Later stages of evolution of an epithermal system: Au–Ag mineralizations at Apigania Bay, Tinos Island, Cyclades, Hellas, Greece

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Abstract Precious metals accompany all types of epithermal deposits. In general, the largest of these deposits occur in intrusive or extrusive rocks of alkaline or calc-alkaline affinity. The Apigania Bay vein system and Au–Ag mineralization is hosted in Mesozoic marbles and schists, and is composed primarily of five nearly parallel, high-angle quartz veins that extend for at least 200 m. Gold–silver mineralization, in association with more than thirty ore and vein minerals, is developed in three stages and occurs at the contact of marbles and schists. Zones of epidote–chlorite–calcite and sericite–albite alteration are associated with precious metal-bearing milky and clear quartz veins. Fluid inclusion studies suggest that hydrothermal mineralization was deposited under hydrostatic pressures of ~100 bars, at temperature

of 120–235°C, from low to moderate, calcium-bearing, saline fluids of 0.2 to 6.8 equiv. wt.% NaCl. Calculated isotope compositions ($\delta^{18}\text{O} = -4.7\text{‰}$ to 1.7‰ and $\delta\text{D} = -120\text{‰}$ to -80‰) for waters in equilibrium with milky and clear quartz are consistent with mixing with dilute, low temperature meteoric ore fluids. Calculated $\delta^{13}\text{C}_{\text{CO}_2}$ (0.6‰ to 1.1‰) and $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ (-7.3 to -0.3‰) compositions of the ore fluids indicate exchange, in an open system, with a metasedimentary source. Gold and silver deposition was associated with degassing of hydrogen due to intense uplift of the mineralizing area. The physicochemical conditions of mineralization stages I to III range between 200°C and 150°C, $f_{\text{S}_2} = 10^{-18.1}$ to $10^{-16.8}$, $f_{\text{O}_2} = 10^{-44.0}$ to $10^{-41.5}$, $\text{pH} = 6.9$ to 7.6 , $f_{\text{H}_2\text{S}} = 10^{-3.4}$ to $10^{-2.6}$ and $a_{\text{H}_2\text{S}} = 10^{-2.7}$ to $10^{-2.6}$. Apigania Bay could be possibly considered the latest evolutionary phase of Tinos hydrothermal system.

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Introduction

Reviews of Au–Ag±Te deposits in Hellas (Greece) reveal that they are hosted within Oligocene to Miocene magmatic systems as epithermal and/or porphyry occurrences in two areas: the Northeastern Hellenic and the Cyclades belts. In the northeastern Hellenic belt the Servomacedonian-Rhodope metallogenic area hosts several major ore deposits (Skarpelis et al. 1999), i.e., replacement style massive Zn–Pb–Au–Ag deposit at Olympias, Chalkidiki (120 g/t Ag and 5.5 g/t Au); Madam Lakkos and Mavres Petres (110 g/t Ag and 1.5 g/t Au; Kalogeropoulos et al. 1989; Nebel et al. 1991; Kiliass et al. 1996), porphyry Cu–Au at Skouries, Chalkidiki (0.9 g/t Au, 2.5 g/t Pd and 0.6% Cu), epithermal Au–Ag–Te at St. Demetrios, Fakos and Perama Hill, Thrace (3.5 to 3.7 g/t Au; Voudouris and Alfieris 2004; Voudouris 2006), and epithermal to porphyry at St. Barbara, Mavrokoryfi and Pefka, Thrace (Voudouris et al. 2006).

Gold–silver mineralization at Apigania Bay, Tinos Island, Hellas (Greece) was first recognized by Melidonis (1980), and subsequently remapped by Tombros (2001). It occurs in a stockwork of early milky and late clear quartz veins in Triassic marbles and schists. Previous studies of the Apigania Bay ores are limited and have focused on the temperature of ore formation (Tombros and St. Seymour 1998) and the reasons for the presence of cassiterite in the mineralization (Tombros and St. Seymour 2003). This study investigates the mineralogical, paragenetic, fluid inclusion, stable isotope (i.e., sulfur, carbon, oxygen, and hydrogen), geochemical characteristics, which have been conducted to constrain the thermochemical conditions of ore formation, and its potential genetical link to the Miocene fluorine- and boron-bearing Tinos leucogranite (Tombros 2001). Epithermal gold mineralization at Apigania Bay is one of several granite-related gold–silver occurrences in Hellas (Greece); as recent investigations include the mineralizations situated at the foot- and hanging-walls of several shear zones all over the Attico-Cycladic Massif (i.e., Lavrion, Mykonos, Paros, Naxos and Ikaria).

Regional geological setting

The Attico–Cycladic belt (ABC) is one of the most spectacular Alpine orogenic belts and is considered to mark the location of an ancient convergence zone (Blake et al. 1981). On Tinos Island, Hellas (Greece), this belt is essentially composed of a package of Alpine nappes (Fig. 1a,b). The so-called Basal unit (Fig. 1a,b) is composed of Late-Triassic to Late-Cretaceous platform of neritic limestones, overlain by Paleocene flysch (Melidonis 1980; Boronkay and Doutsos 1994). The “Blueschist unit” was initially a Mesozoic continental margin of neritic sediments and basic to acid volcanic rocks (Fig. 1a,b; Parra et al. 2002). High-pressure, low-temperature blueschist facies metamorphism occurred during the Eocene–Miocene and was accompanied by a Barrovian overprint, which formed during exhumation of the high-pressure rocks during the Oligocene–Miocene (Avigad and Garfunkel 1989, 1991; Bröcker 1990; Bröcker et al. 1993). The Blueschist unit was overthrust by ophiolites of the “Upper unit”, which was metamorphosed to the greenschist facies (Okrusch and Bröcker 1990; Katzir et al. 1996; Patzak et al. 1994; Bröcker and Enders 1999; Pulitz et al. 2000). The extensional detachment separating the Upper from the Blueschist unit was pierced by a Miocene granodiorite–leucogranite (Altherr and Siebel 2002). Granodiorite have intruded along syn-magmatic ductile faults (Boronkay 1995; Mastrakas and St. Seymour 2000; Zeffren et al. 2005), while its contact with the country rocks served as a conduit for a boron- and fluorine-rich leucogranite, which formed peripherally to the granodiorite (Mastrakas 2007). The Tinos granodiorite was emplaced during the Mid- to Late-Miocene

in a transpressional regime (Mastrakas and St. Seymour 2000; Bröcker et al. 2004), and subsequently deformed under ductile to brittle conditions in a Late Miocene to Pliocene transtensional setting (Boronkay and Doutsos 1994; Mastrakas and St. Seymour 2000). K–Ar ages of ca. 18 to 15 Ma were obtained for the Tinos granodiorite (from amphibole and biotite separates, Altherr et al. 1982). The leucogranite was emplaced under transtension (Mastrakas and St. Seymour 2000) and has been dated at 14 ± 0.1 Ma (whole rock Rb–Sr isochrons from titanite and apatite, Altherr et al. 1982; Henjes-Kunst and Kreuzer 1982). The pluton caused contact metamorphism and formation of scheelite mineralization (Melidonis 1980; Mastrakas 2007). Rb–Sr ages from biotite suggest that the contact aureole formation was at ~ 14 Ma (Bröcker and Franz 2000). The width of the contact aureole ranges from 600 to 2,000 m (Bröcker and Franz 1994, 1998; Mastrakas 2007). The inner zone (~ 1 km wide) consists of pyroxene and amphibole hornfelses, pyroxene–garnet skarns and marbles, whereas the outer zone is composed of albite–epidote hornfelses (Stolz et al. 1997). NE- and NW-trending aplitic dikes and veins intrude the pluton and country rocks (Mastrakas and St. Seymour 2000). A swarm of NW-trending Miocene rhyolitic dikes (with K–Ar ages of 11.5 Ma, Avigad et al. 1994) and tiny outcrops of Miocene–Pliocene clastic sediments complete Tinos tectono-stratigraphy.

The Apigania Bay vein system

The Apigania Bay vein system is hosted in marbles and schists of the Blueschist unit (Fig. 2; Tombros 2001). Thin- to thick-bedded muscovite–chlorite–stilpnomelane–biotite–glaucophane marbles are intercalated with blueschists, greenschists and amphibolites and represent the Blueschist unit base, whereas intercalations of blueschists, greenschists, marbles, and ultramafics occur on the top. The greenschists, in the area, are dominated by the assemblage of quartz–calcite–muscovite–chlorite–actinolite–epidote–biotite–titanite–tourmaline–albite are mineralized with pyrite, Co-bearing pentlandite, pyrrhotite and magnetite (Melidonis 1980).

