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Gold deposits in Greece: Hypogene ore mineralogy as a guide for precious and critical metal exploration

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Abstract: Gold deposits in Greece are spatially associated with back-arc/arc related volcanic, subvolcanic and plutonic rocks, which were controlled by extensional kinematic conditions when metamorphic core complexes in the Rhodope-Serbomacedonian- and Attico-Cycladic Massifs were uplifted to near surface levels over the south-westward retreating Hellenic subduction zone. Porphyry Cu-Mo-Au, high-intermediate sulfidation epithermal Au-Ag deposits and other intrusion-related proximal to distal systems (skarn, carbonate replacement, metamorphic rock-hosted quartz veins) are characterized by enrichment of trace metallic minerals like bismuth sulfosalts and Bi-sulfotellurides, precious- and base metal tellurides and Se-bearing phases, which can be considered as pathfinder minerals for gold as they are intimately associated with gold-bearing ores. Mineralogical studies of various styles of gold deposits in Greece can be applied as an exploration tool and selected examples from well described mineralization/deposits are presented here.

Keywords: Gold deposits, ore mineralogy, pathfinder minerals, critical metals, Greece

1. Introduction

The Rhodope-Serbomacedonian- and Attico-Cycladic Massifs comprise porphyry Cu-Mo-Au and high-intermediate sulfidation epithermal Au-Ag deposits, and several other polymetallic, gold-enriched intrusion-related proximal to distal systems (e.g. intrusion-hosted, skarn, Pb-Zn-Ag-Au carbonate replacement, and Carlin-type mineralization), which are, in part, related to arc-related magmatic rocks and controlled by detachment faults and exhumation of metamorphic core complexes in a back-arc setting [1-7]. This work describes gold-bearing deposits from Greece (Figure 1), emphasizing the widespread occurrences of tellurides and sulfosalts in the

mineralization. Key trace minerals (e.g. tellurides, Bi-sulfosalts and sulfotellurides-selenides, but also common minerals like molybdenite, bornite, galena) from various gold deposits/prospects are discussed demonstrating their genetic significance in relationship to ore formation and their application as exploration tools.

2. Materials and Methods

Samples were studied by optical microscopy and a JEOL JSM 5600 scanning electron microscope, equipped with back-scattered imaging capabilities, at the Department of Mineralogy and Petrology, University of Athens. The chemical compositions of sulfides, sulfosalts and native elements were determined with a Cameca-SX 100 wavelength-dispersive electron microprobe at the Department of Mineralogy and Petrology, University of Hamburg, Germany. Operating conditions were: 20 kV and 20 nA, with a beam diameter <1 μm . The following X-ray lines were used: AgL α , AsL α , AuM α , BiM β , CuK α , FeK α , HgM α , PbM α , SK α , SbL α , SeL α , TeL α , and ZnK α . Pure elements (for Ag, Au, Bi, Se, Te), pyrite and chalcopyrite (for Fe, Cu and S), galena (for Pb), sphalerite (for Zn), HgS (for Hg), Sb₂S₃ (for Sb) and synthetic GaAs (for As) were used as standards.

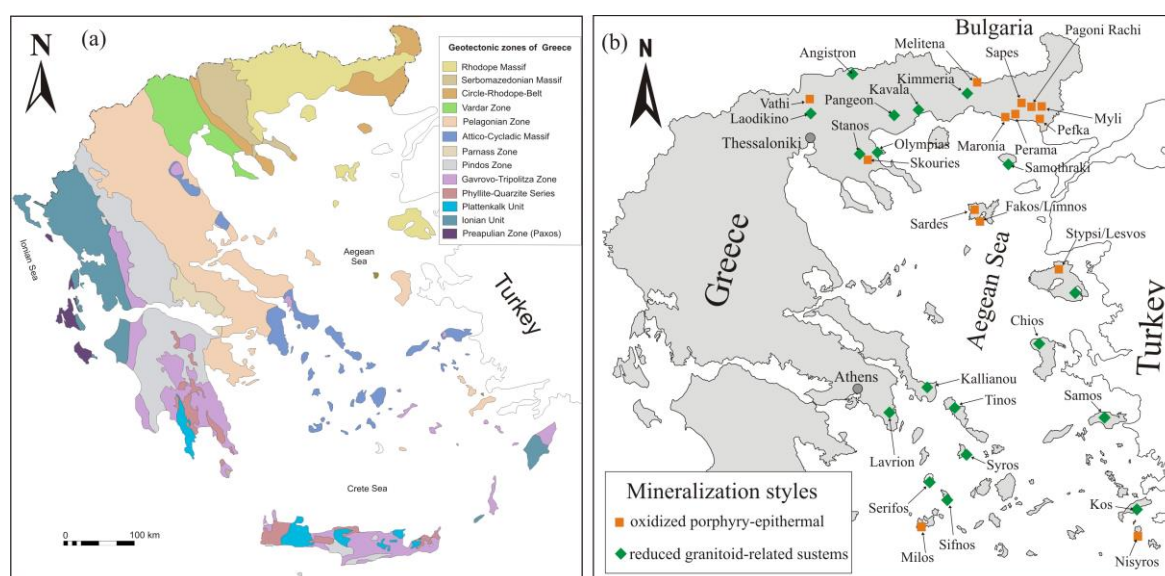


Figure 1. (a) Simplified geologic map of the Hellenides (modified after Ottens and Voudouris [8]) and (b) location of the gold-bearing mineralization (modified from Voudouris et al. [3,4]).

