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# MINERALOGY AND CHEMISTRY OF GOLD IN THE PROFITIS ILIAS EPITHERMAL DEPOSIT, MILOS ISLAND, AEGEAN SEA, GREECE

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## ABSTRACT

The Profitis Ilias epithermal gold deposit, Milos island, Greece, is associated with crustiform banded quartz veins in silicified-sericitized rhyolitic lapilli tuffs and ignimbrites. The mineralization consists mainly of sphalerite, pyrite, galena, chalcopyrite, electrum, native gold and silver bearing minerals, with gangue quartz, adularia and barite. Gold occurs in the main hypogene ore stage and the supergene oxidation stage. Gold fineness indicates three distinct types of gold, reflecting different deposition environments: type I is slightly zoned, showing silver-rich rims (fineness 662), type 2 is characterized by a reverse strong zonation, with rims depleted in silver (fineness 850) and type 3 is pure gold (fineness ~1000). Iron poor sphalerite, (up to 2 mole% FeS), indicates sulfur activities of $10^{-9.8}$ to $10^{-11.2}$ atm during ore stage deposition. The range of sulfur activity and gold fineness, together with all determined mineralogical features are compatible with adularia-sericite type epithermal gold deposits.

**KEY WORDS**: epithermal, gold, mineralogy, sphalerite, sulfur activity, fineness, boiling, Milos, Greece.

## 1. INTRODUCTION

The Profitis Ilias epithermal gold deposit was recently discovered by Midas S.A. on the western end of Milos island. Milos is located towards the western end of Pleiocene-Pleistocene Aegean Volcanic Arc, which was formed as a result of the northward subduction of the African plate beneath the Aegean (Fytikas 1977, Fytikas et al. 1986). The island is built by calc-alkaline volcanic rocks (tuffs, pumice flows, ignimbrites, pyroclastic flows, domes and lava flows of andesitic-dacitic and rhyolitic composition). The volcanic sequence overlies Miocene-Pleiocene clastic and carbonate platform sediments, which unconformably overly Mesozoic (?) metamorphic basement rocks (Fytikas et al. 1986, Fytikas 1989). Except for hosting metalliferous mineralization (Mn, Fe, Pb, Zn, Ag), Milos is currently producing industrial minerals: perlite, pozzolanic earths, kaolin, silica, bentonite and barite (Christidis and Scott 1997, Christidis et al. 1995, Ericsson et al. 1992, Hauck 1983).

The Profitis Ilias deposit is hosted by silicified and sericitized rhyolitic lapilli-tuffs, tuffites and ignimbrites and is characterized by a series of interconnected N-S to NE-NW trending epithermal quartz veins. Vein mineralization consists mainly of sphalerite,pyrite, galena, chalcopyrite, electrum, native gold and halogens of silver with gangue quartz, barite and adularia.

This study presents data on the paragenesis of the veins and the mineralogy and chemistry of gold, bearing on the deposit genesis. In addition certain geochemical parameters of ore deposition, are presented.

## 2. SAMPLES AND ANALYTICAL TECHNIQUES

Paragenesis and mode of gold occurrence has been microscopically studied in 127 thin - polished sections from surface and drill core samples. Electron microprobe analyses on gold and sphalerite were performed using a

