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Silver mineralogy of St. Philippos deposit (NE Greece) and its relationship to a Te-bearing porphyry-Cu-Mo mineralization

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Abstract. Telluride-bearing quartz-carbonate-base metal veins in the Pagoni Rachi porphyry Cu-Mo prospect (W. Thrace, Greece), are developed along the same structural corridor which also controls the polymetallic porphyry-related St. Philippos deposit. New mineralogical evidence from St. Philippos demonstrates the presence of previously unrecognized pearceite, an unnamed Cu-bearing Ag-sulfosalt, and a phase with similarities to watanabeite as the main carriers for silver in the ore. These minerals postdate early galena and sphalerite and are accompanied by plumbian tennantite, plumbian enargite and covellite. Both Pagoni Rachi and St. Philippos mineralization are probable related to distinct porphyry Cu-Mo mineralizing events rather than to represent a lateral metal transition of the same system.

Key words: Silver-sulfosalts, intrusion-related, porphyry-Cu-Mo, tellurides

Introduction

The area between Sappes and Esymi in northern Greece, contains several base- and precious metal-rich mineralizations and includes the HS polymetallic deposit of St. Philippos (Moëlo et al., 1985; Michael et al., 1989; Vavelidis et al., 1989, Michailidis et al., 1989; Dimou, 1993; Skarpelis, 1999), the HS Viper-St. Demetrios deposits (Bridges et al., 1997; Shaw and Constantinides, 2001) and also two Cu ± Mo porphyry-type prospects at Pagoni Rachi and Kassiteres (Arikas and Voudouris, 1998). There is a spatial relationship between St. Philippos (StP) and Pagoni Rachi (PR), the latter characterized by an enrichment in tellurides especially in late-stage veins (Voudouris and Arikas, 2003). This work presents previously unrecognized Ag-sulfosalts from StP and discusses its relationship to the neighboring PR porphyry prospect.

Geology of the area

The geology of the studied area (Fig. 1) is dominated by Oligocene-Miocene synorogenic subvolcanic stocks and dikes of calc-alkaline to high-K calc- alkaline affinity. The magmatism resulted from the underthrusting of the African plate beneath the southern margin of the Eurasian plate and is attributed to slab break-off and/or slab delamination mechanisms (Christofides et al., 1998). A basal-clastic formation of Middle to Upper Eocene age including tuffaceous material (Papadopoulos, 1982) covers discordantly the metamorphic basement (Mposkos and Kostopoulos, 2001).