3. Geology

The Hellenides constitute part of the Alpine-Himalayan orogen and formed when Apulia collided with Europe from the Late Cretaceous to the Tertiary. They are subdivided in several units: the Rhodope Massif, the Serbo-Macedonian Massif, the Vardar Zone, the Pelagonian Zone (Internal Hellenides) and the External Hellenides built up by Mesozoic and Cenozoic rocks [9] (Figure 1a). The Hellenides can be considered an accretionary orogen, resulting from thrusting and SW-verging nappe-stacking of the Rhodopes, Pelagonia and Adria continental blocks, and closure of the Vardar and Pindos oceans domains of the Neotethys [9]. A Permo-Carboniferous igneous event (known from the Pelagonian Zone, the Rhodope Massif, the Attico-Cycladic Zone, Peloponnese and Crete) documents an active continental margin evolution in the Precambrian-Silurian basement of the Hellenides. Final collision between Europe and Pelagonia at the end of the Cretaceous closed the Neotethys Ocean along the Vardar Suture Zone, as evidenced by obducted Jurassic ophiolites on the Pelagonia continental block [10]. Shortening and syn-orogenic exhumation of HP-LT rocks occurred during the late Cretaceous-Eocene, before an acceleration of slab retreat changed the subduction regime and caused the collapse of the Hellenic mountain belt and the thinning of the Aegean Sea

from the middle Eocene/late Oligocene to the present [9]. During this post-orogenic episode large-scale detachments formed, which exhumed metamorphic core complexes in a back-arc setting. Tertiary magmatism in the Aegean region occurred mostly in a back-arc setting behind the active Hellenic subduction zone [10]. The Pliocene to recent volcanic rocks in the active Aegean volcanic arc have been formed as a consequence of active subduction beneath the Hellenic trench.

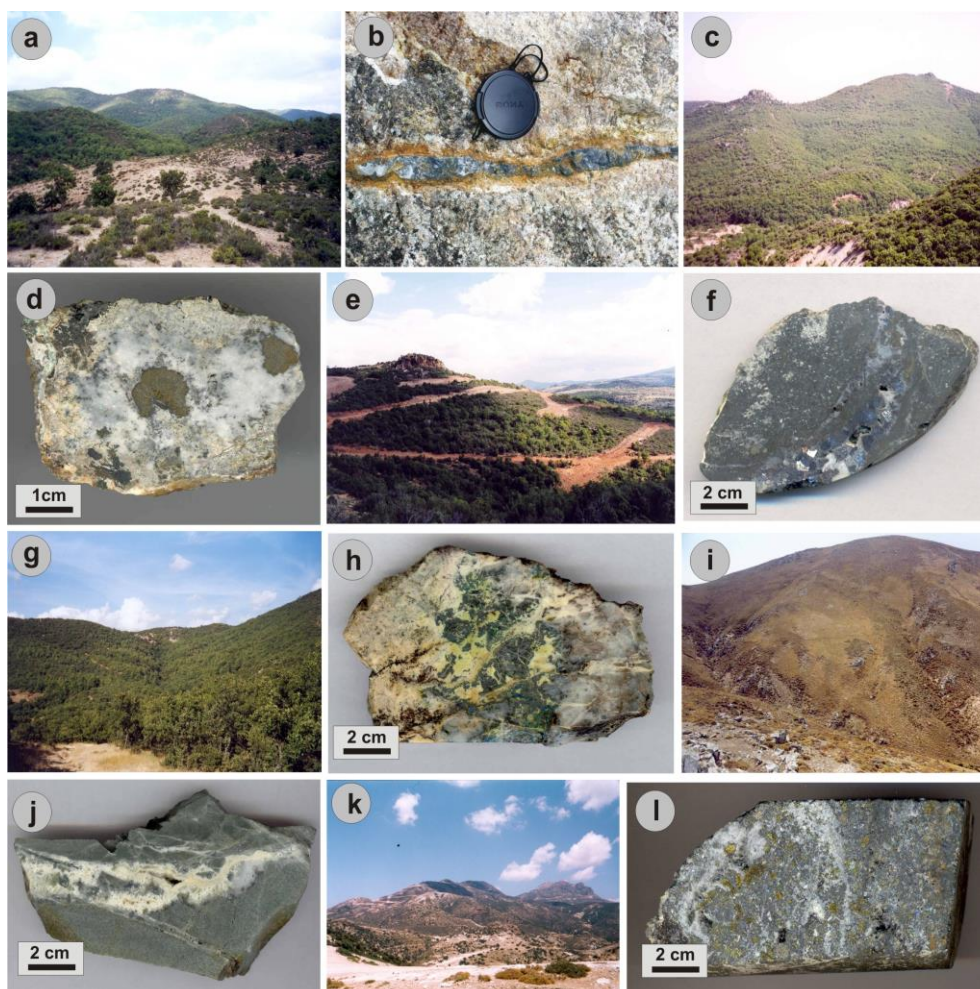


Figure 2. Photographs showing various telluride and Bi sulfosalt/chalcogenide mineralization in porphyry-epithermal systems of Greece: (a) Porphyry-Cu-Mo mineralization in the Pagoni Rachi area; (b) Late-stage carbonate-quartz veins with Bi-sulfosalts and silver tellurides crosscutting sericitized dacitic andesite, Pagoni Rachi area; (c) Porphyry-Cu-Mo and epithermal Au-Ag mineralization in the Kassiteres/Sapes area; (d) Chalcopyrite-telluride mineralization hosted in intermediate sulfidation epithermal carbonate vein at Kassiteres/Sappes area; (e) High-intermediate sulfidation epithermal mineralization at Perama Hill deposit; (f) Early stage enargite-bismuthinite within massive silica, and late-stage galena-tennantite-telluride mineralization related to barite-quartz veins at Perama Hill deposit; (g) High-intermediate sulfidation epithermal mineralization at Pefka deposit; (h) Chalcopyrite-telluride mineralization hosted in intermediate sulfidation epithermal carbonate vein in the Pefka area; (i) Porphyry-epithermal mineralization on Limnos island (Aegean Sea): Fakos prospect; (j) Galena-telluride mineralization hosted in intermediate sulfidation epithermal carbonate-quartz vein at the Fakos prospect, Limnos island. (k) Panoramic view of the shallow submarine epithermal Au-Ag mineralization at the Profitis Ilias deposit, Milos island; (l) Semi-massive base metal-telluride mineralization at Profitis Ilias deposit, Milos island.