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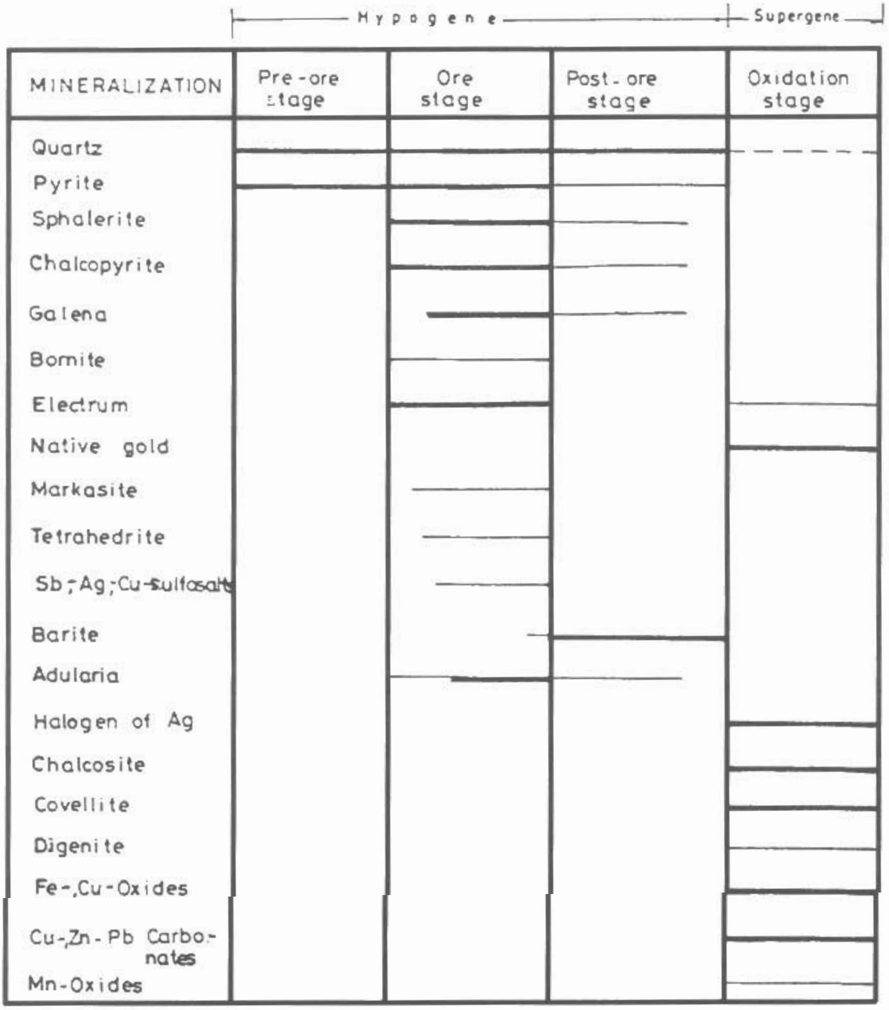
JEOL superprobe 733 electron microprobe analyzer with a Tracor Energy Dispersive Spectrometer. The operating conditions were as follows: 20 kV excitation high voltage, 3nA beam current and 20 seconds counting time. Mineral standards were used and on-line ZAF corrections were carried out. X-Ray Diffraction analyses of alteration and oxidation minerals were performed using an automatic X-Ray Diffractometer, Siemens D500. Qualitative determination was done with SIEMENS software Diffrac AT 3 using the JCPDS database.

## 3. MINERAL PARAGENESIS AND CHEMISTRY

Paragenetic relationships of the vein mineralization can be represented by a sequence consisting of hypogene, pre-ore, ore, post-ore, and supergene oxidation stages (Fig. 1). 1) The earliest pre-ore mineralization consists of barren microcrystalline quartz and pyrite; 2)The main ore-stage is characterized by deposition of coarse- and fine- grained quartz, adularia, sphalerite, chalcopyrite, galena, pyrite, bornite, markasite, tetrahedrite, Sb-Ag-Cu-sulfosalts and electrum (Fig. 2a and b). 3) Lastly post- ore mineralization comprises barite mainly intergrown with fine-grained quartz and rarely with galena, shalerite, pyrite and chalcopyrite. Oxidation stage consists of native gold, electrum, halogens of silver, chalcosite, covellite, digenite, goethite, hematite, lepidocrorite, malachite, tenorite, cerussite, anglesite, smithsonite, jarosite, plumbojarosite, alunite, and Mn-oxides (Fig. 2c and d).



