Δελτίο Ελληνικής Γεωλογικής Εταιρίας τομ. XXXIII, 51 - 60, 1999
Bulletin of the Geological Society of Greece vol. XXXIII, 51 - 60, 1999

The Agios Filippos ore deposit, Kirki (Western Thrace). A base metal part of a high sulfidation epithermal system[1]

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ABSTRACT

The Agios Filippos mineralisation occurs as fracture fillings and breccia-hosted sulfides and sulfosalts in a tectonic zone bounded by two pre-mineral subvertical faults. Rhyolites, which predate the mineralisation, intruded the volcano-sedimentary host lithology. An advanced argillic alteration with alunite and minor pyrophyllite followed an early pervasive grey silicification of the rocks. Propylitic and sericitic hydrothermal alteration zones are developed peripheral to the ore zone. A part of the deposit comprises hydrothermal breccias of previously silicified sedimentary rock and rhyolite. Covellite of hypogene origin was recognised in the upper parts of the ore zone. The Au content of silicified and advanced argillically altered rocks is very low. Concentrates of Cu-sulfosalts do not contain economic Au grades. The overall features of the Agios Filippos mineralisation are considered to be similar to those of high sulfidation deposits. A comparison with conceptual models of high - sulfidation epithermal systems indicates that the upper silicic part of the deposit has been eroded.

ΠΕΡΙΛΗΨΗ

Η μεταλλοφορία του Αγίου Φιλίππου φιλοξενείται σε τέμαχος ενός ηφαιστειο-κλαστικού σχηματισμού, που οριοθετείται από δύο υποπαράλληλα ρήγματα. Κατά μήκος της ρηξιγενούς ζώνης έχει διεισδύσει ρυολιθικής σύστασης τήγμα, που δημιούργησε φλέβα ρυολίθου και ρυολιθικών λατυνοπαγών. Ο ρυόλιθος είναι προγενέστερος της μεταλλοφορίας. Η μεταλλοφορία αναπτύσσεται τόσο μέσα στο ρυόλιθο όσο και στα πετρώματα του τεμάχους του ηφαιστειο-κλαστικού σχηματισμού, τα οποία έχουν υποστεί μία πρώϊμη τεφρή πυριτίωση, που ακολουθήθηκε από προχωρημένη αργιλλική εξαλλοίωση με αλουνίτη. Τα πυριτιωμένα τμήματα σε αρκετές θέσεις έχουν υποστεί υδροθερμική λατυνοποίηση (hydrothermal brecciation). Αναλύσεις Au σε δείγματα τεφρής πυριτίωσης δείχνουν εξαιρετικά μικρές συγκεντρώσεις. Το τμήμα της μεταλλοφορίας η οποία είναι είναι πλούσια σε θειοάλατα του Cu, χαρακτηρίζεται από χαμηλές συγκεντρώσεις Au. Η μεταλλοφορία του Αγίου Φιλίππου ταξινομείται στις επιθερμικές μεταλλοφορίες υψηλής θείωσης (όξινου - θειϊκού τύπου). Συγκρίνοντας τα χαρακτηριστικά του κοιτάσματος με τα ιδεατά μοντέλα των επιθερμικών κοιτασμάτων υψηλής θείωσης, συμπεραίνεται ότι το μεταλλείο του Αγίου Φιλίππου αντιπροσωπεύει το τμήμα των βασικών μετάλλων του αρχικού συστήματος, του οποίου το ανώτερο τμήμα έχει διαβρωθεί.

INTRODUCTION

In the frame of a research project concerning exploration for Ag, Cd, Ga, Ge, and In in sulfide ore bodies and their gossans, the geological setting of the Agios Filippos (AGF) deposit (Kirki, Western Thrace) was investigated. Although the AGF deposit had been thoroughly investigated by various agents or research teams, a closer study of the relevant references revealed that,

[1] **ΤΟ ΚΟΙΤΑΣΜΑ ΑΓΙΟΥ ΦΙΛΙΠΠΟΥ, ΚΙΡΚΗ (ΔΥΤΙΚΗ ΘΡΑΚΗ): ΕΝΑ ΤΜΗΜΑ ΒΑΣΙΚΩΝ ΜΕΤΑΛΛΩΝ ΕΝΟΣ ΕΠΙΘΕΡΜΙΝΟΥ ΣΥΣΤΗΜΑΤΟΣ ΥΨΗΛΗΣ ΘΕΙΩΣΗΣ**

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while the aspect of ore mineralogy was sufficiently covered (MOELO et al., 1985; 1990), the geological setting as well as the hydrothermal alteration pattern of host rocks did n't correlate with our field and laboratory observations. An essential disagreement became evident between the previous ore deposit classifications (polymetallic vein- or Kuroko-type mineralization) as the study of the deposit progressed. Preliminary data on ore deposit geology were then presented by SKARPELIS (1995). The aim of the paper is the description of the mode of occurrence of the mineralization and the hydrothermal alteration of host rocks, as well as the preliminary discussion of metallogenic features and the exploration implications for the Kirki area.

