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Ore mineralogy of transitional submarine to subaerial magmatic-hydrothermal deposits in Western Milos, Greece

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Abstract. Precious metal rich intermediate sulfidation mineralization in W. Milos Island, was formed in a transitional submarine to subaerial environment and is spatially related to a high-sulfidation epithermal center. The latter is exposed in the Triades-Galana-Kondaros corridor and is characterized by a pre-ore advanced argillic alteration, followed by a Cu-rich mineralizing event including chalcopyrite, tetrahedrite/tennantite and enargite. The gold-rich Profitis Ilias-Chondro Vouno system in the south, and a previously unrecognized silver-bearing mineralized system in the north along the Kondaros-Katsimouti-Vani fault, were probably developed contemporaneous to ore introduction in the HS center and followed distinct evolutionary paths due to emergence of the southern volcanic sector.

Key words: high-intermediate sulfidation (HS-IS), transitional volcanics, silver mineralogy

Introduction

Transitional shallow submarine to subaerial arc-volcanic rocks of W. Milos (Stewart and McPhie, 2003) contain epithermal deposits such as the Au-Ag Profitis Ilias and Chondro Vouno, the Pb-Zn-Ag-Ba Triades-Galana and the Mn-Ba-Pb-Zn Vani deposit (Vavelidis and Melfos, 1997; Constadinidou et al., 1998; Hein et al., 2000; Liakopoulos et al., 2001; Kilias et al., 2001; Alfieris et al., 2004). These are closely linked to a mineralized active geothermal system that is characterized by three-component mixing between seawater, meteoric water and a magmatic component (Pflumio et al., 1991). This paper presents new mineralogical data on the W. Milos mineralization and also a previously unrecognized Ag-rich mineralization on the northern part of the island related to the Vani Mn deposit. Genetic considerations are presented concerning the spatial relationship between the three systems.

Geology of the area

Calc-alkaline volcanic activity in W. Milos spans a period from ~ 4 Ma to the present and originated from several emergent eruptive centers (Stewart and McPhie, 2003). The main volcanic units (Fig. 1) are: L. to U. Pliocene submarine acid pyroclastics, U. Pliocene to L. Pleistocene transitional pyroclastics, pumice flows and dacitic-andesitic flow domes and lavas, and L. Pleistocene submarine or subaerial acid subvolcanics. Miocene to Pliocene extensional tectonics resulted in four main fault trends: NW–SE, N-S, NE-SW and a E-W trend. This tectonic regime created a pattern of horst and graben structures and controlled the volcanic and hydrothermal activity.

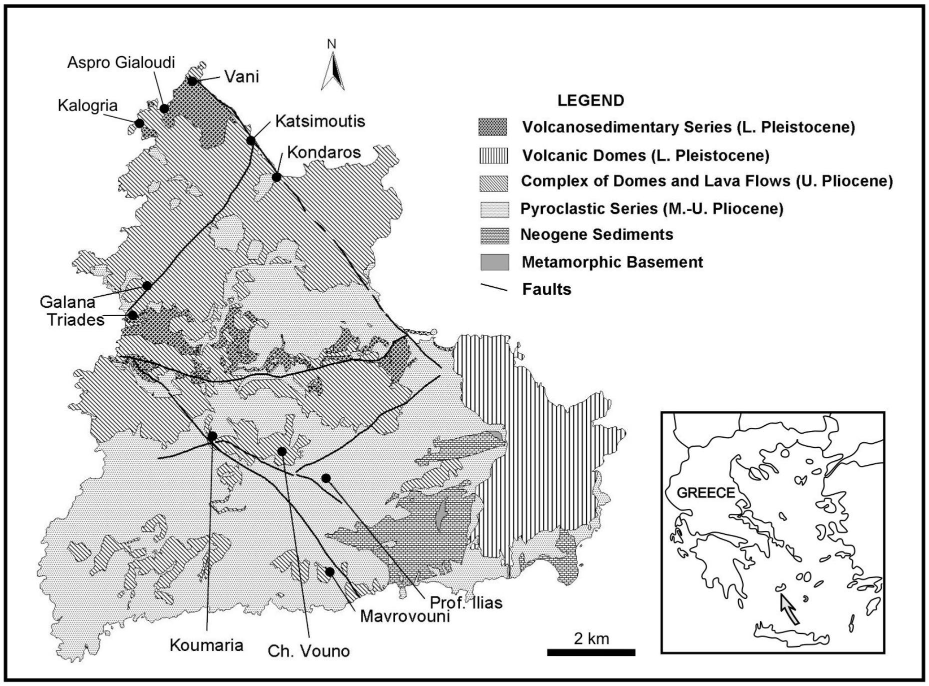

Fig. 1. Generalized geological map of W. Milos area

Mineralization

a) Triades-Galana-Kondaros (TGK)