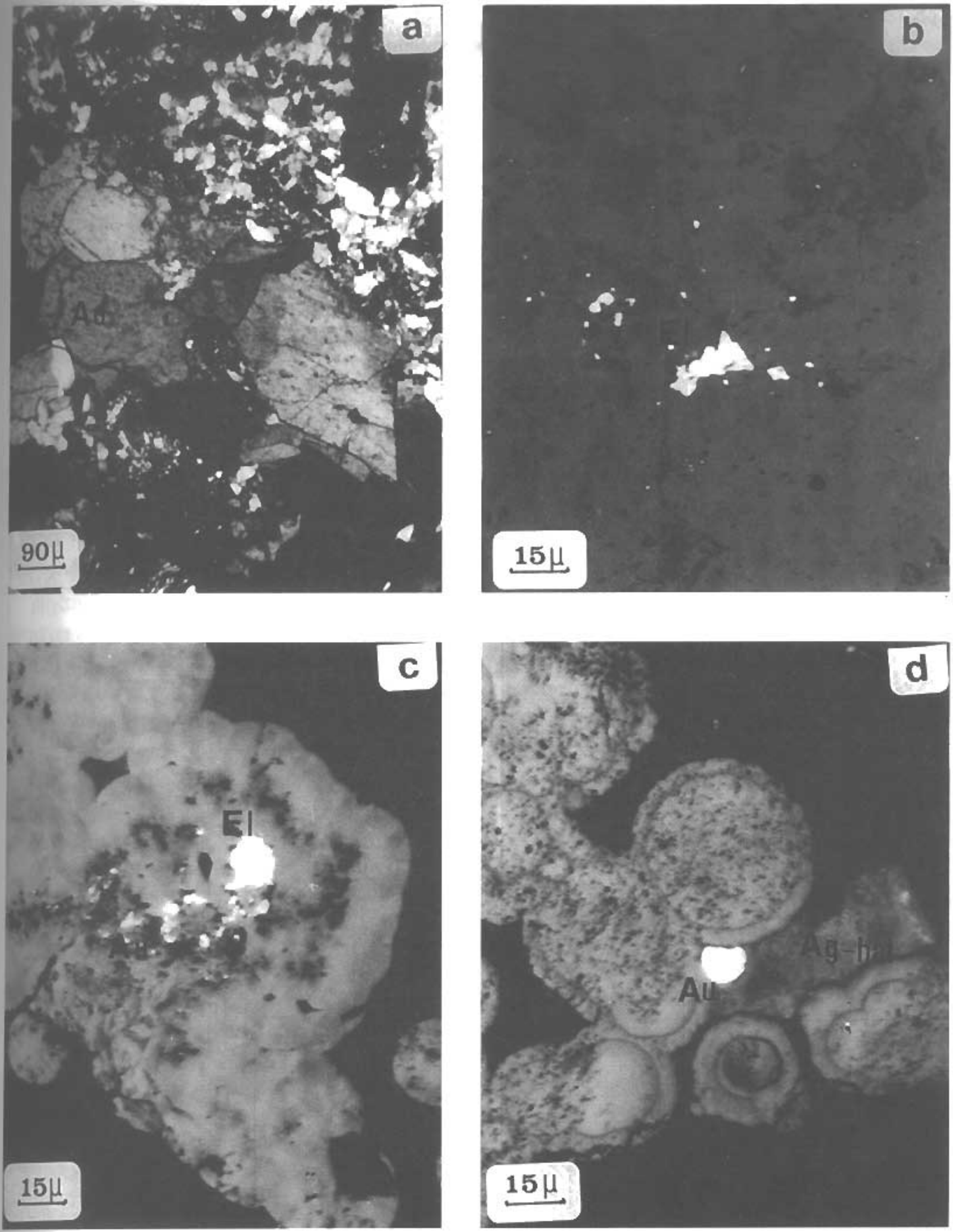


**Fig. 2a-d:** **a.** Sub-rhombic adularia crysrtals, ore stage. (crossed polars) **b.** Electrum aggregates or crystals (type 1) included and/or intersticed between ore-stage fine-grained quartz. **c.** Electrum (type 2) and fine-grained native gold (type 3) included in iron oxides. **d.** Intergrowth of colloform iron oxides, native gold (type 3) and halogens of silver (iodyrite, cerarqyrite).

