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FLUID INCLUSION EVIDENCE FOR THE ORIGIN OF THE BARITE SILVER-GOLD-BEARING Pb-Zn MINERALIZATION OF THE TRIADES AREA, MILOS ISLAND, GREECE

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ABSTRACT

Data from the fluid inclusions of the barite silver-gold-bearing mineralization of the Triades area, Milos island are presented. The highest silver and gold contents were detected in barite-rich black ore layers, reaching up to 855 ppm and 4.1 ppm respectively. The fluid inclusions in barite, which is closely intergrown with the framboidal pyrite, show homogenization temperatures between 280 and 340° C, with a maximum at 300° C. The homogenization temperatures of inclusions in sphalerite, which is formed after framboidal pyrite and is in association with galena, second generation pyrite, gold and silver minerals, range between 160 and 220° C. The estimated minimum pressures of the mineralized fluids range between 9 and 123 bars. There are evidences that dilution by sea water took place during the formation of the mineralization.

KEY WORDS: silver-gold mineralization; fluid inclusions; framboidal pyrite; sphalerite; barite; Triades; Milos volcano; Greece.

1. INTRODUCTION

The island of Milos is situated in the southwest of the Cyclades and belongs to the Southern Aegean active volcanic arc and consists mainly of volcanic rocks of Middle Pliocene (3.5 Ma) - Early to Middle Pleistocene (0.09 Ma) age. Small outcrops of the metamorphic basement and Neogene marine sediments (Figure 1) occur in the southern part of the island (Fytikas 1977, Fytikas et al. 1986, Tsokas 1985).

The volcanic sequence exceeds the 700 m in thickness and was deposited during three or four stages. The extensive volcanic activity started in the western part of Milos island 3.5 Ma ago, with submarine and subaerial eruptions, and continued until relatively recent times (0.09 Ma) (Fytikas 1977, Fytikas et al. 1986). The stratigraphy consists initially of Upper Pliocene felsic pyroclastic rocks as well as ignimbrites, followed by lava domes and flows of dacitic to andesitic composition. Subsequently, large areas of Milos volcano were covered by a green lahar deposits. In the final phase of magmatic activity during Pleistocene, perlitic pyroclastic rocks and rhyolitic to rhyodacitic lavas were deposited. Near the top of the series, a chaotic formation occurs which covers almost half of the island and is considered to be a product of phreatomagmatic eruptions (Fytikas 1977).

Widespread hydrothermal activity evident on Milos island is relatively recent and is related to the thermal anomalies due to the formation of shallow magma chambers. This activity has led to the formation of numerous mineral deposits, such as kaolin, bentonite and barite (Hauck 1988).

Obsidian was intensively mined during the Neolithic era and manganese, silver, barite and industrial minerals in modern times. A number of Pb-Zn-Ba-(Ag-Au), Ba-(Ag) and Mn-Ba-(Ag) ore deposits of

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Milos are situated in the northeastern, eastern, northwestern and western part of the island (Figure 1), hosted in volcanic rocks (Hauck 1984, 1988, Vavelidis 1995). Based on geological and chemical studies these ore deposits were considered to be characteristic examples of Kuroko type deposits formed in an active volcanic arc in Europe. All ore deposits on Milos with the exception of the manganese deposits of cape Vani, reveal a vertical zonation which is characteristic of the Japanese Kuroko deposits: siliceous ore, gypsum ore, black ore and barite ore.

