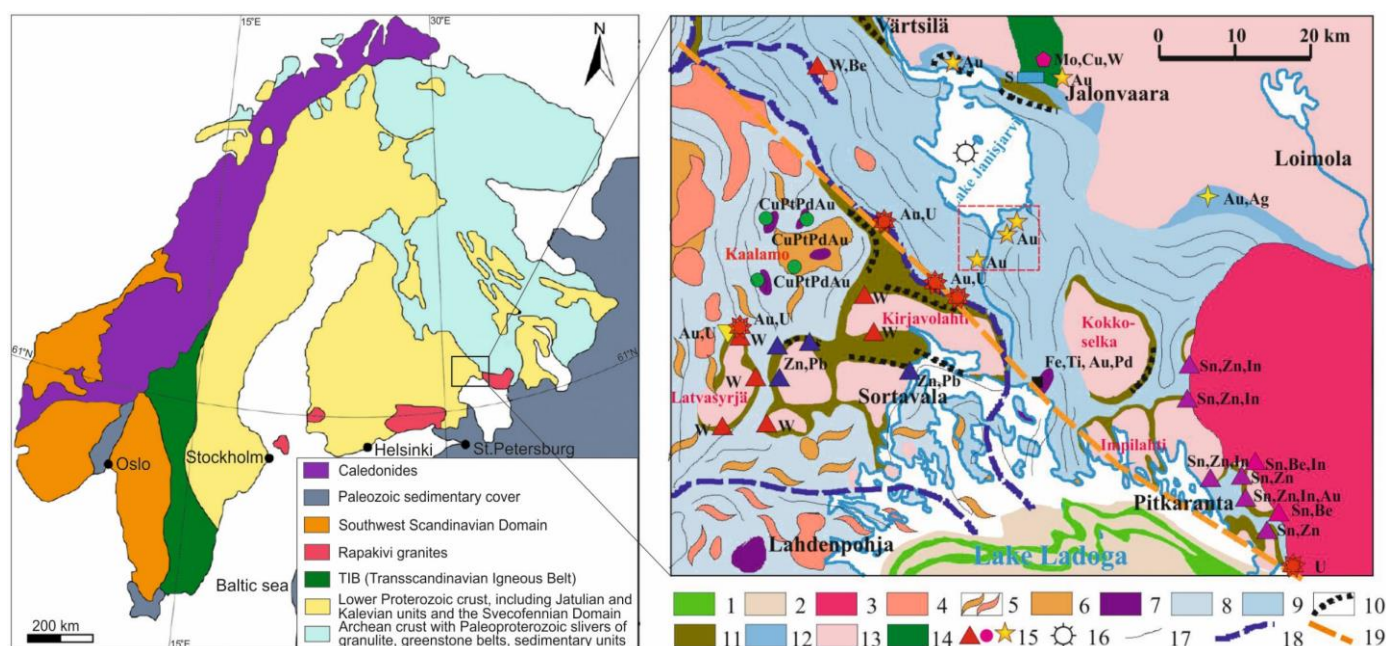


Figure 1. Regional geological map of the Northern Lake Ladoga region with ore prospects. After [14,15], modified. 1–3—Riphean: 1—monzodolerites, ferrodolerites (Valaam sill); 2—tuffs, sandstones, basalt lava (Salmi suite); 3—Salmi anorthosite-rapakivi granite batholith; 4–12—Proterozoic: 4—late- and post-orogenic Svecofennian granitoids; 5—migmatites; 6, 7—early- and synorogenic gabbroic intrusions (6—Kaalamo complex, 7—Välimäki complex); 8–9—Ladoga series (8—mica schists, gneissose schists, 9—phyllites, metaturbidites); 10–11—Sortavala series: 10—carbonaceous shales; 11—mafic metavolcanics (amphibolites), dolomites, marbles, skarns; 12—red dolomites, quartzites (Tulomozero suite); 13, 14—Archean: 13—undivided basement gneissose granites; 14—volcanics and sedimentary rocks of the Jalonvaara-Ilomantsi greenstone belt; 15—ore occurrences and ore deposits; 16—Janisjärvi astrobleme; 17—strike orientation of major folded structures; 18—major dislocations by shearing; 19—Ruskeala fault controlling the distribution of uranium ore prospects; red dotted lines indicate the location of the Alattu, Päskylä and Janis gold occurrences.

New data obtained in the late 20th century have led geologists to conclude that Alattu is an epigenetic gold-porphyry occurrence [16,17]. It was compared with the epithermal Orivesi deposit [18] and, together with other gold occurrences in the Northern Lake Ladoga region, with small gold-arsenic deposits in the Raahe-Ladoga zone, Finland [19]. All workers assumed that the ore occurrence is genetically related to a small shallow-depth stock-like diorite-tonalite-plagiogranite-gabbro-diorite intrusive body (~1.88–1.89 Ga). More recently (2001–2004), the Institute of Geology at the Karelian Research Centre, RAS, together with the Mineral Open Joint Company, found enriched gold (up to 30 ppm Au) mineralization at a Päskylä locality near the Alattu ore occurrence. These gold occurrences were then reinterpreted as one Alattu–Päskylä gold occurrence of mesothermal orogenic type [20–22].

A gold prospecting model for the gold occurrence, applicable to the Suistamo Group of minor intrusion, was constructed, and the related ore occurrences were described as having been derived from one ore-forming system [20,21,23]. The results of studies of ore minerals in these works and in the article by O.B. Lavrov [24] were predominantly of a descriptive nature. However, many problems regarding the detailed description and relationships of ore mineralization of intrusion-related and orogenic types, hydrothermal alterations of arsenopyrite and the distribution of visible and invisible gold are yet to be resolved. The present paper is another attempt to approach these problems.

2. Geological Setting of the Alattu–Päskylä Ore Occurrence

The Alattu–Päskylä ore occurrence is located in the Northern Lake Ladoga region (Figure 1), in the Raahe-Ladoga suprasubduction zone of the Karelian Craton (AR)–Mesoproterozoic Svecofennian foldbelt (PR₁) boundary on the Fennoscandian Shield. The modern structure of the region as the north-eastern flank of the Svecofennian foldbelt is the result of its long evolution (~500 Ma), which included continental and oceanic-marginal rift formation with the opening of the Svecofennian Ocean, followed by the convergent interaction of newly formed oceanic crust with the Archean craton [25,26]. Hence, the formation of structural-rock complexes in the region was split up into several stages, which ended with the formation of an accretionary-collisional orogen, two stages of high-temperature metamorphism (Early Svecofennian, 1.89–1.86 Ga, and Late Svecofennian, 1.83–1.79 Ga) [27], post-collisional uplift, cratonization and discrete intraplate magmatism (Salmi anorthosite-rapakivi granite batholith—1.55–1.53 Ga) [26,28]. The formation of the Janisjärvi astrobleme with its crater, now known as Lake Janisjärvi, was the latest endogenic event in the region (Figure 1). The astrobleme was dated by the paleomagnetic method at 900–850 Ma [29]. Her ³⁹Ar/⁴⁰Ar age, dated from impact glass, is 682 ± 4 Ma [30], and her U/Pb zircon age is 1080 ± 30 Ma [26].

Archean basement rocks (gneisses, granite gneisses and amphibolites; 2.7–2.66 Ga) have only preserved as so-called “rimmed granite gneiss domes” after P. Eskola [31]. Their formation mechanism remains the subject of debate [32–35]. The domes are rimmed by the volcanic-sedimentary rocks of the Pitkäranta suite (Ludicovian, 2.1–1.92 Ga) overlain by Ladoga turbidites (Kalevian 1.92–1.8 Ga) (Figure 1).

Ludicovian and Kalevian rocks were metamorphosed under greenschist and amphibolite facies conditions. They are cut by variably old (1.89–1.80 Ga) Svecofennian intrusions and pegmatites. The Alattu–Päskylä gold occurrence is located in the Janisjärvi prospect (Figure 2) in the small (~1 km) tonalities-gabbro-diorite intrusive body of the Suistamo group of minor intrusions dated at 1884.8 ± 3.2 Ma [36], as well as in the host shales of the Ladoga series.

Suistamo tonalities and gabbro-diorites are part of a calc-alkaline series. Their mantle-crustal origin is supported by geochemical (<HREE, >Ba, >Sr, <Rb) and isotopic data— ϵ Nd (−4–−5) [19]. Suistamo intrusions are accompanied by abundant dikes (Figure 2) consisting mainly of porphyritic rock facies varying in composition from gabbro and diorites to rhyolites. Composite dikes, consisting of gabbro (usually almost completely metamorphosed to amphibolite) and tonalite, also occur. The geological, geochemical and petrological features of these intrusive bodies indicate that they are part of a Svecofennian early orogenic (~1.88–1.89 Ga) magmatic complex with many small, dominantly base metal (some with Au, Ag, W, As, Mo, etc.) and gold deposits in Finland [37–39]. In addition to the Alattu–Päskylä ore occurrence, a similar gold prospect known as Janis (Figure 2), several gold anomalies in other tonalite bodies and tungsten (scheelite mineralization) in gabbro–amphibolite dikes are present in the Janisjärvi prospect.

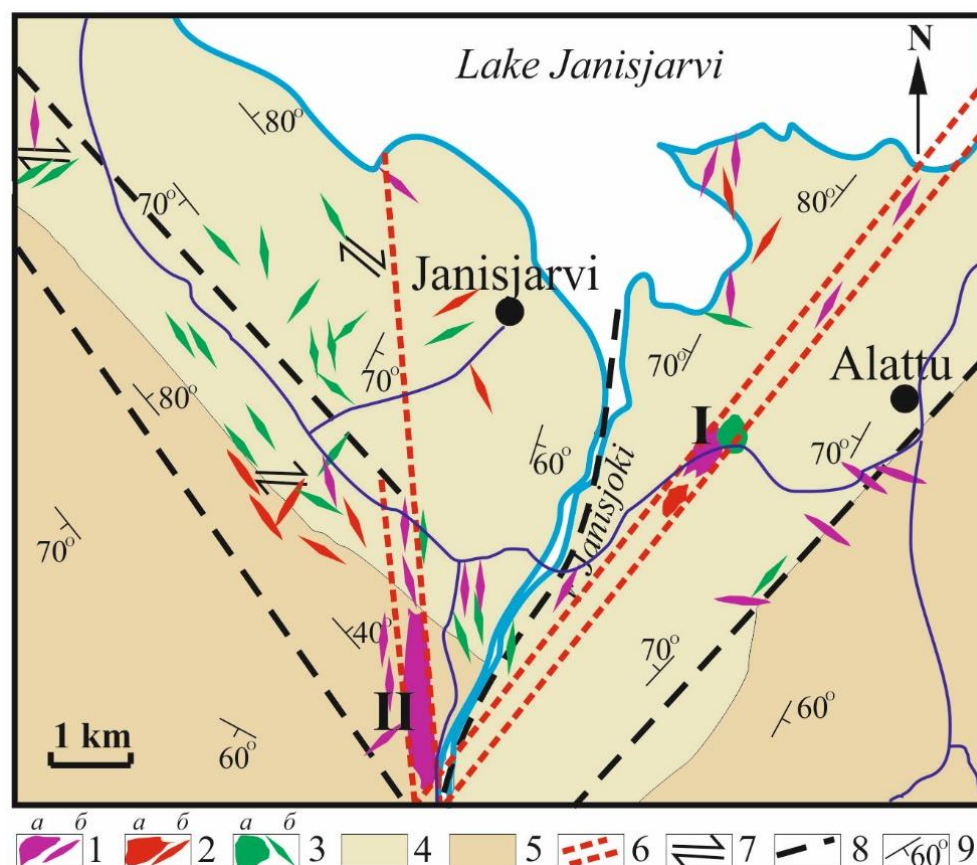


Figure 2. Geological map showing the location of the Alattu-Päskylä-Janis gold occurrences. 1–3—Suistamo Group of shallow-depth intrusions in the Kaalamo magmatic complex: 1—quartz diorites, tonalites, plagiogranites, rhyodacites, etc. (a—stock-shaped bodies, b—dikes); 2—quartz porphyry, granite porphyry (a—stock-shaped bodies, b—dikes); 3—diorites, gabbro-diorites, gabbro (a—stock-shaped bodies, b—dikes); 4, 5—metaturbidites, Ladoga series: 4—coarse and rhythmic interbedding of metasiltstones (biotite schist), sandstones and quartzites (Naatselkä suite); 5—coarse interbedding of metasiltstones (andalusitic, cordieritic-andalusitic and quartz-plagioclase-biotite schists) and sandstones (Pätkjärvi suite); 6—Gold-controlling shear zones with noble-metal occurrences (I—Alattu-Päskylä, II—Janis); 7—elementary shear-structures with gold mineralization points; 8—tectonic dislocations; 9—mode of occurrence of rock bedding.

3. Materials and Methods

Ore minerals and parent rocks were examined using optical microscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), X-ray fluorescence (XRF), inductively coupled plasma mass spectrometer (ICP-MS) and wet chemistry at the Institute of Geology, Karelian Research Centre, Russian Academy of Sciences (IG KRC RAS, Petrozavodsk, Russia). Samples were taken from natural rock exposures and exploration workings. There were a total of over 250 samples. Specimens for ICP MS and XRF analysis were prepared from all samples, and polished sections were made. The polished sections were studied by optical microscopy (an Axiolab pol-u optical microscope equipped with a digital photographic camera and a computer).