The Apigania vein system consists of five high-angle quartz veins “tension gashes” that extend vertically for at least 200 m, filling a conjugate system of NE-trending sinistral and NW dextral strike-slip faults (Tombros and St. Seymour 1998; Tombros 2001). Blueschist unit marbles and schists are intruded by two generations of syntaxial veins: an older, northeasterly trending milky set of quartz veins and a younger group of northwesterly trending clear quartz veins (Fig. 2). The two vein systems form a stockwork, in which milky quartz veins, up to 2 m wide, contain minor amounts of pyrite, sphalerite, tetrahedrite and chalcopyrite, whereas the clear quartz veins (up to 2 m wide) display well-developed comb textures, and contain up to 20 vol.% galena.

Fig. 1 Map showing: **a** generalized geology and **b** tectonic domain of Tinos Island and the location of the Apigania and Panormos Bay Au–Ag–Te mineralization (modified after Melidonis 1980; Mastrakas and Seymour 2000; Skarpelis 2001, and Landsat-Tm, Spot-PAN, and DEM satellite images)

Fig. 2 Location, and geological map and cross section of Apigania Bay vein system, showing the distribution of the milky and clear quartz veins and the Au-Ag mineralization (after Tombros 2001). Apigania Bay vein system is shown at the *upper map* and a cross section of a banded vein in the *lower part*, respectively. In Apigania Bay vein system there is a set of NE-trending banded mineralized veins filled with milky quartz (veins A_2 , A_3 , A_5) with band A (outer) and band B (inner) of the veins. The second group comprises NW-trending banded mineralized veins with clear quartz (A_1 , A_4) and band C (outer) and D (inner). A_1 – A_5 represents the major metalliferous veins in the area

Crustification is apparent in quartz veins which are ≥ 10 cm wide. Four different bands (with widths up to 50 cm; referred to here as, type A to D) have been classified, giving a generalized sequence of: (1) fine-grained milky quartz (>70 vol.%) with abundant fragments of marble and schist (Type A), (2) medium-grained milky quartz (≈ 50 vol. %), epidote (≈ 30 vol. %), albite, sericite (both 10 vol. %), ankerite (≈ 5 vol. %), with pyrite and sphalerite (both 5 vol. %) (type B), (3) fine-grained clear quartz (<60 vol. %) with calcite (≈ 30 vol. %) and chlorite (type C), and (iv) medium- to coarse-grained clear quartz in dogtooth comb textures (<70 vol. %), calcite (<20 vol. %), and chlorite (type D). In a single vein (i.e., vein A_1 , Fig. 2) bands A and B with convolute morphologies are mainly developed in the outer parts of the vein, in a NE direction (Fig. 3a). NW-trending

discontinuous C and D bands cross-cut the former and occupy the central parts of the veins (Fig. 3a). Milky quartz crystals with mottled extinction patterns are symmetrically banded, clear quartz crystals terminate within open cavities, whereas calcite crystals appears bladed (Fig. 3a).

Analytical methods

Mineral compositions from the Apigania Bay vein system were determined with a Joel 8900 Superprobe, equipped with wave and energy dispersive and back-scattered detector at Microprobe Center of the Department of Earth and Planetary Sciences Department, at McGill University. Operating conditions were an acceleration voltage of 15 kV, a beam

Fig. 3 Back-scattered electron images of: **a** stage I pyrite (*py*) developed in the transitional zone of bands A and B in milky quartz (*q*) and calcite (*cc*) (scale bar = 100 μm); **b** stage I (*py*) and zoned sphalerite (sphalerite cores: *sph*₁ and sphalerite rims: *sph*₂) replaced by stage II chalcopyrite (*cp*) and tetrahedrite (*tetr*) (scale bar = 500 μm); **c** Stage III galena (*g*) with argentite-acanthite inclusions (*arg*) (scale bar = 150 μm)

current of 10 nA and counting times of 20 s. Standards used for vein minerals, were natural calcite, chlorite, epidote and muscovite, whereas for ore minerals natural chalcopyrite, tetrahedrite, tennantite, pyrite, sphalerite, galena, CoNiAs,

SnO₂, MnTi, and native Ag, Sb, Au, Se, Ta, and Cd were utilized. The X-ray lines measured were Ag *La*, Sb *La*, Cu *Ka*, Fe *K α* , Au *Ma*, Mn *Ka*, Se *La*, Ta *La*, Cd *La*, Te *La*, and S *Ka*. ZAF corrections were made with proprietary JOEL software. A minimum of ten analyses were obtained from each sample and three from each grain.

Microthermometric determinations were performed on doubly polished wafers 50–100 μm thick using a modified USGS stage, in the Laboratory of High Temperature Processes at the Department of Earth and Planetary Science Department of McGill University. Temperatures were measured with an alumel–chromel thermocouple and the readings were calibrated with synthetic inclusions at -56.6°C (triple point of CO₂), at 0.0°C (melting point of ice) and at $+374.1^\circ\text{C}$ (critical point of H₂O). Measurements are accurate to within 0.2 $^\circ\text{C}$ for temperatures $<31^\circ\text{C}$ and to $\pm 0.1^\circ\text{C}$ for temperatures $>31^\circ\text{C}$. Microthermometric data were reduced using the Flicor software (Brown 1989) employing the equations of Brown and Lamb (1989), and Zhang and Frantz (1990). Results of the fluid inclusion study are listed in Table 4.

Material for stable isotope studies was obtained from vein and alteration minerals, host marbles and schists, and smoky quartz from the Tinos leucogranite (Tombros et al. 2007). All minerals selected were handpicked and checked under a binocular microscope to ensure a purity of $>95\%$. Isotopic compositions of oxygen, hydrogen and carbon were analyzed with a VGSI12 triple collector mass spectrometer and those of sulfur with a VGMM602E double collector mass spectrometer. Analyses were performed at Geochron Laboratory, Massachusetts, USA. Oxygen and hydrogen were released from milky, clear and smoky quartz using the BrF₅ extraction technique of Clayton and Mayeda (1963) and Friedman and O'Neil (1977), whereas carbon and oxygen in calcite by using the CO₂ treating of Clayton et al. (1972). Sulfur was released as SO₂ after the method of Fritz et al. (1974). The isotopic ratios are reported in standard δ notation per mil relative to SMOW for oxygen and hydrogen, Pee Dee belemnite for carbon, and Cañon Diablo troilite for sulfur. Analytical precision was better than $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, $\pm 1\text{‰}$ for δD , and $\pm 0.2\text{‰}$ for $\delta^{34}\text{S}$.

Trace element analyses were obtained from Act Labs (Canada). Major element compositions were obtained by X-ray fluorescence analysis following the method of Taggart et al. (1987). Trace element compositions were measured by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry techniques of Meier et al. (1994), whereas Au was analyzed by flame atomic absorption (Hubert and Chao 1985). Trace element data were collected from samples of Tinos leucogranite and aplites, smoky quartz (Tombros et al. 2007), milky and clear vein quartz, from the epidote-chlorite alteration zone, and host marbles-schists of the Blueschist unit.

Hydrothermal alteration

Alteration zones were developed even around barren milky and clear quartz veins and are widest around the thickest veins, at vein intersections, along fault planes, and in places where host marbles or schists are tectonically brecciated. Discontinuous borders, concentric shells and linear forms are formed, that are parallel to the veins. Marbles develop alteration assemblages enriched in epidote, whereas in schists contain chlorite and calcite. Alteration haloes consist of two zones: an inner epidote and an outer chlorite zone. Adjacent to type A bands are the epidote zones, up to 15 cm, wide which are spatially associated with fine-grained milky quartz. They also contain albite, sericite, ankerite, pyrite and sphalerite. Chlorite zones, with widths up to 10 cm, contain clear quartz, chlorite, calcite, minor albite and sericite, tetrahedrite, chalcopyrite and galena. Representative compositions of vein fill and alteration minerals are given in Table 1.

Ore petrography and chemistry

Apigania Bay ores contain thirty metallic and gangue minerals, including electrum and silver sulfosalts (Tombros and Seymour 1998, 2003). Three paragenetic stages of epithermal mineralization (I to III) are followed by a supergene stage (IV) (Table 2). Mineral stage I (bands A and B) is related to the NE-trending milky quartz veins, while stages II and III to the NW-trending clear quartz ones (bands C and D) (Fig. 3b,c). Representative compositions of Au–Ag sulfides and sulfosalts are given in Table 3.