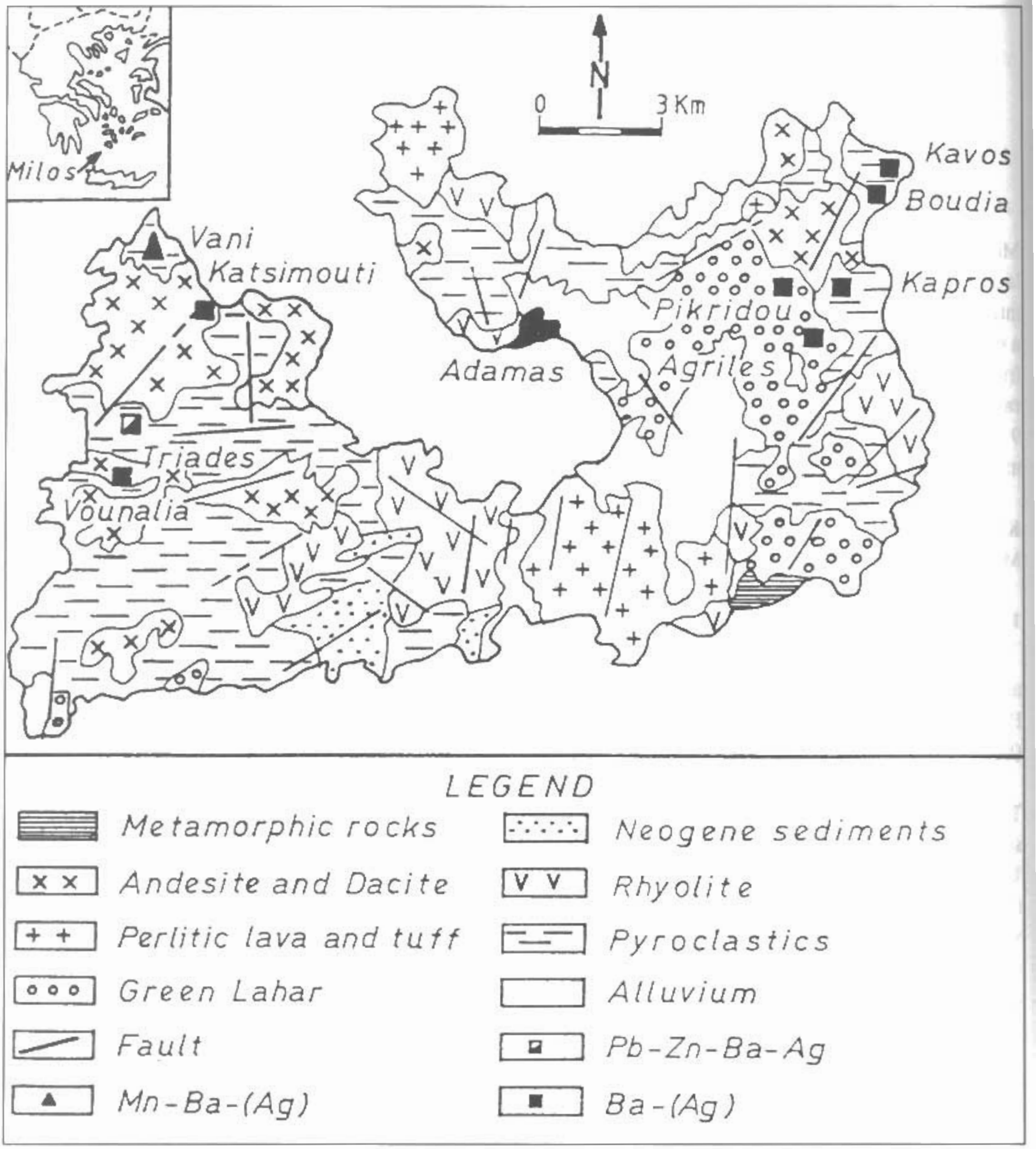

Fig. 1: Simplified geological map of Milos island with location of ore deposits (after Fytikas 1977, with some additions).

The origin and the formation conditions of the Milos Au-Ag bearing ores have been discussed by Hauck (1984, 1988), Vavelidis (1995), Christanis & Seymour (1995) and Kilias et al. (1997) among others. The present fluid inclusion study, obtained from the barite Pb-Zn mineralization of the Triades area

(Figure 1), provide data for the genesis of the deposit. The present work is carried out in the framework of a program financed from the Research Committee of the Aristotle University of Thessaloniki, dealing with the gold deposits in Greece.