4. Porphyry- and epithermal style deposits

Promising porphyry-style prospects/deposits in northern Greece that are enriched in Cu, Au, Mo, Re, include the Pagoni Rachi (Kirki), Kassiteres-Konos (Sapes), Myli at Esymi, Maronia and Melitena (Rhodope Massif), the Skouries (Chalkidiki), Vathi and Gerakario (Kilkis, Serbomacedonian Massif) and five prospects in the northeastern Aegean islands of Limnos and Lesvos (Fakos, Sardes, Kaspakas, Stypsi, Pterounta) [1, 7] (Figure 1, Table 1). In the Attico-Cycladic ore belt, the only well-described porphyry-type deposit is the sub-economic Mo-W Plaka/Lavrion system. Porphyry-style quartz stockworks are hosted by potassic- and/or sericitic altered intrusives.

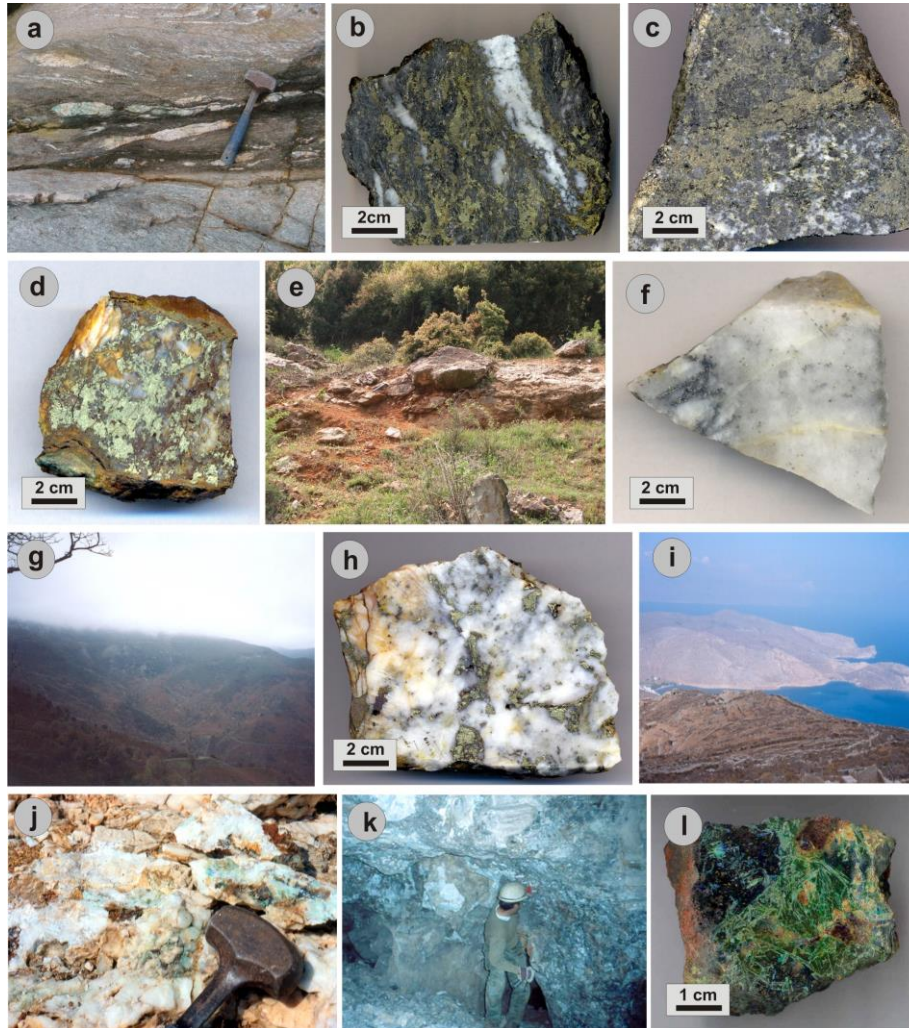


Figure 3. Photographs of various telluride and Bi-sulfosalt mineralization in reduced “granitoid-related” mineralization. *Shear zone-hosted and intrusion-related mineralization in the Serbomacedonian Massif:* (a) Stanos mineralization; (b) Chalcopyrite+tellurides hosted in sheared mica-gneiss, Stanos area; (c) Arsenopyrite+chalcopyrite+tellurides hosted in sheared amphibolite, Laodikino/Kilkis area; (d) Chalcopyrite+tellurides in sheared quartz vein, Koronouda/Kilkis area; *Shear zone-hosted and intrusion-related mineralization in the Rhodope Massif:* (e) Palea Kavala vein mineralization; (f) Bismuthinite+tetradymite hosted in quartz vein from shear zone-related mineralization at Palea Kavala area; (g) Panoramic view of Kallianou deposit, Evia island; (h) Chalcopyrite-telluride mineralization hosted in quartz veins from Kallianou/Evia island; (i) Panoramic view of Panormos deposit, Tinos island; (j) Quartz veins crosscutting marbles at Panormos mineralization; (k) Carbonate replacement mineralization in the Lavrion deposit; (l) Oxidized chalcopyrite-bismuthinite-gold mineralization in the Lavrion area.

