Epithermal type ores in the Aegean. The hot spring mineralisation of northern Chios island, Greece

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ABSTRACT

The mineralisation of Northern Chios, so far considered as stratabound within the Upper Paleozoic sediments, is fracture controlled, crosscutting stratification of clastic sediments or replacing Silurian carbonates. Clastic sedimentary wallrocks are hydrothermally altered to quartz - sericite-pyrite, whereas carbonates are ankeritised. A first stage of silica deposition resulted to the formation of black massive silicification zone, followed by brecciation and sulfide deposition. Ore mineralogy comprises base metal sulfides, tetrahedrite, stibnite and berthierite. Au and Ag values for the major part of the mineralisation indicate low grades.

The data allow a classification of the mineralisation of Northern Chios to the hot spring low grade Au type, related to the Mid-Miocene porphyritic rhyolites which intrude the autochthonous unit. The mineralisation of Northern Chios is comparable to the Miocene epithermal hot spring type deposits of Western Turkey.

Key words: Epithermal, hot-spring, stibnite, hydrothermal alteration, Aegean, Chios island, Greece

ΠΕΡΙΛΗΨΗ

Οι μεταλλοφορίες της Βόρειας Χίου - οι οποίες μέχρι τώρα εθεωρούντο στρωματέγκλειστες εντός Άνω-Παλαιοζωϊκών ιζημάτων - ελέγχονται από διαρρήξεις των πετρωμάτων που τέμνουν τη στρώση ή αντικαθιστούν ανθρακικά του Σιλουρίου. Τα κλαστικά ιζήματα-ξενιστές είναι υδροθερμικά εξαλλοιωμένα προς χαλαζία - σερικίτη - σιδηροπυρίτη, ενώ τα ανθρακικά έχουν αγκεριτιωθεί. Ένα πρώτο στάδιο απόθεσης πυριτίου οδήγησε στο σχηματισμό μαύρης πυριτικής ζώνης εξαλλοίωσης, ενώ στη συνέχεια δημιουργήθηκαν υδροθερμικά λατυποπαγή (breccia) και ακολούθησε απόθεση θειούχων ορυκτών. Θειούχα βασικών μετάλλων, τετραεδρίτης, στιμπνίτης και μπερθιερίτης μετέχουν στη σύσταση της μεταλλοφορίας. Οι περιεκτικότητες σε Au και Ag για το μεγαλύτερο τμήμα της μεταλλοφορίας είναι σχετικά χαμηλές. Τα δεδομένα επιτρέπουν την ταξινόμηση των μεταλλοφοριών της Β. Χίου στον τύπο θερμών πηγών (hot spring type) χαμηλής περιεκτικότητας σε Au. Οι μεταλλοφορίες συνδέονται γενετικά με τους Μεσο-Μειοκαινικούς πορφυριτικούς ρυολίθους, οι οποίοι διεισδύουν εντός της αυτόχθονης ενότητας και συσχετίζονται με τα Μειοκαινικά κοιτάσματα τύπου θερμών πηγών της Δυτ. Τουρκίας.

Introduction

In the frame of our exploration program for epithermal type mineralisation in NE Greece and the NE Aegean islands a re-examination of the geological setting of the antimony and base metals mineralisations of Northern Chios island was carried out. The results presented in the paper came out after detailed field work in idle mines of the area of Kambia village (Pithos and Agrelia), and along the valley of Keramos-Agiasmata (Xygremmos, Koutsonikos). Exploration for "combined Pb-Zn sulfides" in NW Chios dates back to the turkish occupation. Very small scale mining was carried out sporadically up to the 70ies. Ore