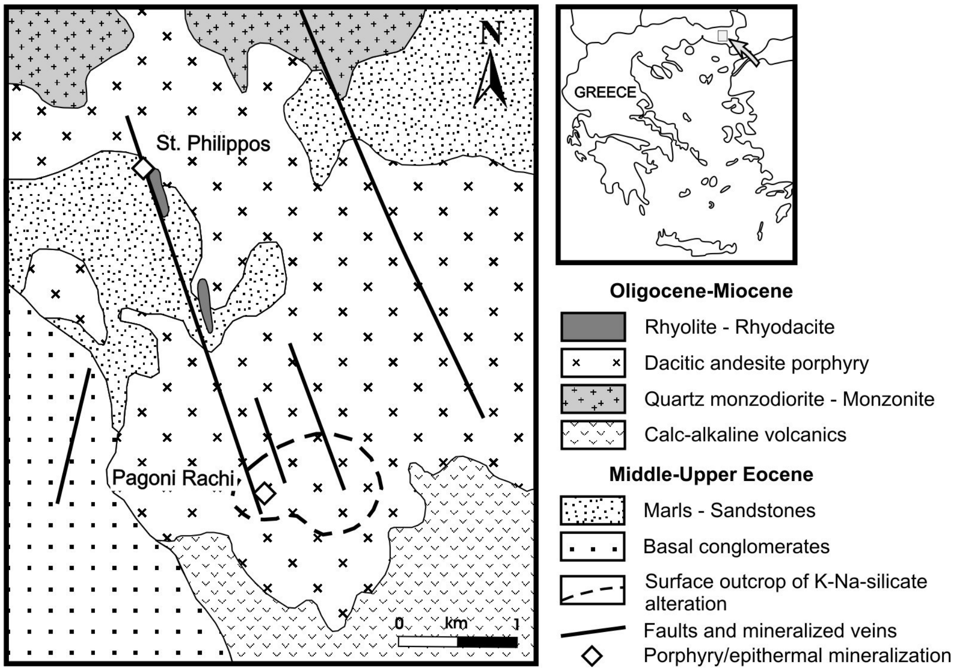

Fig. 1. Generalized geological map of the investigated area (modified after Arikas, 1981)

A volcanic sequence, consisting of lava domes, flows and pyroclastics of andesitic to dacitic composition was intruded at about 32 Ma (Del Moro et al., 1988) by I-type subvolcanic dacite-andesitic and monzodioritic bodies. All these lithologies are cut by rhyolitic dikes, which were intruded mainly along NNW-SSE trending faults.

Mineralization

St. Philippos mineralization is hosted within Eocene sediments and displays spatial relationships to Upper Oligocene rhyolite porphyry exposed at the northern part of the mining area (Fig. 1). The deposit contains an unusual mineralogy consisting of several Pb-As-Cu-Bi-Sn sulfosalts, some of them reported for the first time in the world (Moëlo et al., 1985). Although the deposit is known for its high silver content (up to 2200 ppm, Skarpelis, 1999), no Ag-bearing phases had been reported before now. New paragenetic studies on surface material from the northern site of the open pit indicate the presence of Ag-bearing sulphosalts for the first time. According to our study and previous work, the paragenetic sequence for StP incorporates the initial deposition of early pyrite which is succeeded by sphalerite and minor chalcopyrite and then by a Cu-rich assemblage including jordanite, galena, tennantite, Ag-sulfosalts, enargite and hypogene covellite (Fig. 2b). This assemblage is associated with alunite, dickite and barite, which is consistent with the observations of Skarpelis (1999), who mentioned the presence of pyrophyllite, woodhouseite and alunite in the ore zone. Late calcite and rhodochrosite veins are barren of mineralization. However, previous studies reported the coexistence of early galena and sphalerite with carbonates (Vavelidis et al., 1989; Michailidis et al., 1989). The rhyolite porphyry which is in very close proximity to the ore (<1m) displays a sericite-carbonate alteration. In the south, the veins become richer in galena, sphalerite, chalcopyrite, quartz and carbonates, and at about 3 km distance from the mining area they overprint A- and B-type veins of the PR porphyry-Cu-Mo prospect.

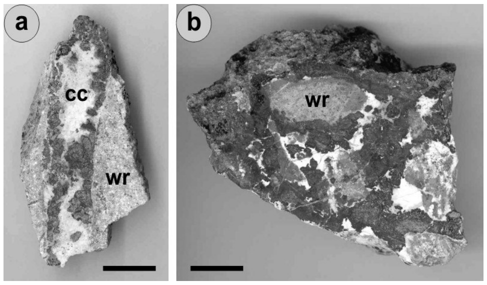

Fig. 2. (a) Quartz-carbonate (cc) veinlet with base metals and hessite, crosscutting sericitized andesite porphyry (wr) PR prospect. (b) Brecciated ore at StP consisting of advanced argillic altered wallrock fragments (wr) cemented by Cu-rich ore (black) and late dickite (white). Scale bars = 2 cm

At PR the quartz-carbonate-base metal veins consist of early pyrite and sphalerite, followed by galena, chalcopyrite, tetrahedrite/ tennantite, minor bornite, covellite and hessite. These veins are related to sericitic alteration of the wallrocks characterized by sericite, chlorite, quartz, carbonate and pyrite (Fig. 2a).

Ore mineralogy

The chemical variation of ore minerals was investigated by a Cameca-SX 100 microprobe at the University of Hamburg and a JEOL JSM 5600 scanning electron microscope in the University of Athens. Representative EPMA results are given in Tables 1 and 2.