HISTORY OF EXPLORATION AND MINING ACTIVITY IN THE AREA

Exploration for Pb and Ag ores in the area began late in the 19th century. In 1932 English mining companies invested in exploration projects, started construction of mine shafts and managed to exploit 20.000 tn of ore. With the onset of the World War II the German company "Thrazische Bergwerke" continued exploration in the AGF area. Small scale exploitation commenced and a part of a flotation plan with an 80 tn/day capacity was installed. Exploration for base metals and Ag in the following years was carried out by several state owned Greek agents. In 1973 the lease was sublet to "Evros Mining Co", which exploited and processed roughly 150.000 tn of ore at 4 to 10% combined Pb and Zn. Pb concentrates at 60-70% Pb, 3-7% Cu and 500 gr/tn Ag, and Zn concentrates at 48-54% Zn and 0.4-0.5% Cd were produced. With long time interruptions small scale open pit mining and processing of the ore continued up to 1998. Production of mineral concentrates remained at very low tonnages. Open pit mining has almost reached level +345m.

ORE DEPOSIT GEOLOGY

Research on the ore deposit geology and proposals on ore deposit model for the AGF had been effectuated by BITSIOS (1973), ARIKAS (1980), KALOGEROPOULOS (1986) and MICHAEL et al.(1989). The data we present come from field observations and sampling in the open pit of AGF and the OP 3 lease. Drill core sampling was carried out so that the ore deposit geology could be validated for depths between +420 to +200m.

a. *Lithology and mode of occurrence*

The mineralized zone at AGF, stretches along two sub-parallel fault planes, which today form the western and eastern boundarties of the open pit. The main fault systems are those with NNW-SSE and NNE-SSW direction. In the AGF zone one may observe two converging fault lines, which unite to the north of the open pit. The western fault dips 80°E and the eastern fault 75°W (Fig. 1). These fault planes tend to converge at depth. The mineralised zone is 25 m wide at the +200 m level. The geological characteristics of the deposit are summarised below:

(i) The western fault plane brings in contact with the mineralised zone a tectonic block consisting of Tertiary (Priambonian?) propylitised sandstones. Limestone intercalations occur within the clastic sediments.

(ii) The eastern fault plane marks the contact between hydrothermally altered sedimentary and felsic volcanic rocks with a rhyolitic dyke, which is the easternmost part of the mineralised zone. These volcanic and sedimentary rocks in the open pit form an anticlinal structure, one limb of which dips to the west, forming strata aligned parallel to the western fault.

(iii) Parts of the rhyolite are hydrothermally brecciated. The rhyolitic dyke narrows out to the northern and the higher parts of the mine, whereas it is widening towards deeper levels. The rhyolite can be traced for several tens of meters to the north and several hundred meters to the south of the pit, and should be considered as a part of extensive rhyolitic intrusions in the