The minerals' composition was analyzed in polished thin sections with a VEGA II LSH scanning electron microscope (Tescan, Brno, Czech Republic). The instrument was equipped with an energy-dispersive spectrometer (EDS) Energy 350 system with SDD X-Act3 detector (Oxford Inca Energy, Oxford, UK). Operating conditions were 20 kV accelerating voltage, 5 nA probe current, 1 μ s EDS process time, 105 cnts/s and 30 s counting time. The spectral lines for each element are CuK α , FeK α , ZnK α , MnK α , SK α , FK α , AgL α , AuL α , SbL α , TeL α , AsL α , BiM α , PbM α , MoL α and WM α . The standards used were

CaCO₃, FeS₂, PbTe, HgTe, TlSbSe₂, NaCl, Cu, Co, Ni, Zn, Mn, As, Ag, Au, Sb, Te, W, Mo and Bi. SEM-EDS quantitative data were obtained and processed using Microanalysis Suite Issue 12, INCA Suite version 4.01; standard deviation (S) for As—0.89–3.13, Sb—0.54–1.30, Au—0.70–4.37, Hg—0.57–2.91, Ni—0.49–1.04, Co—0.23–0.54, Mo—1.09–2.57, W—1.26–2.97, Pb—1.3%–4.4%, Bi—1.40%–5.04%, Te—0.4%–2.0%, Cu—0.7%–2.3%, Zn—1.0%–2.4%, Ag—0.24%–1.91% and S—0.4%–0.7%.

The rocks were analyzed for Au and Ag by fire assay with AAS finish provided by the Central Geological Research Institute for Nonferrous and Precious Metals (Moscow).

Major element concentrations in the granites were estimated by wet chemistry and XRF. XRF analysis was performed using an ARL ADVANT'X-2331 (Thermo Fisher Scientific, Ecublens, Switzerland) wavelength-dispersive spectrometer with a rhodium tube, working voltage of 60 kV, working current of 50 mA and resolution of 0.01. Preliminarily, 2 g of each powdered sample was heated in ceramic crucibles at 1000 °C in a muffle furnace for 30 min. The loss of ignition was determined by a change in sample mass upon heating. For XRF measurements, 1 g of heated sample was mixed with Li-tetraborate flux and heated in an Au-Pt crucible to 1100 °C to form a fused bead.

Trace and rare-earth element concentrations were calculated by ICP-MS using an X 199 Series 2 (Thermo Scientific, Bremen, Germany) mass spectrometer. Powdered samples (200) were digested in acid mixture following a standard procedure [40]. Analytical accuracy was monitored by analyzing the USGS standard BHVO-2.

4. Results

4.1. Geological Structure and Composition of the Alattu–Päkyälä Intrusion

The Alattu–Päkyälä ore occurrence is situated within a small, morphologically complex, stock-like intrusion, with a traceable length of approximately 1 km, a thickness of around 200 m and an area of about 0.15 km². It consists of tonalite-plagiogranite, rhyodacite quartz porphyry, a gabbroic rock stock and their exocontacts (Figure 3). The intrusion is controlled by NW- and NE-trending reverse-shear fault dislocation systems (Figures 2 and 3). It cuts graphite-bearing metaterrigenous rocks (Ladoga series) with scarce thin skarnoid lenses, forming eruptive breccia with an abundance of sharply angular schist and quartzite fragments (Figure S1) at their north-eastern and south-western flanks and is accompanied by comagmatic dikes. The tonalite intrusion is cut at the endocontact by many rhyolite and aplite veins, up to 30 cm thick, a complex injection body and thin cainotypic rhyodacitic porphyry dikes (Figure S2) with sky blue quartz phenocrysts. The rocks that make up the intrusion vary from quartz-diorites to tonalites and plagiogranites. Additionally, thin (0.5–10 cm) streaks units, filled with greenish-gray glass and similar in composition to host Ladoga metasiltstones, occasionally occur at the northeastern contact. They seem to have been produced by an impact event, because they occur only ~1.5 km from the crater of the Janisjärvi astrobleme (Figure 2). The temperature of its impact melt was as high as 1700–1800 °C [26].

All the above rock varieties containing more SiO₂ than diorites display a porphyritic structure. This texture is most pronounced in tonalites, especially within endocontact zones, where quartz phenocrysts exhibit a distinctive pea-like shape and a sky blue color. They are locally pressed at a varying degrees into the contact plane with host Ladoga schists (up to detachment from the matrix), suggesting that they were in a solid state when carried by viscous melt from great depths, i.e., they could have been formed in the intratelluric stage of crystallization. An abundance of complexly zonal plagioclase phenocrysts, up to 1 cm in size (Figure 4), are characteristic of rhyodacitic porphyry. They occur as solitary aggregates, twins, tees or clusters of several adhered tabular crystals. Their cores are of heterogeneous origin. Some occur very seldom as xenogenic fragments of slightly altered plagioclase, which is occasionally also present in the matrix.

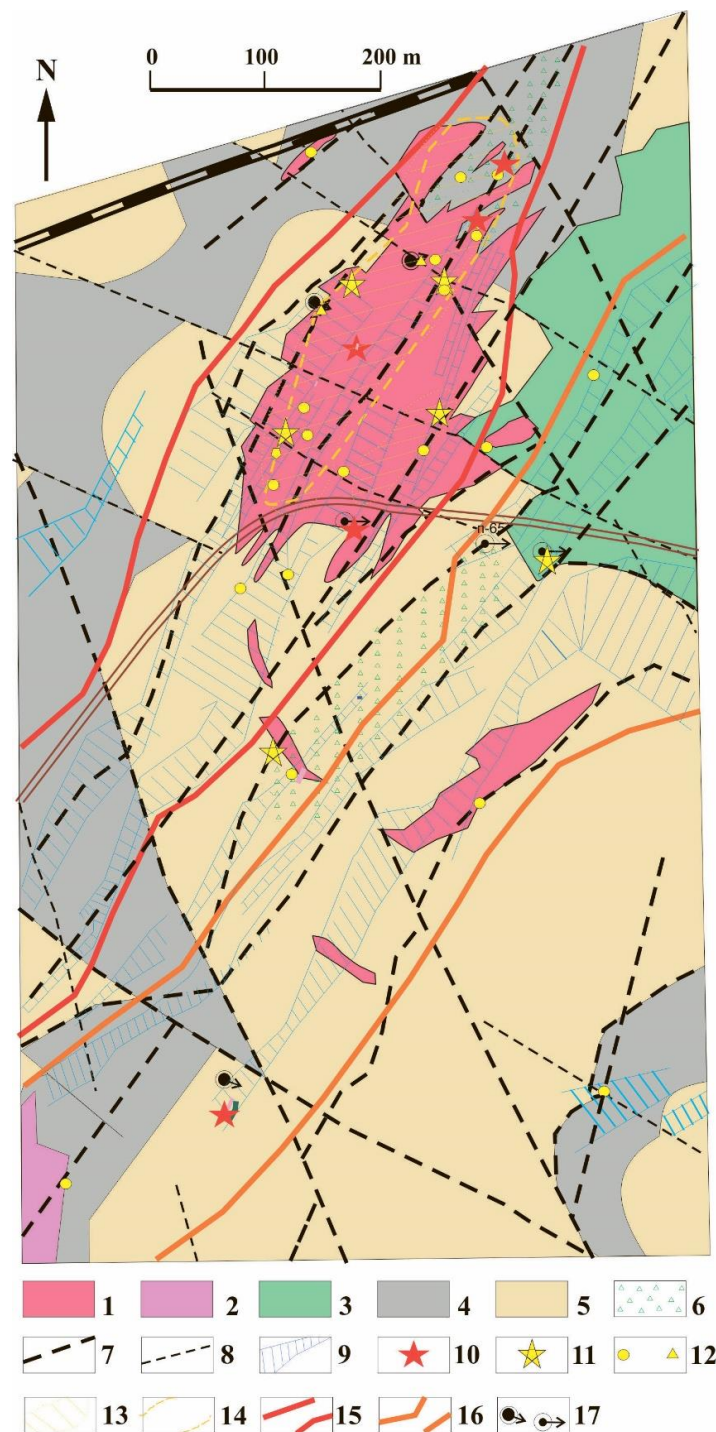


Figure 3. Geological map of the Alattu-Päskylä gold occurrence. After: [22], modified. 1–3—Suistamo magmatic complex (~1.89 Ga): 1—tonalites, quartz diorites, rhyodacitic quartz porphyry; 2—plagiogranites, quartz porphyry; 3—gabbro-diorites, gabbro; 4, 5—metaturbidity, Ladoga series: 4—metasiltstones with sandstone, quartzitic sandstone and quartzite interbeds; 5—thinly-laminated sandstones, quartzitic sandstones, quartzites; 6—eruptive and explosive breccia, tuffite-like rocks; 7, 8—tectonic dislocations: 7—shearing; 8—faults; 9—sulfide mineralization zones; 10–12—gold concentration (sampling data): 10—over 5 ppm; 11—1.0–3.0 ppm; 12—0.1–1.0 ppm; 13—beresitization and quartz-sericite alteration zones; 14—contours of primary dispersion halo with 0.001–0.5 ppm gold; 15, 16—gold ore zone boundaries: 15—North zone derived mainly from tonalites; 16—South zone derived mainly from metaturbidities and gabbroic rocks, Ladoga series; 17—boreholes.

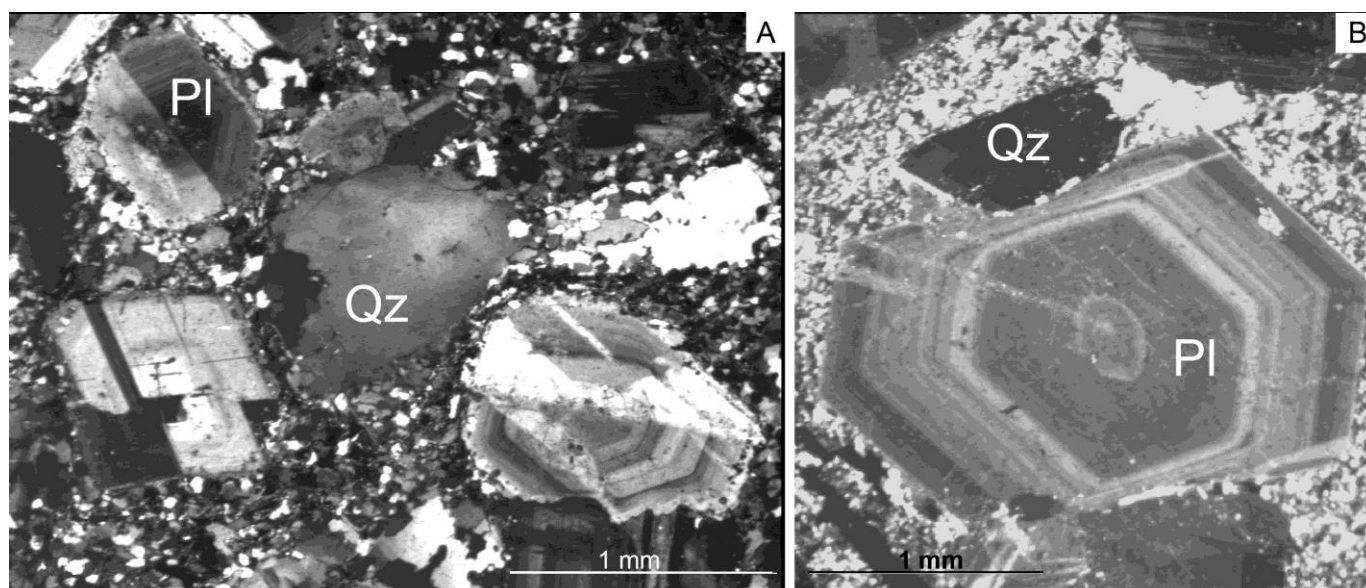


Figure 4. Porphyritic structure of rhyodacites cutting tonalites. (A)—zonal phenocrysts: plagioclase. Non-zonal phenocrysts: quartz; (B)—zonal plagioclase phenocryst with a resorbed core. Pl—plagioclase; Qz—quartz.

Others are typical embryonic crystals, show signs of multiple undermelting, and the overgrowing zones with traces of deformation vary markedly in thickness in different growth directions, indicating disequilibrium crystallization conditions. This, together with other signs (considerable rock variations even within individual outcrops, the presence of several generations of compositionally similar, locally composite, dikes, traces of viscous flow and ductile deformations, the resorption of the external plagioclase and quartz zones, etc.), suggests a long high-gradient crystallization regime, which included an intratelluric stage and probably “magma-mixing” and “magma-mingling”. The crystallization temperature of the melts indicated by a biotite–plagioclase thermometer [41]: for diorites was about 800 °C and for tonalites was over 700 °C and for the cores of plagioclase phenocrysts was much higher than 700 °C. The pressure according to the Ti-biotite geobarometer [42] was 3.29–3.77 kbar.

The above petrographic rock varieties of the intrusion, except for a dike facies, are usually gneissoid, gray, yellowish- to pinkish-gray, fine- to medium-grained, with mineral compositions of the same type. They differ in the abundance of plagioclase (50%–80%), quartz (5%–35%), biotite (3%–20%) and occasionally amphibole. The plagioclase basicity varies mainly from andesine-labrador to oligoclase and oligoclase-albite. The percentage of an anorthite molecule in zonal phenocrysts decreases from 38%–40% in the core to 20%–30% at the margin. The $Mg\# = Mg/(Mg + Fe)$ of biotite in diorites is 0.32, that of tonalites is 0.33–0.41 and that of plagiogranites is 0.38. Amphibole is only present in quartz diorites and tonalites. The $Mg\#$ is much higher than that of the associated biotite (0.54–0.56—amphibole, 0.33–0.41—biotite). Accessory minerals occur as sulfides (pyrite, arsenopyrite, chalcopyrite, molybdenite, pyrrhotite, sphalerite and galena); titanite; scheelite; apatite; xenogenic zircon; monazite; parisite; magnetite; ilmenite; epidote; tourmaline and barite.

