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GOLD COMPOSITION IN THE Fe-Pb-Cu-(Ag-Zn) HYDROTHERMAL QUARTZ VEINS OF KALLIANOU AREA, SOUTHERN EUBOEA (GREECE)

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A B S T R A C T

The gold composition from hydrothermal quartz veins of the Kallianou area, Southern Euboea is studied. The primary mineralogical assemblages found in the quartz veins are Fe-Pb-Cu-(Ag-Zn)-sulphides as well as native gold and silver. Chemical analyses of bulk ore yielded up to 4,6 g/tn gold and 292 g/tn silver. Native gold is hosted in pyrite, chalcopyrite and quartz. A different chemical composition of gold was found in relation with the host mineral. The higher gold fineness (933) has been measured on gold hosted in pyrite and the lower (689) on gold within quartz. The differences in gold composition can be attributed to the time of gold deposition, to the pH of the environment as well as to the composition of the hydrothermal solutions.

Σ Υ Ν Ο Ψ Η

Μελετάται η σύσταση του χρυσού σε υδροθερμικές χαλαζιακές φλέβες της περιοχής Καλλιανού στη Ν. Εύβοια. Η προωτογενής μεταλλοφορία στις χαλαζιακές αυτές φλέβες περιλαμβάνει σουλφίδια Fe-Pb-Cu-(Ag-Zn), καθώς επίσης αυτοφυή χρυσό και άργυρο. Χημικές αναλύσεις δειγμάτων μεταλλεύματος έδωσαν μέχρι 4,6 g/tn χρυσό και 292 g/tn άργυρο. Ο χρυσός φιλοξενείται στο σιδηροπυρίτη, χαλκοπυρίτη και χαλαζία. Εξακριβώθηκε μια διαφορετική χημική σύσταση του χρυσού σε σχέση με το ορυκτό ξενιστής. Η υψηλότερη καθαρότητα (933) μετρήθηκε σε κόκκους χρυσού που φιλοξενούνται σε σιδηροπυρίτη και η χαμηλότερη (689) σ'αυτούς που βρίσκονται μέσα σε χαλαζία. Οι διαφορές στη σύσταση του χρυσού μπορούν να αποδοθούν στο χρόνο απόθεσής του, στο pH του περιβάλλοντος απόθεσης καθώς επίσης και στη σύσταση των υδροθερμικών διαλυμάτων.

INTRODUCTION

The island of Euboea belongs geotectonically to the Pelagonian zone and

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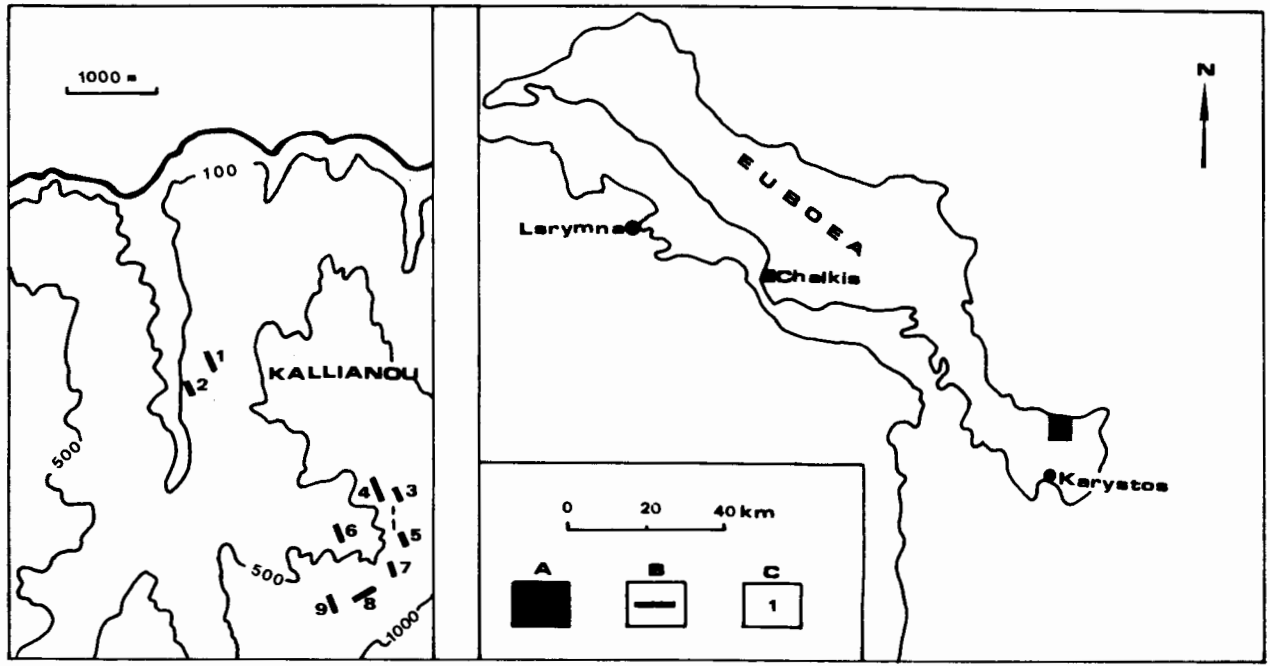