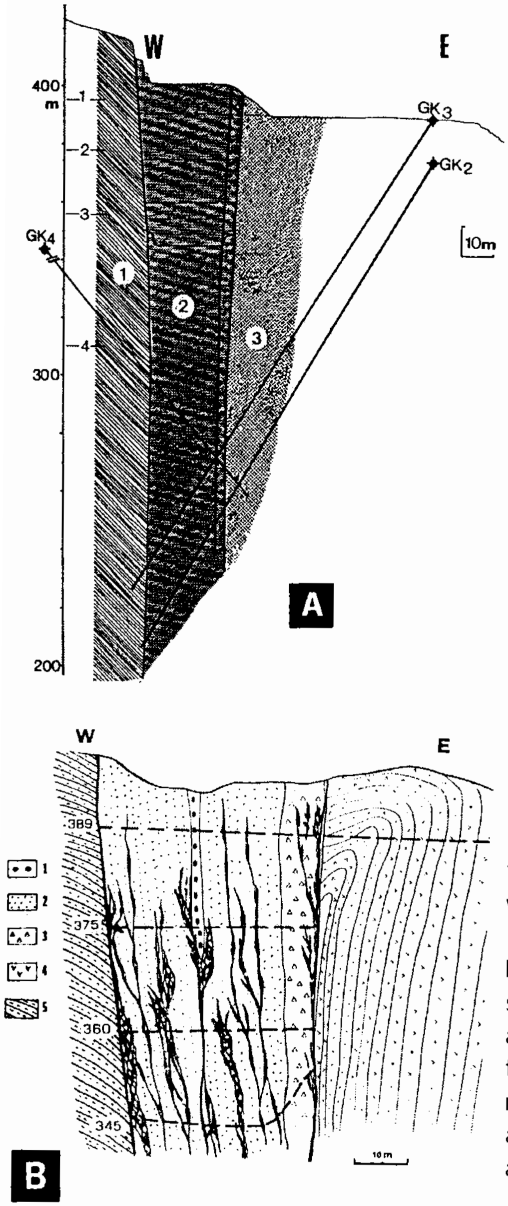

Fig. 1. Cross sections of the Agios Filippos ore deposit
A. Distribution of hydrothermal alteration zones: (1) propylitc (2) advanced argillic (3) sericitic
Numbers 1 to 4 indicate levels of mine shafts; GK3: borehole number
B. Cross section of the upper part of the deposit 1. conglomerates, 2. Hydrothermally altered clastic sediments and felsic tuffs (zones of silicification and advanced argillic alteration), 3. Hydrothermally altered rhyolite and rhyolitic breccia, 4. Bedded felsic tuffs, 5. Propylitised Tertiary sediments;
+389: exploitation level

Εικ. 1. Τομές του κοιτάσματος του Αγ. Φιλίππου.
Α. Τομή του κοιτάσματος με τις κύριες ζώνες εξαλλοίωσης
(1) προπυλιτική (2) χαλαζία - καολινίτη - αλουνίτη (3) σερικιτική
Με τους αριθμούς 1 έως 4 σημειώνονται τα επίπεδα των μεταλλευτικών στοών, GK3: αριθμός γεώτρησης
Β. Τομή του ανώτερου τμήματος του κοιτάσματος
1. κροκαλοπαγή 2. Υδροθερμικά εξαλλοιωμένα κλαστικά πετρώματα και όξινοι τόφφοι (πυριτική και προχωρημένη αργιλλική εξαλλοίωση) 3. Υδροθερμικά εξαλλοιωμένος ρυόλιθος και ρυολιθικά λατυποπαγή 4. Εστρωμμένοι όξινοι τόφφοι 5. Προπυλιτιωμένα Τριτογενή κλαστικά ιζήματα
389: επίπεδο βαθμίδας εκμετάλλευσης

Kirki area. It is clear that the rhyolitic intrusion postdates major extentional faulting in the area and predates the mineralising event. The rhyolitic magmatism in the area is probably of Oligocene age. Besides the intrusive rhyolite the mineralised zone comprises hydrothermally altered sandstones, microconglomerates and felsic volcanics.

(iv) The mineralisation is hosted into the rhyolite and the hydrothermally altered volcanic and sedimentary lithologies. It is aligned along joints and bed planes, as pockets and dispersions within the rocks. The overall impression is that of a mineralisation under tectonic control, forming veins and stockworks of semimassive and massive ore as well as disseminations within the host rocks.

b. *Hydrothermal alteration*

The study of the hydrothermal alteration pattern was based on sampling of the open pit and especially of cores of inclined boreholes penetreting both the wallrocks and the mineralised zone to a depth of 200m. The classification scheme of MEYER & HEMLEY (1967) was used. The rocks