2. 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 samples were analyzed by INAA at Max Planck Institute fur Kernphysik Heidelberg and at the analytical laboratory of Institute for Geology and Mineral Exploration, Xanthi, Greece.

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° C and 600° C. Calibration was performed using the following melting point standards: chloroform (-63.5° C), distilled H_2O (0° C), naphtalene (80.35° C), Merck 135 (135° C), sacharine (228° C) and Merck 247 (247° C). Raman microprobe analysis on the vapour phases of selected fluid inclusions were carried out at the University of Sofia.

3. THE SILVER-GOLD-BEARING BLACK ORE

The investigated silver-gold-bearing Pb-Zn mineralization occurs in the Triades area at the western part of the Milos island (Figure 1) and is similar to the Kuroko black ore, reported from Japan. These ores were exploited with a surface mining activity, of about 100 m in length, in modern times. Tools and extraction techniques, which were found in remnants of underground works, reveal an exploitation from the Prehistoric era to Classical times.

The mineralization is hosted in volcanic rocks of andesitic to dacitic composition, connected with barite and cryptocrystalline quartz. The mineralized zone in the studied area, is up to 100 m long and the thickness of the ore bodies ranges from 20 cm to 5 m. On the basis of the field work and the microscopic study, five types of ore bodies are distinguished: 1) fine grained compact black ore, 2) barite rich black ore layers, 3) barite rich black ore breccias, 4) massive barite bodies and 5) loosely packed black ore and barite. Five bulk sample analyses of these five ore types showed Pb contents from 6.25 to 43.50 wt%, Zn 5.80 to 12.80 wt%, Fe 2.85 to 14.50 wt%, Cu 0.16 to 0.50 wt%, As 325 to 1252 ppm, Sb 870 to 1580 ppm, Ag 670 to 855 ppm and Au 0.80 to 4.10 ppm (Table 1).

Table 1. Chemical analyses of the black ore mineralization of the Triades area. 1) fine grained compact black ore, 2) barite rich black ore, 3) massive barite, 4) barite-rich black ore breccia and 5) loosely packed black ore.

	Pb	Zn	Fe	Cu	As	Sb	Ag	Au
			wt%			ppm		
1	43.50	6.80	5.30	0.48	835	1100	765	3.80
2	14.25	5.80	3.80	0.50	1252	1580	855	4.10
3	7.80	12.80	2.85	0.22	858	1030	720	3.20
4	6.25	12.46	12.30	0.16	325	870	670	0.80
5	20.80	10.25	14.50	0.35	1130	1425	730	2.80

The ore mineralogy consists mainly of barite, sphalerite, galena, pyrite, smithsonite, cerussite, anglesite, tetrahedrite ur. Trace amounts of marcasite, argentite, proustite, polybasite, boulangerite, native silver and gold are also present.

Sphalerite is the main sulphide mineral in the investigated area, associated with barite, galena, pyrite and tetrahedrite. It occurs as massive bands or subhedral grains. Sphalerite often forms colloform concentric or atoll-shaped textures.

Galena is the second main sulphide associated with sphalerite, barite and fahlore. It often shows banded or colloform textures. Well-formed euhedral crystals, measuring up to 2 cm in length, are common. Galena is an economically important mineral concerning its role as a carrier of silver in the investigated mineralization.

Pyrite is one of the main mineral and is found in two distinct generations. The first generation occurs as framboids, spherulites, euhedral crystals or as colloform banded pyrite. The second generation forms anhedral grains or hypidiomorphic crystals surrounding framboids and spherulites. The framboids are spherical in shape and more rarely atoll-shaped. They are found either isolated or in groups, swarms and colonies within barite matrix. The size of the framboids varies from 2 μm to 110 μm, while framboidal groups have a diameter up to 2.3 mm.

