Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, Τομ. XXXIV/3, 1065-1072, 2001 Πρακτικά 9ου Διεθνούς Συνεδρίου, Αθήνα, Σεπτέμβριος 2001 Proceedings of the 9th International Congress, Athens, September 2001

# A NEW OCCURRENCE OF ARGENTOPENTLANDITE AND GOLD FROM THE AU-AG-RICH COPPER MINERALISATION IN THE PALIOMYLOS AREA, SERBOMACEDONIAN MASSIF, CENTRAL MACEDONIA, GREECE V. MELFOS', M. VAVELIDIS', K. ARIKAS<sup>2</sup>

## ABSTRACT

The Au-Ag-Cu mineralisation in the Paliomylos area is associated with quartz segregations and pegmatoids in the form of boudinaged bodies. The Au, Ag and Cu contents in the ore bodies reach 6.8 ppm, 765 ppm and 0.80 wt%. The ore minerals consist of pyrite, chalcopyrite, sphalerite, pyrrhotite, galena, bismuthinite, argentopentlandite, gersdorffite, cobaltite, aikinite, hessite, native bismuth and gold. Pentlandite contains significant amounts in Ag (13.15 wt%), Au (1.59 wt%) and PGM, demonstrating a formula of Fe<sub>537</sub>Ni<sub>2.56</sub>Ag<sub>1.03</sub>Ir<sub>0.03</sub>S<sub>801</sub>. On the basis of geological, textural and chemical data, the mineralisation in the studied area was formed under high temperatures.

**KEY WORDS**: silver-gold-copper mineralisation; argentopentlandite; gold; fluid inclusions; Serbomacedonian massif; Greece

## **1. INTRODUCTION**

Serbomacedonian massif has been recognised as a favourable metallogenetic province for polymetallic, porphyry and skarn type ore deposits as well as for fracture-controlled quartz vein deposits, with significant gold and/or silver concentrations (Vavelidis 1994). Mineral exploration and mining activity of these deposits for precious and base metals, date back to the ancient times due to their economic potential (Wagner et al. 1986, Kiourtzoglou et al. 2001).

A detailed investigation concerning the mineral deposits in the broader area of Thessaloniki and Kilkis districts in northern Greece, revealed a significant Au-Ag-rich copper mineralisation in the Paliomylos area. The Paliomylos area is situated close to the villages Stefania, Lefkochorio and Karteres, 35 km northern of Thessaloniki city and geologically belongs to the Serbomacedonian massif.

The present work aims at studying the sulphide mineralogy and chemistry of the Au-Ag-Cu-bearing mineralisation. Emphasis is given to the chemical composition of the silver minerals, especially to the Ag-bearing pentlandite and to the primary gold chemistry. An attempt to provide data for genetic consideration is based on the fluid inclusion study.

#### 2. GEOLOGICAL SETTING

According to the most recent studies, the Serbomacedonian massif is considered to be the western extension of thrust units belonging to the Rhodope metamorphic core complex (Ricou et al. 1998). It is subdivided into two series: the underlying Kerdilion series to the cast and the overlying Vertiskos series to the west (Kockel et al. 1977). The rocks of the investigated area have a complicated petrotectonic history (Dixon and Dimitriadis 1987, Sakelariou 1989, Kourou 1991, Sidiropoulos 1991, Burg et al. 1995, Kostopoulos et al. 2001) and consist of ortho- and para-gneisses, schists and amphibolites, which belong to the Vertiskos series, as well as ultrabasic rocks (Figure 1). A two-mica and/or biotite granite (of Arnea type) intrudes the Lower Vertiskos sequence. Pliocene to Pleistocene sediments and Quaternary alluvial deposits overlie the older rocks.

Recent zircon Pb-Pb dating, performed by Kostopoulos et al. (2001), revealed an Early Middle Ordovician intrusion of the Vertiskos orthogneisses, as well as Late Triassic migmatitisation of these rocks. Geochronological data from the Arnea-type granite, presented by Kostopoulos et al. (2001), yielded an intrusion zircon Pb-Pb age of Late Triassic, which compares well with the zircon U-Pb age of Vital (1986). De Wet (1989) demonstrated a

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minimum Late Jurassic age (phengite Ar-Ar data) for the Arnea granite, corresponding probably to mixed age between igneous formation and later deformation. An Early Cretaceous underthrusting of the Vertiskos sequence at depths 11-14 kb and temperatures of 500-600 °C, is suggested by Kostopoulos et al. (2001).