Native gold is associated with gold-silver tellurides and Bi sulfosalts/chalcogenides hosted in (a) bornite, chalcopyrite and magnetite ores in the potassic- and the sodic-calcic-altered cores of the systems, and (b) chalcopyrite and pyrite ores in D-veins related to sericitic alteration (Figures 4a and 5-7). In some eastern Greek porphyry prospects, molybdenite is extremely Re-enriched, and rheniite is also present together with high-grade ores [4,11,12]. At Skouries, platinum-group minerals occur in high-grade gold ores [13,14]. The Fakos, Sardes and Stypsi prospect at Limnos and Lesvos island have several characteristics in common with porphyry Au deposits [15,16]. Several high- to intermediate-sulfidation epithermal deposits/prospects endowed with Au, Ag, Te, Se, Bi, In, Ga and Ge occur in the periphery or are superimposed upon porphyry-style mineralization. A genetic relationship to porphyry systems has been suggested (Figure 2, Table 1). Examples in the Rhodope Massif include Kalotycho (northeast of Xanthi), Perama Hill and Mavrokoryfi (Petrota graben), St Demetrios and Viper (Sapes), St Philippos (Kirki) and the Pefka mine [17-22]. Along the South Aegean Active Volcanic Arc, the Milos (and Nisyros) islands host intermediate- to high-sulfidation epithermal Au-Ag mineralization formed in a shallow submarine setting [23]. In all of the above epithermal deposits, which are intimately associated with major, subvertical, normal faults, native gold occurs with enargite-goldfieldite and Se-bearing Bi-chalcogenides in high-sulfidation ores and with Au-Ag-tellurides, Bi-sulfosalts and Bi-chalcogenides and tennantite-tetrahedrite in intermediate-sulfidation ores (Figure 4b,c). However, bornite may also occur in intermediate-sulfidation epithermal veins in the Kassiteres-Sapes and Pagoni Rachi areas (Figure 4d).

5. Other Intrusion-related systems

Mineralization associated with gold-enriched, polymetallic intrusion-related systems in Greece (other than porphyry-type deposits), include intrusion-hosted quartz veins, proximal high-temperature carbonate-replacement deposits (both skarn- and skarn-free massive sulfide replacements), metamorphic rock-hosted quartz veins, and distal "Carlin" style deposits (Figure 3). Common features of all the above examples of metallic mineralization are the presence of a "more reduced" ore mineralogy consisting of pyrite, arsenopyrite and pyrrhotite with native gold that is deposited from CO₂-bearing fluids. In some cases, the presence of magnetite in addition to the above metallic minerals suggests higher fluid sulfidation and oxidation states. The best example of intrusion-hosted gold-bearing veins occurs within the Kavala pluton [24,25]. The sheeted quartz vein system is comprised of quartz with lesser amounts of feldspar, and muscovite. Native gold is associated with pyrite, bismuth sulfosalts and bismuth sulfotellurides. Similar intrusion-hosted sheeted quartz veins are present at Kimmeria/Xanthi [26,27]. At Kimmeria Se-rich bismuth sulfosalts are associated with the gold mineralization in veins (Figure 4d). Significant skarn- and skarn-free carbonate replacement massive sulphide Fe-As-Cu-Au and Pb-Zn-Ag deposits include Palea Kavala and Pangeon Mt at Kavala [25, 28-30], Thasos island [31,32], Thermes [33] and Kimmeria (Xanthi), Angistron Mt (Serres) and Vrontou (Drama) [34], the Aberdeen (Eptadendron) mine in eastern Rhodope Massif [35], the Olympias and Stratoni/NE Chalkidiki [36,37], (Rhodope and Serbomacedonian Massif), Lavrion [38], Serifos, Sifnos, Syros [39] and Tinos islands in the Attic-Cycladic Massif and at Kos Island (on the eastern part of the South Aegean Active Volcanic Arc). Gold occurs in its native form (Figure 4e), as invisible gold and as gold-silver tellurides. Gold-bearing quartz veins hosted in metamorphic rocks were the locus of extensive gold exploitation since the antiquity. Important projects in the Rhodope-Serbomacedonian Massifs include the Palea Kavala and Pangeon Mt at Kavala area, Panagia (Thasos island), the Angistron Mt (Serres), the Aberdeen mine in eastern Rhodope Massif, and the Stanos [40-42], Koronouda [43,44] and Laodikino at Chalkidiki and Kilkis areas. Mineralization occurs, either along foliation planes within strain shadows of quartz boudins at Stanos, Koronouda and Laodikino, or in quartz veins crosscutting the foliation of schists, gneisses and amphibolites. Similar veins in the Attic-Cycladic massif occur at Kallianou area (Evia island) [45], Panormos Bay (Tinos island) [46,47] and Sifnos

island, where gold-rich quartz veins crosscut schists and marbles of the Blueschist Unit. Native gold is associated with various combinations of pyrite, arsenopyrite, pyrrhotite, galena and gold-silver tellurides and/or Bi sulfosalts/chalcogenides in the ores (Figures 4f,g,h and 5-7). Molybdenite at Stanos and on Syros island occurs without any obvious genetic relationship to a granitoid (Figure 4i). Quartz-stibnite-arsenopyrite-realgar veins and disseminations at Samos, Lesvos, Chios and Kos islands in the eastern Aegean and also in the Kallintiri area, NW of Komotini, are hosted in metamorphic rocks and which have affinities with Carlin-style deposits.