Tetrahedrite-group minerals occur in both PR and StP mineralization. In PR they surround pyrite and are intergrown with chalcopyrite, galena and sphalerite. Both As- and Sb-rich members coexist in one sample. All the analyzed tetrahedrite-group minerals show high Zn contents (3.0-8.0 wt.%), and can be classified as zincian tennantites/ tetrahedrites. Their Ag content varies between 0.02 and 1.5 wt.%. Au and Te contents reach up to 0.4 wt.% and 0.3 wt.%, respectively. Bi-, Pb- and Sn-contents are below detection limit. In contrast, the StP deposit includes almost pure tennantite (Fig. 3b) with As-content reaching up to 20.6 wt.%), and Ag up to 0.8 wt.%. The Zn-content is comparable to those at PR (6.5-8.5 wt.%). In addition, another phase which is classified as plumbian tennantite coexists with galena and Ag-bearing sulfosalts. It contains up to 2.3 wt.% Pb, substituting for Zn and Fe (up to 7.3 wt.%) and low Ag, up to 0.8 wt.%. Plumbian tennantite from StP with up to 4 wt.% Pb has also been reported by Michailidis et al. (1989).

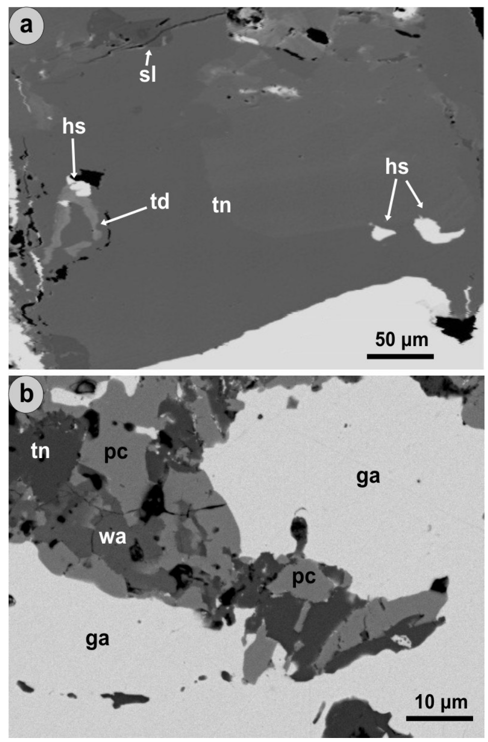

Fig. 3. (a) PR ore: Hessite (hs) and sphalerite (sl) included in tennantite (tn) and associated with tetrahedrite (td), (SEM-BSE image); (b) Back-scattered electron image (SEM-BSE) micrograph of StP ore: Watanabeite-similar phase (wa), tennantite (tn) and pearceite (pc) associated with galena (ga)

Hessite was detected only in PR, as small grains (up to 30 μm), closely related to tennantite-tetrahedrite (Fig. 3a). It contains 56.3-59.4 wt.% Ag and 36.7-41.2 wt.% Te. It also incorporates small amounts of Cu (2.6-2.8 wt.%) in the lattice. The Au content varies between 0.3 and 3.3 wt.%.

Table 1. Representative EPMA data on Ag-bearing phases from Pagoni Rachi porphyry-Cu-Mo prospect

	1	2	3	4	5
Cu	36.78	42.69	40.44	61.62	2.77
Ag	1.47	0.05	0.35	0.24	56.32
Fe	0.26	0.69	<mdl	2.15	0.09
Zn	7.41	7.76	7.99	<mdl	0.50
Pb	<mdl	<mdl	<mdl	<mdl	0.11
Sb	25.07	0.46	10.23	<mdl	0.05
As	3.06	20.16	13.51	<mdl	0.05
Hg	<mdl	<mdl	0.04	<mdl	0.09
Bi	0.03	0.00	<mdl	<mdl	0.02
Te	<mdl	0.25	<mdl	0.02	37.22
Sn	0.05	<mdl	0.05	<mdl	<mdl
Se	0.04	<mdl	0.02	1.03	0.08
Au	<mdl	<mdl	0.43	0.15	3.31
S	25.10	28.44	27.07	34.58	0.18
Total	99.28	100.51	100.63	99.79	100.80