Figure 1. Geological sketch map of the broader area of the Paliomylos Au-Ag-Cu mineralisation.

## **3. ANALYTICAL METHODS**

Polished sections of the ore minerals were systematically studied for gold- and silver-bearing minerals and sulphides using reflected light microscopy. Scanning electron microscopy was performed on a JEOL JSM 840 at the Department of Mineralogy, Petrology, Economic Geology. University of Thessaloniki. Ore and rock whole-samples were analyzed by ICP at ACME Analytical Laboratories, Vancouver, Canada. Microprobe analyses were carried out by a Cameca Camebax Microbeam electron microprobe at the Institute of Mineralogy and Petrology of Hamburg, Germany. The conditioons were 20kv and 20nA, beam diameter  $<1 \mu m$ . Corrections were applied using the Cameca Computer program PAP. Microthermometric measurements on fluid inclusions were carried out on doubly polished thin sections at the Department of Mineralogy-Petrology-Economic Geology, University of Thessaloniki, using a LINKAM THM-600 heating-freezing stage. The equipment is suitable for temperature measurements between  $-180^{\circ}$  C and  $600^{\circ}$  C. Calibration was performed using the following melting point standards: chloroform (-63.5° C), distilled H<sub>2</sub>O (0° C), naphtalene (80.35° C), Merck 135 (135° C), sacharine (228° C) and Merck 247 (247° C).

## 4. ORE MINERALOGY AND TEXTURAL FEATURES

Systematic field working in the Paliomylos area revealed Au-Ag-Cu-bearing quartz segregations and pegmatoids in the form of boudinaged bodies, with a thickness reaching up 2.30 m and a length exceeding over 20 m (Fig. 2a). Structural analyses showed that both quartz segregations and pegmatoids are developed in a NW-SE direction. They are variously deformed and demonstrate a schistosity which is parallel to the dominant schistosity of the host rocks dipping towards NE (20°-50°) with a low angle (20°-40°). A characteristic structural feature of the host metamorphic rocks as well as the quartz segregations and pegmatoids is the presence of kinkfolds, overprinting the dominant ductile fabric with NW-SE b-axis (\*320°/65°). The metamorphic rocks and the mineralised quartz bodies and pegmatoids ERVOS and the mineralised quartz bodies and the mineralised free.



Figure 2. a. Au-Ag-Cu-bearing quartz segregation hosted in the metamorphic rocks of Vertiskos series, Paliomylos area.

b. Argentopentlandite (Ag-pnd) intergrown with sphalerite (sph) within chalcopyrite (cpy). Polished section, //N, picture length=0.4 mm.

c. Euhedral gersdorffite (gersd) within chalcopyrite (cpy). SEM, back scattering image, polished section.

Chemical analyses of the host metamorphic rocks, carried out by ICP, showed elemental composition 0.13-0.17 wt% Fe, 0.02-0.12 wt% Cu, 28-35 ppm Pb, 40-48 ppm Zn, 138-173 ppm Ag and 530-850 ppb Au. The ore bodies contain significant Au and Ag concentrations, reaching 6.80 ppm and 765 ppm, respectively. The bulk composition of the ore bodies is up to 16.50 wt% Fe, 0.80 wt% Cu, 0.12 wt% Pb, 0.46 wt% Zn and 0.18 wt% As.

The ore minerals consist of pyrite, chalcopyrite, sphalerite, pyrrhotite, galena, argentopentlandite, bismuthinite, native bismuth, gersdorffite, cobaltite, aikinite, hessite and native gold, together with quartz as gangue mineral.

**Pyrite** is volumetrically the most important sulphide of the mineralisation and occurs as disseminated euhedral, subhedral and anhedral crystals of 5  $\mu$ m to 3 mm in size. The microprobe analyses (Table 1) showed 0.05 to 2.30 wt% Co and 0.02 to 1.20 wt% Ni. The Co/Ni ratios vary from 0.60 to 5.10 (3.75 in average). The average chemical composition of pyrite is Fe<sub>0.98</sub>Co<sub>0.02</sub>Ni<sub>0.01</sub>S<sub>1.99</sub>.

**Chalcopyrite** is one of the main minerals present and is found mainly as anhedral grains, intergrown with pyrite and pyrrhotite. In some cases chalcopyrite replaces pyrite along fractures. The characteristic feature of chalcopyrite is the development of inversion-twin lamellae. It also contains inclusions of argentopentlandite and Ag-tellurides (Figure 2b,c). Microprobe analyses in chalcopyrite revealed a stoichiometric composition with Ag content up to 0.15 wt% (0.08 wt% on average) (Table 1).