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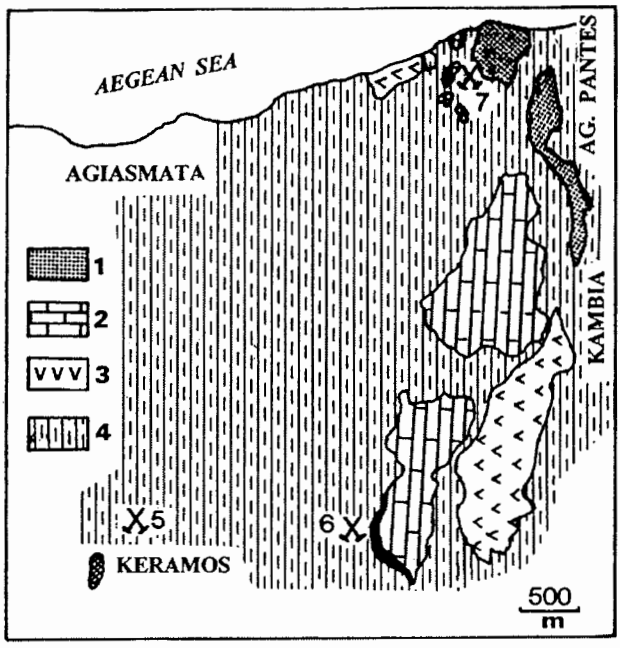

Fig. 1. Geological map of Northern Chios island with the sites of hot spring type mineralisations studied: 1. Mid-Miocene porhyritic rhyolites, 2. Silurian carbonates, 3. Paleozoic volcanics, 4. Clastic sediments (Permian *pro patre*), 5. Xygremmos - Koutsonikos mineralised fractures, 6. Agrelia idle base metal mine, 7. Pithi mineralised zone

reserve estimates by MOUSOULOS (1949) indicated probable reserves of the Agrelia mineralisation to 80.000tn at 4%Pb and 7%Zn.

Geology of Chios

The geology of Chios is characterised by an autocthonous stratigraphically discontinuous Silurian to Jurassic unit and an allocthonous discontinuous Carboniferous to Jurassic unit (KTENAS, 1921a, 1921b; RENZ, 1955, BESENECKER et al., 1968). The allocthonous unit comprises an Upper Carboniferous to Lower Permian clastic sequence with intercalations of limestones, overlain by Middle Permian platform carbonates and trasnsgressively covered by Jurassic carbonates. The mineralisations are hosted within the autocthonous unit of the island, which represents a chaotic clastic sequence comprising blocks of various sizes (centimeter to kilometer scale) of carbonate, volcanic and siliceous rocks, floating within a sandstone to pelitic matrix (Fig. 1). The NW Chios sequence is interpreted as an eastern dipping monocline structure. Carbonate blocks and lydites within greywackes, stratigrapfically belong to Wenlockian, Ludlowian or Ludlowian to Lower Devonian. Upper Devonian to Westfalian greywackes with carbonate blocks, lydites and shales are also reported. The chaotic spatial distribution of the dated carbonate rocks within the unit and the incompatible stratigraphic and lithofacial characteristics of blocks being in immediate contact each to the other, led PAPANIKOLAOU & SIDERIS (1983) to consider the paleozoic terrain of NW Chios as a wildflysch formation, with olistholiths of volcanic rocks. A precise age determination of the matrix was not possible up to now; a Permian age *pro patre* is supposed. PE-PIPER & KOTOPOULI (1994) interpreted the same formation as an accretionary wedge melange intruded in pre-Triassic times by volcanics. Lavas or hypabyssal rocks and pyroclastics of silicic to mafic composition were identified.

The Paleozoic part of the autochtonous unit of Chios is transgressed by Triassic carbonate and clastic sediments. The upper part of the Triassic is represented by a thick sequence of carbonates with bauxite intercalations (TSOFLIAS, 1983).