Barite is the main gangue mineral of the silver-gold-bearing mineralization. It occurs as massive, thin layered or loosely packed crystals, often closely intergrown with cryptocrystalline quartz and amounts of sulphide minerals and sulphosalts. Well-formed barite crystals, over 5 cm in length are common (Figure 2).

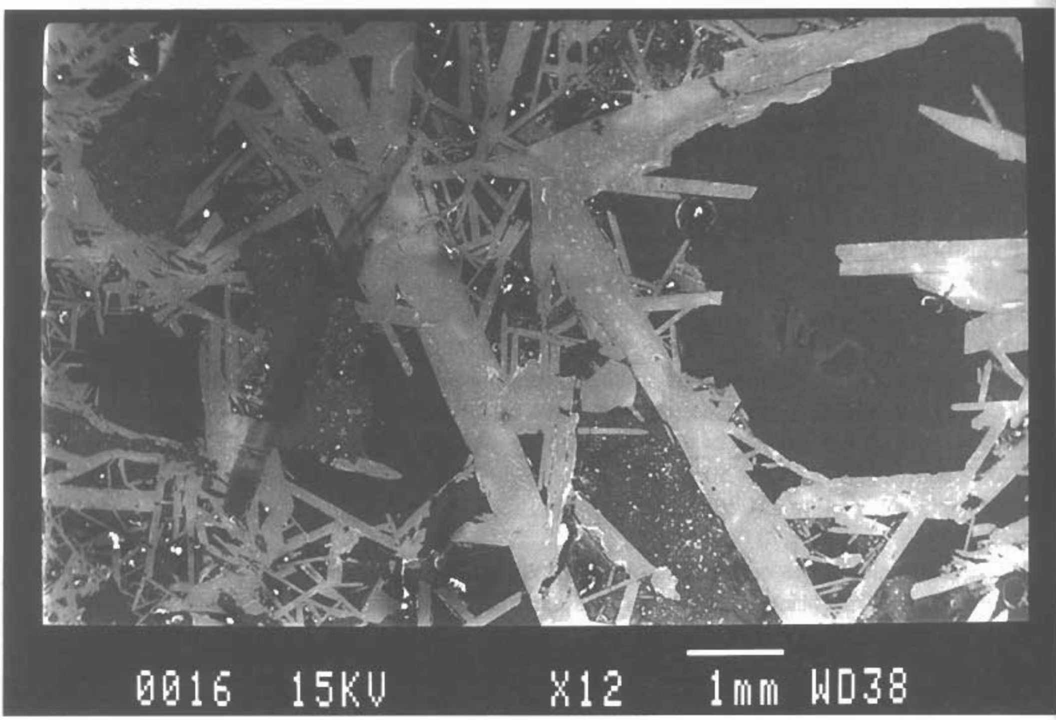

Fig. 2: Electron microphotograph of typical barite crystals.

4. FLUID INCLUSION STUDY

Fluid inclusions were studied in order to estimate the temperature, pressure and composition of the fluids related to the formation of the investigated silver-gold-bearing mineralization. The microthermometric measurements were carried out on 6 double polished thin sections of the mineralized barite bodies from the barite-rich black ore layers. The investigated fluid inclusions are hosted mainly in barite and in some cases are found in sphalerite. The samples examined for fluid inclusions contain clear, transparent, undeformed barite grains intergrown with the sulphides and sulphosalts and appear to be in equilibrium with them. Sphalerite in some cases exhibits semi-transparent areas and fluid inclusions are quite visible. The shapes of the inclusions vary from irregular to subrounded or elongated, while negative-crystal shapes are rarely found. Most of the fluid inclusions occur as individuals or are arranged in clusters or planes. With respect to our microscopic study the subrounded, elongated and negative-crystal shaped fluid inclusions are arranged in clusters and suggested to be primary (Roedder 1984). The irregular inclusions are attributed to leaking and necking-down phenomena and those found in planes, along healed fractures, are suggested to be of secondary origin. These inclusions were avoided during microthermometric determinations. Thus, heating measurements were carried out on 80 primary fluid inclusions, which were found suitable for study. Sixty-seven of these inclusions were found in barite closely intergrown with framboidal pyrite and thirteen in sphalerite in association with galena, gold and silver minerals. Accurate estimates of salinity of fluid inclusions in barite were difficult to determine and were recorded only in ten inclusions.