Pyrrhotite occurs as inclusions in chalcopyrite, as well as intergrown crystals with sphalerite and chalcopyrite.

**Galena** and **sphalerite** are accessory minerals of the copper mineralisation in Paliomylos area. Both minerals are intergrown with pyrite, pyrrhotite and chalcopyrite. Microprobe analyses (Table 1) showed that galena contains up to 0.10 wt% Ag and the average chemical formula is  $Pb_{0.99}S_{1.01}$ . Sphalerite is characterised by relatively high contents of Fe and Cd, up to 5.80 wt% and 2.30 wt%, respectively and its average chemical composition is  $Zn_{0.99}Fe_{0.08}Cd_{0.01}S_{1.01}$ .

Bismuth minerals are unproceen BigAlobories and a method by a state of the big and the big

chalcopyrite in the form of euhedral crystals reaching 35  $\mu$ m in size. Bismuthinite contains Cu (0.49-0.63 wt%), Ag (0.11-0.28 wt%), Pb (0.43-0.89 wt%), Fe (0.06-0.25 wt%), Te (0.15-0.40 wt%) (Table 1), and its average chemical composition is Bi<sub>1.91</sub>Cu<sub>0.04</sub>Pb<sub>0.02</sub>Fe<sub>0.01</sub>Ag<sub>0.01</sub>Te<sub>0.01</sub>S<sub>3.00</sub>.

Aikinite is found within chalcopyrite in association with bismuthinite and in some cases with hessite. The size of the grains ranges between 4 and 25  $\mu$ m. Aikinite contains 0.42 wt% Ag in average (Table 1) and its chemical formula is Cu<sub>0.94</sub>Ag<sub>0.02</sub>Fe<sub>0.05</sub>Pb<sub>1.00</sub>Bi<sub>0.98</sub>S<sub>3.00</sub>.

**Cobaltite** occurs as small euhedral crystals in chalcopyrite, with a size of up to 40  $\mu$ m. Microprobe analyses revealed 1.75 wt% Ni and 4.70 wt% Fe in average (Table 1). The chemical formula of cobaltite is  $Co_{0.84}Fe_{0.14}Ni_{0.05}As_{0.95}S_{1.02}$ .

**Gersdorffite** is mainly euhedral and is intergrown with chalcopyrite. A zonal growth has been observed in some grains (Figure 2c). Fe contents are 2.08 wt% in average (Table 1) and the chemical formula is  $As_{101}Ni_{0.05}Fe_{0.06}S_{0.08}$ .

**Argentopentlandite** is a high-silver variety of pentlandite and has so far been identified as an accessory mineral in a few sulphide deposits in the world. Several investigations, during the last 30 years, have shown that argentopentlandite is a discrete mineral phase, with an average composition of  $(Fe_5 \pm_{0.77}Ni_3 \pm_{0.78})_{28} \pm_s Ag_1 \pm_s S_8 \pm_s with 0 < [x] < 0.30$ , 0 < [y] < 0.23 and 0 < [z] < 0.30 (Kontny et al. 1994, Morales and Fenoll Hach-Alv 1996). In Paliomylos area it is found within chalcopyrite in the form of small reddish-brown anhedral crystals or patches, with a size ranging between 5 and 65  $\mu$ m (Figure 2b). Microprobe analyses revealed significant amounts in Ag, Au and PGM (Table 2). The Ag content vary between 12.78 and 13.50 wt% (13.15 wt% on average), while the maximum Au, Pt and Ir contents reach 1.59 wt%, 0.65 wt% and 0.85 wt%, respectively. This is the first documented report so far concerning PGM contents in argentopentlandite. The average chemical formula of argentopentlandite in Paliomylos area is  $Fe_{5.44}Ni_{2.47}Ag_{1.01}Au_{0.01}Ir_{0.01}S_{8.05}$ , which agrees with the general formula proposed by Morales and Fenol Hach-Alv (1996).