Several small, mid-Miocene (14-17 Ma) volcanic centres with high-Mg calc-alkaline (adakitic) andesite, ne-normative basalt, and calc-alkaline rhyolite are exposed in Chios island (BESENECKER, 1973; PE-PIPER et al. 1995). The andesites are

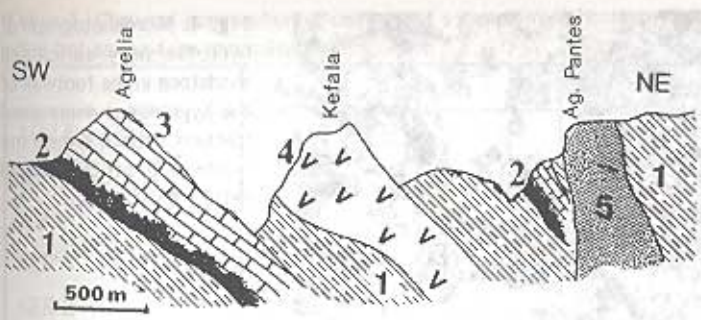

Fig. 2. Schematic geological section showing the setting of the Agrelia mineralisation (based on the geological section given by PAPANIKOLAOU & SIDERIS, 1983): 1. Clastic sediments (Permian *pro patre*), 2. Mineralised zone, 3. Silurian carbonates, 4. Paleozoic volcanics, 5. Mid-Miocene porhyritic rhyolites

typical of subduction-related calc-alkaline rocks. Highly porphyritic rhyolites (14.3□0.7 Ma), bearing an alkaline geochemical signature and being hydrothermally altered, crop out between Kambia and Ag. Pantes (Fig. 1). They intrude the autocthonous unit of N. Chios and show trace element concentrations typical of alkaline "within plate" granites (PE-PIPER et al., o.c). Thermal springs are located on the northernmost part of the Keramos valley (location: Agiasmata).

Geology and mineralogy of ore occurrences

a. The base metal sulfide mineralisations of Agrelia and Pithi

Small scale mining for base metals was carried out in Agrelia area.The ore zone is restricted at the lower contact of Silurian thick bedded massive limestone blocks with the clastic Permian sediments (Fig. 2). The contact of the ore zone with the carbonates is typical of replacement type. Massive calcite replacement by silica and hydrothermal breccias are recognised. The Silurian carbonates are locally ankeritised. Field observations indicate that a first stage of silica deposition resulted to the formation of a black massive silicification zone with thicknesses up to 6m, followed by brecciation and later deposition of sulfides (Fig. 3).

Sericite, quartz and pyrite are the alteration minerals. Locally, the mineralised zone contains open spaces, possibly resulting from calcite dissolution, that are lined with euhedral quartz crystals. Late deposited large rhombohedral crystals of calcite and dolomite form a network of veins and veinlets within the

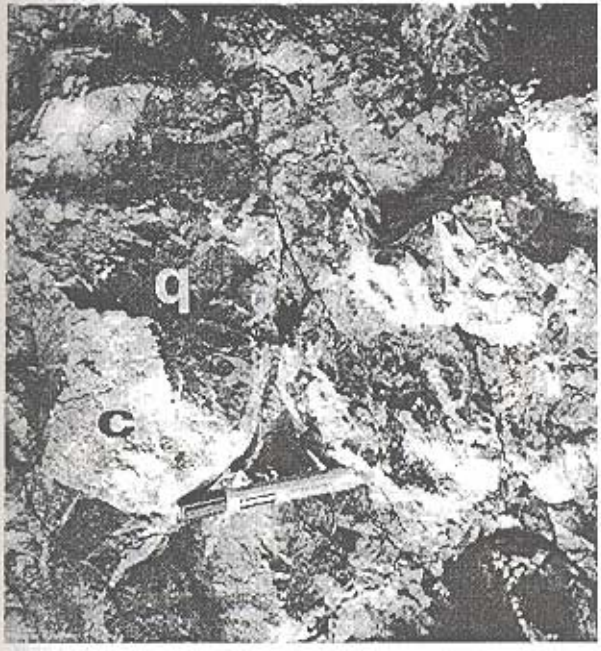

Fig. 3. The silicification zone of Agrelia: (q) grey silicification with sulfide disseminations and veining, (c) Recrystallised carbonates