Stage I is associated with type B bands, and comprises with pyrite (~35 vol.%), sphalerite (~30 vol. %), minor pyrrhotite, senopyrite, magnetite, argentite, electrum, stephanite [Ag₅SbS₄], xanthoconite [Ag₃AsS₃], proustite [Ag₃AsS₃] and canfieldite [Ag₈SnS₆]. Pyrite develops at the vein margins in massive aggregates which are granular, and intensely brecciated. It also appears as coarse-grained pyritohedra (up to 15 mm) and/or as disseminations in

Table 1 Representative electron microprobe analyses of the vein fill and alteration minerals from Apigania Bay vein system

Mineral	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	36.91	39.80	49.12	46.00	66.95	64.10	28.25	30.09	(b.d.)	(b.d.)	(b.d.)	(b.d.)
Al ₂ O ₃	21.94	24.42	35.27	34.97	21.01	23.87	16.98	14.91	(b.d.)	(b.d.)	(b.d.)	(b.d.)
Fe ₂ O ₃	14.18	11.35	0.02	0.03	0.09	(b.d.)	(b.d.)	(b.d.)	(b.d.)	(b.d.)	(b.d.)	(b.d.)
FeO	(b.d.)	(b.d.)	1.24	3.92	(b.d.)	(b.d.)	19.90	20.43	1.09	2.57	17.92	22.74
MgO	(b.d.)	0.03	0.80	0.69	(b.d.)	0.01	19.52	18.49	0.94	0.01	3.61	2.11
CaO	23.67	23.79	(b.d.)	0.08	1.31	2.06	0.08	0.15	57.96	51.23	19.38	18.90
MnO	0.25	0.08	0.02	0.21	0.03	0.01	1.62	1.59	0.38	0.50	3.19	2.95
Na ₂ O	(b.d.)	(b.d.)	0.92	1.25	10.59	9.05	0.01	(b.d.)	(b.d.)	(b.d.)	(b.d.)	(b.d.)
K ₂ O	(b.d.)	(b.d.)	9.24	9.98	0.02	(b.d.)	0.01	0.02	(b.d.)	(b.d.)	(b.d.)	(b.d.)
ZnO	(b.d.)	(b.d.)	(b.d.)	(b.d.)	(b.d.)	(b.d.)	(b.d.)	(b.d.)	0.58	(b.d.)	(b.d.)	(b.d.)
LOI	2.92	0.33	3.04	2.45	0.00	0.75	13.50	10.78	38.94	44.71	55.35	53.13
Total	99.87	99.77	99.67	99.58	99.99	99.94	99.86	99.42	99.89	99.02	99.45	99.83
No. of atoms based on												
Si	3.01	2.93	2.57	2.10	2.95	2.89	5.75	6.05	0.00	0.00	0.00	0.00
Al	2.11	2.35	3.90	3.83	0.98	1.15	4.00	3.50	0.00	0.00	0.00	0.00
Fe	0.97	0.77	0.56	1.09	0.02	0.00	3.39	3.44	0.02	0.12	0.39	0.45
Mg	0.00	0.00	0.08	0.07	0.01	0.00	5.92	5.55	0.02	0.00	0.09	0.06
Ca	2.07	2.08	0.00	0.00	0.1	0.12	0.02	0.03	0.95	0.87	0.45	0.43
Mn	0.02	0.01	0.00	0.00	0.00	0.00	0.28	0.27	0.00	0.01	0.07	0.06
K	0.00	0.00	0.78	0.77	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.12	0.16	0.99	0.92	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
OH	0.94 ^a	0.96 ^a	1.99 ^b	1.98 ^b	0.00	0.00	15.92 ^d	15.95 ^d	0.00	0.00	0.00	0.00
O	12.00 ^a	12.00 ^a	8.00 ^b	8.00 ^b	4.00 ^c	4.00 ^c	12.00 ^d	12.00 ^d	3.00 ^e	3.00 ^e	3.00 ^e	3.00 ^e

Samples analysed were A4, A5 and A7. The calculated An (%), Ab (%), and Or (%) for albite, range from 0.4 to 6.4, 93.5 to 99.6 and ~0.1, respectively.

1 Vein fill epidote (Band B), 2 epidote from alteration zone, 3 vein fill sericite (Band B), 4 sericite from alteration zone, 5 vein fill albite, 6 albite from alteration zone, 7 vein fill chlorite, 8 chlorite from alteration zone, 9 vein fill calcite, 10 calcite from alteration zone, 11 vein fill ankerite, 12 ankerite from alteration zone

^a Number of ions basis of 13 atoms of (O, OH)

^b Number of ions basis of 10 atoms of (O, OH)

^c Number of ions basis of 4 atoms of O

^d Number of ions basis of 28 atoms of (O, OH)

^e Number of ions basis of 3 atoms of O

Table 2 Ore paragenesis and crustification banding of vein fill minerals

	Bands				
	A ^a	B ^a	C ^a	D ^a	
Mineral stages		Stage I	Stage II	Stage III	Stage IV
T (°C)	235–223	213–177	173–160	160–125	<100
Milky quartz	■■■■■■■■ ^b	■■■■■■■■■■			
Clear quartz			■■■■■■■	■■■■■	■■
Calcite			■■■	■■■■■	
Sericite		■■■■■	■■■■■		
Chlorite			■■■	■■■■■	
Epidote		■■■■	■■		
Albite		■■■	■■■		
Ankerite		■■■	■■■	■■■	
Sphalerite		■■			
Pyrite		■■			
Pyrrhotite		■			
Magnetite		■			
Arsenopyrite		■			
Argentite		■		■	
Electrum		■		■	
Stephanite		■			
Canfieldite		■			
Xanthoconite		■			
Proustite		■			
Tetrahedrite			■■		
Chalcopryrite			■■		
Famatinite			■		
Rammelsbergite			■		
Laggisite			■		
Cassiterite			■		
Galena				■■■	
Acanthite				■	
Polybasite				■	
Argentopyrite				■	
Covellite					■
Anglesite					■
Cerussite					■
Goethite					■
Hematite					■■

^a The number of boxes represents the abundance.

^b Mineral stage I (bands A and B) is related to the NE-trending banded mineralized milky quartz veins, while stages II and III to the NW-trending banded mineralized clear quartz veins.

Ag₅SbS₄ Stephanite, *Ag₈SnS₆* Canfieldite, *Ag₃AsS₃* Xanthoconite, *Ag₃AsS₃* Proustite, *Cu₃SbS₄* Famatinite, *(Ni,Co,Fe)As₂* Rammelsbergite, *Co_{0.8}Ni_{0.2}As* Laggisite, *Ag₁₆Sb₂S₁₁* Polybasite, *AgFe₂S₃* Argentopyrite.

medium-grained milky quartz matrix (Fig. 3b). Pyrite contains up to 2.24 wt.% As interpreted as native As nanoparticles (Table 3). Aggregates of intensely brecciated, anhedral and zoned sphalerite are intergrown with pyrite (Fig. 3b). Zoning in sphalerite is visible as green-brown cores and green-yellow rims reflecting zonation of the iron content, which range from 6.51 to 0.02 wt.% (Fig. 3b). Sphalerite contains up to 11.3 mol% FeS in the cores and up to 0.4 mol% FeS in the rims (Table 3). Crystals with Fe/Zn+Fe+Cb+Co values <0.01 are wurtzite and display a Co/

Fe+Cu+Co ratio ranging up to 0.01. Pyrite and sphalerite are intimately intergrown with fine-grained disseminations of subhedral arsenopyrite, anhedral hexagonal pyrrhotite and minor magnetite. Arsenopyrite with 44.44 to 44.85 wt.% As contains gold nanoparticles; so it appears, in some sites, rich in Au up to 1.12 wt.%. Specks or laths of stephanite, proustite, xanthoconite, argentite and canfieldite (up to 1 mm) are intergrown with pyrite and sphalerite. Electrum occurs as minute specks (up to 2 µm) and pseudo-cubic grains in intergrowths with sphalerite, pyrite and argentite.

Table 3 Representative electron microprobe analyses compositions of native metals, sulfosalts, and sulfides from Apigania Bay

Mineral	1	2 core	2 rim	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Wt. %																	
Ag	0.05	0.00	0.00	0.00	83.75	82.19	19.93	17.93	63.70	65.51	73.33	68.08	0.00	0.03	3.49	60.03	34.02
Cu	0.06	0.00	0.00	0.00	1.42	3.24	0.19	0.06	0.01	0.00	0.00	0.10	0.00	0.01	0.15	11.70	0.24
Pb	0.15	0.00	0.01	0.00	0.15	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	83.22	0.01	0.03
Zn	0.01	60.03	66.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au	0.00	0.00	0.00	1.12E	0.00	0.00	79.85	81.91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	27.83	8.77	0.00	0.00	0.00
Fe	46.62	6.51	0.02	33.80	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.01	0.01	0.00	35.05
Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.13	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.09	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.53	35.18	0.00	0.00	0.00
Te	0.00	0.00	0.00	0.00	1.62	0.79	0.02	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.00
As	1.85F	0.01	0.00	44.85	0.01	0.01	0.00	0.01	15.02	14.99	0.00	1.50	68.28	55.53	0.00	1.52	0.19
Sb	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	1.22	0.50	0.00	13.80	0.03	0.05	0.02	8.14	0.05
S	50.83	33.41	33.61	20.10	12.61	12.52	0.00	0.01	19.90	18.99	16.52	15.89	0.46	0.09	13.10	18.30	30.18
Total	99.67	99.99	99.99	99.89	99.57	99.04	99.99	99.97	99.85	99.99	99.98	99.37	99.38	99.71	99.99	99.95	99.77
No. of atoms based on																	
Ag	0.00	0.00	0.00	0.00	1.96 ^c	1.87 ^c	0.33 ^g	0.31 ^g	2.93 ^h	3.00 ^h	8.00	4.99 ^j	0.00	0.00	0.07 ⁿ	12.02 ^o	0.98 ^r
Cu	0.01 ^a	0.00	0.00	0.00	0.04 ^c	0.13 ^c	0.00	0.00	0.07 ^h	0.00	0.00	0.01 ^j	0.00	0.00	0.00	3.98 ^o	0.02 ^r
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.92 ⁿ	0.00	0.00
Zn	0.00	1.01 ^c	0.92 ^c	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au	0.00	0.00	0.00	0.01 ^d	0.00	0.00	0.67 ^g	0.69 ^g	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.91 ^k	0.20 ^m	0.00	0.00	0.00
Fe	0.98 ^a	0.00	0.11 ^c	0.99 ^d	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01 ^k	0.00	0.00	0.00	2.00
Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.01 ^a	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08 ^k	0.80 ^m	0.00	0.00	0.00
Te	0.00	0.00	0.00	0.00	0.02 ^f	0.01 ^f	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02 ^q	0.00
Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05 ^j	0.02 ⁱ	0.00	0.85 ⁱ	0.00	0.00	0.00	1.54 ^p	0.00
As	0.04 ^b	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.95 ^j	0.98 ⁱ	0.00	0.15 ^j	0.98 ⁱ	1.00	0.00	0.46 ^p	0.00
S	1.96 ^b	1.05	1.04	1.00	0.98 ^f	0.99 ^f	0.00	0.00	3.00	3.00	6.00	4.00	0.02 ^j	0.00	1.00	10.98 ^q	2.99
As/As + S	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.01	0.00	0.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
D	0.00	0.01	0.00	0.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00