Table 1. Average microprobe analyses of pyrite (1), chalcopyrite (2), galena (3), sphalerite (4), bismuthinite (5),
aikinite (6), cobaltite (7), gersdorffite (8), hessite (9), gold in pyrite (10) and gold in quartz (11) from the Au-
Ag-rich copper mineralisation in the Paliomylos area. bdl=below detection limit

Wt8	1	2	3	4	5	6	7	8	9	10	11
Bi	bdl	bdl	bdl	bd1	78.89	35.52	bdl	bdl	bdl	bdl	bdl
Pb	bdl	bdl	86.32	bdl	0.89	35.89	bdl	bdl	0.08	bd1	bdl
Au	bdl	bd1	82.65	97.06							
Pt	bdl	bdl	bdl	bdl	bd1	bdl	bdl	bd1	bdl	bdl	bdl
Ir	bdl	bdl	bdl	bdl							
Те	bdl	bdl	bdl	bdl	0.23	bdl	bdl	bdl	36.80	bdl	bdl
Sb	bd1	bdl	bdl	bdl	bdl						
Cd	bdl	bdl	bdl	1.74	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ag	bdl	0.08	0.08	0.05	0.16	0.42	bdl	bdl	62.65	17.26	2.71
Pd	bdl	bdl	bdl	bdl							
Rh	bdl	bdl	bdl	bdl							
Ru	bdl	bd1	bdl	bdl	bdl						
Se	0.05	bdl	bdl	bdl	bdl	bdl	bdl	bd1	bdl	bdl	bdl
As	bd1	bdl	bdl	bdl	bdl	bdl	43.35	45.38	bdl	bdl	bdl
Zn	bd1	bdl	bdl	59.92	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cu	bdl	34.25	bdl	0.05	0.50	10.35	bdl	bd1	0.12	0.23	0.16
Ni	0.32	bdl	bdl	bd1	bdl	bdl	1.75	33.55	bdl	bdl	bdl
Co	1.20	bdl	bdl	bdl	bd1	bdl	30.25	0.25	bd1	bdl	bdl
Fe	45.40	30.58	bd1	4.32	0.12	0.52	4.70	2.08	bdl	bdl	bdl
Min	bdl	bdl	bdl	0.10	bdl	bdl	bdl	bdl	bdl	bdl	bdl
S	52.75	34.89	13.57	33.11	18.97	16.65	19.85	18.85	bdl	bdl	bd1
Tot	99.72	99.80	99.97	99.29	99.76	99.35	99.90	100.11	99.65	100.14	99.93

Hessite is found within chalcopyrite, intergrown with bismuth minerals and in some cases with galena. The size of hessite grains ranges between 2 and 25  $\mu$ m. According to the microprobe analyses (Table 1) the average chemical formula is Ag<sub>200</sub>Cu<sub>001</sub>Te<sub>0.99</sub>.

Gold occurs within pyrite and in some cases in quartz. The grain size ranges from 5 to 480 μm. Gold grains hosted in pyrite are characterised by high Ag content ranging between 16.25 and 18.25 wt% (17.26 wt% on average), whereas gold in quartz contains lower Ag (2.15 to 3.25 wt%, 2.71 on average). Copper is generally low and in both cases does not exceed 0.57 wt%. Based on the analytical results (Table 1), the chemical formula of gold in pyrite is Au<sub>0.72</sub>Ag<sub>1</sub>Ψhdtakf<sup>18</sup>BiblioBihkh<sup>10</sup>ØέcobaceToc<sup>70</sup> Tuήμα Γεωλογίας. Α.Π.Θ.

Wt8 10 11 12 Fe 37.40 37.70 37.20 36.85 37.20 35.96 36.38 37.25 36.65 36.25 36.71 37.46 36.15 36.30 36.82 372

Table 2. Selected microprobe analyses and the calculated chemical formulae of the argentopentlandite from the
Au-Ag-Cu mineralisation in the Paliomylos area.