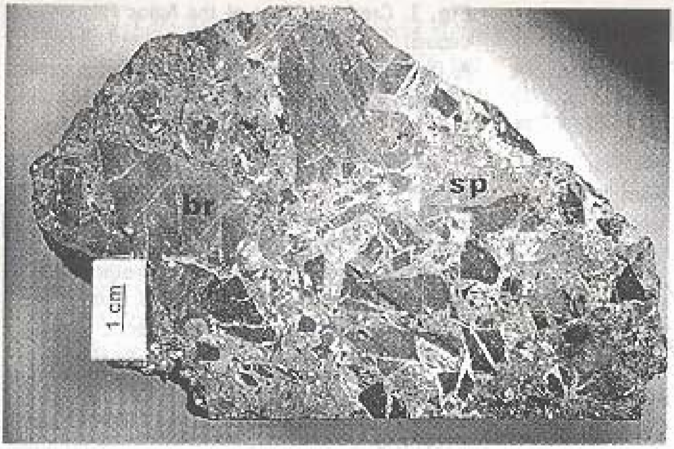

Fig. 2. (a) Breccia of silicified rock (br) cemented by sphalerite (sp) (b) Breccia of silicified rock (br) comprising quartz, alunite and kaolinite, cemented by sphalerite, Cu-sulfosalts and covellite

Εικ. 2. (α) Λατύπες πυριτιωμένου πετρώματος (br) συγκολλώνται από σφαλερίτη (sp)
(β) Λατύπες πυριτιωμένου πετρώματος (br) με αλουνίτη και καολινίτη συγκολλώνται από σφαλερίτη, θειοάλατα Cu και κοβελλίνη

into the mineralised zone are intensely to pervasively altered, so that characterisation of the type of protoliths is difficult.

Propylitisation is the prevailing alteration of the clastic sedimentary rocks in the western sector of the open pit. Argilically altered rocks of the mineralised zone are roughly separated from the propylitised sediments by the western fault. Chlorite, goethite, minor epidote and calcite filling microveinlets, are the main alteration minerals.

Early silicification. An early grey to grey-whitish massive silicification with disseminated pyrite or semimassive pyritic aggregates preceded deposition of the ore minerals and resulted to texture destruction (1st pyrite generation). Quartz appears as fine replacements of primary minerals. Quartz and pyrite veinlets crosscut the massive silicification. Silicification is a result of acid leaching of the rocks. Parts of the silicification zone are hydrothermally brecciated. Angular fragments are cemented by sphalerite and late formed sulfides, sulfosalts and gangue minerals (Fig. 2a, b).

Advanced argillic alteration with alunite. This alteration type affected mainly the rhyolite and rhyolitic breccia, giving them a white to pinkish-white hue. It also affected parts of the rocks in the mineralised zone which hadn't been entirely silicified, a fact indicating that this alteration succeeded silicification of the rocks. It further indicates that acidic, sulfate rich solutions leached the protoliths and were later neutralised by reaction with the wall rocks producing the advanced argillic assemblages. This is also evident in the development of kaolinite/dickite-quartz aggregates as cement of the hydrothermal breccia, or as veinlets intersecting silicified rock. Alunite is found intimately intergrown with quartz, kaolinite and pyrite. The relative proportion of these minerals in individual samples is highly variable. Illite was detected in the outer part of the advanced argillic zone, towards the propylitic and sericitic haloes, and in drill cores at the deepest parts of the deposit. Minor pyrophyllite was found in the western part of the open pit close to the propylitic zone and in altered rhyolitic breccia at the immediate contact with sphalerite-covellite veins (eploitation level +389). Gypsum aggregates, found in the uppermost parts of the open pit, cann't be attributed with certainty to either a hypogene or supergene origin.

Sericitic alteration: A sericitic alteration halo is well exposed in the western sector of the open pit. The alteration mineralogy of the rocks consists of compact aggregates of sericite, quartz and pyrite, or as veinlet-fillings of sericite, quartz and pyrite. Minor illite, kaolinite and alunite were found in the altered rocks close to the mineralised zone, indicating grading of alteration from the argillic to the sericitic zones.