Fig. 1: Location map of the studied metalliferous quartz veins. A: Studied area, B: Metalliferous quartz veins, C: Locality names: Kyparissi (1), Pikiza (2), Kordella (3), Agia Barbara (4), Asbestocamino (5), Klikeriza (6), Mpampanioti (7), Mouskies (8), Salesa (9).

Σχ. 1: Χάρτης θέσεων μεταλλοφόρων χαλαζιακών φλεβών. A: Περιοχή μελέτης, B: Μεταλλοφόρες χαλαζιακές φλέβες, : Τοπονύμια: Κυπαρίσσι (1), Πίκιζα (2), Κορδέλλα (3), Αγία Βαρβάρα (4), Ασβεστοκάμινο (5), Κλικέριζα (6), Μπαμπανιώτη (7), Μουσκιές (8), Σάλεζα (9).

especially its southern part to the Attica-Cyclades massif (AUBOUIN, 1959). The district of the southern and eastern part of S. Euboea consists of a series of crystalline schists, marbles and cipolins which constitute the Styra-Ochi formation (KATSIKATSOS, 1978). The Upper horizon of this formation consists mainly of glaucophane schists with intercalated lenses of manganese-rich quartzites and small ophiolitic masses.

At many sites, discordant quartz veins cut the metamorphic rocks. The width of the veins ranges from a few centimeters to some meters and their length is relatively small. They strike to a general NW direction and dip 30^{o}-70^{o} NE (THEOFILOPOULOS and VACONTIOS, 1982). There are also quartz veins and stocks parallel to the schistosity of the rocks of probable metamorphic origin.

The ore mineralization of S. Euboea consists mainly of Fe-Pb-Cu-(partly Zn)-sulfides. It is enclosed in the discordant quartz veins cutting the schists or within the calcareous rocks in the form of lenses.

The most important metalliferous sites are: Agia Barbara, Kordella, Mpampanioti, Mouskies, Salesa, Argos, Kyparissi, Pikiza, Klikeriza, Asbestokamino of the broader area of Kallianou (Fig. 1). On these sites galleries, shafts and dumps of rock waste are found today, displaying an intense mining and metallurgical activity, which probably refers to antiquity as stated also by ZACHOS and MARATOS (1965).

Chemical analyses by Neutron activation on samples from different sites of the discordant quartz veins yielded the following Au and Ag contents:

a. gangue 119 g/tn Ag and 0,6 g/tn Au

b. massive ore 105 g/tn Ag and 4,6 g/tn Au

c. disperse ore 202 g/tn Ag and 1,3 g/tn Au

ZACHOS and MARATOS (1965) report up to 9 g/tn, while THEOFILOPOULOS and VACONTIOS (1982) up to 6,8 g/tn gold contents for the same metalliferous area.

MINERALOGY OF THE METALLIFEROUS QUARTZ VEINS.

The ore mineralization of the Kallianou district, within the quartz veins, consists of pyrite, galena, chalcopyrite, sphalerite and scanty bornite. The hypergene minerals limonite, cerussite, smithsonite, agglesite, malachite, azurite and calcocite, covellite have been also observed as a result of oxidation and secondary enrichment respectively. The main gangue minerals of the veins are quartz and in subordinate amounts calcite.

The most interesting feature of mineralization in the Kallianou area is the presense of native gold and silver, argentite as well as silverous fahlore.