Ag       13.35       12.78       12.97       12.88       13.05       13.15       13.50       12.88       12.90       13.05       13.35       13.30       13.50       13.50       13.15         Au       bdl	NI	17.70	17,25	17.50	17.25	11.35	17,05	17.90	17.68	17.60	17.30	17.35	17.95	17.90	18.16	17.57
An         bdl	Co	bdl	0.04	bdl	0.02	0.08	0.03	0.04	0.02	bdl	bdl	0.05	bdl	bdl	0.05	0.02
Ir       bdl       bd	Ag	13.35	12.78	12.97	12.88	13.05	13.15	13.50	12.88	12.90	13.05	13.35	13.30	13.50	13.50	13.15
Pd         bdl         bdl         0.05         bdl         0.05         bdl         bdl <td>Au</td> <td>bdl</td> <td>bdl</td> <td>bdl</td> <td>0.65</td> <td>0.55</td> <td>0.45</td> <td>0.65</td> <td>0.68</td> <td>1.59</td> <td>bdl</td> <td>bdl</td> <td>bd1</td> <td>bdl</td> <td>bdl</td> <td>0.33</td>	Au	bdl	bdl	bdl	0.65	0.55	0.45	0.65	0.68	1.59	bdl	bdl	bd1	bdl	bdl	0.33
Pt         bdl         bdl         bdl         0.85         0.58         0.62         0.50         bdl         bdl         0.65         0.50         bdl         bd	Ir	bdl	bdl	0.05	bdl	bd1	bdl	bd1	bd1	0.05	0.45	0.55	0.85	0.75	0.63	0.24
Bu         bdl	Pd	bdl	bdl	0.05	0.05	bd1	0.05	bdl	bd1	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Bdl         0.05         bdl         bdl <td>Pt</td> <td>bdl</td> <td>bdl</td> <td>bdl</td> <td>0.85</td> <td>0.58</td> <td>0.62</td> <td>0.50</td> <td>bdl</td> <td>bdl</td> <td>0.65</td> <td>0.50</td> <td>bdl</td> <td>bdl</td> <td>0.05</td> <td>0.27</td>	Pt	bdl	bdl	bdl	0.85	0.58	0.62	0.50	bdl	bdl	0.65	0.50	bdl	bdl	0.05	0.27
As         bdl         0.06         0.25         bdl         0.22         bdl         bdl </td <td>Ru</td> <td>bdl</td> <td>bdl</td> <td>bdl</td> <td>bdl</td> <td>bdl</td> <td>bdl</td> <td>0.05</td> <td>0.05</td> <td>0.05</td> <td>0.05</td> <td>bdl</td> <td>bdl</td> <td>bdl</td> <td>bd1</td> <td>bdl</td>	Ru	bdl	bdl	bdl	bdl	bdl	bdl	0.05	0.05	0.05	0.05	bdl	bdl	bdl	bd1	bdl
Cu       0.03       0.05       bdl       bdl       0.05       bdl       bdl       0.05       bdl       bdl <t< td=""><td>Rh</td><td>bdl</td><td>0.05</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td><td>0.07</td><td>bdl</td><td>bdl</td><td>bd1</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td></t<>	Rh	bdl	0.05	bdl	bdl	bdl	bdl	bdl	0.07	bdl	bdl	bd1	bdl	bdl	bdl	bdl
S       31.38       31.45       31.49       31.48       31.62       31.46       31.35       31.45       31.08       31.15       31.15       31.20       31.10       31.37         Tot       99.86       99.44       99.47       100.04       100.07       100.17       100.06       100.24       100.29       99.83       99.60       99.50       99.84       99.70         Chemical formulae       on the basis of 17 atoms         Fe       5.50       5.48       5.44       5.43       5.47       2.47       2.43       2.46       2.53       2.52       2.55       2.47       2.43       2.46       2.43       2.46       2.53       2.52       2.55       2.47       2.43       2.46       2.43       2.46       2.53       2.52       2.57       2.46       2.53       2.52       2.47       2.43 <th< td=""><td>As</td><td>bdl</td><td>0.06</td><td>0.25</td><td>bdl</td><td>0.22</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td><td>bdl</td><td>0.04</td></th<>	As	bdl	0.06	0.25	bdl	0.22	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.04
Fe         5.50         5.54         5.48         5.44         5.43         5.47         5.32         5.50         5.38         5.51         5.44         5.37         5.36         5.38         5.4           Ni         2.47         2.43         2.46         2.42         2.45         2.39         2.51         2.47         2.43         2.46         2.53         2.52         2.55         2.4           Ag         1.01         0.97         1.00         0.98         1.00         1.03         0.99         0.99         1.00         1.02         1.02         1.04         1.03         1.0           Au         -         -         -         -         -         -         -         -         0.03         0.03         0.07         -         -         -         -         0.00           Ir         -         -         -         -         -         -         -         -         -         -         0.01         1.03         0.99         1.00         1.02         1.02         1.04         1.03         1.00           Ir         -         -         -         -         -         -         -         -         -	Cu	0.03	0.05	bd1	bd1	0.05	bdl	bd1	0.05	bdl	bdl	bdl	bdl	bdl	0.05	bdl
Chemical formulae on the basis of 17 atoms           Fe 5.50 5.54 5.48 5.44 5.43 5.47 5.32 5.50 5.38 5.51 5.44 5.37 5.36 5.38 5.4           N1 2.47 2.43 2.46 2.42 2.45 2.39 2.51 2.47 2.47 2.43 2.46 2.53 2.52 2.55 2.4           Ag 1.01 0.97 1.00 0.98 1.00 1.00 1.03 0.99 0.99 1.00 1.02 1.02 1.04 1.03 1.0           Au         -         -         -         -         -         -         -         0.03         0.03 0.03 0.07         -         -         -         -         0.00           Ir         -         -         -         -         -         -         -         0.03 0.03         0.02         0.03 0.02         -         0.03 0.02         -         -         0.03 0.03         0.01           Pt         -         -         -         -         -         -         -         -         -         0.02	S	31.38	31.51	31.45	31.49	31.48	31.62	31.46	31.35	31.45	31.08	31.15	31.15	31.20	31.10	31.35