### Sphalerite

On the basis of textural, paragenetic and chemical relationships two types of sphalerite were distinguished:

Type 1, the most abundant type, occurs as subhedral coarse grains in ore- stage assemblages. The iron composition shows insignificant variation between 0.31 and 1.20 wt %, corresponding to 0.55-2.09 mole % FeS (Table 1).

Type 2 sphalerite occurs as anhedral to subhedral fine-grained crystals included in post-ore barite. Iron contents are slightly lower than type 1 sphalerite (Fig.3) and vary between 0.20-0.98 wt%, corresponding to 0.35-1.71 mole % FeS. The chemical composition of type 1 sphalerite is characterized by the systematic presence of Mn and Cd whereas these elements are erratically distributed in type 2 sphalerite.

**TABLE 1: Chemical composition of sphalerite.**

| No | Zn | S | Fe | Mn | Cd | Cu | Total | Mol% FeS |
|---|---|---|---|---|---|---|---|---|
| 1 | 64.92 | 32.87 | 0.47 | 0.24 | 0.20 | | 98.70 | 0.84 |
| 2 | 64.07 | 33.02 | 1.09 | 0.38 | 0.35 | 0.25 | 99.16 | 1.93 |
| 3 | 65.31 | 33.49 | 0.48 | 0.22 | 0.35 | | 99.85 | 0.85 |
| 4 | 60.83 | 32.88 | 0.31 | 0.22 | 4.41 | 1.15 | 99.80 | 0.55 |
| 5 | 64.06 | 32.90 | 0.76 | 0.48 | 0.76 | 0.34 | 99.30 | 1.34 |
| 6 | 64.86 | 32.93 | 0.62 | 0.68 | 0.48 | | 99.57 | 1.09 |
| 7 | 64.12 | 32.98 | 0.98 | 0.46 | 0.79 | | 99.33 | 1.73 |
| 8 | 64.08 | 32.67 | 1.20 | 0.41 | 0.56 | 0.98 | 99.90 | 2.09 |
| 9 | 64.26 | 33.07 | 0.64 | 0.34 | 0.98 | | 99.20 | 1.14 |
| 10 | 64.84 | 32.85 | 0.49 | 0.45 | 0.93 | 0.24 | 99.80 | 0.86 |
| 11 | 64.98 | 33.03 | 0.50 | 0.48 | 0.20 | | 99.10 | 0.89 |
| 12 | 64.76 | 32.89 | 0.57 | 0.52 | 0.73 | | 99.47 | 1.01 |
| 13 | 65.88 | 32.99 | 0.77 | 0.00 | 0.22 | | 99.77 | 1.34 |
| 14 | 64.85 | 33.11 | 0.70 | 0.12 | | 0.47 | 99.25 | 1.22 |
| 15 | 65.03 | 33.29 | 0.76 | | | 0.35 | 99.43 | 1.32 |
| 16 | 64.65 | 32.96 | 0.73 | 0.24 | 0.61 | | 99.19 | 1.30 |
| 17 | 65.03 | 33.13 | 0.87 | | 0.20 | | 99.23 | 1.55 |
| 18 | 65.08 | 33.44 | 0.37 | 0.12 | 0.29 | | 99.30 | 0.66 |
| 19 | 64.99 | 33.04 | 0.28 | 0.20 | | 0.46 | 98.97 | 0.48 |
| 20 | 67.50 | 32.20 | 0.20 | | 0.23 | | 100.13 | 0.35 |

No 1-12: sphalerite 1, No 13-20: sphalerite 2.