Samples analyzed were A1, A3, A5, A6, A7, A9, and A10.

1 Pyrite from Stage I (Band B), 2 sphalerite from Stage I (Band B), 3 arsenopyrite from Stage I (Band B), 4 argentite from Stage I (Band B), 5 acanthite from Stage III (Band D), 6 electrum from Stage I (Band B), 7 electrum from Stage III (Band D), 8 xanthoconite from Stage I (Band B), 9 proustite from Stage I (Band B), 10 canfieldite from Stage I (Band B), 11 stephanite from Stage I (Band B), 12 rammelsbergite (with rose to green-blue anisotropy) from Stage II (Band C), 13 laggisite from Stage II (Band C), 14 galena from Stage III (Band D), 15 polybasite from Stage III (Band D), 16 argentopyrite from Stage III (Band D); A Cu + Co/Fe + Cu + Co, B Fe/Zn + Fe + Cu + Co, C Co/Fe + Cu + Co, D Cu/Pb + Fe + Cu + Co, E Au inclusion, F As inclusion

^a Fe+Co+Cu=1

^b As+S=2

^c Zn+Fe=1

^d Fe+Au=1

^e Ag+Cu=2

^f S+Te=1

^g Au+Ag=1

^h Ag+Cu=3

ⁱ As+Sb=1

^j Ag+Cu=1

^k Ni+Co+Fe=1

^l As+S=1

^m Co+Ni=1

ⁿ Pb+Ag=1

^o Ag+Cu=16

^p As+Sb=2

^q S+Te=11

^r Ag+Cu=1

Stage II, which is associated with type C bands, is dominated by the granular and massive aggregates of tetrahedrite, famatinite, chalcopryrite, rammelsbergite $[(\text{Ni}, \text{Co}, \text{Fe})\text{As}_2]$, laggisite $[\text{Co}_{0.8}\text{Ni}_{0.2}\text{As}]$ and cassiterite (Tombros and St. Seymour 2003). These minerals form massive grains and are commonly interstitial to fine-grained clear quartz. They replace stage I pyrite and sphalerite and were themselves replaced by galena (stage III). Intergrowths of tetrahedrite, famatinite and chalcopryrite occur as irregular masses of subhedral or anhedral crystals. Tetrahedrite contains up to 1.14 wt.% Ni and has a $\text{Sb}/(\text{As}+\text{Sb})$ ratio of 0.99. Tetrahedrite and chalcopryrite contain large inclusions of rammelsbergite and laggisite. Occasionally chalcopryrite is intergrown with cassiterite and commonly replaced by covellite (Tombros and St. Seymour 2003).

The central parts of the veins (type D bands) are characterized by stage III galena and argentite-acanthite, polybasite $[\text{Ag}_{16}\text{Sb}_2\text{S}_{11}]$, electrum and argentopyrite. Coarse-grained crystals of galena occur in massive aggregates, strongly deformed and replaced by cerussite and anglesite (Fig. 3c). Polybasite, argentite in intergrowths with acanthite, electrum and argentopyrite occur in association with galena (Fig. 3c). Stage I argentite contains up to 1.2 wt.% Cu and 1.6 wt.% Te, whereas stage III acanthite up to 3.4 wt.% Cu and 0.8 wt.% Te (Table 3). Stage I electrum bears 79.85 wt.% Au (fineness of 0.683) and up to 0.19 wt.% Cu, whereas stage III electrum contains 81.91 wt.% Au (fineness of 0.672) and traces of Cu (Table 3).

Fluid inclusion studies

Fluid inclusion data were obtained from milky and clear quartz (vein fill, epidote and chlorite zone), from fine- to medium-grained calcite, and stage I-sphalerite (Table 4). Fluid inclusions used in microthermometric studies ranged from 5 to 25 μm in length and their nature was based on the criteria of Roedder (1984). They were considered as primary due to their formation adjacent to growth zones and to planar arrays outlining growth zones. Isolated inclusions within the crystals were also analyzed. Secondary inclusions in milky quartz occurred in planes of healed fractures that cut across grain boundaries. Many of the primary milky quartz fluid inclusions studied were decrepitated, as they appear with halos of small secondary inclusions (Fig. 4).

At room temperature, only one type of fluid inclusions was identified: Type L–V inclusions consist of aqueous liquid+vapor, with the liquid phase being dominant in most inclusions (10 to 20 vol.%). Temperatures of initial ice melting (T_c) of these inclusions range from -47.2°C to -34.0°C , suggesting the presence of appreciable CaCl_2 in addition to NaCl (Oakes et al. 1990). Temperatures of last melting of ice range from -4.3°C to -0.1°C . Using the equation of Brown and Lamb (1989), the salinities range from 0.2 to 6.8 wt.% NaCl equivalent (Table 4). No gas hydrates were observed during freezing and no daughter crystalline solids were identified.

The L–V fluid inclusions homogenize to the liquid phase, upon heating, from 235°C to 125°C (Figs. 4 and 5, Table 4). As suggested by Roedder (1984) a pressure correction of $+5^\circ\text{C}$

Table 4 Fluid inclusion microthermometric data for primary liquid–vapor inclusions from Apigania Bay

Sample ^a	Mineral	V/L%	T_c Range	T_m Range	T_h Range	wt.% NaCl Range	Density Range
A10	2	4 to 22	–47 to –41	–4.3 to –2.3	195 to 212	3.4 to 6.8	0.88 to 0.91
A6	2	7 to 12	–43 to –40	–3.6 to –2.3	203 to 210	3.0 to 5.0	0.89 to 0.91
A5	1	10 to 20	–45 to –39	–3.6 to –0.4	173 to 235	3.5 to 5.8	0.86 to 0.90
A6	1	12 to 22	–45 to –40	–3.7 to –2.2	217 to 220	3.8 to 5.9	0.88 to 0.90
A7	3	5 to 27	–46 to –36	–3.4 to –0.1	153 to 168	0.2 to 5.5	0.91 to 0.96
A4	3	2 to 19	–36 to –34	–3.6 to –0.1	151 to 162	1.3 to 5.2	0.87 to 0.97
A10	4	5 to 10	–42 to –40	–3.0 to –1.1	125 to 143	1.8 to 3.3	0.95 to 0.97
A10	5	7 to 10	–41 to –38	–3.0 to –2.3	193 to 197	3.7 to 4.9	0.90 to 0.93
A7	6	10 to 30	–39 to –37	–0.9 to –0.2	150 to 160	0.2 to 1.5	0.91 to 0.93
A7	7	11 to 20	–39 to –38	–0.8 to –0.7	138 to 143	1.2 to 1.3	0.96 to 0.97
A1	8	10 to 15	–44 to –43	–3.0 to –2.4	197 to 212	3.9 to 4.8	0.88 to 0.91
A1	9	15 to 20	–46 to –38	–3.4 to –0.7	151 to 166	1.2 to 5.1	0.91 to 0.95
A1	10	10 to 20	–39 to –38	–1.0 to –0.7	138 to 152	1.2 to 1.6	0.93 to 0.94

Mineral: 1 Milky quartz from band A, 2 milky quartz from stage I and band B, 3 clear quartz from stage II and band C, 4 clear quartz from stage III and band D, 5 sphalerite from stage I and band B, 6 calcite from stage II and band C, 7 calcite from stage III and band D, 8 fine-grained milky quartz from epidote alteration zone 9 fine-grained clear quartz from chlorite alteration zone, 10 fine-grained calcite from chlorite alteration zone

^a The total of fluid inclusions analyzed were 50

Fig. 4 Fluid inclusions in milky quartz veins, at the Apigania Bay, Au–Ag mineralization. The inclusions are two-phase L–V primary inclusions, which show evidence of decrepitation (L liquid, V vapour)

was applied on homogenization temperatures up to 250°C. The pressure correction was calculated by Flncon software using independent pressure determinations from the Tinos pluton ($P=7$ and $P=2$ kbars for the granodiorite and leucogranite, respectively; based on the Al-hornblende and garnet–biotite–muscovite–plagioclase geobarometers, Mastrakas 2007).