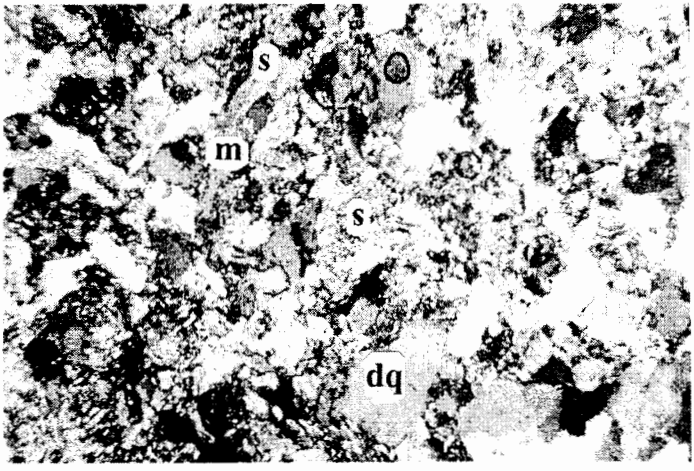

Fig. 4. Microphotograph of hydrothermally sericitised sandstone in the footwall of the Xygremmos mineralised fracture: detrital K-mica (m) is altered to sericite (s); (dq) detrital quartz grain.

mineralised zone and the hanging wall Silurian carbonates. Galena, sphalerite, chalcopyrite, pyrite and tetrahedrite were identified as fillings in veinlets or were interstitially developed between quartz grains. Bournonite and freibergite inclusions in galena, and chalcopyrite disease in sphalerite were observed. Microprobe analyses of tetrahedrite indicate a high Ag content (2.00 - 2.50 per structural formula).

b. The low grade Au mineralisations of Keramos

Numerous mineralised fracture zones are set on a N-S line from Keramos to Agiasmata areas. We focused are study on mineral occurrences around the Keramos village (Xygremmos and Koutsonikos). The mineralisation is evidently fracture controlled, cross-cutting the stratification of the country sedimentary rocks and occurs as low-angle veins. The clastic sediments are fine to medium grained, moderately sorted sandstones with detrital K-mica and quartz as the main rock forming minerals. Quartz grains are angular to subangular with low sphericity and mostly polycrystalline. Detrital K-feldspar and zircon grains are rare. Detrital K-mica is hydrothermally altered to sericite (Fig. 4). At the site Xygremmos, where the idle mine, a NW-SE trending fracture within the clastic sediments of the autocthon hosts stockworks of irregular multidirectional quartz veinlets in a pervasively silicified and locally hydrothermally brecciated sandstone. Individual veinlets do not attain widths greater than 5cm. The sulfide content of the veinlets is judged to be low (say, 2 vol%). The vein has irregular envelopes of quartz-sericite-pyrite alteration towards the fresh sandstone.

On top of the mineralised fracture a weather resistant massive silicified sandstone is developed, bearing typical moss quartz texture. Veinlets of late quartz crosscut the aggregates of quartz and altered K-mica. We have looked for but have not found evidence of a silica sinter.The fracture zone of Xygremmos is not capped by a typical sinter.

Stibnite and berthierite appear in radial aggregates of euhedral to subhedral crystals on the walls of uncemented breccias, in late formed quartz veinlets and rarely as massive aggregates within the silicified rock. HOLL (1966) described cinnabar as a rare mineral in the hanging- and the footwall of the mineralised zone. Sphalerite, galena, Ag-rich tetrahedrite, marcasite and rare chalcopyrite are associated with stibnite. Goethite and Sb-oxides occur as oxidation ninerals.