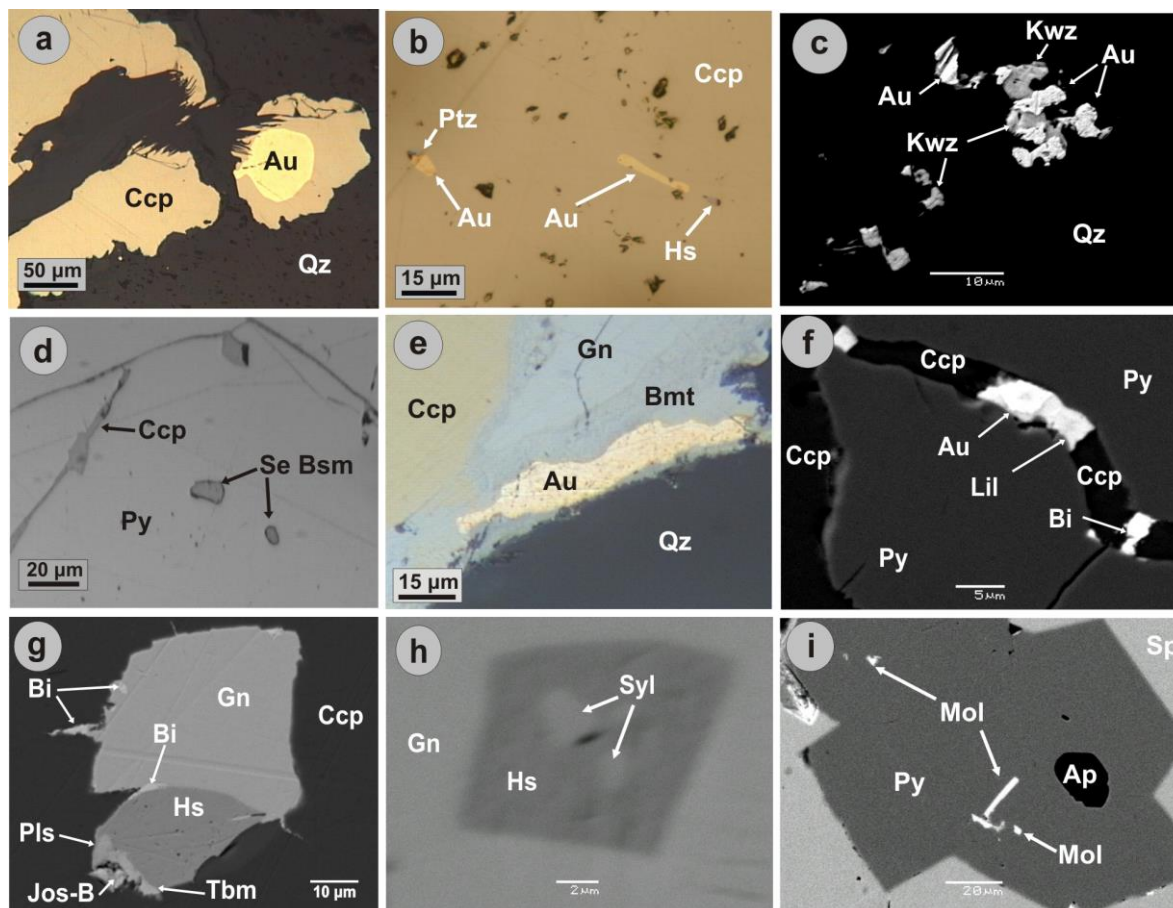


Figure 4. Reflected light and BSE microphotographs of ore parageneses of various Au-Ag telluride and Bi sulfosalts/chalcogenide bearing gold ore systems in Greece: (a) Native gold (Au) included in chalcopyrite (Ccp), Skouries porphyry Cu-Au deposit. Quartz (Qz) is gangue; (b) Native gold (Au), hessite (Hs) and petzite (Ptz) included in chalcopyrite. Viper high-sulfidation epithermal gold deposits, Sapes; (c) Native gold and kawazulite (Kwz) intergrowth; high-sulfidation epithermal Perama Hill deposit; (d) Se-bearing bismuthinite (Se-Bsm) included in pyrite (py). Kimmeria granodiorite-hosted quartz vein mineralization; (e) Native gold included in bismuthinite (Bmt) and associated with chalcopyrite and galena. Kamariza, Lavrion carbonate-replacement deposit; (f) Lillianite homologue (Lil), native gold (Au), native bismuth (Bi) and chalcopyrite (Ccp) filling fissure in pyrite (Py), Stanos intrusion-related deposit; (g) Bleb of galena (Gn) within chalcopyrite (Ccp) associated with hessite (Hs), native bismuth (Bi), pilsenite (Pls), josite-B (Jos-B) and tellurobismuthite (Tbm), Koronouda intrusion-related deposit; (h) Sylvanite (Syl) and hessite (Hs) included in galena (Gn). Kallianou intrusion-related deposit; (i) Molybdenite (Mol) and apatite (Ap) included in pyrite. Sphalerite (Sp) is also present. Syros island carbonate-replacement deposit.