Stable isotopes studies

Sulfur isotopes

Sulfur isotope analyses were obtained on pyrite and sphalerite (stage I), chalcopyrite (stage II) and galena (stage III). The $\delta^{34}\text{S}$ values range from 0.0 to -9.1‰ (Table 5). The calculated $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values of the mineralizing fluids, using

the fluid inclusions average homogenization temperatures reported in Table 5, range from -0.3 to -7.3‰ (Table 5). The cores of sphalerite exhibited $\delta^{34}\text{S}$ values of -0.4‰ and -0.5‰ , whereas the rims showed a value of -4.7‰ . These $\delta^{34}\text{S}$ values correspond to $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values of -0.9‰ , -1.0‰ and -5.5‰ , respectively.

Oxygen and hydrogen isotopes

Oxygen and hydrogen isotope compositions are given in Table 6 and were obtained from fluids released from samples of vein milky and clear quartz. The $\delta^{18}\text{O}$ and δD values of milky quartz range from 13.2‰ to 15.7‰ and -85‰ to -97‰ and of the epidote zone from 12.7‰ to 14.7‰ and -79‰ to -94‰ , respectively. For the calculations we have used the average temperature of fluid inclusions in milky and clear quartz, reported in Table 6. The calculated $\delta^{18}\text{O}$ and δD values of the mineralizing fluids range from -0.6‰ to 1.7‰ and -80‰ to -93‰ , respectively (Fig. 7, Table 6).

Clear quartz in veins and alteration possesses $\delta^{18}\text{O}$ and δD values of 15.9‰ to 18.0‰ and -99‰ to -112‰ and of 15.8‰ to 16.5‰ and -85‰ to -101‰ , respectively. The corresponding $\delta^{18}\text{O}$ and values of the mineralizing fluid in equilibrium with clear quartz range from -4.2‰ to -0.1‰ and -90‰ to -110‰ , respectively. These values are approximately 3.0 (for $\delta^{18}\text{O}$) and 30.0‰ (for δD) heavier than of those of milky quartz, respectively. The isotopic $\delta^{18}\text{O}$ compositions of the blueschists and greenschists of the Blueschists unit, range from 10.7‰ to 14.5‰ (Bröcker et al. 1993; Ganor et al. 1991, 1996).

Carbon and oxygen isotopes of carbonates

Carbon and oxygen isotope compositions were obtained from fine- to medium-calcite from clear quartz veins, and fine-

Fig. 5 Liquid–vapor homogenization temperature versus salinity plot in the NaCl–H₂O system from fluid inclusions of Apigania Bay and Panormos Bay mineralizations

Table 5 Sulfur isotope compositions of pyrite, sphalerite, chalcopyrite and galena from Apigania Bay

Sample	Mineral	<i>T</i> (°C)	δS34	δ ³⁴ S _{–H₂S} ^a
A7	1	200	–0.2	–0.9
A1	1	195	–0.3	–1.0
A6	1	205	–0.5	–0.8
A6	2	200	–0.5	–0.8
A5	2	210	0.0	–0.3
A6	2	205	–0.1	–0.7
A10	2a	195	–0.4	–0.9
A10	2b	177	–4.7	–5.5
A7	2a	198	–0.5	–1.0
A7	3	165	–3.2	–4.2
A4	3	155	–4.7	–5.1
A4	4	160	–6.7	–5.9
A10	4	160	–6.4	–5.7
A7	4	150	–9.1	–7.3
A7	4	150	–7.7	–6.2

Mineral: 1 Pyrite from stage I (band B), 2 sphalerite from stage I (band B), 2a sphalerite cores, 2b sphalerite rims, 3 chalcopyrite from stage II (band C), 4 galena from stage III (band D)

^aUtilizing the H₂S–water equations of Ohmoto and Rye (1979), and Ohmoto and Lasaga (1982)

grained calcite from chlorite alteration zone. δ¹⁸O values are between 17.9‰ to 19.2‰ (Table 7), whereas fine-grained calcite from chlorite zone yielded a value of 17.5‰ (Table 7). The calculated δ¹⁸O values of the fluids in equilibrium with calcite range from 9.0‰ to 10.3‰ (Table 7). An isotopic

analysis was conducted on metamorphic calcite from the marbles of Blueschists unit and yielded δ¹⁸O values of 20.7‰. The corresponding calculated δ¹⁸O values for the fluid are of 16.9, assuming a metamorphic temperature of 400°C (Tombros et al. 2007). Reported δ¹⁸O values from dolomites and calcites in the marbles of the Blueschist unit range from ~20.0‰ to 31.5‰, and ~20 to 29.1‰, respectively (Bröcker et al. 1993; Ganor et al. 1991, 1996).

The δ¹³C values for the same samples range from 0.85‰ to 1.2‰, corresponding to calculated values of δ¹³C_{CO₂} from 0.7 to 1.1‰. A measured value of δ¹³C for a sample from the chlorite zone was 0.7‰, with a corresponding δ¹³C_{CO₂} value of 0.6‰. Lastly, the sample of metamorphic calcite yielded δ¹³C values of 1.6‰, corresponding to δ¹³C_{CO₂} value of 1.4 (Fig. 8, Table 7).

Discussion

Fluid evolution

The relationship between homogenization temperatures and salinities of fluids at Apigania Bay is displayed in Fig. 5 (with addition of selective fluid inclusions analyses from Panormos Bay for comparisons, Tombros et al. 2007). As it has already discussed for Panormos Bay, these trends indicate a history of CO₂ effervescence (Tombros et al. 2007). H₂O-rich inclusions in milky quartz and clear quartz-calcite

Table 6 Oxygen and hydrogen isotope compositions of milky and clear quartz vein from Apigania Bay

Sample	Mineral	<i>T</i> (°C)	Δ ¹⁸ O-quartz	δ ¹⁸ O-water ^a	δD-quartz	δD-water ^b
A10	1	235	13.9	1.7	–89	–85
A6	1	225	13.2	1.3	–85	–80
A10	1	223	14.6	1.5	–93	–90
A5	2	207	14.3	0.2	–89	–86
A10	2	212	14.9	1.2	–95	–92
A7	2	195	15.0	–0.1	–97	–93
A6	2	200	15.7	–0.6	–94	–90
A10	3	165	15.9	–1.8	–99	–98
A10	3	150	16.8	–2.4	–108	–102
A4	3	155	16.2	–2.0	–112	–104
A7	4	143	17.0	–2.8	–111	–107
A7	4	125	17.2	–4.2	–110	–110
A7	4	130	18.0	–4.7	–120	–114
A1	5	210	13.0	1.1	–84	–80
A6	5	205	12.7	0.8	–79	–84
A1	5	197	14.7	0.1	–94	–91
A10	6	166	15.8	–0.1	–92	–90
A7	6	165	15.2	–0.2	–85	–92
A10	6	151	16.5	–1.9	–101	–98

Mineral: 1 Milky quartz from stage I (band A), 2 milky quartz from stage II (band B), 3 clear quartz from stage III (band C), 4 clear quartz from stage IV (band D), 5 milky quartz from epidote alteration zone, 6 clear quartz from chlorite alteration zone

^aUtilizing the quartz–water equation of Clayton et al. (1972)

^bUtilizing the quartz–water, and muscovite–water equations of O’Neil and Taylor (1972), and Suzuoki and Epstein (1976)

Table 7 Oxygen and carbon isotope data obtained from calcite at Apigania Bay

Sample	Mineral	T (°C)	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$ -water ^a	$\delta^{13}\text{C}$	$\delta^{13}\text{C}_{\text{fluid}}^b$
A7	1	165	17.9	9.2	0.85	0.7
A7	1	150	18.0	9.3	0.9	0.8
A7	2	145	18.9	10.1	1.0	0.9
A7	2	125	19.2	10.3	1.2	1.1
A7	3	165	17.5	9.0	0.7	0.6
A7	4	400 ^c	20.7	16.9	1.6	1.4

Mineral: 1 Calcite from stage II and band C, 2 calcite from stage III and band D, 3 fine-grained calcite from chlorite alteration zone, 4 metamorphic calcite from Blueschist unit marbles

^a Utilizing the calcite–water equation of O'Neil et al. (1969)

^b Utilizing the CO_2 –water equation of Ohmoto and Rye (1979)

^c Tombros (2001)

veins (Stage I and Stages II and III, respectively) display a parabolic trend of increasing salinities (from 3.4 to 6.8 wt.% equivalent NaCl and 0.2 to 5.5 wt.% equivalent NaCl) with decreasing temperatures (from 125°C to 235°C; Fig. 5). This negative correlation can be attributed to either boiling of the hydrothermal fluid (Hedenquist and Henley 1985a, b) or tectonic uplift of the system, causing degassing due to depressurization (Vityk et al. 1994; Vityk and Bodnar 1995). Positive correlation of temperature and salinity in the same diagrams indicate that the hydrothermal fluids ores evolved due to mixing with local meteoric waters (Fig. 5).