Granitoid intrusion and gabbroic stock rocks are interlinked in space and structure, making up a bimodal association. The zircon ages of gabbro-diorites and granitoids coincide within the error limits: 1884.8 ± 3.3 Ma and 1872 ± 13 Ma [22,36]. The coexistence of two magmas could have resulted in hybridization events responsible for the highly variable chemical composition of the intrusion rocks (Table S1), which, judging by their position on the multication R1-R2 diagram [43] (Figure S3), are pre- and syncollisional in a geotectonic aspect. On the $(Na_2O + K_2O)$ vs. SiO_2 diagram [44] (Figure S4), they form a common trend in the fields from quartz diorites and quartz monzodiorites to

tonalites, granodiorites and granites, the elevated alkalinity of which is due to ubiquitous sericitization and multiple metamorphisms in the rocks. Gabbroic rocks and quartz diorites are moderately aluminous (meta-aluminous), and the more felsic members of the complex are alumina-oversaturated S-type granitoids (Figure 5).

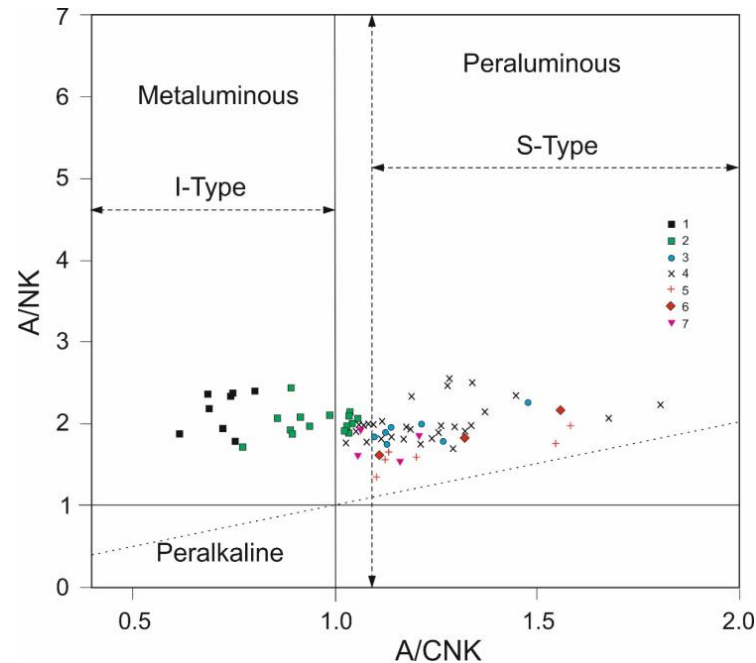


Figure 5. A/NK and A/CNK diagram [45] showing the composition of Alattu-Päskylä granitoids. A/CNK is molecular $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ and A/NK molecular $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$. Boundary I- and S-type granites are borrowed from [46]. 1—gabbro, gabbro-diorites; 2—diorites; 3—quartz diorites; 4—tonalites; 5—plagiogranites; 6—quartz porphyry, rhyolites; 7—rhyodacitic quartz porphyry.

On the Y–Nb, Y+Ta–Rb discriminant diagrams of J. Pearse [47], the felsic rocks of the Alattu-Päskylä intrusion are plotted in the island arc and syncollisional granitoid field (Figure 6).

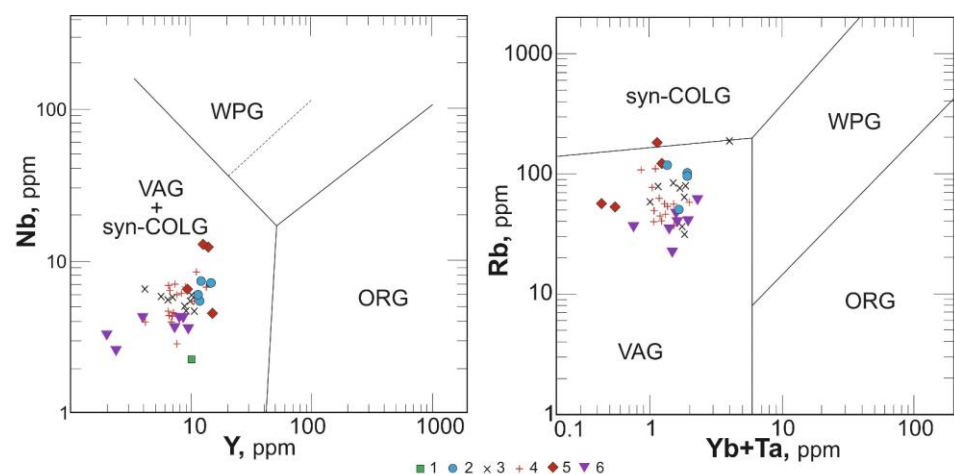


Figure 6. Discriminant Y–Nb and Y+Ta–Rb diagrams for granitoids of J. Pearse [47] (dotted line on Y–Nb diagram: ORG boundary for anomalous rifts); fields on diagrams: ORG—oceanic ridge granites; WPG—within-plaite granites; VAG—volcanic arc granites; syn-COLG—syn-collisional granites. 1—diorites; 2—quartz diorites; 3—tonalites; 4—plagiogranites; 5—quartz porphyry, rhyolites; 6—rhyodacitic quartz porphyry.

Some distinctive petrochemical features are displayed by the rocks making up the Alattu–Päskylä intrusion, such as rhyodacitic quartz porphyry (Table S1). Their median percentage of SiO_2 is 65.5%, and their Mg content ($\text{Mg\#}=0.48$) is even higher than that of gabbro (0.45). They contain Cr_2O_3 —147 ppm, while gabbro is 134 ppm. They also contain barium and strontium ($>0.1\%$ each), as well as alkalis (2.79% K_2O and 3.39% Na_2O). This distinctive feature of rhyodacitic porphyry makes it similar to granitoid of M-type and sanukitoid of mantle origin.

All the rock varieties of the Alattu–Päskylä intrusion, including a dike facies, are similar in the abundance of REE (Table S2) and their distribution spectra (Figure 7). Their median total REE content varies slightly (73–87 ppm), and their distribution is fractionated with moderate enrichment in light lanthanides (LREE/HREE 7.74–10.62, $\text{La}_\text{N}/\text{Yb}_\text{N}$ 8.15–25.62). They are enriched in large ion lithophile elements (LIL) K, Rb and Ba and high field strength (HFS) Th, U, Hf, Ta and Nb, but they are impoverished in transient elements, such as Sc, Cr, Co, Ni and V (Table S3, Figure 8).

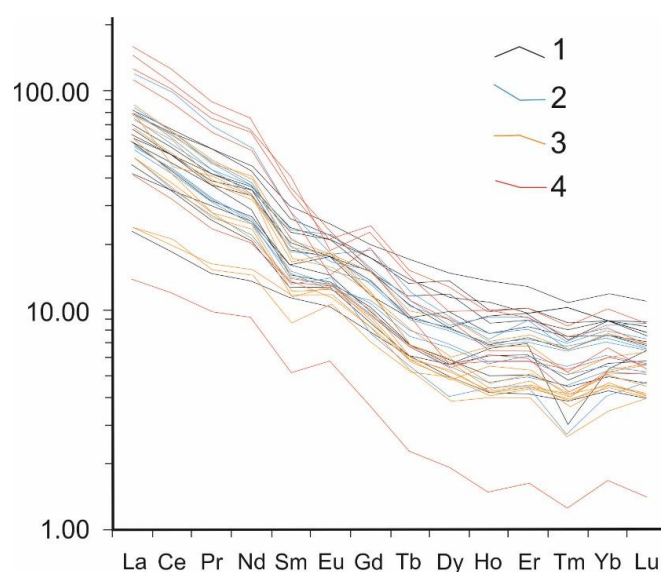


Figure 7. Chondrite-normalized REE patterns [48] of Alattu–Päskylä intrusion rocks and cutting dikes. 1—gabbro, diorites; 2—tonalites; 3—plagiogranites; 4—rhyolites, rhyodacites.

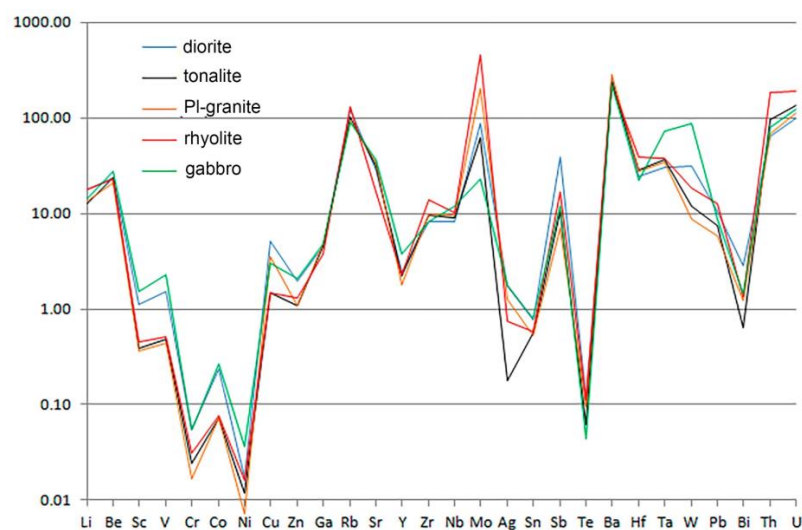


Figure 8. Primitive mantle-normalized trace element spider diagram of rock samples from the Suistamo magmatic complex; NMORB normalization by [48].

4.2. Types of Ore Mineralization in the Alattu–Päskylä Occurrence

4.2.1. Copper–Molybdenum–Porphyry with Gold (Intrusion–Related)-Type Mineralization

This type is represented by quartz–molybdenite ($\pm$ pyrite, chalcopyrite, arsenopyrite, pyrrhotite, sphalerite and gold) stockwork mineralization (Figure 9) in the central portion of the tonalite intrusion, in its south-eastern and south-western endo- and exocontacts, in thin comagmatic dikes and in host metasiltstones.

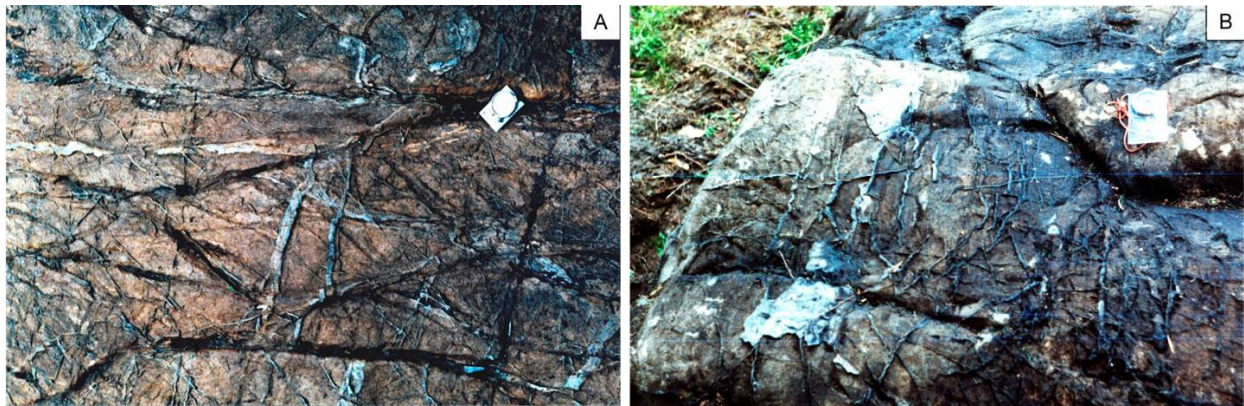


Figure 9. Quartz stockworks with Mo-Cu-As-Au mineralization of porphyry type in tonalites (A) and metasiltstones (B).

Quartz streaks vary markedly in strike from NW to NE and in thickness from 1–2 mm to 1.5–2 cm. Molybdenite-quartz stockwork zones are traced with some intervals over tens of meters. Quartz in the ore streaks shows a distinctive bluish-gray shade of color, and their molybdenite is present as a mixture of polytypes 3R and 2H with 68–175 ppm of rhenium [19,36]. It is concentrated as fine scales and rosette-like intergrowths up to 1.5 cm across and associated with pyrite, chalcopyrite, pyrrhotite and sphalerite. Micron-sized molybdenite inclusions occur in chalcopyrite, and its coarser scales clearly cut associated sulfide grains (Figure 10B). At the exocontacts of quartz streaks, molybdenite is associated with rutile (Figure 10A). It also occurs as 1–3 mm thick monomineral units confined to the earliest “dry” micron-sized fractures. The isochron Re-Os age of Alattu–Päskylä molybdenite is 1914 ± 34 Ma [49].