c. *Ore mineralogy and mineral parageneses*

Extended studies of the ore mineralogy were carried out by BITSIOS (1973), MOELO et al. (1985), DEMOU (1987), VAVELIDIS et al. (1989), MOELO et al. (1990), which showed the complexity of the ore mineral assemblages. It is worth mentioning that two new minerals were discovered by MOELO et al. (1985) and MOELO et al. (1990) respectively: kirkiite and levyclaudite. On the basis of these studies and our own microscopic and microprobe work, the following mineral composition has been determined: *sphalerite, wutrzite, pyrite, galena, jordanite, Bi-jordanite, kirkiite, cosalite, bismuthinite, tennantite, koesterite, luzonite, stibioluzonite (fammatinite),enargite-stibioenargite, selligmanite, bournonite, levyclaudite, hypogene covellite, supergene covellite*. Quartz, kaolinite/dickite, alunite and barite are the gangue minerals closely associated with the ore. Two generations of pyrite were distinguished: the first is associated with the advanced argillic alteration and the second with the main mineralisation stage. In the latter case euhedral to subhedral pyrite coexists with tennantite. Sphalerite formation preceded that of the Cu- and Pb-sulfosalts and the other sulfide minerals. Sphalerite coexisting with pyrite is Fe-poor (0.1 to 0.4 mole % Fe). Enargite and luzonite were early formed relative to tennantite and galena (Fig. 3a). Coarse grained covellite (Fig. 3b) which does not replace other sulfides and is characteristic of hypogene origin, was found in samples only from the upper part of the open pit (exploitation level +389). It should be mentioned for comparison that the assemblage "covellite-luzonite - gold" appears only in the upper part of the high - sulfidation Summitville deposit, passing downward to the assemblage "chalcopyrite-tennantite" (ARRIBAS, 1995). Supergene fine-grained covellite replacing Cu-sulfosalts is widespread. Massive wurtzite aggregates fill open spaces either of the ore or the silicified rocks, usually filling the inner wall of cavities. It is evident that wurtzite was the last formed sulfide mineral. Euhedral to subhedral barite crystals accompany sulfides and sulfosalts throughout the ore zone. Calcite, dolomite and rarely rhodochrosite are found in veins and veinlets crosscuting the ore (Fig. 4), especially in the deeper parts of the mineralised zone, indicating they were the late formed hydrothermal minerals.

d. *Gold and Silver grades*

Gold assays of rock samples characterised by grey silicification indicate very low concentrations (range: 8-75mgs/tn). Gold and silver values ranging from 100 to 500 mgr/tn and 100 to 2200gr/tn respectively were detected in samples rich in Cu-sulfosalts. Silver grade of the galena concentrates is 500gr/tn (GEMEE, 1987). Representative analyses of mineral concentrates and ore samples for base metals and Ag, Cd, Ga, Ge, In, are given in TABLE 1. It is worth to be