For the early mineralizing stages a temperature interval of 235°C to $\approx 177^\circ\text{C}$ is obtained, which ends with precipitation of stage I-minerals (Table 2), from dilute fluids (3.4 to 6.8 wt.% NaCl equivalent). Application of the pyrite–sphalerite–argentite–electrum geothermometer (Shikazono 1985), brackets stage I-ore assemblages between 177°C and 195°C, whereas fluid inclusion temperatures in sphalerite

indicate a range of 193°C to 197°C (Table 4). Clear quartz veins, which represent the later sulfide mineralization (stages II to III) were deposited between $176 \pm 0.5^\circ\text{C}$ to 125°C, as indicated by the coexistence of argentite–acanthite and fluid inclusion data, from low salinity fluids (0.2 to 5.5 wt.% NaCl equivalent; Fig. 5).

The maximum pressure of fluid entrapment can be calculated from the thickness of the overlying Upper unit rock column, which at Apigania Bay area is estimated to be ≈ 1.5 km (Melidonis 1980). These depths correspond to a lithostatic pressure of 400 bars or a hydrostatic pressure of 150 bars. Geological features indicate that pressure conditions were hydrostatic (i.e., the high-porosity and abundance of vugs in marbles, the brittle character of mineralized fractures in schists, and the main occurrence of milky quartz veins as stockworks and of clear quartz veins with “open-space” filling and comb textures). A combined plot of temperatures versus pressure, for Apigania and Panormos Bay, suggests that the Apigania mineralization formed under hydrostatic pressures of 50 to 380 bars, with average of ≈ 100 bars (Fig. 6). The continuation of pressure and temperature values indicates that the Apigania Bay mineralization could have formed at shallower levels (Fig. 6). Statistical analyses for the documented pressures for the fluid inclusion from milky and clear quartz, sphalerite and calcite reveal that the correlation coefficients were 0.59, 0.61, 0.77, and 0.56, respectively.

The fluid inclusion data reveal that there is a positive linear trend of decreasing temperatures and increasing pressures (Fig. 6). These trends (Figs. 5 and 6) can be explained by boiling and CO_2 -effervescence for the Panormos Bay mineralization, but cannot be the case for Apigania Bay because of the absence of vapor rich inclusions. Alternatively it can be explained by the decrepitation of the inclusions

Fig. 6 Temperature versus pressure plot in the NaCl–H₂O system, from fluid inclusions from Apigania and Panormos Bay mineralizations

due to rapid tectonic uplifting in successive steps. According to Roedder (1984), Vityk et al. (1994) and Vityk and Bodnar (1995) the external pressure of the fluid inclusions decreases rapidly during tectonic uplift with a slight drop of temperature (less than $\approx 50^\circ\text{C}$ for Apigania Bay). This mechanism could produce overpressure conditions that will cause decrepitation of the inclusions, intense degassing and release of enough fluid to permit resealing of the inclusions leaving a fluid with higher density. It appears that in Apigania Bay the internal pressures recorded from fluid inclusions are greater than the confining pressures (Fig. 6).

Source of metallic and hydrothermal component

Regardless of the fact that the sulfur isotope data are few in number ($n=15$), the calculated $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values of mineralizing fluids show a considerable range of isotopic values ranging from -0.9‰ to -6.2‰ (Table 5). Values of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ of stage I (i.e., 0‰ to -1.0‰) exhibit a transitional minor magmatic to metasedimentary origin with contribution of sulfur from the Blueschist unit. Values of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ throughout stages II and III, become progressively lighter (i.e. -4.2‰ to -7.3‰ , respectively). The reason for such a progressive reduction in $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values is possibly due to the progressive exchange of the ore fluid with the metamorphic country rocks. This hypothesis is supported by a single sample of pyrite from the Blueschist unit schists just 1 km away from Apigania Bay, which has a calculated sulfur isotope value of -18.2‰ (Tombros et al. 2007).

Oxygen, hydrogen, and carbon isotope data suggest a combined magmatic-meteoric origin for the ore fluid. The O and H isotope compositions for the early and late stages of the Apigania Bay fluid reflect the dominance of

meteoric waters, which evolved due to mixing and isotopic exchange, at low water-to-rock ratios (Fig. 7). A trend of decreasing $\delta^{13}\text{C}_{\text{CO}_2}$ compositions, with decreasing temperatures and increasing $\delta^{18}\text{O}$ values indicates interaction of the ore fluids with the wall-rocks (Fig. 8). Sulfur isotopes also indicate a magmatic-metasedimentary origin in the early stages of mineralization. With falling temperature and increased fluid circulation, as mixing and wall-rock to fluid interactions proceed, gradual addition of sulfur is apparent due to increasing degree of leaching from a same source. The source of precious and other metals can be assigned to the metamorphic country rocks (Table 8). Trace element contents in the Apigania Bay mineralization suggest contribution to the ore fluid from the Blueschist unit and Upper unit rocks, although some of them were partly derived from Tinos leucogranite, which also acted as heat engine. The host rocks are characterized by high values of Cu (up to 676 ppm), Zn (up to 378 ppm), Ag (up to 372 ppm), Au (up to 592 ppm), V (up to 46 ppm), Cd (up to 4 ppm), Sb (up to 37 ppm) As (up to 67 ppm), Cr (up to 93 ppm), Co (up to 8 ppm) and Ni (up to 57 ppm). On the contrary leucogranite and miarolitic smoky quartz may have contributed Pb (up to 172 ppm), Br (up to 0.8 ppm-rich in volatiles), Sn (up to 1,000 ppm) and Re (Table 8).

Physicochemical conditions of metallic mineral formation

Chemical conditions of mineralization were estimated from phase stability relationships at temperatures of 200°C , 175°C and 150°C and the pressure of vapor-saturated liquid using SUPCRT92 (Johnson et al. 1992). All phases were considered to be ideal and individual ion activity coef-

Fig. 7 Hydrogen versus oxygen isotope diagram and histogram, displaying stable isotope systematics of hydrothermal fluids from Apigania Bay mineralization. The “Meteoric water line” and the “Subduction-related vapor, arc and crystal felsic magma” (Hedenquist and Lowenstern 1994) are also displayed

Fig. 8 Carbon versus oxygen isotope diagram from vein and alteration calcites, displaying stable isotope systematics of hydrothermal fluids from Apigania Bay mineralization. Temperatures represent the equilibrium temperatures obtained from fluid inclusions between calcite and clear quartz

ficients of dissolved species were derived from Helgeson and Kirkham (1974a, b), Harvie et al. (1984), Henley et al. (1984), Ahmad et al. (1987) and Zhang and Spry (1994).

From the reaction (1) $\log a_{\text{SiO}_2(\text{aq})}$ values of -1.9 , -2.5 and -2.8 were derived at 200°C , 175°C , and 150°C , respectively:

Values of pH were obtained, at the same temperatures, from albite-sericite ($\pm$ quartz) equilibria (Eq. 2):

Based on the albite-orthoclase equilibrium (reaction 3) the calculated $\log(\text{Na/K})$ values were 0.64 , 0.78 and 0.95 . These values correspond to activity coefficients of Na^+ ($\log \gamma_{\text{Na}^+}$) of 0.85 , 0.79 and 0.72 [based on the Debye-Hückel expression of Helgeson et al. (1981), reaction 3], and concentrations of Na^+ ($m\gamma_{\text{Na}^+}$) of 0.67 , 0.74 and 0.81 mg/l, respectively (based on the molal calculations obtained from salinities determinations of fluid inclusions studies; assuming that all salts are NaCl). Using the latter concentrations the $\log a_{\text{Na}^+}$ values of -0.38 , -0.34 , and -0.45 were obtained at 200°C , 175°C , and 150°C , respectively, and pH values of 6.9 , 7.2 and 7.6 , respectively.