on the basis of 17 atoms           Fe 5.50 5.54 5.48 5.44 5.43 5.47 5.32 5.50 5.38 5.51 5.44 5.37 5.36 5.38 5.4           N1 2.47 2.43 2.46 2.42 2.45 2.39 2.51 2.47 2.47 2.43 2.46 2.53 2.52 2.55 2.4           Ag 1.01 0.97 1.00 0.98 1.00 1.00 1.03 0.99 0.99 1.00 1.02 1.02 1.04 1.03 1.0           Au         -         -         -         -         -         -         -         0.03         0.03 0.03 0.07         -         -         -         0.00         0.03         0.07         -         -         -         0.00         0.01         0.02         0.03 0.03 0.07         -         -         -         0.00         0.03         0.02         0.02         0.03 0.03         0.07         -         -         -         0.00         0.03         0.07         -         -         -         0.00         0.03         0.03         0.07         -         -         -         0.00         0.03         0.03         0.07         -         -         -         0.00         0.03         0.03         0.07         -         -         -         0.00         0.03         0.03         0.07         -         -         -         0.00         0.03         0.03         0.03         0.00         0.00         0.00         0.00 </td <td>Tot</td> <td>99.86</td> <td>99.44</td> <td>99.47</td> <td>100.04</td> <td>100.07</td> <td>100.17</td> <td>100.06</td> <td>100.24</td> <td>100.02</td> <td>99.83</td> <td>99.60</td> <td>99.50</td> <td>99.50</td> <td>99.84</td> <td>99.78</td>	Tot	99.86	99.44	99.47	100.04	100.07	100.17	100.06	100.24	100.02	99.83	99.60	99.50	99.50	99.84	99.78
Fe         5.50         5.54         5.48         5.44         5.43         5.47         5.32         5.50         5.38         5.51         5.44         5.37         5.36         5.38         5.4           N1         2.47         2.43         2.46         2.42         2.45         2.39         2.51         2.47         2.47         2.43         2.46         2.53         2.52         2.55         2.4           Ag         1.01         0.97         1.00         0.98         1.00         1.03         0.99         0.99         1.00         1.02         1.02         1.04         1.03         1.0           Au         -         -         -         0.03         0.02         0.03         0.03         0.07         -         -         -         -         0.01           Ir         -         -         -         -         -         -         -         -         -         0.03         0.03         0.00           Ir         -         -         -         -         -         -         -         -         -         -         -         -         -         -         -         0.03 <th0.03< th=""> <th0.03< th=""></th0.03<></th0.03<>	128 4															
Ni       2.47       2.43       2.46       2.42       2.45       2.39       2.51       2.47       2.43       2.46       2.53       2.52       2.55       2.4         Ag       1.01       0.97       1.00       0.98       1.00       1.03       0.99       0.99       1.00       1.02       1.02       1.04       1.03       1.0         Au       -       -       -       0.03       0.02       0.03       0.03       0.07       -       -       -       -       0.03       0.03         Ir       -       -       -       -       -       -       -       -       0.03       0.02       0.02       0.03       0.03       0.07       -       -       -       -       0.03       0.00         Ir       -       -       -       -       -       -       -       -       -       0.03       0.02       0.02       0.03       0.02       0.02       0.03       0.02       0.04       0.03       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03 <td< td=""><td>100</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></td<>	100															
Ag       1.01       0.97       1.00       0.98       1.00       1.03       0.99       0.99       1.00       1.02       1.02       1.04       1.03       1.0         Au       -       -       -       0.03       0.02       0.03       0.03       0.07       -       -       -       -       0.03       0.01         Ir       -       -       -       -       -       -       -       -       0.03       0.02         Pt       -       -       0.04       0.02       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.03       0.02	Fe	5.50	5.54	5.48	5.44	5.43	5.47	5.32	5.50	5.38	5.51	5.44	5.37	5.36	5.38	5.44
Au       -       -       -       0.03       0.02       0.03       0.03       0.07       -       -       -       -       0.03         Ir       -       -       -       -       -       -       -       0.03       0.03       0.07       -       -       -       0.03         Pt       -       -       -       -       -       -       -       0.03       0.02       0.03       0.02       0.03       0.02       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.02       -       -       0.03       0.03       0.03       0.03       0.03       0.03       0.03       0.03       0.03       0.03       0.03       0.03	Ni	2.47	2.43	2.46	2.42	2.45	2.39	2.51	2.47	2.47	2.43	2.46	2.53	2.52	2.55	2.47
Ir 0.02 0.02 0.0	Ag	1.01	0.97	1.00	0.98	1.00	1.00	1.03	0.99	0.99	1.00	1.02	1.02	1.04	1.03	1.01
Pt 0.04 0.02 0.03 0.02 0.03 0.02 0.0	Au		-		0.03	0.02	0.02	0.03	0.03	0.07	_	-	-	-	-	0.01
	Ir	7	-	-	2	-	-	-		-	0.02	0.02	0.04	0.03	0.03	0.01
8.02 8.06 8.06 8.09 8.08 8.09 8.09 8.01 8.09 8.01 8.04 8.04 8.05 8.01 8.0	Pt	<u> </u>	-	-	0.04	0.02	0.03	0.02	-	-	0.03	0.02		-		0.01
	S	8.02	8.06	8.06	8.09	8.08	8.09	8.09	8.01	8.09	8.01	8.04	8.04	8.05	8.01	8.05