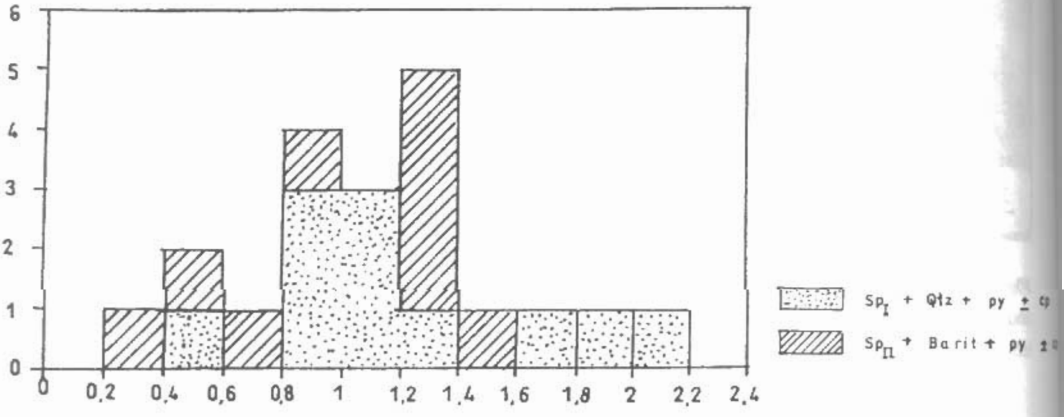


Fig.3 Chemical composition of sphalerite

### Pyrite

Three characteristic textural forms of pyrite have been observed, corresponding to three different paragenetic stages. Pyrite 1, is the earliest phase occurring as fine-grained, usually cubic crystals, disseminated in pre-ore microcrystalline quartz. Pyrite 2 occurs as coarser-grained subhedral to anhedral grains associated with ore-stage minerals. It is characterized by zoned development determined by chalcopyrite blebs defining individual growth zones.

### Galena

An earlier type of galena occurs as coarse-grained patches in the main ore-stage, and a later type is included in post-ore barite. Moreover, a characteristic type of fine-grained galena has been observed, forming thin rims around coarse sphalerite 1; it is intergrown with chalcosite, covellite and digenite and it is believed to be of supergene origin (Ramdohr 1980).

### Chalcopyrite

Occurs disseminated in main ore-stage quartz, or along growth zones in pyrite 2 and it has also been observed in barite, as inclusions.

### Silver minerals

On the basis of qualitative microprobe analyses Sb-Ag-Cu- sulfosalts and silver halogens (iodyrite and cerargyrite) were recognized in ore- and oxidation stage assemblages, respectively.

## 4. GOLD MINERALOGY AND CHEMISTRY

Electrum occurs in two associations: 1. As isolated grains either occupying interstices between, or included in ore-stage fine-grained quartz (Fig.2b), and 2. As inclusions in goethite, covellite, quartz, as well as in contact with clay minerals in the oxidation stage (Fig. 2c). Native gold was mainly found associated with iron- and copper-oxides, quartz, as well as with silver halogens (Fig. 2d). In one case, electrum was found in contact with barite. Figure 4 shows the distribution of gold grains (electrum and native gold) per host mineral.

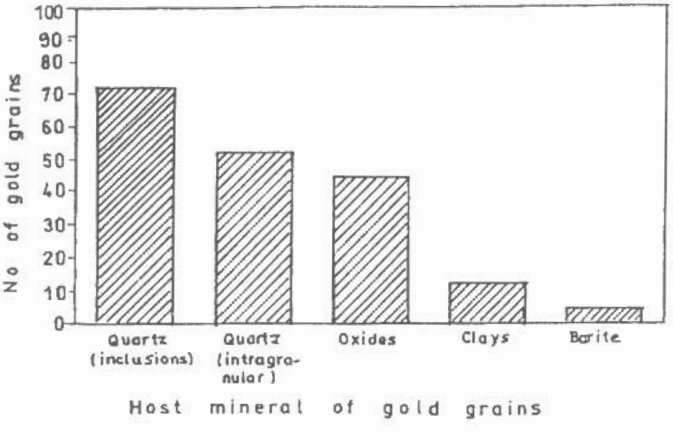


Fig.4 Distribution of gold grains per host mineral.