Mineralization occurs mostly in NE–SW and E–W trending faults and is expressed as multi-stage breccia zones and barite-galena veins (Fig. 2a, b), related to massive-vuggy silica, quartz-sericite and quartz-kaolinite/alunite alteration. The textural features of the ore, indicate early deposition of pyrite with minor bornite and Fe-rich sphalerite inclusions, followed by chalcopyrite, galena and Fe-poor sphalerite and then by a HS Cu-bearing assemblage composed of tetrahedrite-group minerals and enargite. Gangue minerals are barite, kaolinite, sericite, adularia and quartz.

b) Profitis Ilias-Chondro Vouno (PI-CV)

Mineralization is of IS type and is expressed as a series of N–S to NE–SW trending crustiform/colloform banded veins related to the quartz-sericite-illite and quartz-adularia-sericite alteration. It comprises quartz, chalcedony, adularia and barite, with pyrite, chalcopyrite, galena, Fe-poor sphalerite, native gold and electrum (Constadinidou et al., 1998). Surface material sampled during this study indicates contemporaneous deposition of base metal sulfides (galena, sphalerite, chalcopyrite) and tetrahedrite to both chalcedonic and late comb amethystine quartz (Fig. 2 e, f).

c) Kondaros-Katsimouti-Vani (KKV)

A previously unrecognized Ag-bearing IS epithermal mineralization occurs along the major NW-SE trending KKV fault. It shows features like cockade structures, colloform banding and consists of carbonate, adularia and chalcedony gangue (Fig. 2c, d). Early deposition of sphalerite was followed by pyrite, galena, polybasite, argentian tetrahedrite, chalcopyrite, minor bornite and late Mnoxides. The above mineralization and also the presence of NE-trending Mn-barite outflow zones (white smokers) and crustiform banded amethyst-chalcedony feeder zones on the SW of Vani (Aspro Gialoudi, Kalogria, Fig. 1), suggests Vani manganese deposit to be the final hydrothermal manifestation of a major Pb-Ag-Mn epithermal system.

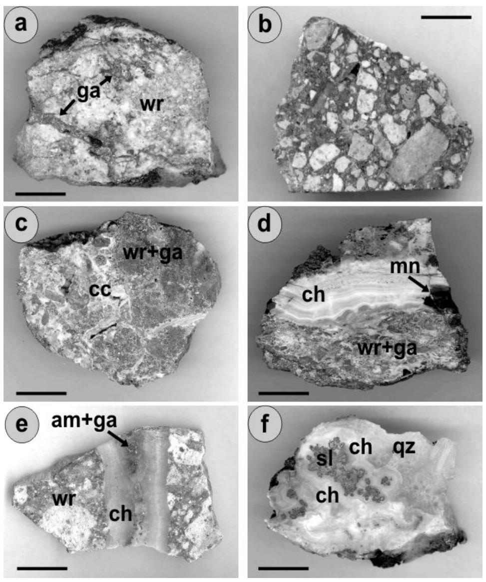

Fig. 2. Hand specimens of W. Milos mineralization. (a) Advanced argillic altered dacitic wallrock (wr) crosscuted by galena-rich ore (ga) (Galana); (b) Sericitic altered dacite fragments cemented by base metal sulfides (Triades); (c) Cockade breccia composed of quartz-base metal bearing (ga) and volcanic (wr) fragments surrounded by colloform banded chalcedony + calcite (cc) (Kondaros). (d) Colloform banded chalcedonic silica (ch) and late carbonate and manganese mineralization (mn) postdate early brecciated base metal mineralization (wr+ga) (Kondaros). (e) Colloform banded chalcedonic quartz vein (ch) with late amethyst (am) and galena (ga) crosscutting adularized wallrock (wr) (Profitis Ilias); (f) Chalcedonic silica (ch) with sphalerite-rich (sl) base metal mineralization, and quartz (qz) (Chondro Vouno). Scale bars = 0.5cm

Ore mineralogy

Variation in chemical composition among ore minerals was investigated using a Cameca-SX 100 microprobe at the University of Hamburg and a JEOL JSM 5600 SEM in the University of Athens. Representative EPMA results are given in Tables 1 and 2.