The vein mineralization is of the massive and in places of the dispersed

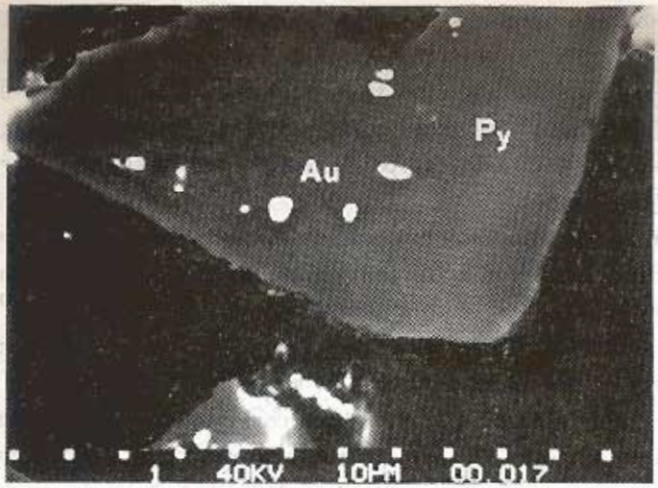

Fig. 2: Electron microphotograph of gold grains (Au) in host pyrite (Py) surrounded by quartz (black).

Σχ. 2: Φωτογραφία από ηλεκτρονικό μικροσκόπιο κόκκων χρυσού (Au) σε σιδηροπυρίτη (Py) μέσα σε χαλαζία (μαύρο).

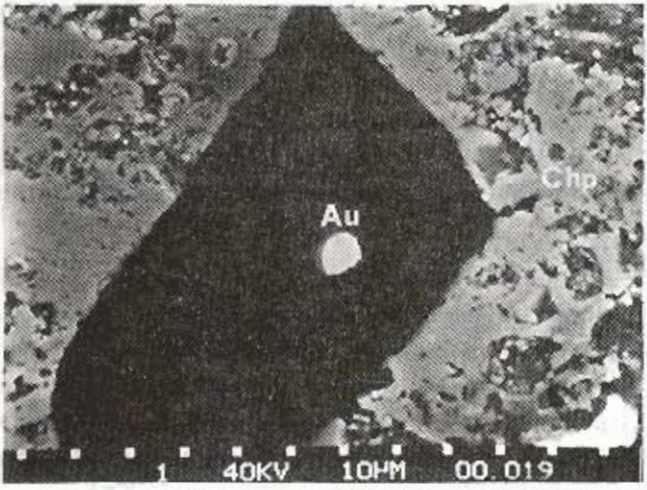

Fig. 3: Electron microphotograph of gold grains (Au) in quartz (black) surrounded by chalcopyrite (Chp).

Σχ. 3: Φωτογραφία από ηλεκτρονικό μικροσκόπιο κόκκου χρυσού (Au) σε χαλαζία (μαύρο) μέσα σε χαλκοπυρίτη (Chp).

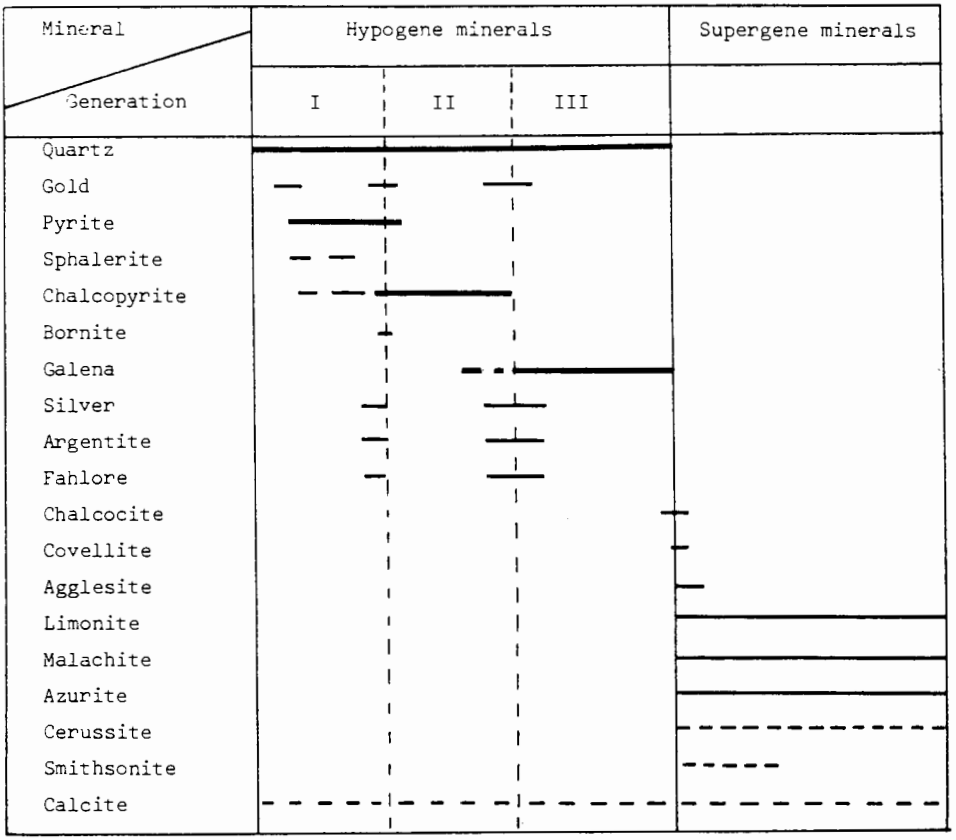

Fig. 4: Mineral formation series in the Kallianou metalliferous quartz veins.