Geochemistry

Bulk samples of silicified mineralised rocks were commercially analysed by atomic absorption spectroscopy for the critical in hot spring type deposits elements. The data are presented

Table 1. Chemical composition of mineralised samples from Northern Chios island, and comparison with other hot spring type mineralisations

	Au	Ag	Sb	Zn	Pb	As	Hg
AGR 4	-	18	-	1.8	2.4	-	40
X 7	-	11	-	0.21	0.46	-	6
X 3	-	13	0.01	2.4	1.44	-	85
KER 4	0.01	-	-	0.1	0.1	-	0.1
KER 2	0.46	1	0.36	0.01	0.01	0.19	0.8
KER 3/1	0.04	64	-	5.9	7.2	-	177
KER 3/2	0.01	20	-	2.85	3.0	-	20
KER 3/4	0.88	-	0.01	0.01	0.01	0.09	0.2
KER 3/5	1.09	2	0.4	0.01	0.01	0.07	0.2
KER 3/12	0.59	2	0.5	0.01	0.01	0.23	0.1
KER 3/13	0.05	1	0.48	0.01	0.01	0.03	0.1
KER 5/9	0.7	6	5.44	0.01	0.01	0.1	0.4
Steamboat Springs, Nevada (1)	0.2-1.5	15	0.007-<0.02	n.a.	n.a	0.001-0.007	1000-<2000
Steamboat Springs, Nevada (sinter and stibnite) (2)	1.5	1	1.0	0.0002	n.a.	0.005	30
Veins, Wirralie Queensland (1)	2.8	7	700-<2000	n.a	n.a.	0.027	0.3
Lower sinter, Verbena, Queensland (1)	<0.008	<1	0.0004	n.a.	n.a	0.003	<0.005
Bolivia, Cosuno (3)	2.7	29	n.a.	n.a.	n.a.	0.07	56.1
Bolivia, Caracota (3)	0.04	380	n.a.	n.a.	n.a.	0.02	0.4

* Tl is below the detection limit in all samples analysed

** Au, Ag, Hg in gr/tn; Sb, Zn, Pb, As in wt %

*** Samples AGR 4 and X 7 from Agrelia, X 3 from Pithi, all other from Keramos

**** n.a. = not analysed

(1) CUNNEEN & SILLITOE (1989); (2) WHITE (1981); (3) DILL (1998)

in Table 1, which also summarizes analytical data from other hot spring type mineralisations throughout the world.

It is evident that the mineralisation of Agrelia and Pithi is a base metal one. The same is true for a part of the mineralised fracture zones of Keramos, as is indicated by elevated Zn+Pb values (samples KER 3/1, 3/2 from the ore stockpiled at Xygremmos). Au and Ag values for the Keramos mineralisation indicate low grades if compared with vein material from hot spring deposits being exploited throughout the world, which usually have grades be-

tween 1 and 2 gr/tn Au (PANTELEYEV, 1996). Detectable Au at 0.02 ppm was found in silicified zones beneath the sinter at Round Mountain (BERGER et al., 1981; in BERGER & EIMON (1983). Thalium values are below the detection limit of the analytical method, possibly because nearly all of the Tl in hot spring systems is concentrated in the sinter, with samples below it having about crustal average content. Samples with high Zn+Pb values are depleted in Sb and As and vice versa. Unfortunately sampling of the mineralised fracture zone at depth is n't possible; thus metal zoning can't be defined. According to the grade and tonnage model, grades of "simple Sb deposits" range between 8 to 63% Sb and grades of "Hot-spring Hg deposits" range between 0.18 to 0.64 %Hg. Thus the characterisation of the Keramos mineralisation as Sb or/and Hg one is not justified. The pervasively silicified sandstone on top of the mineralised fracture zone of Xygremmos (sample KER 4) is depleted in minor elements if compared to samples from the fracture zone, geochemically resembling sinter material.

Discussion

The Pb-Zn mineralisations of Kambia were interpreted as hydrothermal in origin related to the "quartz porphyries" of Agioi Pantes hill by MOUSOULOS (1949). The mineralisations of Agrelia and Keramos were interpreted by HOLL (1966) as stratabound associated with a paleozoic submarine volcanic activity. CHALKIAS & VAVELIDIS (1989) estimated the age of the mineralisation as being around 320 □20Ma, when interpreted the Pb isotopic data given by WAGNER et al. (1985) for one sample of galena from Agrelia.