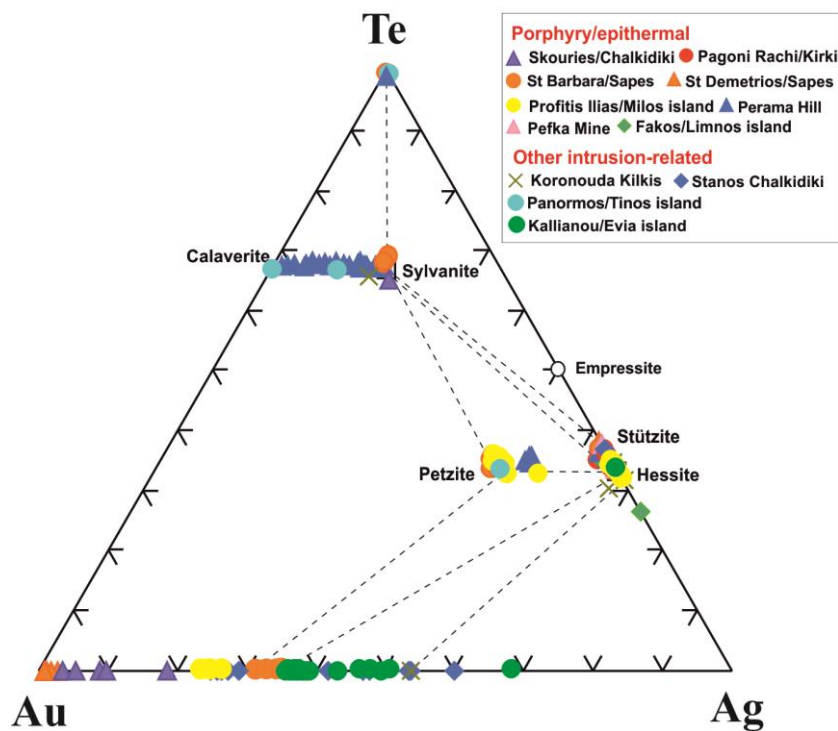


Figure 5. Ternary Au-Ag-Te diagram (atomic proportions) for mineral compositions (literature data) in porphyry, epithermal and other intrusion related systems. For references see Table 1.

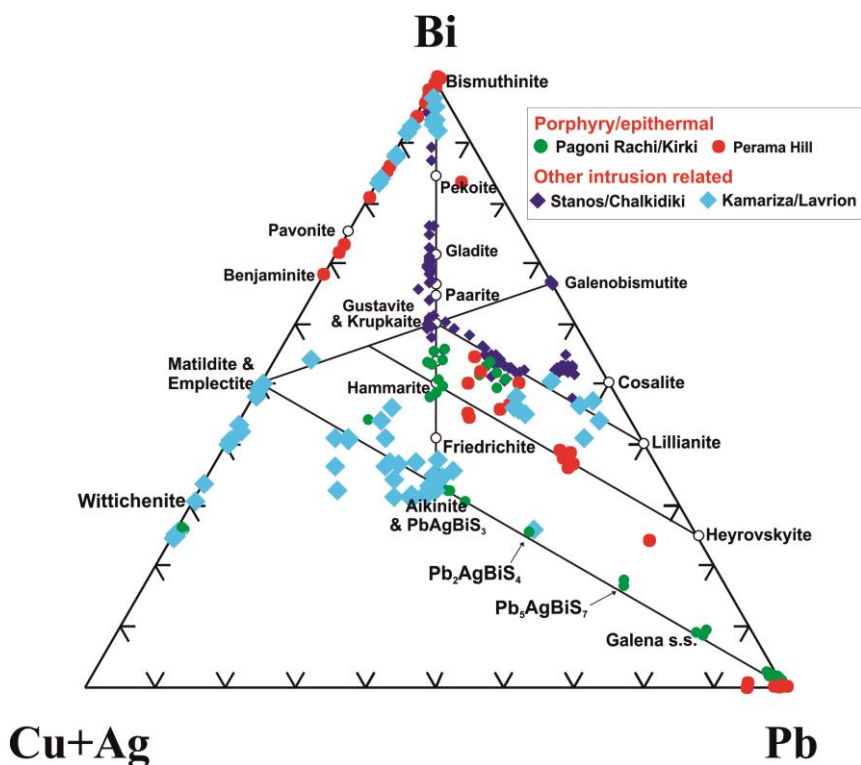


Figure 6. (a) Ternary Bi-(Cu+Ag)-Pb diagram (atomic proportions) for mineral compositions (literature data) in porphyry, epithermal and other intrusion related systems. For references see Table 1.