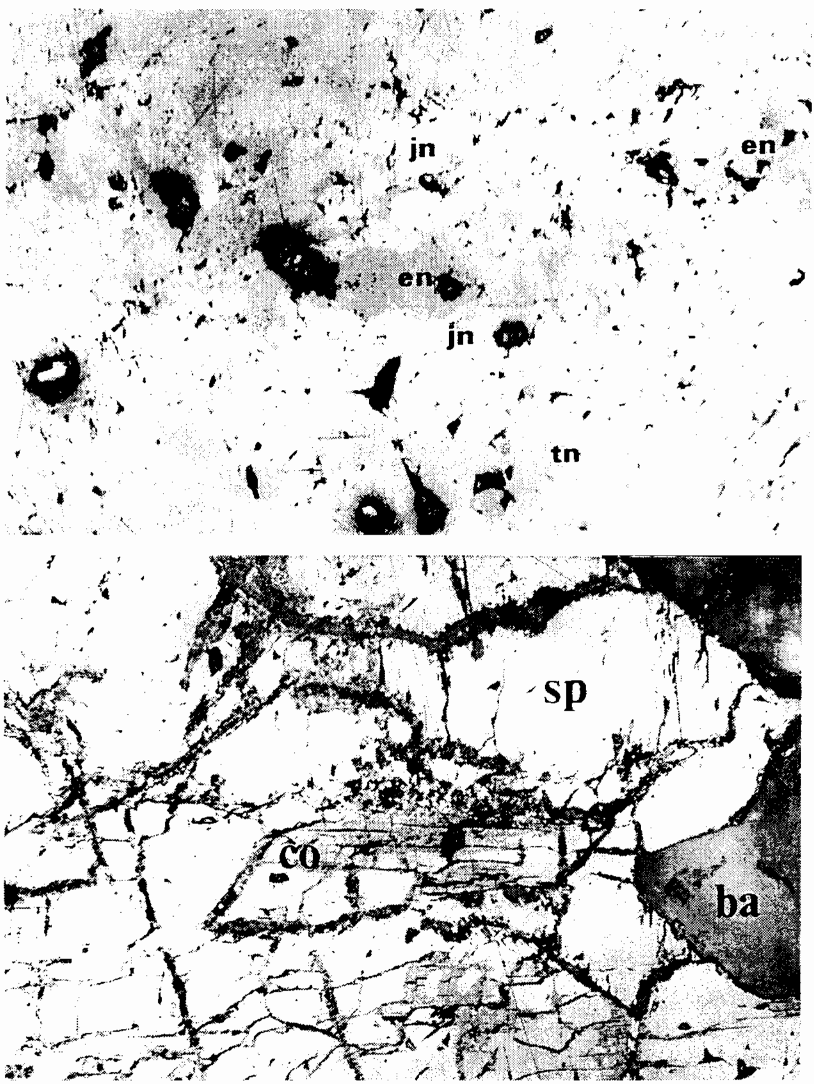

Fig. 3. (a) Microphotograph of relictic enargite (en) associated with jordanite (jn) and tennantite (tn) (b) Hypogene covellite (co) interstitially developed between Sphalerite grains (sp). Euhedral barite crystals (ba)

Εικ. 3. (α) Υπολλειματικός εναργίτης (en) με ιορδανίτη (jn) και τενναντίτη (tn) (β) Υπογενετικός κοβελλίνης (co) αναπτυγμένος μεταξύ κόκκων σφαλερίτη (sp). Ιδιόμορφοι κρύσταλλοι βαρίτη (ba)

mentioning that the sphalerite - wurtzite concentrates are rich in Cd, Ga, Ge and In (SKARPELIS, 1995).

e. *Temperatures of mineral deposition*

Primary fluid inclusion data in wurtzite-sphalerite showed homogenization temperatures of around 230°C (DRIESNER & PINTEA, 1994). The aqueous fluid had a low salinity (<5% NaCl eq.) with NaCl probably the dominant salt. Tem-

TABLE 1. Representative analyses of mineral concentrates and ore samples (SKARPELIS, 1995)

Sample	Description	Zn	Pb	Cu	Ag	Cd	Ga	Ge	In	Sn
K 103	Sphalerite conc.	53.7	0.2	0.1	130	5390	637	91	272	65
K 112	wurtzite conc.	65.1	0.1	0.13	220	3500	2862	811	1090	12
K 115	Cu - rich ore	12.1	9.3	25.6	65	470	407	134	77	75
K 148	Cu - rich ore	1.6	8.9	22.7	2210	180	46	18	40	3400
K 142	Zn-Pb ore	15.9	4.1	0.04	10	1140	116	4	86	9
K 176	Zn-Pb-Cu ore	2.2	7.1	9.1	380	240	139	1	80	1100

Zn, Pb, Cu in wt%; All other metals in gr/tn

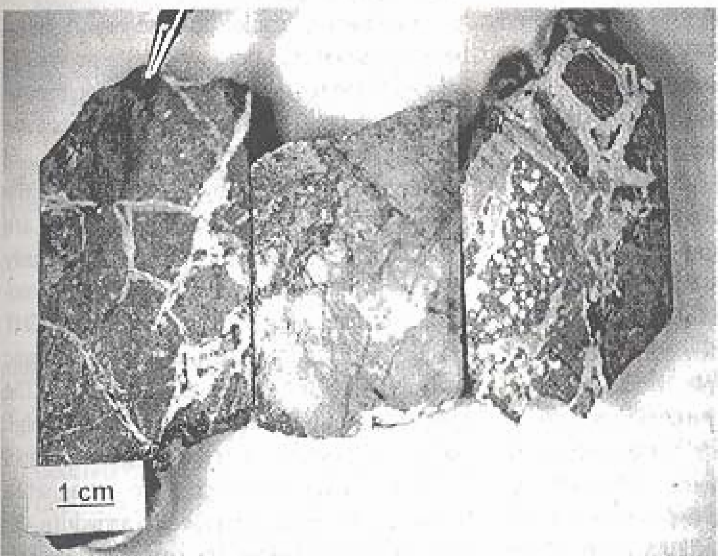

Fig. 4. Calcite and dolomite veinlets crosscutting silicified and mineralised rock
Εικ. 4. Φλεβίδια ασβεστίτη και δολομίτη τέμνουν την πυριτίωση και τη μεταλλοφορία

peratures in the range 230-268°C and a low salinity (4.9% NaCl eq.) were determined in fluid inclusions in barite (KALOGEROPOULOS & KATIRTZOGLOU, 1989). A further indication of the temperature of formation is the coexistence of the polymorphs of Cu_3AsS_4: luzonite and enargite; luzonite is the low temperature form. MASKE & SKINNER (1971) have concluded that the inversion from luzonite to enargite takes place between 275° and 300°C. Calcite and dolomite in veinlets crosscuting the ore were deposited at lower temperatures (140-200°C) as concluded by MICHAEL et al. (1989) on the basis of oxygen and carbon isotope geothermometry. Although further fluid inclusion work is necessary, the available data allow one to consider the mineralisation as being formed at the epithermal stage.