1. $(Cu_{9.64}Ag_{0.23})(Zn_{1.89}Fe_{0.08})(As_{0.68}Sb_{3.43})S_{13.04}$
2. $(Cu_{9.91}Ag_{0.01})(Zn_{1.75}Fe_{0.18})(As_{3.97}Sb_{0.06}Te_{0.03})S_{13.09}$
3. $(Cu_{9.80}Ag_{0.05}Au_{0.03})(Zn_{1.88}Fe_{0.14})(As_{2.78}Sb_{1.29})S_{13.01}$
4. $(Cu_{0.92}Fe_{0.04}Se_{0.01})S_{1.02}$
5. $(Ag_{1.76}Au_{0.06}Cu_{0.15})(Te_{0.98}S_{0.02})$

1. tetrahedrite, 2. tennantite, 3. tennantite/ tetrahedrite, 4. covellite, 5. hessite; <mdl: below micro-probe detection limit

Sphalerite from both occurrences is characterized by low Fe content which varies from 0.25 to 1.6 wt.% or 0.4-2.7 mol. % FeS. Sphalerite contains low Mn (<0.3 wt.%), and Cd varying between 0.25 and 1.25 wt.%.

Enargite was observed only in StP. It is closely related to covellite and crosscuts and also rims earlier phases. It also occurs as small inclusions within galena. It contains small amounts of Pb (up to 2 wt.%), being classified as plumbian enargite.

A phase with similarities to *watanabeite* (Shimizu et al., 1993) is closely associated with Ag-sulfosalts and tennantite, postdating galena in StP (Fig. 3b). It contains up to 4 wt.% Ag, but also significant amounts of Pb (6.5-12.9 wt.%). This is the first occurrence of this rare sulfosalt, which could be a Pb-bearing variant of watanabeite, in Greece.

*Pearceite***,** rich in Cu (14-16 wt.%) represents the main Ag-bearing phase in StP. It occurs in the form of small grains (up to 20 μm) closely related to the watanabeite-similar phase and tennantite (Fig. 3b). The Ag content varies between 58.8 and 61.9 wt.%; Sb is below detection limit. It also incorporates minor amounts of Te (<0.15 wt.%).

An unnamed *Ag-phase*, As-analog to stephanite, accompanies pearceite and watanabeite in StP. It contains 48.7 wt.% Ag, 20.8 wt.% Cu and 9.8 wt.% As.

Jordanite and *selligmanite* are closely related to Ag-bearing phases in StP deposit. They do not incorporate any Ag in their structures.

Covellite, a minor phase in PR, contains Se, Ag and Au substituting for Cu (Table 1).

Discussion and conclusions

The St. Philippos deposit, developed on the periphery of the Pagoni Rachi porphyry prospect, is a typical porphyry-related vein system with many similarities to polymetallic vein deposits elsewhere, such as Butte (Montana), Rosario vein and Chuquicamata (Chile) (Einaudi et al., 2003). Porphyry-related base metal deposits have many similarities to the epithermal high-sulfidation ores. However they are formed in greater depths than typical epithermal ores and are characterized by base metal- and Ag-rich ore mineralogy (Einaudi et al., 2003). Minerals indicative of a high-, to very high sulfidation state as enargite and covellite are deposited late in the paragenetic sequence of porphyry-related base metal deposits, and this is a feature typical for StP. The available data suggest that ore deposition underwent an evolution from an intermediate-sulfidation state (deposition of sphalerite-galena-tennantite) towards high-, or very high states of sulfidation (deposition of enargite and covellite with dickite, alunite and pyrophyllite)

Table 2. Representative EPMA data on Ag-bearing phases from St. Philippos deposit