The fluid inclusions in barite occur as individuals or as clusters and range in size from 5 to 45 μm. Based on their phase assemblages at room temperatures, one main type of inclusions was distinguished, containing two phases: a liquid aqueous solution and a vapour bubble, which occupies 5 to 35 % of the total volume (Figure 3, 4). Only a few vapour-rich fluid inclusions (>50 % by volume) were observed,

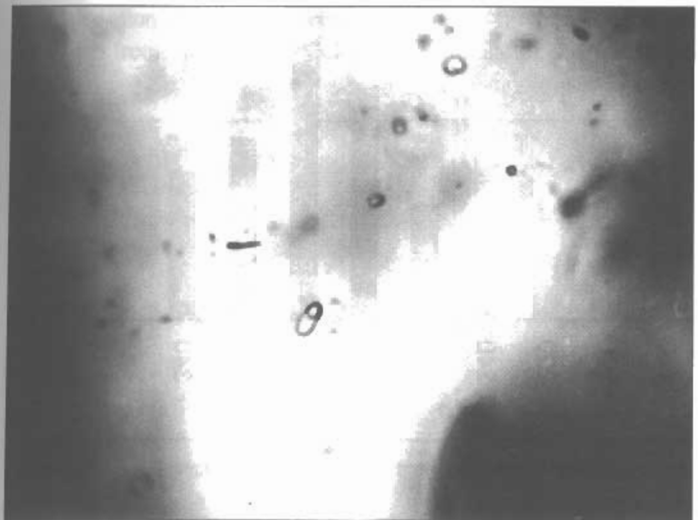

Fig. 3: Liquid-rich fluid inclusion in barite intergrown with sulphides (dark), picture length 75 μm.

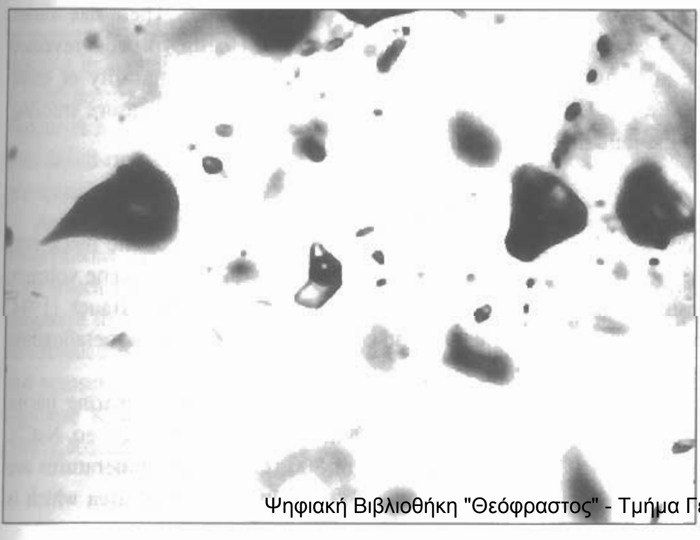

Fig. 4: Liquid-rich fluid inclusion in barite and decripitated fluid inclusions (dark spots) due to necking-down, picture length 50 μm.

which decrepitated during the heating process. This possibly suggests that they originated from leaking and necking-down and were not taken into further consideration. According to Spooner (1981), high vapour/liquid ratio inclusions observed in barite from Kuroko-type deposits are interpreted to be the result of necking-down.