Σχ. 4: Σειρά κρυσταλλώσεως στις μεταλλοφόρες χαλαζιακές φλέβες της περιοχής Καλλιανού.

type, while the mineralogical composition varies from one site to another. Pyrite forms euhedral to subhedral crystals, while the rest hypogene minerals form individual anhedral grains and massive aggregates. Pyrite is enclosed in the other sulphides, while chalcopyrite only in galena. In some cases droplets of chalcopyrite are observed in sphalerite.

Detailed microscopic studies if the ore samples reveal that native gold occurs mainly in the form of drop-like inclusions in pyrite, chalcopyrite and quartz, which may be characterized as three different generations of gold deposi-

Table 1: Representative analyses of gold grains in different host minerals.

Πιν. 1: Αντιπροσωπευτικές αναλύσεις κόκκων χρυσού σε διαφορετικά ορυκτά ξενιστές.

	Au(%)	Ag(%)	Cu(%)	Gold fineness F*
		Gold in Pyrite		
1.	93.35	6.40	0.20	934
2.	93.09	6.75	0.16	931
3.	93.45	6.50	0.05	935
4.	92.95	7.00	0.05	930
M.V**	93.21	6.67	0.11	933
		Gold in Chalcopyrite		
1.	81.26	18.58	0.16	813
2.	80.75	19.22	0.03	808
3.	81.03	18.72	0.25	810
4.	81.28	18.24	0.48	813
M.V.	81.08	18.69	0.23	811
		Gold in Quartz		
1.	68.48	31.52	0.00	685
2.	70.40	29.60	0.00	704
3.	68.29	31.71	0.00	683
4.	68.40	31.60	0.00	684
M.V.	68.89	31.11	0.00	689

*F=Au X 1000/Au+Ag

**M.V.=Mean Value

tion. Gold grains have sizes between 1 and 3 μm in diameter and occasionally up to 30 μm (Fig. 2, 3). In Fig. 4 the mineral formation series in the quartz veins of Kallianou district is given.

AGIORGITIS and BECKER (1975) indicate the existence of gold in galena, but such a case was not identified in our study.

CHEMICAL COMPOSITION OF GOLD

Microprobe analyses of gold were carried out at the Max-Planck Institute for Nuclear Physics, Hiedelberg, on a EIRL probe, operated at 15KV, 20nA specimen current, using natural minerals as standards. Element concentrations have been calculated with the ZAF program. These analyses revealed differences in the Ag- and partly the Cu- contents of gold in relation to the host mineral. Representative analytical data of 12 gold grains, occurring in different host minerals, are given in Table 1. From this table results that:

1. Gold hosted in pyrite shows the higher fineness (933) with average contents: 93.3% (92.9-93.4%) in Au, 6.7% (6.4-7.0%) in Ag and 0.1% (0.05-0.20%) in Cu.

2. Gold in host chalcopyrite shows a lower fineness (811) with average contents: 81.1% (80.8-81.3%) in Au, 18.7% (18.2-19.2%) in Ag and 0.2 (0.03-0.50%) in Cu.

3. Gold hosted in quartz shows the higher silver content (lowest fineness 689) averaging to 31.1% (29.6-31.7%) and it can be characterized as electrum (RAMDOHR, 1975). The absence of copper in this case is also remarkable.

DISCUSSION ON THE ORE DEPOSITION AND THE GOLD COMPOSITION

Different suggestions have been proposed up to now as regards the quartz veins ore mineralization of the Kallianou district. MARINOS and PETRASCHECK (1955) and ALEXOULI-LIVADITI (1978) suggest a hydrothermal origin of the quartz veins and ore mineralization. AGIORGITIS and BECKER (1975), on the basis of the analytical data on trace elements accept also an hydrothermal origin. To the above authors the low concentration of the elements Ag, Bi, As, Te and probably Se in galena, pyrite and chalcopyrite suggests a low temperatute of formation. On the contrary, THEOFILOPOULOS and VACONTIOS (1982) propose that the ore minerals of the veins do not result from solutions of magmatic origin. The metallic elements, instead, preexisting in the primary sediments which gave the schists, have been mobilized into the veins during a low grade metamorphism.