	1	2	3	4	5	6	7	8	9	10	11
Cu	40.66	39.23	40.33	34.67	37.26	13.86	14.01	16.38	20.76	40.77	46.13
Ag	3.03	3.09	2.84	3.68	2.94	61.63	61.87	58.82	48.66	0.24	<mdl
Fe	<mdl	0.01	<mdl	na	na	<mdl	0.01	<mdl	0.02	7.28	<mdl
Zn	0.17	0.83	0.16	0.47	0.38	0.14	0.05	0.37	0.17	0.18	<mdl
Pb	6.53	8.11	6.84	12.86	12.06	<mdl	<mdl	<mdl	0.06	2.35	1.84
Sb	0.61	0.18	0.28	na	na	<mdl	<mdl	<mdl	<mdl	<mdl	<mdl
As	21.81	21.09	21.72	22.95	22.66	7.06	6.91	7.50	9.85	21.88	21.13
Te	<mdl	<mdl	<mdl	<mdl	<mdl	0.09	0.14	<mdl	0.15	<mdl	<mdl
S	28.05	27.41	27.57	23.95	23.89	17.26	17.03	16.55	19.87	27.29	30.76
Total	100.96	99.95	99.75	98.57	99.18	100.04	100.03	99.62	99.50	100.00	99.80
Atoms	11	11	11	11	11	29	29	29	10	29	8
Cu	3.757	3.698	3.777	3.526	3.739	4.439	4.504	5.246	2.131	9.634	2.940
Ag	0.165	0.172	0.156	0.220	0.174	11.630	11.716	11.098	2.944	0.035	0.000
Fe	0.000	0.001	0.000	-	-	0.001	0.003	0.000	0.002	1.958	0.000
Zn	0.016	0.076	0.014	0.046	0.036	0.043	0.014	0.116	0.018	0.041	0.000
Pb	0.185	0.234	0.197	0.401	0.371	0.000	0.000	0.000	0.002	0.170	0.036
Sb	0.029	0.009	0.014	-	-	0.000	0.000	0.000	0.000	0.000	0.000
As	1.709	1.686	1.725	1.980	1.928	1.918	1.885	2.036	0.849	4.385	1.142
Te	0.000	0.000	0.000	0.000	0.000	0.015	0.023	0.000	0.008	0.000	0.000
S	5.136	5.122	5.116	4.828	4.751	10.953	10.852	10.504	4.044	12.780	3.886

1-5. watanabeite-similar phase included in galena; 6-8. cuprian pearceite associated with plumbian-tennantite; 9. unnamed Cu-bearing phase, As-analog of stephanite; 10. plumbian tennantite included in galena; 11. plumbian enargite; <mdl: below microprobe detection limit; na: not analyzed

and ended under lower sulfidation state conditions (deposition of calcite and rhodochrosite veins). Silver-bearing sulfosalts were introduced together with tennantite under intermediate sulfidation states. The intermediate sulfidation-type, telluride-bearing quartz-carbonate veins of Pagoni Rachi occur along the same structural corridor and furthermore they resemble the early galena-sphalerite-tennantite association of StP. Further investigation will be needed to establish if PR and StP were formed by two different hydrothermal fluids related to distinct porphyry events, or alternatively if they represent a lateral metal transition of a same system, or formed as a result of successive phases within a single, evolving magmatic-hydrothermal system. The close spatial relationship of StP mineralization and rhyolitic dikes support the hypothesis that these dikes may have played a major role in supplying the system with volatiles and with metals. A granitic body burried at depth beneath StP probably hosts porphyry-Cu-Mo mineralization like that described in Maronia area by Melfos et al., (2002). The presence of plumbian tetrahedrite/tennantite in both Maronia (Vavelidis and Melfos, 1999) and StP supports the above assumption. The presence of tellurides in the porphyry-related veins at PR is of importance because it offers the possibility for comparisons with other Te-rich systems in western Thrace, such as Kassiteres, St. Demetrios, Perama Hill and Mavrokoryfi.

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