Tetrahedrite-group minerals represent an important constituent of all mineralization (Fig. 3). EPMA data are plotted in Fig. 4. In Triades, both As- and Sb-rich members coexist in individual samples, but there is a dominance of tennantite over tetrahedrite. All the analyzed tetrahedrite ss show high Zn contents (between 6.3 and 10.9 wt.%) and are classified as zincian tennantites/tetrahedrites. Silver, substituting for Cu, shows a broad compositional range and reach values up to 9.98 wt.% (in Sb-rich members). Vavelidis and Melfos (1997) also reported Ag-values in the order of 11.8-12.6 wt.%. The Ag content in tennantites (As <1.0 apfu) is low and varies between 0.03 and 1.4 wt.%. The Bi, Te and Pb contents in measured tetrahedrites ss are all below detection limit. Hg reaches values up to 0.29 wt.%. At Galana, tetrahedrite/tennantite, with As/(As+Sb) ratios ranging between <0.1 and 1.0, show similarly to Triades, high contents in Zn (6.8 to 10.9 wt.%) and Fe (<1.5 wt.%). Silver substituting for copper varies between 0.02-2.5 wt.%. The KKV system contains almost pure tetrahedrite (Sb-content varies between 26.5 and 28.1 wt.%). Their Ag-content is the also the highest measured in W. Milos, reaching values up to 16.2 wt.%. The Zn-content is lower compared to that from TG (ranging between 3 and 5 wt.%. In addition, a plumbian variety is detected containing up to 7.5 wt.% Pb and 6.7 wt.% Ag. It forms small inclusions in galena. Plumbian tetrahedrite-tennantite with up to 2.3 wt.% Pb was previously reported from Triades mineralization by Vavelidis and Melfos (1997).

Enargite (Cu_3AsS_4) is a common constituent in Triades-Galana deposits. At Triades enargite surrounds early pyrite and tennantite but also occurs as inclusions in tennantite indicating contemporaneous deposition (Fig. 3a, b). Enargite from Galana contains small inclusions of galena (Fig. 3c). Microprobe analysis indicated an almost ideal chemical formula (Table 1). It contains small amounts of Ag (<0.25 wt.%), Fe (<1.2 wt.%), Zn (<2.4 wt.%), Sb (<0.35 wt.%) and Hg (<0.07 wt.%). An argentian enargite surrounds sphalerite and coexists with zincian tennan-tites/tetrahedrites in Triades (Fig. 3b). It contains Ag (7.1 wt.%), Zn (1.6 wt.%), and 5.3 wt.% Sb substituting for As.

Table 1. Representative EPMA data on tetrahedrite/tennantite (1-8) and enargite (9-11) from W. Milos

	1	2	3	4	5	6	7	8	9	10	11
Cu	41.23	34.14	31.59	41.71	35.08	32.05	25.30	26.32	41.09	45.70	46.89
Ag	1.40	5.57	7.67	0.08	1.81	6.69	16.16	14.62	7.13	0.16	0.23
Fe	0.46	0.09	0.07	1.52	1.32	3.38	2.41	4.45	0.25	0.11	0.13
Zn	8.57	7.14	6.45	8.24	7.29	0.45	3.14	4.96	1.60	2.38	0.52
Sb	3.36	24.42	27.65	<mdl	20.99	26.48	28.12	26.87	5.34	0.34	0.03
As	18.53	3.52	1.35	20.71	7.19	<mdl	<mdl	0.57	14.05	18.99	18.94
Hg	0.02	0.06	0.02	0.03	<mdl	<mdl	<mdl	<mdl	0.04	0.05	<mdl
Pb	<mdl	<mdl	<mdl	<mdl	<mdl	7.48	2.38	<mdl	<mdl	<mdl	<mdl
S	27.91	24.80	24.41	28.11	25.53	22.18	22.09	21.91	29.85	31.91	32.77
Total	101.48	99.74	99.20	100.40	99.46	99.18	99.51	99.71	99.35	99.63	99.50
Atoms	29	29	29	29	29	29	29	29	8	8	8
Cu	9.667	9.053	8.608	9.694	9.042	9.213	7.357	7.142	2.717	2.861	2.914
Ag	0.193	0.867	1.231	0.011	0.276	1.134	2.770	2.346	0.278	0.006	0.008
Fe	0.122	0.027	0.022	0.401	0.386	1.262	0.797	1.380	0.019	0.008	0.009
Zn	1.952	1.839	1.707	1.862	1.827	0.128	0.887	1.311	0.103	0.145	0.031
Sb	0.412	3.379	3.932	0.000	2.822	3.973	4.269	3.813	0.184	0.011	0.001
As	3.684	0.792	0.312	4.083	1.572	0.000	0.000	0.138	0.788	1.008	0.998
Hg	0.002	0.005	0.002	0.002	0.000	0.000	0.000	0.000	0.001	0.001	0.000
Pb	0.000	0.000	0.000	0.000	0.000	0.661	0.212	0.000	0.000	0.000	0.000
S	12.968	13.035	13.185	12.947	13.038	12.635	12.728	12.870	3.911	3.960	4.037