FYFE and HENLEY (1973) and GOTTESMANN (1976) refer that during the temperature conditions of the greenschist facies gold has been shown to be highly mobile in the presence of adequate conditions, and the metamorphism can create gold concentration.

This aspect is known as the "metamorphic secretion theory" which is based on the assumption that from a favourable primary gold source as a result of regional metamorphic overprinting, gold is extracted and concentrated in suitable

structures (BOYLE, 1955; VILJOEN et al., 1969). The mineralogical siting of gold is of great importance for this process (BOYLE, 1979; GOTTFRIED et al., 1972; KEAYS and SCOTT, 1976: MEYER and SAAGER, 1985 and others).

From our investigation results that the mineralization is more probably of a hydrothermal origin and this idea can be supported by the followings:

(a) Field work observations showed that the studied metalliferous quartz veins are always discordant, while their mineralogical composition varies from site to site. On the contrary, the concordant quartz veins and stocks were always found to be free of ore mineralization.

(b) The gold-content of the schists, which host the quartz veins, is 0.1-0.2 g/tn (after THEOFILOPOULOS and VACONTIOS, 1978). This high concentration of gold in the schists, could explain the presense of this mineral in the quartz veins if the mineralogical siting of gold was not the native state and the concordant veins were mineralized too. The dissolution of native gold (being the most probable mineral phase in the primary sediments) during metamorphism is unclear according to the up date available literature.

(c) It is difficult to explain the differences in the Ag-content of the gold grains found even in the same vein, with the "metamorphic secretion theory". The observed differences in Ag-content of gold can be more convincingly explained as the result of a gradual deposition from hydrothermal solutions.

The deposition of native gold in hydrothermal deposits is defined by various factors like temperature, pressure, redox potential, pH and type of solutions. According to SAKHAROVA et al. (1981) the hydrothermal gold deposits are formed in a temperature range between 50^{o} and 250^{o}C. The purity of gold is governed primarily by the ratio of gold to silver valences in solution, while on the other hand the pH value of the evnironment determines the differences in behaviour of gold (chemical affinity) of different valence states (MARAKUSHEV, 1977). Scherbina (1956, in SAKHAROVA et al., 1981) has stated that the ratio Au:Ag in native gold increases with the alkalinity of the solutions, while MOISEYENKO (1976, 1977) showed that the most favorable pH values for gold deposition are 5.7-8.6. The experimental study of SAKHAROVA et al. (1981), showed that the Ag-content of native gold depends not only on the pH value but on other properties of the gold-bearing solutions too. Some investigators state that in hydrothermal gold deposits the Ag-content of gold increases along with falling temperature of the solutions (KOROLEVA et al., 1981), and others that gold, formed later than pyrite, is enriched in silver (BALTON et al., 1969).

On the basis of the above mentioned suggestions, it is possible to make the following statements about the variation of the Ag-content in the investiga-

ted native gold:

(a) The low Ag-content of gold in host pyrite can be attributed to the higher temperature of formation, in relation to the other two cases.

(b) The high Ag-content of gold in host quartz can be interpreted with the acid conditions during gold deposition or/and the lower temperature of formation.

(c) The intermediate Ag-content of gold in host chalcopyrite is the result of a corresponding temperature of formation.

We must not also ignore the influence of the solution composition changes with proceeding metallogenesis, which also causes a variation in the Au:Ag ratio of native gold deposited.

However, we believe that the interpretation of gold composition in its hydrothermal vein deposits, needs a further study of some more cases in order to confirm the above statements by means of comparisons and statistical results.

The investigation of gold has proceeded to a high stage during the last years, but the solution of the problem of gold origin has not yet been successfully defined. There are also many controversies as regards the geochemical-metallogenic behavior of gold during ore deposition.

CONCLUSIONS

The study of the Fe-Pb-Cu-(Ag-Zn) sulphide mineralization enclosed in the concordant quartz veins of the Kallianou area (S. Euboea) revealed the presence of native gold hosted in pyrite, chalcopyrite and quartz. The metalliferous quartz veins are considered as hydrothermal in origin. Electron microprobe analyses on gold grains showed different Ag-contents in relation with the host mineral.

These differences in the gold grains composition are attributed to the various factors defining the deposition of gold from hydrothermal solutions.

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