Grain sizes vary from submicroscopic (<1μm) up to 30μm for both electrum and native gold; typically (56.5%) 0.5-3μm, 30.5% 4-10μm and 13% 12-30μm (Fig.5).

The chemical composition of 29 individual gold grains was determined by core to rim analyses; silver contents range from 0 up to 38.49 wt %.

Gold fineness, defined as 1000 x [wt% Au/wt % Au + wt% Ag] (Morrison et al. 1991), show a large variation between 610-1000 (mode: 843) (Fig.6). However, individual grains are not homogeneous in terms of silver content. Based on the distribution of silver, three types of gold grains were distinguished (Fig.7). Type 1, (ore-stage), with average fineness ranging from 610-728 (mode: 662), is slightly zoned, showing silver-rich rims. Type

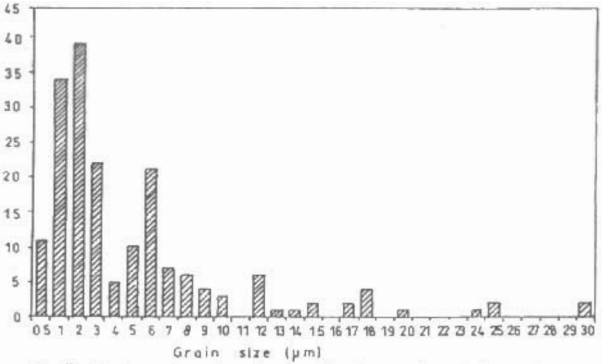


Fig.5 Grain size (μm) distribution of gold grains.

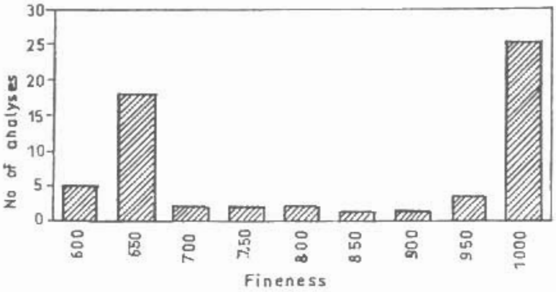


Fig.6 Histogran showing the distribution of gold fineness.

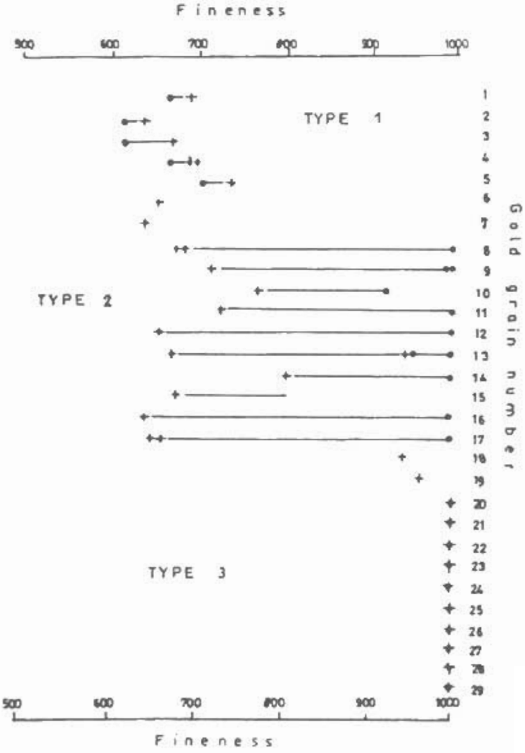


Fig.7 Range of fineness in gold grains

— range + core • rim.

2, oxidation stage, with average fineness between 656 and 1000 (mode: 840), is characterized by a reverse zonation, in relation to type 1, with rims depleted in silver. Type 3, oxidation stage, represents homogeneous pure gold grains (fineness~1000).

## 5. DISCUSSION

The chemical composition of sphalerite as well as the composition of gold, in terms of the silver content combined with paragenetic data, provide important clues on the geochemical environment of gold deposition.