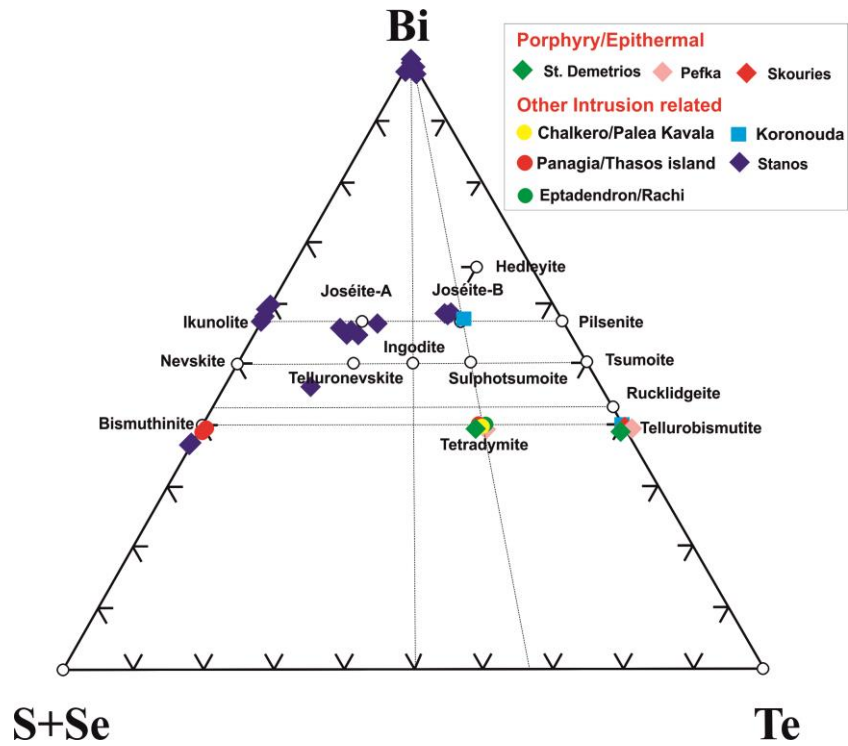


Figure 7. Ternary Bi-(S+Se)-Te diagram (atomic proportions) for mineral compositions (literature data) in porphyry, epithermal and other intrusion related systems. For references see Table 1.

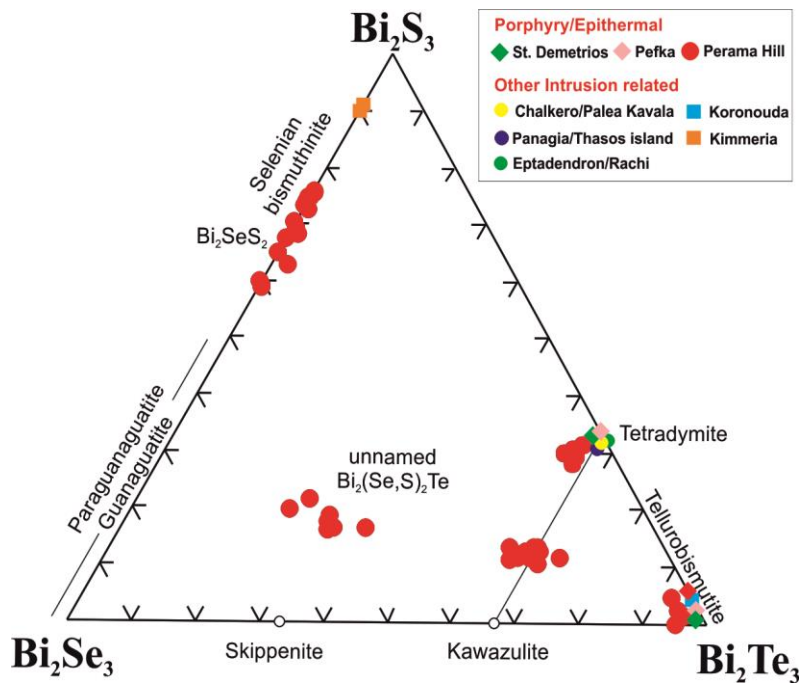


Figure 7. (a) Ternary Bi-Se-Te diagrams for mineral compositions (literature data) in porphyry, epithermal and other intrusion related systems. For references see Table 1.

Table 1. Characteristics of the Magmatic-Hydrothermal Au-Ag Deposits in Greece

Deposit name	Deposit style	Critical and precious metal mineralogy	References
Konos Hill	Porphyry-epithermal	Re-Mol, Rhn	[18,4,12]
Koryfes Hill	Porphyry-epithermal	Ttd	[18]
Pagoni Rachi	Porphyry-epithermal	Bn, Re-Mol, Au, Rhn, Ttd, Hes, Ptz, Stz, Alt, Ag-Au, Aik, Hmr, Ber, Lnd, Gus-Lill ss, Se-Bi sulf, Wtc	[11,4,5]
Myli	Porphyry-epithermal	Re-Mol, Au	[4]
Maronia	Porphyry-epithermal	Re-Mol, Bsm	[2]
Melitena	Porphyry-epithermal	Re-Mol	[4]
Skouries	Porphyry	Syl, Hs, Clv, Tbm, Mer, Au, Bn	[13,14]
Fakos, Sardes	Porphyry-epithermal	Mol, Au, Hes, Ptz, Alt, Ag-sulf	[15,16]
Stypsi	Porphyry-epithermal	Re-Mol, Bsm	[15]
St. Demetrios	HS-IS epithermal	Clv, Syl, Hs, Stz, Alt, Au, Glf	[17, 18]
Viper			
St Barbara	HS epithermal	Bn, Hs, Ptz, Syl, Alt, Te, Au	[18,19]
St Philippos	HS-IS epithermal	Bsm, Eng, Hs, Alt, Tbm	[5]
Perama Hill	HS-IS epithermal	Gn, Bsm, Hey, Gus-Lill ss, Hs, Ptz, Syl, Kre, Clv, Col, Te, Mln	[21]
Mavrokoryfi	HS-IS epithermal	Gld, Au	[20]
Pefka	HS-IS epithermal	Ttd, Hs, Stz, Alt, Te, Au, Col, Syl, Glf	[19,22]
Milos	IS Epithermal	Hs, Ptz, Au, Alt	[23]
Kavala	Intrusion-related	Bsm, Ttd, Bi-sulfosalts, Cos, Au	[24,25,28]
Kimmeria	Intrusion-related	Bsm, Aik, Pek, Mat	[26,27]
Pangeon Mt	Intrusion-related	Ttd, Bsm, Au	[29,30]
Thasos	Intrusion-related	Bsm, Grf, Ttd, Hs, Au	[31,32]
Thermes	Intrusion-related	Grf, Hs, Alt, Au	[33]
Angiaron Mt	Intrusion-related	Bsm, Bi, Cos, Jos-A, Lill hom	[34]
Aberdeen	Intrusion-related	Bsm, Emp, Aik, Wtc, Ttd, Hs, Au	[35]
Madem Lakkos, Mavres Petres	Intrusion-related	Bsm, Gbm, Cos, Aik, Au	[36,37]
Lavrio	Intrusion-related	Au, Bsm, Aik, Lill, Grf	[38]
Syros	Intrusion-related	Mol, Au	[39]
Stanos	Intrusion-related	Bsm, Pek, Gla, Kru, Gus-Lill ss, Cos, Emp, Bi, Au, Jos-A	[40-42]
Laodikino	Intrusion-related	Au, Pls	[3]
Koronouda	Intrusion-related	Bsm, Aik, Bi, Au, Hs, Ptz, Syl, Pls, Tbm, Jos-B	[43,44]
Kallianoi	Intrusion-related	Hs, Syl, Cvl, Stz, Ptz, Emr, Te, Col, Au	[45]
Tinos	Intrusion-related	Hs, Syl, Alt, Te, Stz, Crv, Mln, Rck, Vul, Wei, Kos, Kre, Ptz, Clv	[46,47]