Triades: tetrahedrite/tennantite (1-3), enargite (9, 10); Galana: tetrahedrite/tennantite (4, 5), enargite (11); Kontaros-Katsimouti: tetrahedrite/tennantite (6-8); <mdl: below microprobe detection limit

Galena postdates sphalerite, is intergrown with chalcopyrite, and also occurs as small inclusions in enargite and tetrahedrite group minerals. EPMA data from TG indicate no Ag- and Bi contents and only minor (<0.09 wt.%) Sb.

Sphalerite is a common constituent in the mineralizations studied. All sphalerites analyzed are generally of the low-Fe variety with no more than 0.8 wt.% Fe. Early sphalerites from Galana represent an exception. These occur as inclusions in pyrite (Fig. 3d) and contain 2.6 wt.% Fe (4.6 mol.% FeS). Late sphalerite from the same locality is Fe-poor (0.02-0.8 wt.% Fe), corresponding to 0.04-1.4 mol.% FeS. The Triades sphalerite (Fig. 3a, d) contains 0.01 to 0.7 wt.% Fe (0.03 to 1.2 mol.% FeS), quite similar to those from Galana. The EPMA data on sphalerite from Kondaros-Katsimouti coexisting with the Ag-rich assemblage, revealed Fe contents between 0.8 and 2.5 wt.% (1.4-4.3 mol.% FeS). All sphalerites contains Mn (<0.7 wt.%), and Cd (0.2-0.8 wt.%). The sphalerites analyzed are similar in composition to those from PI deposit with Fe content varying between 0.2 and 1.2 wt.% (0.35-2.09 mol.% FeS; Constadinidou et al., 1998).

Bornite is detected as small inclusions within early pyrite in Galana (Fig. 3d) and is associated with chalcopyrite and galena as inclusions in sphalerite at Katsimouti. It contains up to 0.6 wt.% Ag. Bornite is also present in ore-stage mineralization of Profitis

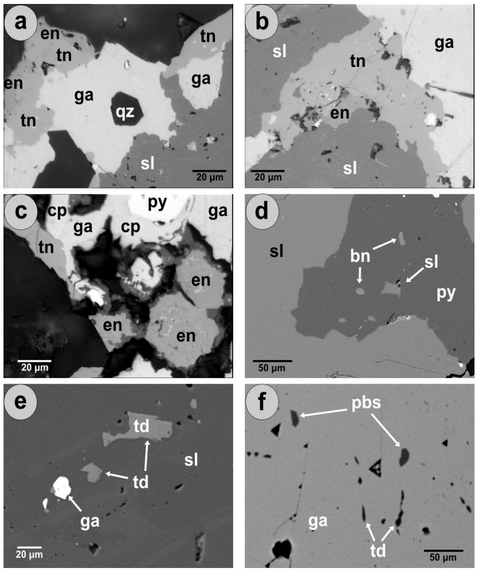

Fig 3. (a-c): Reflected light microphotographs of W. Milos ores. (a) Sphalerite (sl) surrounded by galena (ga) and tennantite (tn) – enargite (en). qz: quartz (Triades); (b) Argentian enargite (en) and tennantite (tn) postdate galena (ga) and sphalerite (sl). (Triades); (c) pyrite (py) surrounded by chalcopyrite (cp), galena (ga), tennantite (tn) and enargite (en). (Galana); (d-f) SEM-BSE micrographs: (d) Fe-rich sphalerite (sl), bornite (bn) included in pyrite (py) surrounded by Fe-poor sphalerite (sl). (Galana); (e) Argentian tetrahedrite (td) and galena (ga) included in sphalerite (sl). (Kontaros); (f) polybasite (pbs) and argentian tetrahedrite (td) included in galena (ga). (Katsimouti)

Ilias (Constadinidou et al., 1998).