## 5. FLUID INCLUSIONS

Fluid inclusions were studied in double-polished thin sections, in order to estimate the temperature, pressure and composition of the fluids related to the formation of the investigated gold-bearing quartz veins and the associated mineralisation. Microscopic observations indicate two types of quartz, an older (Oz1) and a younger generation (Qz2). Qz1, which is the main carrier of the mineralisation, is related to the quartz segregations and pegmatoids and has been affected by the subsequent tectonic deformation, resulting in the recrystallisation of quartz and the destruction of its primary texture. Qz2 is undeformed and not related to the mineralisation and is associated to the the crosscuting quartz veins. Both generations of quartz contain only a few fluid inclusions suitable for thermometric measurements.

The studied fluid inclusions contain two phases: a liquid aqueous solution and a vapour bubble, which occupies 10 to 25% by volume and their size ranges between 3 and 15 µm. The homogenisation temperatures of the fluid inclusions hosted in Qz1, exceeds 400 °C, and they are mainly above 600 °C, which is the limit of the measurement ability of the LINKAM THM-600 stage. The freezing point of the Qz1 inclusions could not be measured, because of their small size. The temperatures of initial melting of inclusions in the undeformed Oz2 vary approximately from -19 to -20 °C indicating that the solutions consist mainly of H<sub>2</sub>O and NaCl. Ice melting temperatures (-12 to -7 °C) indicate salinities of 16 to 10.5 wt% NaCl equiv. The homogenisation temperatures of these inclusions vary between 220 and 350 °C, with a maximum at 250 °C.

## 6. DISCUSSION

The gold bearing quartz pegmatoids at Paliomylos area are of special interest due to the relatively high Au concentrations (up to 6.80 ppm), as well as to high silver content (up to 765 ppm). Gold is found as native with elevated Ag contents, while the main Ag carriers are hessite and argentopentlandite.

Argentopentlandite is a rare mineral and it has been described in only ten deposits worldwide, since it was first reported by Shishkin et al. (1971). Investigations on its occurrence, composition, structure and phase relations (Kontny et al. 1994, Morales and Fenoll Hach-Alv 1996, and references therein) revealed that it is a distinct mineral species, rather than a member of an isomorphous solid solution series with pentlandite. Argentopentlandite from Paliomylos area is the second documented report of this mineral in Greece (Vavelidis et al. 2000). Previously, Mposkos (1983a,b) and Vavelidis et al. (1996) demonstrated the mode of occurrence and the chemistry of argentopentlandite from Koronouda Cu-deposit, which is located about 10 km northwestern of Paliomylos area. Argentopentlanidite in Koronouda area is found in boudinaged quartz segregations and pegmatoids, intergrown with chalcopyrite and the Ag contents range between 11.95 and 13.40 wt% (12.76wt% on average) corresponding to a chemical formula of  $Fe_{5,44}Ni_{2,40}Ag_{0.97}As_{0.02}Au_{0.01}Ir_{0.01}Pt_{0.01}S_{8.14}$  (Vavelidis et al. 1996). The present study confirms the similarities of the two Greek argentopentlandite occurrences concerning their mineralogical, textural and chemical features.