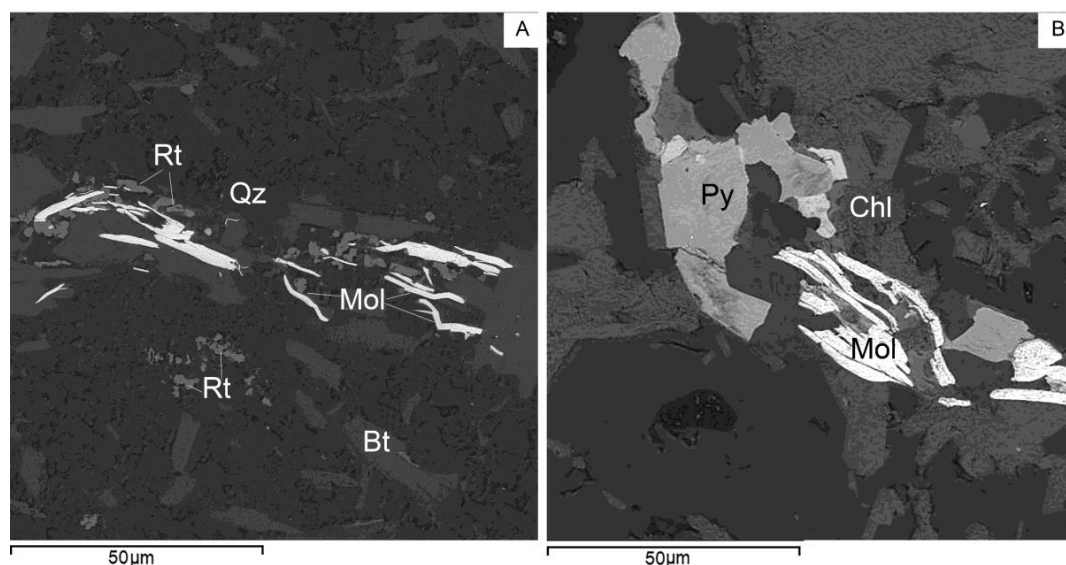


Figure 10. BSE images. Molybdenite (A,B) mineralization in Alattu–Päskylä ores; for more detail, see text. Ccp—chalcopyrite; Mol—molybdenite; Py—pyrite; Qz—quartz; Rt—rutile.

Stockwork molybdenitic mineralization was simultaneous with the crystallization pyrite, pyrrhotite and euhedral acicular arsenopyrite dissemination (Figure S5) along schistosity and silicification planes in host rocks. These sulfides are usually enriched in cobalt (up to 0.2%, up to 0.6% and up to 3.5%, respectively) [21], and arsenopyrite shows the highest percentages of invisible gold (up to 234 ppm) and $\delta^{34}\text{S}$ (−2.10). Micron-sized (1–3 μm) gold, acanthite, hedleyite, bismuth and matildite grains are occasionally present in quartz.

Gabbroic rock dikes accompanying the tonalite intrusion display quartz vein scheelite mineralization. Most gabbroic rocks are highly amphibolized and transformed into amphibolites. Only gabbroic rocks occasionally contain the coarsest quartz-scheelite aggregates, with crystals varying in size up to several centimeters.

4.2.2. Gold–Arsenopyrite–Sulfide Mineralization in Shear–Zones

The structural-rock complex, which controls gold–arsenopyrite–sulfide mineralization, is present as a system of variably large shear zones (Figure 11) with syngenetic metasomatic rocks, corresponding to beresites in granitoids and similar in chemical composition to Ladoga schists, as well as propylites in gabbroic rocks, amphibole schists and skarnoids. Shear zones contrast most in the tonalite intrusion. Elementary planar shearing (Figure 11A), their parallel series (Figure 11B) and shear zones up to 2 m thick, in which tonalities are altered to thin tabular schists, are present (Figure 11D). The displacement range of individual rock fragments occasionally varies in trend and degree. This pattern is best defined when shearing is superposed on thin rhyolite dikes (Figure 11C) and tourmaline veins (Figure 12A), the displacement planes of which are occasionally filled with quartz veins (Figure 12B).

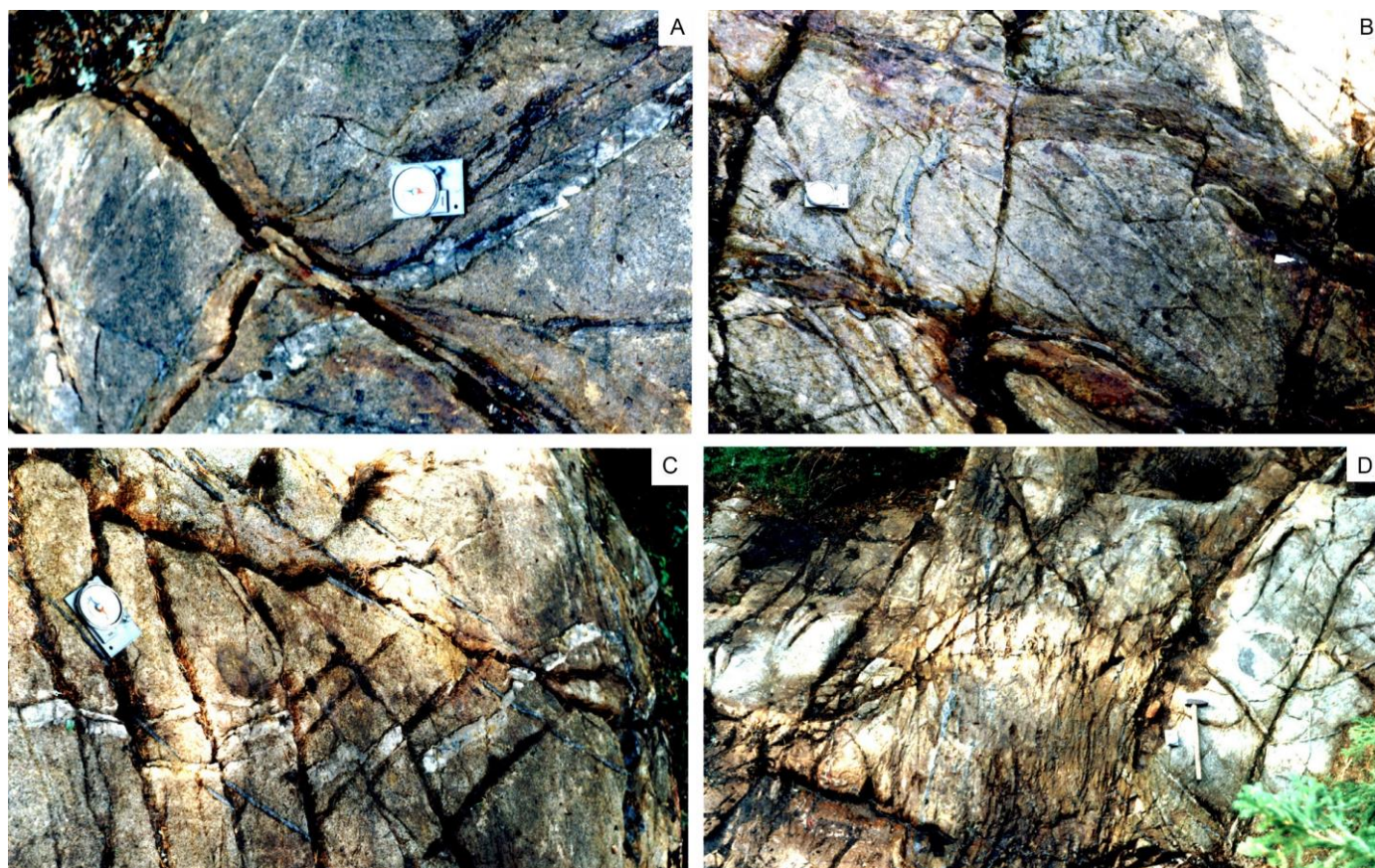


Figure 11. Ore-controlling displacements by shearing in Alattu–Päskylä tonalites (for more details, see text).

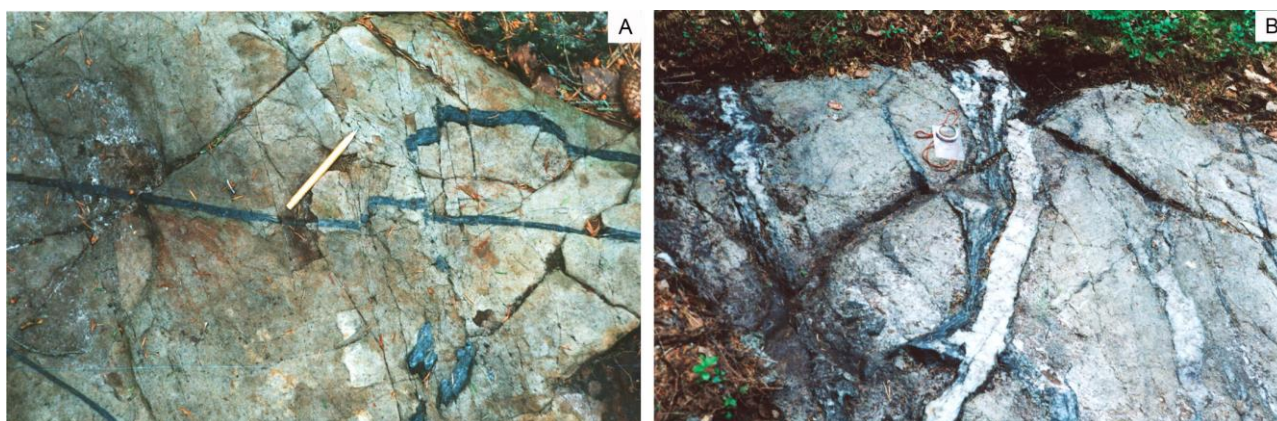


Figure 12. Quartz and tourmaline veins in metasilstones (A) and tonalites (B), subjected to shearing (for more details, see text).

The mineral associations of this type of gold mineralization were formed in several stages, the earliest of which was *gold–arsenopyrite*. Auriferous arsenopyritic mineralization is located in 1–2 m thick linear schistosity zones derived from metasilstones at the exocontacts of metasomatically altered plagioporphphyry dikes and gabbroic stock in the southern portion of the Alattu–Päskylä occurrence. Arsenopyrite ($\delta^{34}\text{S} = +4.99$) occurs as euhedral acicular metacrystals. The arsenopyrite content of the ore is 20%–30%. Visible micron-sized gold in this association is scarce. It is usually present as single micron-sized inclusions in arsenopyrite (Figure 13E), sometimes together with native bismuth, bismuthine, johnassonite and Pb–Sb–S system minerals. Also present here are micron-sized (2–3 μm) rounded Au–Bi alloy grains. Isometric scheelite grains, up to 50 μm , are occasionally connected with this association (Figure S6). The gold content of the samples is 1–3 ppm, that of arsenopyritic concentrate is over 100 ppm and that of arsenopyrite is 71 ppm. This association seems to contain mostly invisible gold.

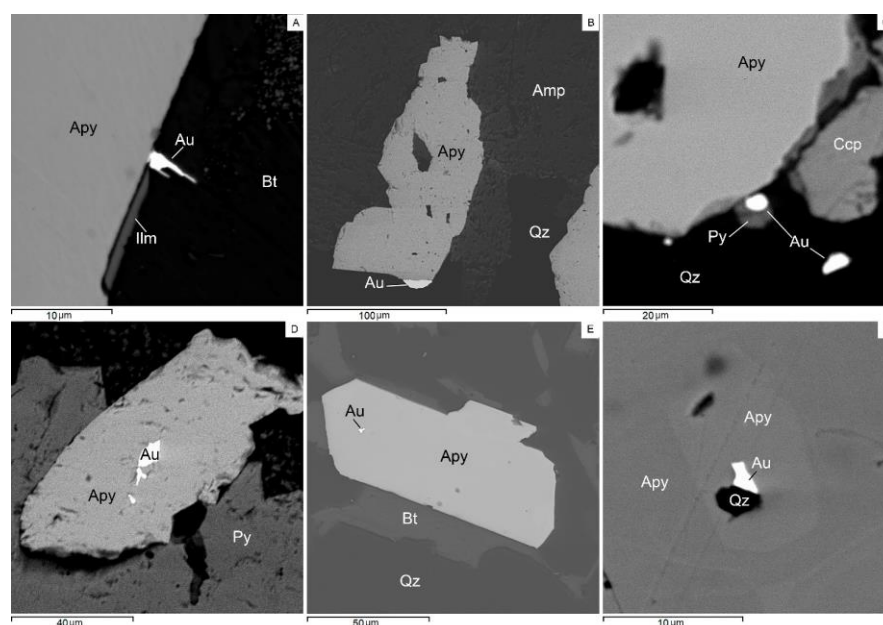


Figure 13. BSE images. Mineralization of gold associated with arsenopyrite: (A–C) gold on arsenopyrite crystal faces; (D–F) gold present as micron-sized inclusions in arsenopyrite. Amp—amphibole; Apy—arsenopyrite; Au—gold; Bt—biotite; Ccp—chalcopyrite; Ilm—ilmenite; Py—pyrite; Qz—quartz. (for more detail, see text).

The next mineral association is *quartz–arsenopyrite*. It is associated with the formation of north-eastern–near-N-S schistosity zones and quartz vein mineralization within the intrusion and at its exocontacts, so that also quartz-biotite streaks with scheelite are formed (Figure S6). NE-trending quartz veins, ranging from 1–3 cm to 20–30 cm in thickness, with arsenopyrite, intersect and sometimes displace quartz-molybdenite veins. Their morphology is often irregular, characterized by pinches and swells. They usually consist of several generations of quartz ranging from colorless to dark-gray varieties with finely dispersed arsenopyrite, pyrite, pyrrhotite, galena, sphalerite and chalcopyrite, which are present in highly variable amounts. Vein minerals, e.g., biotite and feldspar, are common, while brown and black tourmalines are scarcer. Quartz streaks with arsenopyrite are cut by schistosity zones with near-N-S-trending quartz–arsenopyrite streaks. The central portion of the schistosity zones consists of either gray quartz or beresite-like metasomatic rock, and the external portion is made up of quartz-sericitic metasomatic rocks with arsenopyrite dissemination. Such ore bodies are 5–7 m thick, and their arsenopyrite content varies from 2%–3% to 20%–30%. Arsenopyrite ($\delta^{34}\text{S} = +1.19$) is present as coarse euhedral crystals, up to 5–7 mm in size, and granular aggregates, the fractures of which host more recent ore minerals: pyrrhotite, chalcopyrite, jamesonite, boulangerite, falkmanite, meneghinite and other antimony lead sulfosalts, as well as sphalerite, pyrite, galena, hypogenic marcasite and occasionally molybdenite. Micron-sized gold grows on arsenopyrite crystal faces (Figure 13A–C) and is present as micron-sized inclusions in it (Figure 13D,F) and in quartz (Figure S7a,b,d) and biotite (Figure S7c). Coarser gold forms intergrowths with arsenopyrite (Figure 14A,B,F) and micron-sized veinlets, filling its fractures. Gold grains are up to 0.2 mm across. The maximum amount of gold in the samples is 5.6 ppm, that in ore concentrate is over 30 ppm and that of arsenopyrite is 6–24 ppm.