Polybasite represents a minor but abundant constituent in the mineralization of Katsimouti-Kondaros (Table 2). It occurs in the form of small (<50μm) grains within galena and is associated with argentian tetrahedrite (Fig. 3f). It contains up to 70 wt.% Ag, up to 8.3 wt.% Cu, 10.8 wt.% Sb and minor amounts of Pb (< 1.5 wt.%). Polybasite together with pyrargyrite, argentite and proustite, has been reported but not documented by various authors from TG and PI (Vavelidis and Melfos, 1998; Constadinidou et al., 1998; Liakopoulos et al., 2001).

Table 2. Representative EPMA data on polybasite from Kondaros-Katsimouti

	1	2	3	4
Ag	68.41	67.62	64.11	64.49
Cu	5.33	6.39	8.33	7.74
Sb	10.73	9.89	10.84	10.85
As	<mdl	0.29	<mdl	0.41
S	15.36	15.58	16.17	15.93
Total	99.83	99.77	99.45	99.42
Atoms	29	29	29	29
Ag	14.308	13.901	13.070	13.228
Cu	1.896	2.239	2.882	2.669
Sb	1.986	1.796	1.958	1.969
As	0.000	0.089	0.000	0.111
S	10.810	10.975	11.089	10.994

<mdl: below microprobe detection limit

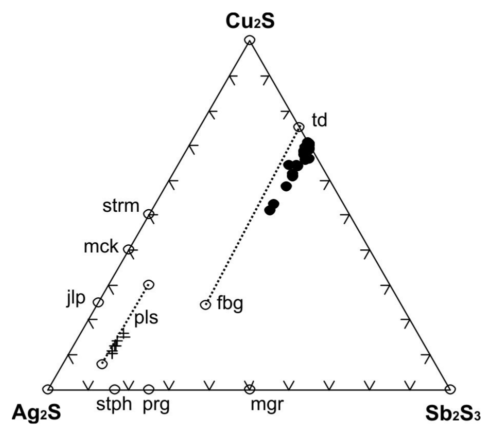

Fig. 4. Ternary diagram of Ag-Cu-Sb sulfosalts. Theoretical compositions are shown as open circles. Filled circles represent composition of tetrahedrite group minerals analyzed in the present study. Crosses are representative compositions of polybasite from Kontaros-Katsimouti. Compositional ranges of polybasite and tetrahedrite-freibergite are shown by dashed lines. Abbreviations: td: tetrahedrite, fbg: freibergite, strm: stromeyerite, mck: mckinstryite, jlp: jalpaite, stph: stephanite, prg: pyrargyrite, mrg: miargyrite

Discussion and conclusions

Mineralization in W. Milos was developed during the U. Miocene to Pleistocene in an emerging volcanic setting under transitional shallow submarine to subaerial conditions (Alfieris et al., 2004). This work reinterprets previous results and presents new data suggesting that precious metal deposits in W. Milos are rather of IS than of LS type (according to the scheme proposed by Einaudi et al., 2003). Mineralogical data presented in this study indicate common features between the PI-CV, KKV and TG mineralized centers: all of them are characterized by the occurrence of galena + Fe-poor sphalerite + chalcopyrite + bornite and abundance of barite, adularia and sericite/chlorite, features typical of IS epithermal type deposits. Mineralization of TG evolves from an IS character toward HS character with time. This evolution could be the result of acidification of IS fluids as they enter the advanced argillic lithocaps, as proposed by Sillitoe and Hedenquist (2003). The high silver content of KKV is accounted to inclusions of argentian tetrahedrite and polybasite in galena (as discussed by Sharp and Buseck, 1993) and in sphalerite. The enrichment of Au vs. Ag in PI-CV relative to KKV could be either the result of a deeper exposure lever (deeper base metal and silver rich part for KKV, shallower gold-rich levels for PI-CV) or to primary geochemical characteristics of these systems.

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