The iron content of sphalerite 1 (0.55-2.09 mole % FeS) coexisting with pyrite 2 and chalcopyrite, combined with ore-stage fluid inclusion derived temperatures of 250°C (Kilias et al. 1997) indicate sulfur activity of $10^{-9.8}$ to $10^{-112}$ atm (Barton et al 1977), during deposition of ore-stage minerals. This range falls within the characteristic sulfur activity limits of adularia-sericite type epithermal gold deposits (Heald et al. 1987). The slightly lower iron content of sphalerite 2 (0.35-1.71 mole % FeS) suggests lower sulfur activity conditions and temperatures, during post-ore mineral deposition, supported by fluid inclusion homogenization temperatures (Kilias et al. 1997).

Electrum deposition with silver-enriched rims may be caused by temperature decrease and/or pH increase (Huston et al. 1992) Increase in fluid pH may be caused by fluid boiling due to volatile gases loss (Drummond and Ohmoto 1985). On the basis of adularia presence and of fluid inclusion evidence for boiling in the Profitis Ilias epithermal system (Killias et al. 1997), it is highly suggested that the zonation of type 1 electrum is due to boiling of the mineralizing fluids. Ore stage gold was most probably transported as a bisulfide complex, as in most epithermal environments (e.g. Berger and Henley 1989, Dong and Morisson 1995) and deposited according to the following reaction (Drummond and Ohmoto 1985):

$$8Au^0+15H_2S(aq)+SO_4^{-2}(aq) \rightleftarrows 8Au(HS)_2^-(aq)+4H_2O(aq)+6H^+(aq)$$

The differences in the chemistry between type 1 electrum and types 2 and 3 may be explained by precipitation of electrum 1 under alkaline conditions during boiling at deeper parts in the epithermal-hydrothermal system, and precipitation of type 2 electrum and type 3 pure gold during acidification and oxidation at near surface environments; in addition, assemblages of the oxidation stage may have been formed by mixing of boiled ascending waters with descending acid-sulfate waters, and/or cold oxygenated ground waters (Spycher and Reed 1989, Reed and Spycher 1985).

If the oxidation stage was formed in a weathering environment the presence of amorphous or colloform Fe-oxides indicates acid conditions, due to ferrolysis (Mann 1984). This combined with the presence of supergene type 2 electrum, with Ag-depleted rims and supergene type 3 pure gold, suggest that supergene gold may have been transported by chloride complexes (e.g. Webster 1986, Stoffregen 1986, Simmons et al. 1990, Herzig et al. 1991). This is supported by the association of gold grains with silver halogens and amorphous to colloform iron oxides. Precipitation of gold in this environment may be expressed by the following reaction (Mann 1984):

$$AuCl^-_4 + 3Fe^{2+} + 6H_2O \rightarrow Au + 4Cl^- + 3FeOOH + 9H^+$$

## 6. CONCLUSIONS

The epithermal quartz-vein gold mineralization at Profitis Ilias deposit of Milos island, was formed during three broad hypogene paragenetic stages: pre-ore, ore stage, post-ore and a supergene oxidation stage. Gold is associated with: 1) the main ore-stage occurring as primary, type 1, electrum grains with silver-enriched rims (fineness 610-728) and 2) the oxidation stage either as supergene, type 2, electrum grains with silver-depleted rims (finennes 656-1000), or as supergene, type 3, pure native gold (fineness ~1000). Sulfur activities, during ore stage deposition, range between $10^{-9.8}$-$10^{-11.2}$ atm at 250°C. Electrum of type 1, probably precipitated under alkaline conditions during boiling at deeper parts in the epithermal-hydrothermal system and type 2 electrum and type 3 pure gold precipitated during acidification and oxidation at near surface environments. The gold fineness, together with sulfur activities range and the mineralogical paragenesis of the Profitis Ilias mineralization are strong indicators for adularia-sericite type epithermal gold deposit.

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