The initial melting temperatures of the liquid-rich fluid inclusions in barite range between -31.4 and -33.8° C, which indicate that the dissolved salt in the inclusions is dominated by NaCl with minor contribution of $CaCl_2$ and/or $MgCl_2$ (Davis et al. 1990). The final ice melting temperatures range from -1.3 to -3.5° C, corresponding to salinities from 2.14 to 5.62 wt% eq. NaCl in the system H_2O-NaCl (Potter et al. 1978). Raman microprobe analyses of the vapour phase revealed the presence of small amounts of SO_4, while other components, such as CO_2 or CH_4, were not detected. The fluid inclusions in barite homogenize by vapour disappearance at temperatures varying from 135 to 380° C. This wide variation in homogenization temperatures of inclusions in barite is interpreted to be the result of continued necking-down of inclusions at low temperatures after nucleation of the vapour phase (Bodnar et al. 1985). However the distribution histogram of the T_h values display a frequency peak between 280 and 340° C, with a maximum at 300° C (Figure 5).

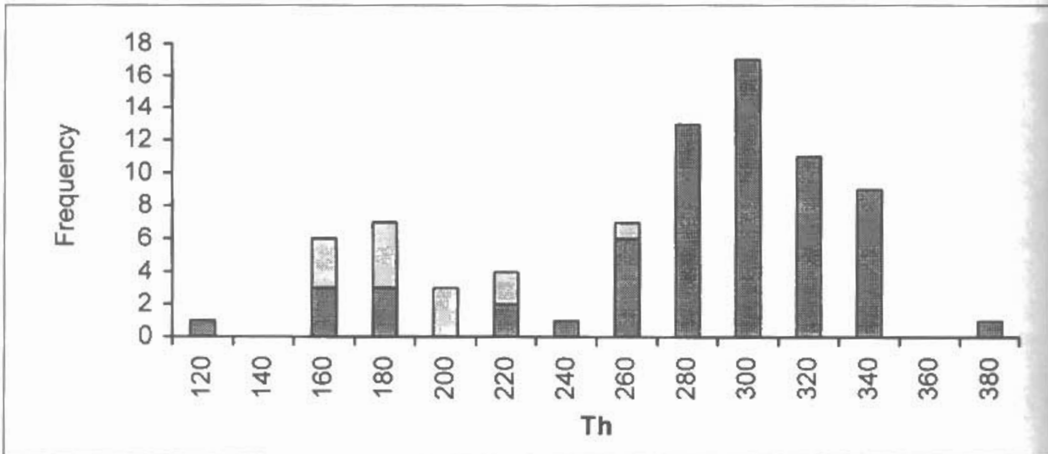

Fig. 5: Homogenization temperature (T_h) - Frequency diagram for fluid incluions in barite (dark grey) and sphalerite (light grey).

Fluid inclusions in sphalerite from the studied mineralization are relatively rare. Their size varies between 3 and 8 mm and the bubble occupies 5 to 25 % of the total inclusion. Heating process revealed homogenization to the liquid phase at temperatures from 160 to 260° C, while the majority of these inclusions homogenized between 160 and 220° C (Figure 5). It was not possible to measure freezing temperatures due to the small size of the fluid inclusions and the dark colour of sphalerite.

5. DISCUSSION

The silver-gold bearing barite deposit in the Triades area shows typical features of the black ore, similar to those described from the Japanese Kuroko type deposits. It occurs within Pleistocene volcanic rocks of andesitic to dacitic composition. Based on the isotopic and geochemical studies, Hauck (1984, 1988) suggests a continuous interaction between andesitic tuffs and circulating sea water as a metallogenic model for the Kuroko-type deposits of Milos.