DISCUSSION

The mode of occurrence and mineralogy, the hydrothermal alteration mineral assemblages and the temperatures of formation indicate that the AGF ore deposit bears a resemblance to high - sulfidation type epithermal systems. A depositional environment at high sulfur fugacities is proved by the following data: a. The occurrence of very high and high sulfidation state minerals:

hypogene covellite, enargite-luzonite, koesterite, pyrite. b. The very low Fe content of sphalerite coexisting with pyrite, a feature characterising high fS_2 of the hydrothermal solution (SCOTT & BARNES, 1971) c. the abundant alunite and the major amount of kaolinite closely associated with ore.

It is known that the zones of alteration in high-sulfidation systems typically grade from a shallow silicic zone through advanced argillic, argillic, into a sericitic with increasing depth. This alteration sequence may extend a few hundred to more than 1000m (ARRIBAS, 1995). A comparison with conceptual models of high - sulfidation epithermal systems indicates that the upper silicic part of the AGF deposit has been eroded.

The available geochemical data indicate that the AGF mineralisation is very low in Au. Concentrates of Cu-sulfosalts do not contain economic Au grades (max. Au content 0.5gr/tn). It is possible that Au was associated with the upper (now eroded) silicic zone as is the case with similar ore deposits. As an example, it could be mentioned that, in Rodalquilar, Au mineralisation occurred in the shallowest parts of the central core of hydrothermal activity in association with hydrothermal brecciation and deposition of amorphous silica and pyrite (ARRIBAS et al., 1995). Detailed studies on El Indio and Lepanto deposits have resulted in identification of two metal stages: an early Cu-rich, Au-poor dominated by enargire-luzonite, and a late Au-rich, Cu-poor stage with tennantite-tetrahedrite, chalcopyrite and tellurides. The lack of the latter minerals in the AGF mineralisation may explain the low Au content of the ore.

The transition of alteration assemblages from quartz-alunite-pyrite to enargite-pyrite and finally to tennantite indicates a hydrothermal fluid which gradually became more reducing and less acidic. This is confirmed by the late formation of wurtzite in open spaces and cavities in the latest stages of the mineralising event. According to SCOTT & BARNES (1972) wurtzite is stable at lower fS_2 relative to sphalerite, whereas at temperatures lower than 250°C it may be deposited in a highly reducing environment. Rhodochrosite is most commonly absent from high sulfidation deposits except at Red Mountain (HEALD et al., 1987). Its occurrence as a late vein filling mineral in AGF, along with calcite/dolomite, is a further indication of the neutralisation of hydrothermal fluids at the late evolutionary stages of the system.

From the exploration point of view it should be emphasised that porphyry systems are developed at the roots of high-sulfidation epithermal deposits and that high-sulfidation deposits form in a position intermediate between intrusions and the surface. As stated by KNIGHT (1971), the alteration mineralogy above plutons which are anomalously rich in sulfur reflect anomalously large activities of sulfur in the pluton environment. The chemical relations presented by KNIGHT (o.c.) predict the formation of copper - arsenic sulfosalts and alunite under these conditions. The predicted spatial zoning in and below high sulfidation systems is from copper - arsenic sulfosalts above to chalcopyrite - magnetite below, and from alunite above to anhydrite - K-feldspar - biotite below. The spatial and genetic relation of high sulfidation epithermal deposits with porphyry systems has been documented in several ore districts around the world (SILLITOE, 1983; 1989; ARRIBAS et al., 1995). Taking in consideration the ore deposit type of the AGF mineralisation, along with the occurrence of porphyry type mineralisation in the nearby area (ARIKAS, 1979), a follow-up exploration work for porphyry Cu-Au and/or Mo is suggested.

Acknowledgements

This work was carried out as part of the project "Exploration for metals used by the electronic industry, in sulfide ore bodies and their gossans". The Greek Secretariat for Research & Technology is kindly acknowledged for providing the necessary funds. Thanks are due, both to Mr. Minos Kypriadis (Evros Mining Co) and Prof. St. Skounakis (former President, Board of Directors of the General Company for Mineral Exploration & Exploitation - ΓΕΜΕΕ) for permission of sampling available borehole cores.

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