The Au-Ag-Cu bearing quartz segregations and pegmatoids are probably genetically associated with the adjacent granite of Arnea type, which occurs 5 km to the south (Figure 1). The emplacement of the Arnea granite took place during Late Triassic and was related to continental rifting (Kostopoulos et al. 2001). Christofides et al. (2000) and Kostopoulos et al. (2001) suggested that the Arnea granite is a high evolved granitic intrusion resulting from crustal anatexis.

The ascending magma of the granite was possibly the main source for the metals Bi, Pb, As, Zn, Cu, Ni, Co, Fe, Te, Au and Ag. Arnea granite is interpreted as crustal melt and hence it is considered that the surrounding host rocks could probably supply the magmatic system with basic and precious metals. This assumption is based also on the fact that the Vertiskos formation is enriched in base and precious metals and is considered to be the source for part of the gold and silver mineralisations in the Serbomacedonian massif (Vavelidis 1994, Vavelidis and Tarkian 1995, Vavelidis et al. 1996).

The structural analyses revealed that the quartz segregations and pegmatoids in Paliomylos area are syntectonic to the formation of metamorphic rocks. Papadopoulos and Kilias (1985) consider that the dominant schistosity of the metamorphic rocks is of Middle to Late Cretaceous age, whereas Kostopoulos et al. (2001) suggest an Early Cretaceous underthrusting of the Vertiskos sequence resulting in high pressure (11-14 kb) and temperature (500-600 'IC) metamorphic rocks. For this event Sidiropoulos (1991) and Kourou (1991) reported metamorphic conditions of 500 to 640 'IC and >5.3 kb for the rock formations of the western Vertiskos group.

The metal-bearing quartz pegmatoids in the Paliomylos area were affected by the same tectonic phase, that also affected the host metamorphic rocks. As a result of that, the ore shows recrystallisation textures. This is also evidenced by the Co/Ni ratio of pyrites (0.60-5.10), which is plotted in the field of the reformed ore deposits (Bralia et al. 1979).

The temperature of formation of the ore paragenetic assemblage is difficult to establish exactly. However, the determination of an interval of temperature is possible. Different events occurred within this interval. The characteristic inversion twins developed in chalcopyrite show that this mineral was formed at temperatures between 400 and 550 °C (Craig and Kullerud 1969). Argentopentlandite coexisting with chalcopyrite, has an upper stability limit at 455 °C, according to Mandzuik and Scott (1977). The most probable interval ranges from 400 to 550 °C. This interval is in accordance with the range in the temperature of homogenisation obtained from fluid inclusions of the quartz of first generation (400 to >600 °C). Kourou (1991) and Kostopoulos et al. (2001) suggested similar temperatures for the metamorphic rocks of the Vertiskos group.

Concerning gold formation, it is assumed that gold grains in pyrite, which are Ag-rich (17.26 wt%), were crystallised during the first stages of the mineralisation. In contrast, gold grains in quartz are Ag-poor (2.71 wt%) and they are interpreted to have been formed after the silver-bearing minerals, hessite and argentopentlandite, at the final mineralisation stage.

## 7. CONCLUSION

It is obvious that argentopentlandites from Paliomylos and Koronouda Cu-deposits display similar mineralogical and chemical features, giving the impression that these two deposits belong to the same metallogenetic zone in the Serbomacedonian massif. Based on the data published so far on Au-Ag-bearing Cu mineralisations hosted in quartz segregations in the metamorphic rocks of the Vertiskos series (Serbomacedonian massif), we could suggest that the metallogenetic zone extends in a NW-SE direction from Koronouda to Paliomylos area, with a possible extension to the more southern quartz-vein-associated Au-bearing deposits from Drakontio (Vavelidis et al. 1999) and Nea Madytos-Stanos area (Vavelidis and Tarkian 1995).

ACKNOWLEDGEMENTS: The first author (V. Melfos) would like to thank the State Scholarships Foundation of Greece for the financial support of the fluid inclusions study (1<sup>st</sup> Project for Post-Doctoral Research). We also thank Dr. Dimitrios Kostopoulos (University of Thessaloniki) for his thorough and helpful comments on the manuscript, especially on the Geological Setting section.

#### Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.

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