Using data from Barton and Toulmin (1964) and Barton (1980) for the assemblages pyrite-sphalerite-pyrrhotite and pyrite-sphalerite-electrum-argentite, respectively; values of $\log f_{\text{S}_2}$ obtained for stages I and III are: for sphalerite

cores and rims values of $\log f_{\text{S}_2} = -16.8$, and -18.1 , and for the pyrite-sphalerite-electrum-argentite assemblage of $\log f_{\text{S}_2} = -16.6$, and $\log f_{\text{S}_2} = -17.7$, respectively. The assemblage of famatinite-tetrahedrite $\pm$ chalcocopyrite for $T = 175^\circ\text{C}$, yields a maximum $\log f_{\text{S}_2}$ value of -17.2 for stage II (Craig and Barton 1973). At 200°C the assemblage pyrite-pyrrhotite-magnetite “buffers” the $\log f_{\text{O}_2}$ values at -44 (Barton and Skinner 1971; Barton and Toulmin 1964). The appearance of galena in stage III, in the absence of anglesite, at $T = 150^\circ\text{C}$ and $\text{pH} = 7.6$, requires a maximum $\log f_{\text{O}_2} = -41.5$ (Craig and Barton 1973).

Table 8 Representative major (wt.%) and trace (ppm) element analyses of vein and host rocks from the Apigania Bay

	1	2	3	4	5	6	7	8
SiO ₂	76.03	96.34	75.98	0.50	45.70	85.65	85.37	55.79
TiO ₂	0.03	0.01	0.03	0.02	0.08	0.01	0.01	1.31
Al ₂ O ₃	13.35	0.05	13.22	0.57	15.14	0.27	0.03	10.26
Fe ₂ O ₃	0.40	1.21	1.28	7.71	6.35	0.80	0.35	16.13
MnO	0.17	0.00	0.01	0.01	0.01	0.00	0.00	0.20
MgO	0.04	0.01	0.06	5.48	5.46	0.08	0.55	7.61
CaO	0.46	0.02	1.08	53.58	20.49	11.52	12.72	4.17
Na ₂ O	3.24	1.31	3.22	0.01	2.72	0.01	0.02	2.78
K ₂ O	5.99	1.02	5.09	2.01	4.02	1.20	1.10	1.71
P ₂ O ₅	0.02	0.00	0.02	0.01	0.02	0.08	0.02	0.01
LOI	0.20	0.00	0.00	30.13	0.00	0.31	0.00	0.00
Total	99.93	99.97	99.99	99.98	99.99	99.93	99.99	99.97
Sr	13	22	67	357	871	15	437	70
Y	53	20	13	12	8	5	35	13
Zr	56	40	35	25	26	20	24	11
Cu	4	8	2	676	14	20	6	40
Pb	167	155	154	57	6	38	55	13
Zn	28	23	7	282	378	211	11	45
Ag	5	4	5	372	140	173	43	35
Ni	2	8	2	37	36	9	3	57
Cd	5	0.3	0.4	3.3	4	1.3	1	0.3
V	2	2	2	40	46	2	8	145
Au	2	5	40	352	592	202	1.5	15
As	1	1.2	0.9	66	67	41	18	0.5
Br	0.5	0.8	0.3	0.3	0.3	0.8	1.4	0.1
Co	6	2	1	8	34	7	6	38
Cr	17	11	1.5	28	26	6	5	93
Cs	63	11	7	1	1	1	1	11
Hf	5.1	2.1	1.7	0.5	0.6	0.8	0.8	1
Rb	820	265	225	15	14	13	11	8
Sb	1.5	0.2	0.2	18	37	7.2	0.3	0.6
Th	15	25	11	0.3	0.6	0.2	0.4	0.9
U	19.5	15	3.7	0.8	0.5	0.2	0.3	0.1
Nb	66	3	3	1	1	1	1	1
Sn	20	1000	980	2	1	875	192	2
La	4.7	3.5	3.9	3	1.6	4.2	35	15
Ce	13	10	9	6	4	<3	49	39
Nd	8	5	4	2	1	5	28	21
Sm	2.9	0.7	0.6	0.8	0.4	0.5	5.2	6.4
Eu	0.33	0.2	0.19	0.3	0.1	0.2	1.1	1
Tb	1	0.5	0.5	0.2	0.1	0.2	1	0.6
Yb	3.9	0.8	0.6	0.5	0.6	0.3	1.8	4.5
Lu	0.6	0.2	0.1	0.1	0.1	0	0.3	0.8

1 Tinos leucogranite (average of $n=7$), 2 smoky quartz (average of $n=2$), 3 aplites (average of $n=4$), 4 marbles of the Blueschists unit (average of $n=5$), 5 schists of the Blueschists unit (average of $n=5$), 6 milky quartz veins (average of $n=20$), 7 clear quartz veins (average of $n=20$), 8 schists of the upper unit (average of $n=15$)

Using reactions 4, 5, 6, 7 and 8, for $T=200^\circ\text{C}$ and $\text{pH}=6.9$, and $T=150^\circ\text{C}$ and $\text{pH}=7.6$ the values of $\log a_{\text{H}_2\text{S}(\text{aq})} = -2.6$ and -3.4 , $\log a_{\text{HS}^-} = -2.3$ and -3.3 , and $\log f_{\text{H}_2\text{S}} = -2.2$ and -2.7 , were obtained, respectively. The calculated values of the ions Fe^{+2} and Zn^{+2} , in solution, were $\log a_{\text{Fe}^{+2}} = -5.7$ and $\log a_{\text{Zn}^{+2}} = -8.7$, corresponding to a ferrous and zinc content of

Table 9 Calculated physicochemical parameters of stage I, II, and III fluids of Apigania Bay mineralization

Physicochemical Parameters	Stage I	Stage II	Stage III
Temperature (°C)	235–176.5	176.5–160	160–152
pH	6.9	7.2	7.6
$\log a_{\text{SiO}_2(\text{aq})}$	–1.9	–2.5	–2.7
$\log f_{\text{S}_2}$	–16.8 to –18.1	–17.2	–17.7
$\log a_{\text{H}_2\text{S}(\text{aq})}$	–2.6	–	–2.7
$\log f_{\text{H}_2\text{S}(\text{g})}$	–2.2	–	–3.4
$\log \bar{f}_{\text{HS}(\text{aq})}$	–2.3	–	–3.3
$\log f_{\text{O}_2}$	–44	–	–41.5
$\log a_{\text{Fe}^{+2}}$	–5.7	–	–
$\log a_{\text{Zn}^{+2}}$	–8.7	–	–
$\log a_{\text{Au}^+}$	–11.5	–	–12.7
$\log a_{\text{Ag}^+}$	–14.4	–	–15.7
$\log a_{\text{Pb}^{+2}}$	–	–	–7.3

Mean temperatures for stages I, II, and III of 200°C, 175°C and 150°C and ionic strength $I=0.1$.

8.3 and 0.95 ppb, respectively (Table 9). Based on equilibria 9, 10 and 11 for the formation of electrum at $T=190^\circ\text{C}$ and $T=150^\circ\text{C}$ and $\text{pH}=6.9$ and 7.6 respectively, the minimum calculated values of $\text{Au}^+(\text{aq})$ and $\text{Ag}^+(\text{aq})$ are $\log a_{\text{Au}^+} = -11.5$ and $\log a_{\text{Ag}^+} = -14.4$ (stage I), and -12.7 and -15.7 (stage III). These values correspond to gold and silver concentrations of 1.3, 0.8, 1.0 and 0.4 ppb, respectively (Table 9), whereas values of $\log[a_{\text{Au}^+}/a_{\text{Ag}^+}]$ range from 0.1 to 0.3. From equilibrium 12 for galena, and stage III conditions, the minimum calculated value of $\text{Pb}^{+2}(\text{aq})$ is $\log a_{\text{Pb}^{+2}} = -7.2$, corresponding to lead concentration of 1.8 ppb (Table 9).

Precipitation of ores

There is an overall decrease in homogenization temperatures from type A to D crustification bands (type A bands are characterized by $T=235^\circ\text{C}$ to 220°C , for type B the $T=215^\circ\text{C}$ to 170°C , for type C the $T=168^\circ\text{C}$ to 150°C , and for type D the $T=145^\circ\text{C}$ to 125°C). This temperature drop was likely caused by mixing of the precious metal laden fluid with waters of meteoric origin, as it entered the intensely fractured hydrothermal system. This scenario is also reflected by stable isotope data (Fig. 7). The progressive decrease of average salinity with decreasing temperature (from ≈ 5 wt.% NaCl-stage I to ≈ 0.2 wt.% NaCl-stage III) suggests progressive dilution of the ore fluids with meteoric waters. Precipitation of base metal sulfides was the consequence of the temperature drop from 200°C to 177°C , coupled with the decreasing f_{S_2} from -16.8 to -18.1 . Calcite deposition occurred at low temperatures ($\approx 160^\circ\text{C}$ to 140°C) as a result of continuous cooling, dilution and mixing, and represents the final closure of the hydrothermal system (Fig. 5).