¹ Abbreviations: Ag-sulf = silver sulfotellurides; Aik = aikinite; Alt = altaite; Au = native gold; Ber = berryite; Bn = bornite; Bsm = bismuthinite; Clv = calaverite; Col = coloradoite; Cos = cosalite; Crv = cervelleite; Emp = emplectite; Emr = empressite; Gbm = galenobismutite; Gla = gladite; Glf = goldfieldite; Grf = gersdorffite; Gus-Lil ss = gustavite-lillianite solid solution; Hey = heyrovskyite; Hmr = hammarite; Hs = hessite; Jos-A = joséite-A; Kos = kostovite; Kre = krennerite; Kru = krupkaite; Lill = lillianite; Lnd = lindströmite; Mat = matildite; Mer = merenskyite; Mln = melonite; Re-Mol = Re-rich molybdenite; Pek = pekoite; Pls = pilsenite; Ptz = petzite; Rck = rickardite; Rhn = rheniite; Se-Bi sulf = Se-Bi sulfosalts; Stz = stützite; Syl = sylvanite; Te = native tellurium; Tbm = tellurobismuthite; Ttd = tetradymite; Vul = vulcanite; Wei = weissite; Wtc = wittichenite. HS = High-sulfidation; IS = Intermediate-sulfidation.

6. Discussion and Conclusions

A common feature of the metallic mineralization in Greece is the close relationship between gold (either in form of native element and/or as gold-silver tellurides) and other trace minerals that incorporate Bi, Te and Se in their structure. These minerals can be considered as pathfinders for gold and they may guide exploration to discover distinct types of gold-bearing ores. Primary gold mineralization in Greece can be subdivided into three groups [4]: (A1) Mineralization where native gold and Au-Ag tellurides accompany either Bi-sulfosalts, native Bi and reduced-type Bi-sulfotellurides (joséite-A, joséite-B, pilsenite) at Koronouda, Laodikino/Kilkis area, Stanos (Figure 2a), Olympias-Stratoni and Fissoka at Chalkidiki area and Angistron Mt/W. Rhodope), or accompany Bi-sulfosalts with oxidized-type Bi-sulfotellurides (e.g. tetradyrite and tellurobismuthite) that is found at Eptadendron, Palea Kavala, Thasos island, as well as being associated with calc-alkaline and alkaline-hosted porphyry and epithermal deposits/prospects in western Thrace, Limnos island and Skouries; (B) Deposits which lack tellurides but include Bi-sulfosalts and native gold (e.g. the carbonate replacement deposit of Lavrion, the porphyry-Cu-Mo-Au deposits of Maronia and Stypsi, Lesvos Island, and the intrusion-related Kimmeria Cu-Mo-Au deposit); and (C) Deposits/prospects where native gold and Au-Ag-tellurides and other base metal tellurides are abundant and Bi-tellurides and Bi-sulfosalts are absent (the metamorphic rock-hosted quartz veins at Panormos/Tinos and Kallianou/Evia islands (Figure 2b), and the epithermal shallow submarine mineralization at Milos). Bismuth and tellurium are considered to be derived from a magma while the presence of bismuth sulfosalts and bismuth tellurides/selenides, as well as of various types of base (and precious) metal tellurides in the mineralization, are strong evidence of a magmatic-hydrothermal contribution to the ore fluid and of potentially concealed intrusives (e.g. Perama Hill and Pefka deposits are cases where no granitoids are exposed). The absence of bismuth minerals and the presence of precious and base metal tellurides (as is the case for Milos, Tinos and Evia islands) may still suggest magmatic contributions but in more distal setting from a buried granitoid at depth. Selenium (and/or bismuth) bearing galena and Se-bearing bismuth chalcogenides at Kimmeria intrusion-hosted veins, at Lavrion, as well as in several porphyry-epithermal deposits in northern Greece (e.g. Kassiteres-Sapes, Pagoni Rachi, Perama Hill, Pefka and Skouries) (Figure 2c) are indicative of high-temperature, magmatic-hydrothermal fluids, during the initial stages of ore deposition and proximity to porphyry mineralized centers. When recognized as an accessory mineral, Se-bearing galena could guide exploration towards unexposed granitoids. Bornite and molybdenite are present in the potassic and sericitic alteration zones of Skouries and Pagoni Rachi porphyry deposits, where they are intimately associated with native gold and gold-silver tellurides.

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