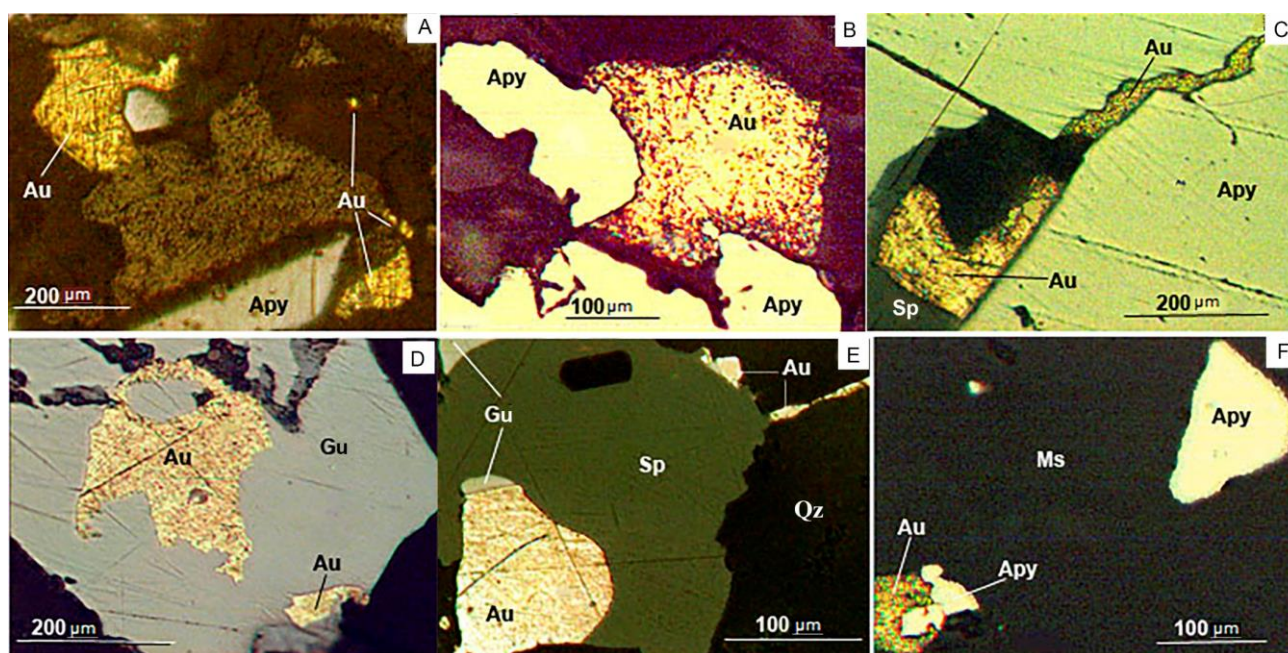


Figure 14. Characteristic morphotypes of native gold (Au) associated with arsenopyrite (Apy), gudmundite (Gu), sphalerite (Sp), quartz (Qz) and muscovite (Ms) (for more detail, see text), reflected by light (for more detail, see text).

A *Gold-polysulfide* mineral association is present mostly in the northern and north-eastern portions of the tonalite intrusion. It is concentrated in thin NW-trending quartz veinlets filling rejuvenated fractures with quartz-molybdenitic or quartz-arsenopyritic mineralization formed earlier and is accompanied by the beresitization of tonalites. One of major minerals in this association is galena. It occurs as separate grains, up to 1–2 mm across, and complex aggregates with many braided and worm-like chalcopyrite, gudmundite and

tetrahedrite inclusions (Figures S8d and 15A,B). Its micron-sized inclusions sometimes occur together with gudmundite and sphalerite inclusions (Figure S8c). Gudmundite is commonly intergrown with chalcopyrite and pyrite (Figure S8a,b), and tetrahedrite occurs as separate galena-rimmed grains (Figure 15A) intergrown with bournonite and galena (Figure 15C) and chalcopyrite and sphalerite (Figure 15E) as micron-sized veinlets cutting chalcopyrite (Figure 15D) and as micron-sized inclusions in sphalerite (Figure 15F). The composition of tetrahedrite varies considerably up to argentotetrahedrite with up to 31% Ag (Table 1), which is strongly correlated negatively with Cu (Figure 16). Its other secondary elements are poor in Zn (0%–4.5%) and As (0%–4.96%). The composition of gudmundite is close to stoichiometric (Table S4). Sphalerite has a relatively stable composition (Table S5). It contains variable amounts of iron, no copper, as shown by most analyses, and small amounts of cadmium.

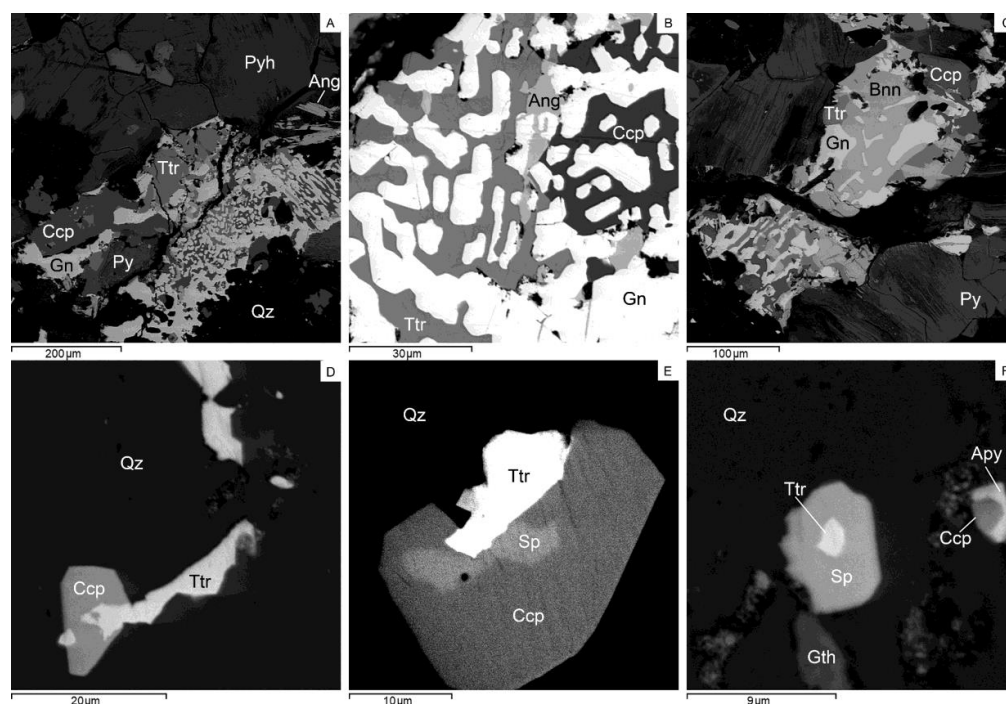


Figure 15. BSE images. Mineral associations of tetrahedrite [Ttr, $(\text{Cu},\text{Ag})_{10}(\text{Fe},\text{Zn},\text{Mn},\text{Cd},\text{Hg})_2(\text{Sb},\text{As},\text{Bi},\text{Te})_4(\text{S},\text{Se})_{13}$]. Ang—anglesite, PbSO_4 ; Apy—arsenopyrite; Bnn—bournonite, PbCuSbS_3 ; Ccp—chalcopyrite; Gn—galena; Gth—goethite; Py—pyrite; Pyh—pyrrhotite; Qz—quartz; Sp—sphalerite. (for more detail, see text).

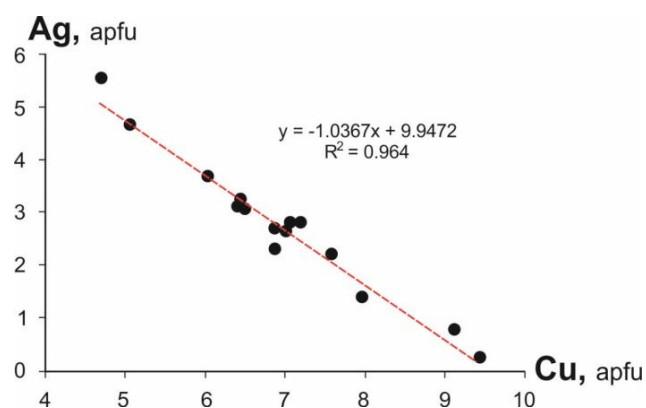


Figure 16. Plot of Cu vs. Ag (apfu) of tetrahedrite – group minerals from the Alattu–Päskylä ore occurrence. (for more detail, see text).

Table 1. Representative electron microanalyses and atomic proportions of tetrahedrite, $(\text{CuFeAgZn})_{12}(\text{SbAs})_4\text{S}_{13}$.

wt. %	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cu	37.24	33.81	29.66	27.20	25.31	24.98	24.44	25.44	23.21	22.55	22.65	21.10	17.31	15.61
Fe	5.09	5.81	4.35	6.14	5.76	5.37	5.62	5.13	5.22	5.75	5.87	5.69	7.65	5.72
Zn	2.10	2.44	2.89	1.29	4.50	1.11	1.33	bd	1.45	bd	bd	bd	1.15	bd
Ag	1.78	4.88	8.81	13.49	14.37	16.04	16.27	16.83	18.58	18.83	19.35	22.00	27.05	31.33
Sb	22.82	28.92	29.47	28.13	25.52	28.16	27.85	28.56	27.88	27.13	27.80	27.58	25.20	26.19
As	4.96	bd	bd	bd	0.58	bd	bd	bd	bd	bd	bd	bd	bd	bd
S	26.39	23.67	25.30	23.26	24.36	23.76	23.64	23.42	24.04	23.70	23.53	23.48	21.65	21.28
U	bd	bd	bd	bd	bd	bd	bd	bd	bd	1.17	bd	bd	bd	bd
Total	100.38	99.53	100.51	99.51	100.40	99.42	99.15	99.38	100.38	99.14	99.19	99.87	99.72	100.13
Chemical formula														
Cu	9.431	9.121	7.955	7.572	6.873	7.006	6.876	7.195	6.490	6.435	6.447	6.029	5.063	4.695
Fe	1.467	1.784	1.328	1.946	1.781	1.714	1.801	1.650	1.662	1.858	1.900	1.853	2.549	1.957
Zn	0.516	0.638	0.757	0.351	1.186	0.305	0.365		0.394				0.325	
Ag	0.267	0.777	1.392	2.213	2.300	2.648	2.697	2.804	3.060	3.164	3.248	3.703	4.663	5.551
Sb	3.016	4.072	4.124	4.086	3.619	4.121	4.089	4.217	4.069	4.040	4.130	4.115	3.848	4.112
As	1.064				0.133									
S	13.241	12.609	13.444	12.833	13.108	13.204	13.175	13.134	13.325	13.403	13.273	13.299	12.551	12.682
U										0.090				

bd—below detection limit.

Bournonite and Pb–Sb–S system sulfosalts are widespread in this association. Bournonite often contains micron-sized sulfosalt, galena and chalcopyrite inclusions (Figure 17A–C). The chemical composition of bournonite does not depend on the associated minerals and is consistent with the stoichiometric composition (Table 2). Pb–Sb–S sulfosalts (boulangerite— $\text{Pb}_5\text{Sb}_4\text{S}_{11}$, jamesonite— $\text{FePb}_4\text{Sb}_6\text{S}_{14}$, robinsonite— $\text{Pb}_4\text{Sb}_6\text{S}_{13}$, freieslebenite— $\text{AgPb}(\text{SbS}_3)$ (Figure 17D–F), meneghinite— $\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$, twinnite— $\text{Pb}(\text{Sb},\text{As})_2\text{S}_4$, plumosite— $\text{Pb}_2\text{Sb}_2\text{S}_5$, plagionite— $\text{Pb}_5\text{Sb}_8\text{S}_{17}$, heteromorphite— $\text{Pb}_7\text{Sb}_8\text{S}_{19}$, falkmanite— $\text{Pb}_3\text{Sb}_2\text{S}_6$, geocronite— $\text{Pb}_{14}(\text{SbS}_3)_6\text{S}_{23}$ and fülöppite— $\text{Pb}_3\text{Sb}_8\text{S}_{15}$), except for boulangerite, jamesonite, robinsonite and falkmanite, are often present as cryptogranular aggregates intergrown with other minerals. Hence, their compositions differ from stoichiometric compositions, as shown by microprobe analysis (Tables S6–S10). Therefore, their position on the triple Pb–Sb–S diagram (Figure S9) is not sufficiently accurate and informative.