At Apigania Bay, there is evidence of decrepitation the inclusions. As it was pointed out by Avigad and Garfunkel (1991), Gautier and Brun (1994a, b), Avigad et al. (1994), Famin et al. (2004), Jolivet et al. (2003, 2004), Tinos hydrothermal system evolved into an interconnected network as the exhuming footwall moved rapidly to the surface. This uplift was controlled by large-scale en-echelon normal-oblique faults accompany the Tinos extensional shear zone and the elongated dome due to a regional extensional stress field with NE-direction (Fig. 1b). Due to the uplift the external pressure of the fluid inclusions decreases rapidly, with a slight temperature drop, and resulted overpressure conditions which will produce degassing of the fluid. Escape of H_2S and O_2 due to overpressure drove reactions 4 to the right and reactions 5, 6, 9, 10 and 11 to the left. As a consequence such conditions will produce intense hydraulic fracturing, increase in the pH into slightly alkaline of gold and silver-bearing hydrothermal fluid and destabilization of the bisulphide ligand (Gammons and Williams-Jones 1995b). Deposition of native metal alloys, via reactions 9, 10 and 11, coincided with a decrease in $f_{\text{H}_2\text{S}}$ and pH from $10^{-2.6}$ and 6.9 , at $T=200^\circ\text{C}$, to $10^{-3.4}$ and 7.6 , at $T=150^\circ\text{C}$.

Comparisons between the Apigania and Panormos Bay epithermal ore systems

Although the Apigania and Panormos Bay mineralizations, are different by more than one feature; they share several geological, mineralogical, and geochemical attributes. These similarities suggest a common origin, but a different evolutionary phase of the same major ore event in the Tinos hydrothermal system. The Panormos Bay ores are hosted exclusively in the marbles of both the Basal and Blueschist units, whereas the Apigania Bay in the marbles and schists of the Blueschist unit. These ore systems exhibit the same styles of epithermal stockworks (i.e., the Panormos Bay mineralization is characterized by the abundance of numerous veins, more than thirty major against five; and of hydrothermal vein breccias, against of tectonic origin), in directions, steep faults, banding, and mineralogical sequence of earlier milky and later clear quartz veins.

Major differences in alteration patterns, include the formation of talc-brucite-calcite versus epidote-ankerite and chlorite-epidote-ankerite versus chlorite-calcite paragenetic sequences (of the inner and outer zones, respectively). Ore paragenesis, generally, evolves from base metals in the early stages to precious metals in the late ones. Pyrite, tetrahedrite, chalcopyrite, Ni–Co arsenides, galena, and Sn-bearing minerals are common in both of the mineralizations. The occurrence of the Sn-minerals suggests the possible link to the Tinos pluton leucogranitic phase. The Panormos Bay assemblages contain

exclusively tellurides (both of base and precious metals) and native precious metals, whereas the Apigania Bay precious metals are deposited, even in the early stages, as alloys (electrum) and Ag-sulfosalts. In the Panormos Bay mineralization, pyrite contains Au (3.34 wt.) and Te (0.13 wt.%), whereas at Apigania Bay As (1.85 wt.%) and Ag (0.15 wt.%), respectively. In comparison, arsenopyrite is As-rich, whereas sphalerite is Fe-poor. Chalcopyrite, tetrahedrite, and galena from Panormos Bay are rich in Ag (up to 1.2, 3.5 and 1.0 wt.%) and Te (up to 6.5, 9.2, and 6.0 wt.%). In both systems deposition of Ag-bearing minerals proceeded of the Au-bearing, and Sn- and Ni, Cr-bearing phases are deposited.

Homogenization temperatures of Panormos Bay fluid inclusions were from 200°C to 300°C, with the telluride ore to be precipitated from 230°C to 260°C, and native precious metals below 210°C, whereas at Apigania Bay the inclusions homogenize to liquid from 125°C to 235°C, with the ores precipitate from 150°C to 195°C. Fluids responsible for Apigania Bay mineralization were non boiling, cooler (~235°C to 125°C), with salinities overlapping the ones of Panormos Bay (0.8 to 6.8, against 0.6 to 13.3 wt.% NaCl equivalent). Ore-bearing fluids cooled, mixed, and progressively diluted from early to late stages in both systems. CO₂-bearing fluid inclusions showing evidence for effervescence characterize the Panormos Bay (Tombros et al. 2007), whereas at the Apigania Bay decrepitated inclusions related to intensive uplift assisted deposition to shallower depths (at ~100 bars). The Panormos Bay mineralization has been deposited under the same hydrothermal conditions, from pressures below 500 bars, at the deeper parts of the hydrothermal system, although there is evidence of uplifting in the late stages.

The $\delta^{18}\text{O}$ values from Apigania Bay overlap these from Panormos Bay (i.e., -0.1‰ to 1.7‰ against -3.3‰ to 5.1‰, Tombros et al. 2007) whereas the δD values are heavier (i.e., -62‰ to -73‰ against -100‰ to -103‰). There is a recognizable overlap of the obtained values from milky and clear quartz of the mineralizing fluid, and of the metamorphic rocks of the Blueschist unit. The values of water-to-rock ratios in the Apigania Bay rose up to 16%, against the 6% from Panormos Bay (Tombros 2001). Calculations of water-to-rock ratios were performed by assuming an open system, based on the equations adopted from Taylor (1974). The Apigania Bay calculated $\delta^{34}\text{S}_{\text{H}_2\text{S}}$, $\delta^{18}\text{S}_{\text{H}_2\text{O}}$, and $\delta^{13}\text{C}_{\text{CO}_2}$ values overlap the ones from Panormos Bay (i.e., -0.3‰ to -5.9‰ against 0.8‰ to -10.5‰, 7.3‰ to 12.2‰ against 9.0‰ to 10.3‰, and 0.6‰ to 1.1‰ against -0.3‰ to -2.0‰, respectively, Tables 5, 7 and Fig. 8).

From the isotope data it appears that the Apigania Bay mineralizing fluid has been interacted with the metamorphic wall-rocks, and mixed with meteoric waters. This can be attributed to the alkaline nature of the fluid and the open

character of the hydrothermal system, as it was revealed from the water-to-rock ratios calculations. Zoning in sphalerite also points out that the ore minerals were out of equilibrium and precipitated in an open environment. In the Panormos Bay system the contribution from magmatic fluids is apparent, and isotopic exchange with the marble wall-rocks is in a lesser degree. Metals and sulfur were mainly contributed from the metasedimentary Blueschist rocks, although a part of them could have been derived from the leucogranite. Likely sources of the host rocks for the metallic components in the Apigania Bay mineralization are the schists and marbles of the Blueschist unit, whereas in the Panormos Bay ore there is also contribution from the Basal and Upper unit rocks.

The Panormos Bay mineralizing fluid bears a more sulfidized, acidic, auriferous and telluric signature, whereas the Apigania Bay a more oxidized, H₂S and silver-bearing. In the Panormos Bay and Apigania Bay mineralization the major physicochemical parameters were: $\log f_{\text{S}_2} = -10.9$ to -15.0 , and -16.8 to -18.1 , $\log f_{\text{O}_2} = -37.0$ to -41.0 , and -44.0 to -41.5 , pH=4.6 to 6.5, and 6.9 to 7.6, and $\log f_{\text{H}_2\text{S}} = -1.7$ to -1.8 , and -2.2 to -3.4 , respectively.

The main difference between the two ore occurrences is the absence of tellurium deposition in the Apigania Bay. Possible explanations for the non deposition of tellurides can be attributed to the non occurrence of CO₂-effervescence of the mineralizing fluid, in the absence of available tellurium content due to pre-deposition in the Panormos Bay, in the minor volume of the highly reactive marbles in the area and in absence of magnesium the marbles or in solution, which may have played a catalytic role and helped tellurium to condense. Experimental studies have showed that magnesium has the capacity to increase the rate of hydrogen dissociation, slow down its adsorption kinetics, and lead hydrogen-bearing gases to condense (Swartz et al. 1999). This hypothesis is supported by the presence of magnesium minerals in the most studied Ag-Au-Te ore deposits such as: dolomite-talc-brucite (Panormos Bay; Tombros et al. 2004, 2005, 2007), Mg-chlorite (Acupan; Cooke et al. 1996; Cooke and McPhail (2001), dolomite (Cripple Creek; Thompson et al. 1985; Kelley et al. 1998), dolomite and Mg-chlorite (Emperor, Tuvatu; Ahmad et al. 1987; Scherbarth and Spry 2006), roscoelite and dolomite (Porgera; Richards and Kerrich 1993; Ronacher et al. 2004) and Mg-chlorite and manganese ores (Sunnyside mine; Casadevall and Ohmoto 1977).

The Apigania Bay system could be regarded as a small occurrence contemporaneous to the Panormos Bay, which most likely formed at shallower crustal level (Fig. 6). Both of the mineralizations were most likely formed by the processes generated by the leucogranite phase of the Tinos pluton, with Apigania Bay representing the latest evolutionary phase of the hydrothermal system. The evolution of the mineralizing hydrothermal fluids began with the

deposition of scheelite in the skarn rocks nearby Tinos granodiorite-leucogranite (Fig. 1b); continued with the tellurium-bearing precious metals ores at the Panormos Bay and ended with precious metals ores tellurium absent at Apigania Bay.

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