Our field, mineralogical and geochemical data lead us to support an alternative model: that of a hot spring epithermal system. This proposal is based on the following arguments:

a. The mineralisation is evidently fracture controlled, cross-cutting the stratification of the country sedimentary rocks.
b. Intense silicification affected the country rocks in Keramos and replacement of Silurian carbonate blocks in Agrelia and Pithi.
c. The alteration and ore mineralogy and the geochemical features of the mineralisation are identical to those of hot spring type deposits.

It is proposed that the mineralisations of Northern Chios were formed by ascending hydrothermal fluids. The heat necessary to drive the hydrothermal fluids could be provided by sub-volcanic magmatic activity. Surface expression of this magmatism are the highly porphyritic and hydrothermally altered rhyolites of Agioi Pantes and Kambia areas. A fluid inclusion study will shed light on physicochemical conditions of formation. The Agrelia and Pithi mineralised zone was eroded down to the base metal part of the epithermal system, whereas the Keramos fracture zones retained the upper part, which is enriched in "epithermal" chemical elements, that selectively concentrate near the surface. It is possible that the thermal springs of Agiasmata represent remnants of the fossil geothermal system.

Hot spring deposits are localised in shallow parts of fossil geothermal systems. Hot springs deposit silica near the paleo groundwater table and as subaerial, ponded precipitates. Deaper fluids are channeled by permeable stratigraphic units, hydrothermal breccia bodies and faulted/fractured rocks. Gangue mineralogy includes silica minerals, calcite, dolomite and barite (PANTELEYEV, 1996). Breccias in the fracture zones are interpreted to have resulted from sudden eruptions of locally over-pressured vapor enriched fluids with the brecciation resulting from the rapid expansion of the gases upon breaching of the sealing and consequent boiling (BERGER & SILBERMAN, 1985). Hot spring deposits show a depth zoning of the "epithermal" chemical elements, Au, As, Sb, Hg, Tl and some Ag, that selectively concentrate near the surface. Much Ag and base metals precipitate at somewhat greater depths. The alteration at the top of the system consists characteristically of silicification underlain by a zone of mixed-layer illite-montmorillonite. This clay zone changes with depth into a sericite zone. At Steamboat Springs, K-feldspar occurs from a depth of 45 to 135 m. Comparing the alteration pattern of a complete hot spring type deposit with the alteration assem-

blages characterising the fracture zones of Northern Chios island, we may conclude that the latter represent the parts of the system which underlie the silica caps. This is supported also by the brecciation of the vein material, which is a typical textural feature of this part of the system. Thus one may conclude that sinters of the epithermal system of Chios were eroded.

Epithermal stibnite ores are found in fissures with breccia usually associated with faults and shear zones developed in various lithologies (BLISS & ORRIS, 1986). Silicification, sericitisation and argillic alteration are characteristic of this deposit type. Stibnite and minor base metal sulfides (frequently less than 1% of the deposit) are the main ore minerals. At least a third of the deposits contain gold or silver.

Similar epithermal hot spring type deposits are located in Western Turkey. The Hg, Sb and Au deposits of Halikoy, Emirli and Kure are localised in the Kucuk Menderes rift zone, which formed as a result of extensional tectonics prevailing in the area in Middle Miocene. The mineralisations are genetically related to calkalkaline volcanism (OZGUR, 1993; OZGUR et al., 1997). The *Halikoy* Hg deposit has estimated ore reserves of 300.000 tn and a Hg grade of 0.3%. The *Emirli* deposit is located in the southern part of the Kucuk Menderes rift zone, with ore reserves at 450.000 tn with 6% Sb content. Quartz veins in mica schists and gneisses and the hanging wall mica schists are the hosts of the antimony mineralisation, which appears as veinlets and disseminations. Stibnite, sphalerite, tetrahedrite, pyrite, marcasite, realgar, orpiment, arsenopyrite and cinnabar are the major ore minerals. In the *Ivrindi* (Balikesir) area many antimony occurrences are restricted to fault zones in silicified paleozoic clastic sediments. The ores consist of stibnite, base metal sulfides and rare cinnabar. Ore reserves at 300.000 tn with Sb concentrations at 8% are reported.

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