Table 2. Representative electron microanalyses and atomic proportions of bournonite, $\text{PbCu}(\text{SbS}_3)$.

wt. %	1	2	3	4	5	6	7	8	9	10
Pb	41.93	41.85	41.57	41.90	41.35	40.37	41.99	42.45	42.59	41.89
Cu	12.81	12.46	12.47	12.84	12.63	12.93	12.43	12.53	12.05	12.42
Sb	25.54	25.70	25.54	25.44	24.82	25.53	25.17	25.01	25.32	25.13
S	18.51	19.34	19.57	19.59	20.05	20.19	19.62	19.08	19.35	19.33
Total	98.79	99.36	99.14	99.77	98.85	99.03	99.20	99.07	99.31	98.96
Chemical formula										
Pb	1.019	0.999	0.989	0.991	0.976	0.944	0.999	1.022	1.022	1.009
Cu	1.015	0.970	0.968	0.991	0.972	0.986	0.964	0.984	0.943	0.971
Sb	1.057	1.045	1.034	1.024	0.997	1.016	1.019	1.025	1.034	1.025
S	2.909	2.986	3.009	2.995	3.056	3.053	3.017	2.969	3.001	2.995

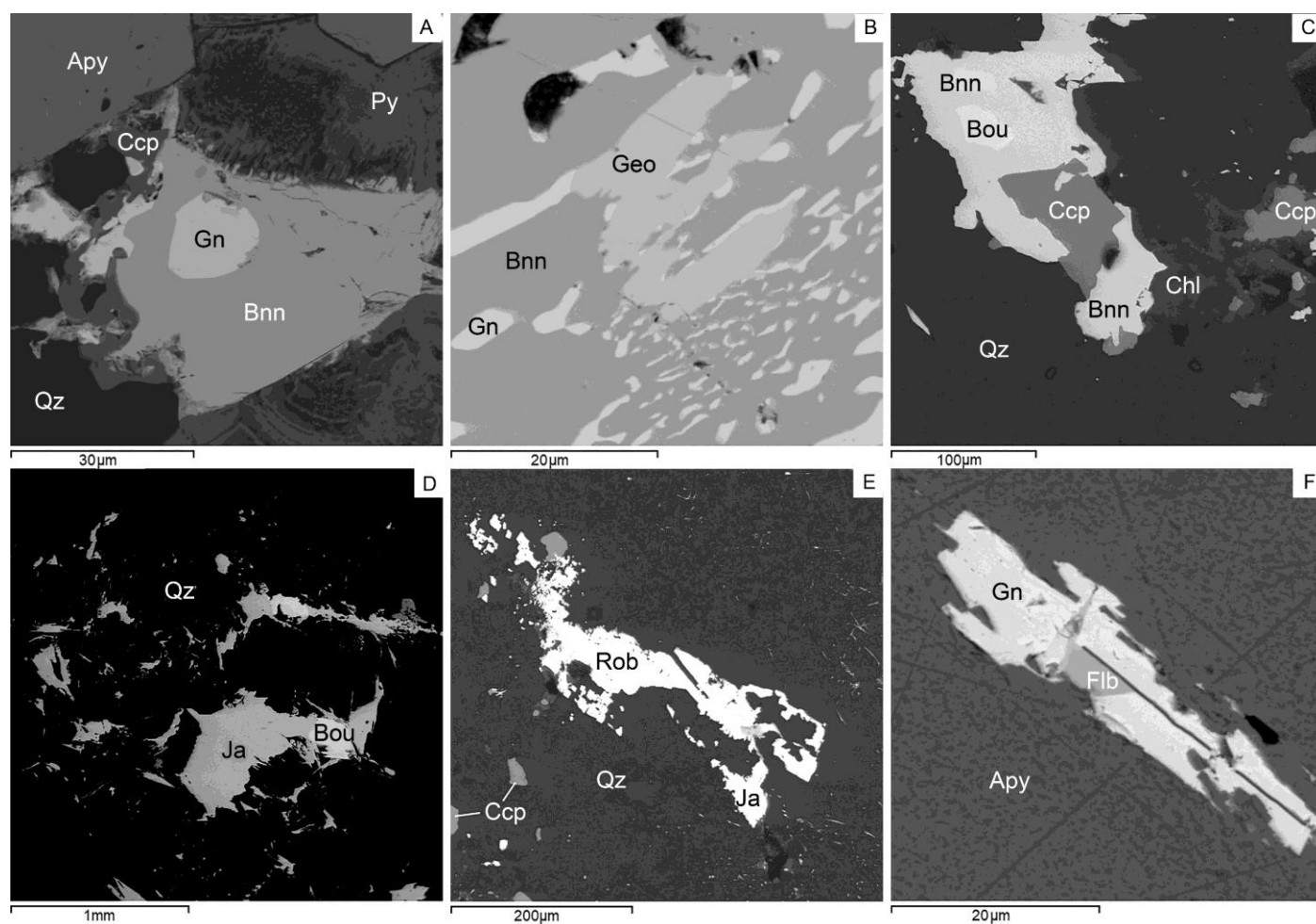


Figure 17. BSE images. Bournonite (Bnn, PbCuSbS_3) and Pb–Sb–S system minerals of gold–polysulfide mineral association. Apy—arsenopyrite; Bou—boulangerite, $\text{Pb}_5\text{Sb}_4\text{S}_{11}$; Ccp—chalcopyrite; Chl—chlorite; Flb—freieslebenite, $\text{AgPb}(\text{SbS}_3)$; Geo—geocronite, $\text{Pb}_{14}(\text{SbS}_3)_6\text{S}_{23}$; Gn—galena; Ja—jamesonite, $\text{FePb}_4\text{Sb}_6\text{S}_{14}$; Pyh—pyrrhotite; Qz—quartz; Rob—robinsonite, $\text{Pb}_4\text{Sb}_6\text{S}_{13}$. (for more detail, see text).

Micron-sized gold is present in galena, tetrahedrite and quartz. Its coarser aggregates occur in gudmundite and sphalerite (Figure 14D,E). Micron-sized aggregates occasionally occur together with sphalerite and arsenopyrite (Figure 14C). The highest amounts of gold are 30 ppm in point samples and 2–6 ppm in arsenopyrite. The $\delta^{34}\text{S}$ of arsenopyrite is +0.70.

Ore genesis was terminated by the formation of a *gold–antimony* mineral association, which is present only in the shear zone cutting eruptive tonalite breccia in the north-eastern portion of the intrusion. The zone strikes north-east (20°), dips subvertically and is 20–40 cm thick. It is made up of two generations of quartz: a gray generation highly ochred by iron oxides with disseminated ore mineralization and a light-gray almost white ore-free generation. Ore minerals are dominated by auriferous (up to 100 ppm Au) gudmundite forming radiate-fibrous aggregates and intergrowths of rhomboprismatic crystals up to 1 cm in length. Gudmundite is also present as intergrowths with native auriferous (up to 0.25% Au) antimony (Figure 18A) characterized by a variety of forms of existence and grain morphology (isometric, drop-shaped, romb-like, etc.) (Figure 18B). Antimony is often intergrown with pyrrhotite, as well as chalcopyrite and sphalerite. Similar forms of presence and morphological features are displayed by stibnite. It occurs as prismatic crystals, intergrown crystals in kaolinitized feldspar and veinlets in quartz and pyrrhotite

(Figure 18C,D), Stibnite locally replaces pyrrhotite. The chemical composition of stibnite and berthierite, which often occur together with it, is near-stoichiometric (Table 3).

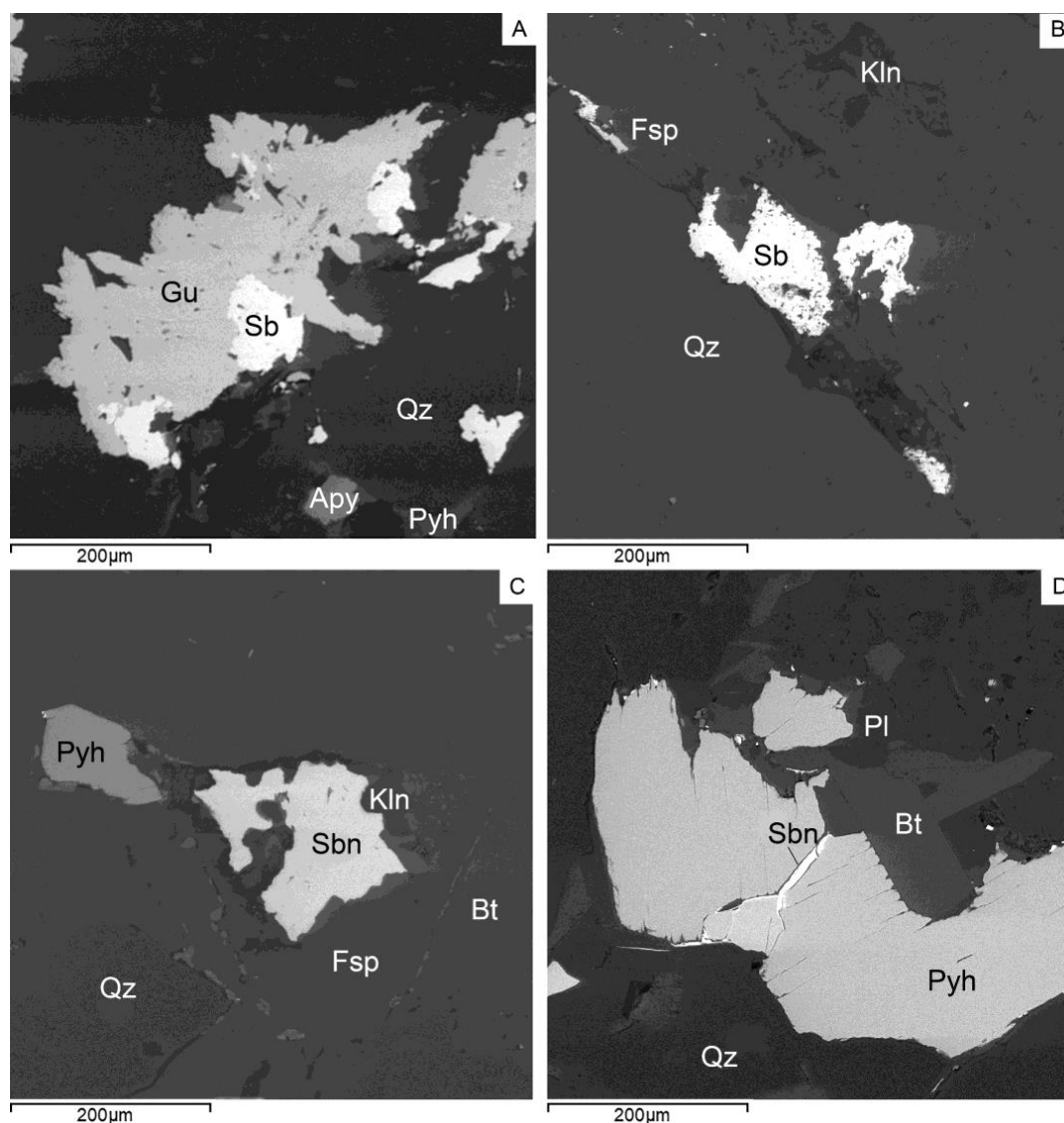


Figure 18. BSE images. Gudmundite, native antimony and stibnite of gold–antimony association. Apy—arsenopyrite; Bt—biotite; Fsp—feldspar; Gu—gudmundite; Kln—kaolinite; Pyh—pyrrhotite; Pl—plagioclase; Qz—quartz; Sb—antimony; Sbn—stibnite. (for more detail, see text).

Table 3. Representative electron microanalyses and atomic proportions of stibnite, Sb_2S_3 (1,2) and berthierite, FeSb_2S_4 (3).

wt. %	1	2	3
Fe	1.63	bd	12.61
Sb	71.18	72.39	57.56
S	26.57	27.25	28.98
Total	99.38	99.64	99.16
Chemical formula			
Fe	0.101		0.987
Sb	2.026	2.058	2.065
S	2.873	2.942	3.948

bd—below detection limit.

Ullmannite is a widespread mineral in gold–antimony association. It is closely associated with pyrrhotite, growing on its crystal faces or forming graphic intergrowths with chalcopyrite (Figure 19A,B,D). Ullmannite often contains a few percent to 21 percent cobalt, which corresponds to the composition of costibite (Table 4). On the triple NiSbS–CoSbS–FeSbS diagram (Figure S10), the compositions of these minerals display a wide range of immiscibility. Costibite is present as anhedral grains, no more than 10 μm in size. It is usually associated with pyrite (Figure 19C). Other minerals present in this association in small amounts are arsenopyrite, sphalerite, antimonial lead sulfosalts and gray ore (fahlore). Submicron-sized native gold is present in quartz and in metasomatized metasilstone fragments. Its content of point samples is up to 17 ppm.