The microthermometric study in the investigated area revealed that the silver-gold bearing barite deposit is dominated by liquid-rich aqueous fluid inclusions with low salinities (2.14 to 5.62 wt% eq. NaCl). These inclusions homogenize mainly at 280 to 340° C (a maximum at 300° C). These temperatures are similar to those suggested by Vavelidis (1995) in the barite mineralization in Katsimouti area which is located at about 5 km northeast of the studied area. The homogenization temperatures of the investigated mineralization are slightly higher than the temperatures (220-260° C) derived from sulphur isotope geochemistry conducted by Hauck (1984, 1988) on sulphur-sulphate pairs from Milos, Kimolos, Polyaigos and Antimilos islands. Kalogeropoulos and Mitropoulos (1983) report lower temperatures (140-170° C), based on oxygen isotope studies of three barite samples from Voudia area, which is located in the northeastern part of Milos island. The majority of the temperatures of sphalerite in the investigated area, which is associated with galena, second generation pyrite, sulphosalts, native silver and gold and was formed after the framboids, were determined between 160 and 260A C with the majority to lie between 160 and 220° C.

The minimum pressures of the mineralized fluids were estimated, by applying the Brown and Lamb (1989) equation of state to the microthermometric data of the H_2O-NaCl system. They range from 9 to 123 bars, indicating that the mineralization was formed at shallow depths. Figure 6 shows a plot of the salinity data versus the homogenization temperatures for the liquid-rich aqueous fluid inclusions. From this diagram, a distinct positive correlation is evident, indicating that the salinity decreases with the temperature decrease. This implies that the simultaneous decrease of the temperature and salinity of the metal-bearing brines due to the mixing with sea water is considered to be the main depositional process. This explanation is consistent with Hauck's (1988) isotopic results. In such case the metals have been leached-out from the volcanic rocks by the circulating sea water, which was heated up by the volcanic activity.

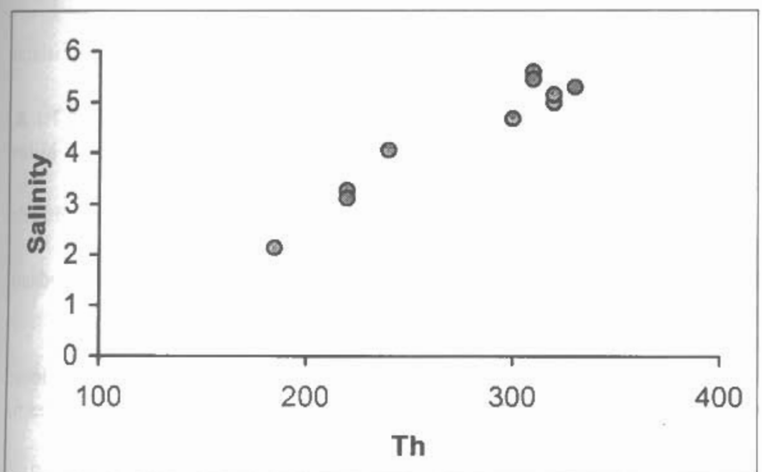

Fig. 6: Homogenization temperatures (T_h) (° C) versus salinity (wt% eq. NaCl) diagram of the fluid inclusions in barite.

In their recent studies on gold-bearing ore deposits in Milos island, Christanis & Seymour (1995) and Kilias et al. (1997) suggested that boiling was the major process for ore deposition. As indicated above, in the Triades ore deposit, there were a few vapour-rich fluid inclusions in the studied barite, which decrepitated before anticipated homoganization, during heating process. These vapour-rich inclusions could support the presence of boiling, only if we suggest that they are cogenetic with liquid-rich inclusions. In this case boiling should not be excluded as a possible mechanism for ore precipitation.

As a conclusion the present microthermometric data combined with our geological and mineralogical observations, support a possible hydrothermal derivation with a magmatic fluid component of the fluids from which the silver-gold bearing mineralization originated. Mixing of heated fluids with sea water is suggested to be the most acceptable process for the formation of mineralization, while boiling should not be excluded. The fluid inclusion phases and homogenization temperatures as well as the observed salinites and pressures of barite and sphalerite from the studied mineralization show similarities with those from Japanese Kuroko-type deposits, described by Lambert & Sato (1974), Urabe & Sato (1978), Spooner (1981), Roedder (1984).

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