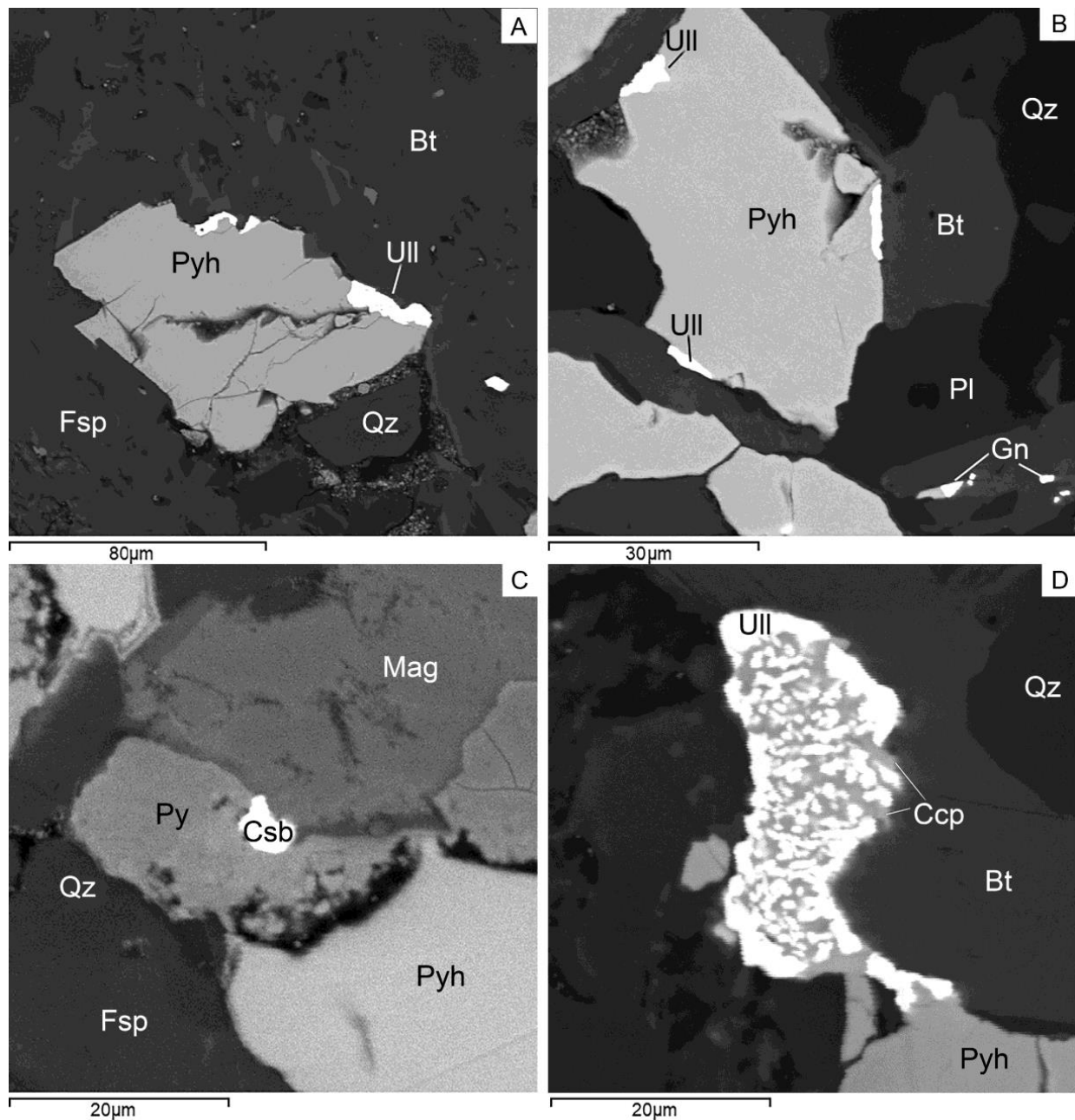


Figure 19. BSE images. Typical mineral associations of ullmannite (Ull, NiSbS) and costibite (Csb, CoSbS) of gold–antimony mineral associations. Bt—biotite; Ccp—chalcopyrite; Fsp—feldspar; Gn—galena; Mag—magnetite; Pl—plagioclase; Pyh—pyrrhotite; Qz—quartz. (for more detail, see text).

Table 4. Representative electron microanalyses and atomic proportions of ullmannite, NiSbS (1–13) and costibite, CoSbS (13–14).

wt. %	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ni	28.36	27.76	26.44	25.86	25.24	25.71	25.62	27.14	25.15	24.00	23.36	18.52	6.96	4.11
Co	bd	bd	bd	bd	bd	0.59	1.33	1.50	1.70	1.79	3.30	5.45	17.71	21.24
Fe	bd	1.28	1.04	bd	bd	2.81	3.38	1.31	bd	3.09	1.54	4.73	4.90	2.66
Sb	55.19	56.70	57.86	58.38	59.37	56.55	54.96	56.50	56.99	56.12	55.81	53.40	52.87	56.43
S	15.86	13.39	15.17	15.07	15.06	13.97	15.37	14.03	15.61	14.54	15.15	17.31	18.17	15.89
Total	99.41	99.13	100.51	99.31	99.67	99.62	100.66	100.48	99.45	99.54	99.16	99.41	100.61	100.33
Chemical formula														
Ni	1.030	1.028	0.953	0.951	0.929	0.940	0.910	0.982	0.911	0.870	0.845	0.644	0.236	0.146
Co						0.021	0.047	0.054	0.061	0.065	0.119	0.188	0.598	0.752
Fe		0.050	0.039			0.108	0.101	0.050		0.118	0.059	0.173	0.175	0.099
Sb	0.967	1.013	1.006	1.035	1.055	0.997	0.941	0.986	0.994	0.981	0.974	0.895	0.864	0.968
S	1.004	0.909	1.001	1.014	1.016	0.935	1.000	0.929	1.034	0.966	1.004	1.101	1.128	1.034

bd—below detection limit.

The ubiquitous mineral in all the mineral associations revealed is arsenopyrite. It varies in composition in each association but shows no significant differences (Tables S11 and S12). However, arsenopyrites with invisible and visible gold differ in the morphology of aggregates and the degree of heterogeneity of their composition (Table 5).

Table 5. Variations in the chemical composition, formation temperature and sulfur fugacity of arsenopyrite [50,51] with visible and invisible gold from the various mineral associations of the Alattu-Päkylä ore occurrence.

	Cu–Mo with Apy and Au Mineralization		Au–Apy Mineral Association		Qz–Apy Mineral Association		Polysulfide Mineral Association	
	Apy with Visible Au	Apy with Invisible Au	Apy with Visible Au	Apy with Invisible Au	Apy with Visible Au	Apy with Invisible Au	Apy with Visible Au	Apy with Invisible Au
As/S	0.763–0.926	0.804–1.028	0.734–1.145	0.748–0.975	0.753–0.931	0.882–1.033	0.891	0.773–0.989
Fe, at. %	33.50–33.60	31.53–34.67	32.17–34.40	32.37–34.63	32.67–34.27	32.30–33.87	33.87	32.00–33.87
As, at. %	28.73–31.97	30.51–33.10	28.65–35.30	28.63–32.24	28.74–32.07	31.70–34.33	33.55	29.08–33.04
S, at. %	34.53–37.67	32.23–37.96	30.83–39.02	34.23–38.70	34.43–38.13	33.37–35.93	34.96	33.25–37.75
T °C	270–410	310–490	260–560	260–370	270–420	340–470	330	280–490
Log <i>f</i> S ₂	−12.5–−7.0	−12.6–−4.3	−14–−4.3	−13.8–−8.5	−11.3–7.0	−11.3–−7.7	−11.8	−12.0–−4.6

Arsenopyrites with invisible gold usually occur as euhedral compositionally homogeneous crystals (Figure S5). Arsenopyrites closely associated with visible gold (micron-sized inclusions, buildups on crystal faces and intergranular filling) bear traces of multiple late hydrothermal-metasomatic alterations. Their grain structure includes BSE domains with considerable variations in the amounts of As and S, as indicated by BSE images (Figure 20). Most domains lose primary grain morphology, showing an irregularly mottled and striated structure produced by different As and S concentrations (Figure 20A–C). Rims enriched in As and depleted in S (Figure 20D–F) are formed on arsenopyrite more seldomly. The Fe concentration does not vary markedly.

Gold is present in all veined material and metasomatic rock samples from each of the above mineral associations. Its concentration varies from tens of ppb to 30 ppm, and its size ranges from less than 1 µm to 0.2 mm. Hence, the gold concentration estimated by assay could be much lower, because it was impossible to convert a certain part of finely dispersed (<50 µm) gold, which cannot be extracted upon attrition of the samples, into the alloy analyzed [52]. Native gold varies in composition from high-grade gold to electrum and silver gold (Table S13). These variations were shown to be most considerable for micron-sized gold inclusions in arsenopyrite (25%–40% Ag) and in crystals grown on its crystal faces (11%–50% Ag) and less considerable for micron-sized streaky gold (40%–50%),

with the highest Hg concentration of 8% (Table S13) but with twice the maximum possible low concentration of 19.8% [53]. The ores of gold-arsenopyritic mineral concentration occasionally contain micron-sized aggregates of Au–Bi alloys (Figure 21B, Table 6) and the gold mineral johnnassonite (Table 6). In addition, the ores contain silver minerals, such as acanthite, matildite and miargyrite (Figure 21A, Table 6). Hence, they contain 0.22% Ag, 0.11%–>1% As, 0.3% Sb and Bi, 0.001%–1% Pb, 0.2% Zn, 0.15% Mo, 0.003%–0.02% Cu and 0.1% B.

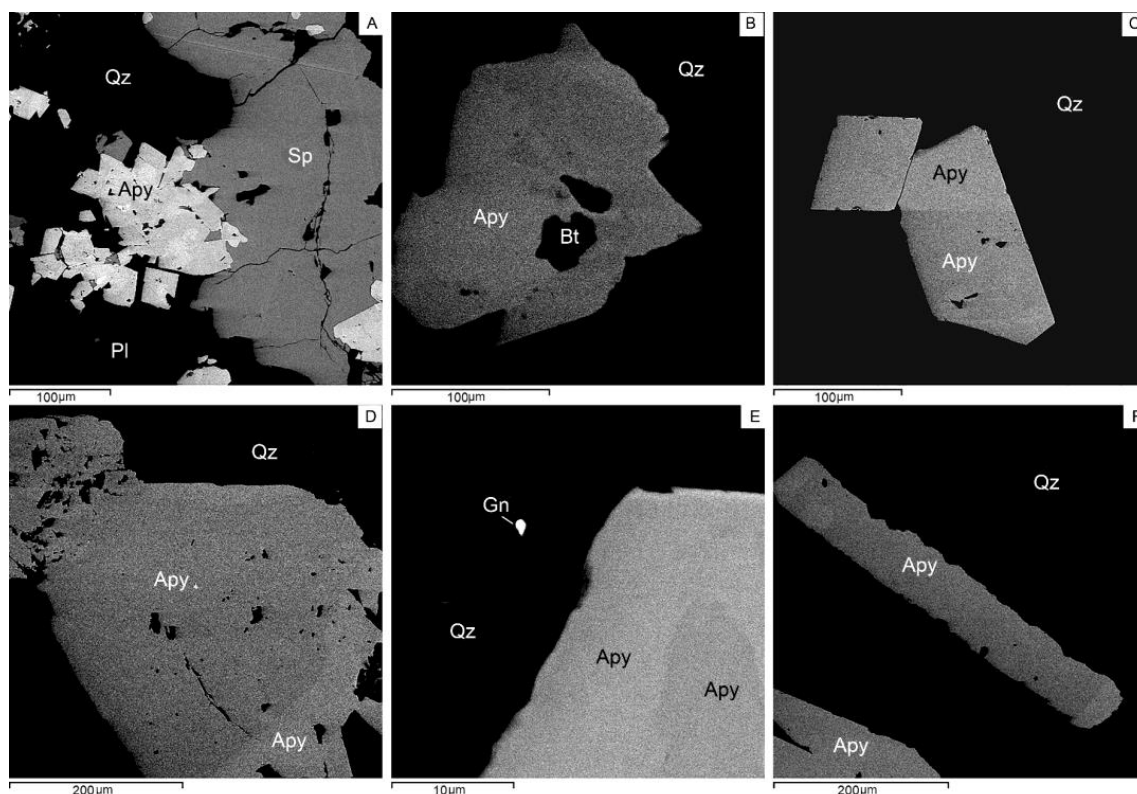


Figure 20. BSE images. Characteristic forms of alterations (lighter) in Alattu–Päkylä auriferous arsenopyrites (for more detail, see text). Altered domains in arsenopyrite are enriched in As and depleted in S. Apy—arsenopyrite; Bt—biotite; Gn—galena; Pl—plagioclase; Qz—quartz; Sp—sphalerite. (for more detail, see text).

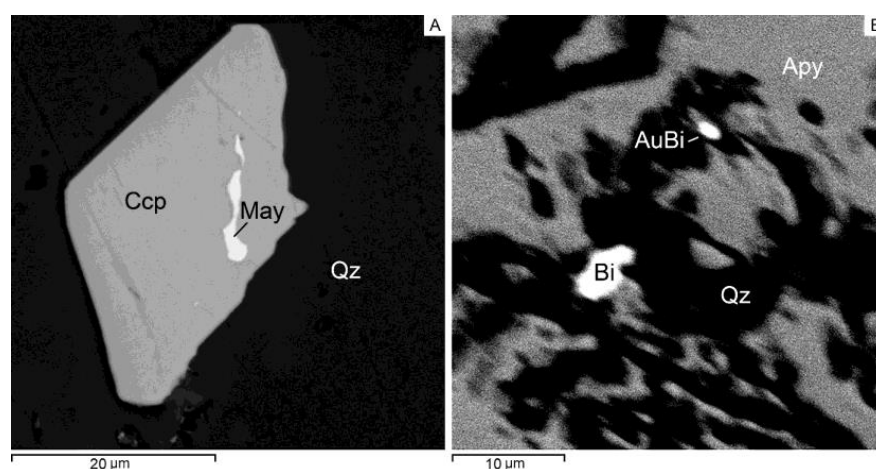


Figure 21. BSE images. Miargyrite (May, AgSbS_2), AuBi alloy (AuBi , $\text{Au}_{0.54-0.55}\text{Bi}_{0.45-0.46}$) and native bismuth (Bi) associated with chalcopyrite (Ccp), arsenopyrite (Apy) and quartz (Qz). (for more detail, see text).

Table 6. Representative electron microanalyses and atomic proportions of jonassonite $\text{Au}(\text{BiPb})_5\text{S}_4$ (1), matildite AgBiS_2 (2), miargyrite AgSbS_2 (3) and Au–Bi alloy (4,5).

wt. %	1	2	3	4	5
Ag	bd	26.52	34.95	bd	bd
Au	15.06	4.76	bd	52.37	53.42
Bi	70.06	45.26	bd	48.22	47.31
Sb	bd	bd	41.54	bd	bd
Pb	4.61	bd	bd	bd	bd
S	9.44	23.24	22.42	bd	bd
Total	99.17	99.76	98.91	100.59	100.73
Chemical formula					
Ag		0.811	0.950		
Au	1.051	0.080		0.535	0.545
Bi	4.606	0.715		0.465	0.455
Sb			1.000		
Pb	0.306				
S	4.036	2.394	1.050		

bd—below detection limit.

5. Discussion

The gold mineral associations of the Alattu–Päskylä ore occurrence are of two types of mineralization: (1) a copper–molybdenum–porphyritic type with gold (intrusion-related) and (2) a gold–arsenopyrite–sulfide type in shear zones. An early type of Cu–Mo–Au mineralization is present mainly within the tonalite intrusion dated at 1884.8 ± 3.2 Ma [36]. Molybdenite was dated at 1914 ± 34 Ma [49]. After this, there were two stages of regional metamorphism in the Ladoga structure, including the Alattu–Päskylä area: an Early Svecofennian stage, 1.89–1.86 Ga, and a Late Svecofennian stage, 1.83–1.79 Ga [27], in which gold mineralization was formed in shear zones. According to Y.L. Gulbin [54], the metamorphic parameters of Ladoga metapelites at the prospect adjacent on the north-west to the Alattu–Päskylä occurrence were T 519–522 °C, P 7–7.2 kbar (early) and 570–600 °C, P 3.6–4.1 kbar (late). Shear zones with low-temperature metasomatites and gold–arsenopyrite and quartz–arsenopyrite mineralization are superimposed on lenses of garnet-bearing skarnoids in the Ladoga shales at the ore occurrence.

Consequently, the formation of the mineralization seems to have fallen into three stages: 1—a post-magmatic stage associated with tonalite intrusion; stages 2 and 3 are associated with Early and Late Svecofennian metamorphism. The mineralization formed at stage 1 was remobilized, and new mineralization was formed in shear zones resting on all the rocks, including tonalites. The similar values of the Pb model age (2150–2200 Ma) and those of the isotopic composition of Pb and $^{238}\text{U}/^{204}\text{Pb}$ (9.4–9.75) for the feldspars of the tonalite intrusion and pyrite of the gold mineralization [55] and ϵNd (−4 up to −5) [19] suggest that they were formed during Svecofennian plutonic and tectono-thermal events, in which the substances of the mantle–crustal reservoir were involved in the formation of magma and mineralization. The model Pb age of feldspars and sulfides, which is older than that of zircon (1884.8 ± 3.2), seems to be due to the effect of the Archean crust, because the tonalite intrusion is located near the Archean Karelian Craton (Figure 1).

Thus, the Alattu–Päskylä gold occurrence was completely produced by the evolution of three endogenic processes separated in time by ~100 Ma, although the possible effect of the Janisjärvi astrobleme cannot be ruled out. The assumed multi-stage genesis of the ore occurrence affected the complex correlations of various mineral associations, the hydrothermal alterations of ore minerals and considerable variations in their composition. This is clearly applicable to arsenopyrite, which often has intragranular composite zones (Figure 20A) produced by hydrothermal alterations. Its composition differs greatly (Tables S11 and S12) from stoichiometric (Figure 22A). Fe in arsenopyrite varies less markedly than As and S, for which a strong negative correlation was revealed (Figure 22B).

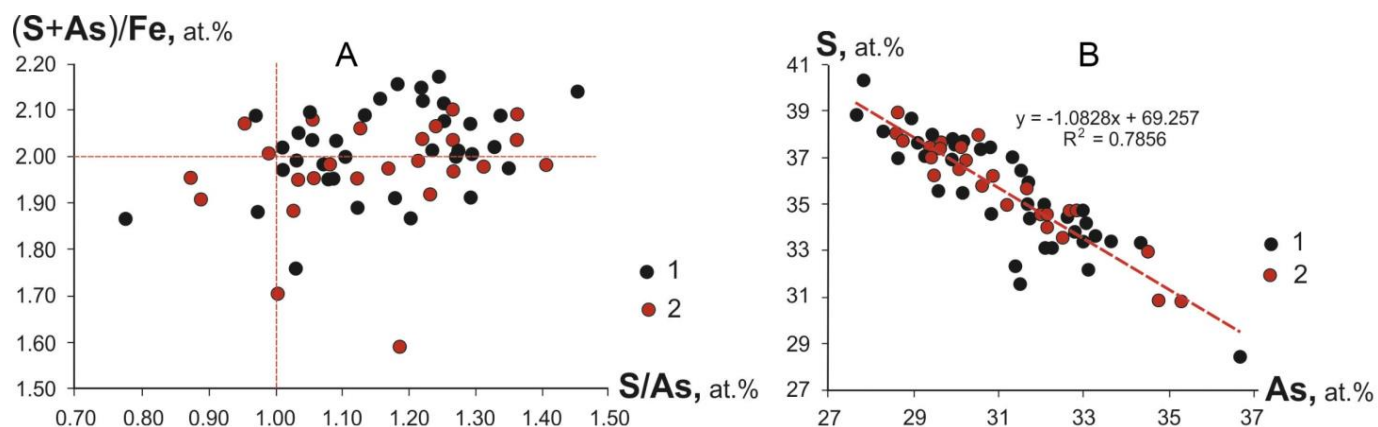


Figure 22. (A). Chemical composition of arsenopyrite in coordinates S/As and (S + As)/Fe. Intersection of the composition lines S/As = 1 and (S + As)/Fe = 2 is consistent with chemical stoichiometry. (B). Plot of As vs. S (at.%) of Alattu-Päskylä arsenopyrite. 1—arsenopyrites with invisible gold; 2—arsenopyrites with visible gold.

Similar variations in the composition of original arsenopyrite were reported for many deposits [1]. The $\delta^{34}\text{S}$ values in arsenopyrite varied from -2.10 to $+4.99$, suggesting [56] that granites acted as a source and that a mantle source was involved as well. Alattu-Päskylä arsenopyrites of various mineral associations with visible and invisible gold, as well as their physicochemical parameters (T °C, $\log f\text{S}_2$) of formation, did not differ greatly in composition (Table 5, Tables S11 and S12; Figure 22), presumably due to their multiple metamorphisms. Only in a few cases was visible gold confined to altered arsenopyrite domains inside original arsenopyrite grains with invisible gold (Figure 13F). Micron-sized gold aggregates were deposited more commonly on arsenopyrite crystal faces due to chemisorption [57,58] (Figure 13A,B). Altered arsenopyrite shows higher (to >500 °C) formation temperatures (after) [50,51] than original arsenopyrite (<500 °C). These temperature and sulfur fugacity values are doubtful due to the two-fold effect of metamorphism on the original arsenopyrite mineralization and the possible involvement of more recent (~ 1 Ga) impactogenesis. The remobilization of invisible gold in arsenopyrite is due to a decline in its solubility in this sulfoarsenide with a rise in temperature [4,59,60]. The paragenetic sequence, associated with the deposition of invisible and visible gold at the Alattu-Päskylä ore occurrence, is generally similar to that in the Archean Boorara and Bardoc Shear Systems, Yilgarn Craton, Western Australia [1]: pyrrhotite (present occasionally as inclusions in arsenopyrite) + unaltered arsenopyrite (with invisible gold) $\rightarrow$ altered arsenopyrite (arsenic-enriched) + pyrite $\pm$ pyrrhotite + visible gold.

However, Alattu-Päskylä ores also contain gold that is not associated with arsenopyrite. It is associated with quartz, mica (Figure S7a,c), gudmundite and sphalerite and is present in an unknown form (Figure 14D,E) in native antimony and gudmundite. This gold mineralization has been reported only from the northern portion of the tonalite intrusion, which is cut here by rhyodacitic porphyry of unknown age. Therefore, this gold, like the entire antimony mineralization, including argentotetrahedrite, the formation temperature of which is below 170 °C, as indicated by the geothermometer [61] (Figure S11), could have been produced by hydrothermal processes in connection with rhyodacitic porphyry or with a retrograde stage in late Svecofennian metamorphism.

6. Conclusions

The Alattu-Päskylä gold occurrence is of polygenetic origin. Its gold mineral associations fall into two types of mineralization: (1) a copper-molybdenum-porphyry type with gold (intrusion-related) and (2) a gold-arsenopyrite-sulfide type in shear zones. Type 1 was produced by shallow-depth tonalite and type 2 by two stages of Svecofennian metamorphism. Hence, ore mineralization is present as several consecutive mineral associations:

a pyrite-molybdenite association with arsenopyrite and gold, a gold–arsenopyrite association, a quartz–arsenopyrite association with antimonial lead sulfosalts, a gold–polysulfide association with tetrahedrite–argentotetrahedrite series minerals and a gold–antimony association with Pb–Sb–S system minerals and native antimony. The Alattu–Päskylä occurrence was completely formed by three endogenic processes spaced apart by ~100 Ma (1.89–1.8 Ga) and possibly by the impactogenesis of the Janisjärvi astrobleme. These events were responsible for the complex correlations of various mineral associations, the hydrothermal alteration of ore minerals and considerable variations in their composition. The latter is mostly characteristic of arsenopyrite. Fe in arsenopyrite varies less markedly than As and S. Arsenopyrites with visible gold do not differ greatly from those with invisible gold due to multiple hydrothermal-metamorphic events. The maximum invisible gold concentration in arsenopyrite is 234 ppm, and the minimum concentration is 2 ppm. Visible gold in arsenopyrite occurs in its altered As-enriched high-temperature domains and on its crystal faces. Altered arsenopyrite with visible gold shows a higher formation temperature (up to >500 °C) than original arsenopyrite with invisible gold (<500 °C). Gold, which is not associated with arsenopyrite but is associated with quartz, mica, gudmundite, sphalerite and native antimony, seems to have been formed by hydrothermal processes in connection with kainotypic rhyodacitic porphyry, which cuts the tonalite intrusion, or with a retrograde stage in late Svecofennian metamorphism. The similar values of Pb model age (2150–2200 Ma), the isotopic composition of Pb and $^{238}\text{U}/^{204}\text{Pb}$ (9.4–9.75) for the feldspar of the tonalite intrusion and the pyrite of gold mineralization [55], ϵNd (−4 to −5) [19] and $\delta^{34}\text{S}$ values in arsenopyrite (2.10–4.99) indicate that the Alattu–Päskylä gold occurrence was formed during Svecofennian plutonic and tectono-thermal events and that the substance of the mantle-lower crustal reservoir was involved in magma formation and mineralization.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14111172/s1>, Figure S1: Eruptive tonalite breccias; Figure S2: Exo- and endocontacts of tonalite intrusion; Figure S3: Distribution of the major petrographic rock varieties in the Alattu–Päskylä bimodal magmatic complex on the R1–R2 diagram [43]. $R1 = 4\text{Si} - 11(\text{Na} + \text{K}) - 2(\text{Fe} + \text{Ti})$; $R2 = 6\text{Ca} + 2\text{Mg} + \text{Al}$; Figure S4: $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ vs. SiO_2 variation diagram [44] for the Suistam igneous complex; Figure S5: BSE images. Euhedral acicular arsenopyrite in the schistosity and silicification zones of Ladoga metasiltstones; Figure S6: BSE images. Scheelite mineralization in Alattu–Päskylä ores; Figure S7: BSE images. Mineralization of gold associated with quartz and mica; Figure S8: BSE images. Typical mineral associations of gudmundite (Gu, FeSbS); Figure S9: Ternary Pb–Sb–S plot showing the composition of Pb–Sb sulfosalts; Figure S10: Ternary NiSbS–CoSbS–FeSbS plot showing the composition of ullmannite and costibite; Figure S11. Molar $\text{Ag}/(\text{Ag} + \text{Cu})$ and $\text{Zn}/(\text{Zn} + \text{Fe})$ of high-Ag fahlore from the Alattu–Päskylä compared with curves calculated for the maximum solubility of Ag in fahlore in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{ZnS}-\text{FeS}-\text{Sb}_2\text{S}_3$ at 170, 200, 250, 300 and 400 °C by [61]; Table S1: Average chemical composition of rocks of the Alattu–Päskylä intrusion, wt.%; Table S2: REE content (ppm) in rocks of the Alattu–Päskylä intrusion, ICP MS; Table S3: Trace element contents (ppm) of rocks of the Alattu–Päskylä intrusion, ICP MS; Table S4: Representative electron microanalyses and atomic proportions of gudmundite, FeSbS; Table S5: Representative electron microanalyses and atomic proportions of sphalerite; Table S6: Representative electron microanalyses and atomic proportions of boulangerite, $\text{Pb}_5\text{Sb}_4\text{S}_{11}$; Table S7: Representative electron microanalyses and atomic proportions of jamesonite, $\text{FePb}_4\text{Sb}_6\text{S}_{14}$; Table S8: Representative electron microanalyses and atomic proportions of falkmanite— $\text{Pb}_3\text{Sb}_2\text{S}_6$ (1–4), robinsonite— $\text{Pb}_4\text{Sb}_6\text{S}_{13}$ (5–8), geocronite— $\text{Pb}_{14}(\text{SbS}_3)_6\text{S}_{23}$ (9) and fülöppite— $\text{Pb}_3\text{Sb}_8\text{S}_{15}$ (10); Table S9: Representative electron microanalyses and atomic proportions of meneghinite— $\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$ (1–7), freieslebenite— $\text{AgPb}(\text{SbS}_3)$ (8) and twinnite— $\text{Pb}(\text{Sb,As})_2\text{S}_4$ (9–10); Table S10: Representative electron microanalyses and atomic proportions of plumosite— $\text{Pb}_2\text{Sb}_2\text{S}_5$ (1–5), plagionite— $\text{Pb}_5\text{Sb}_8\text{S}_{17}$ (6–9) and heteromorphite— $\text{Pb}_7\text{Sb}_8\text{S}_{19}$ (10); Table S11: Representative electron microanalyses and atomic proportions of arsenopyrite with visible gold; Table S12: Representative electron microanalyses and atomic proportions of arsenopyrite with invisible gold; Table S13: Representative electron microanalyses and atomic proportions of Alattu–Päskylä native gold.

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