FLUID EVOLUTION IN THE BOLCANA ORE DEPOSIT, METALIFERI MOUNTAINS (ROMANIA)

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Abstract: Bolcana is one of the porphyry Cu-Au ore deposits associated with the Neogene metallogenesis from Metaliferi Mountains. This deposit is characterized by the spatial association between the porphyry Cu-Au type mineralization, superimposed on a microdioritic subvolcanic structure and the base metal and gold-silver low sulfidation hydrothermal veins that cross cuts the subvolcano and the surrounded andesitic rocks. Fluid inclusions are found both in the quartz stockwork veins and in the hydrothermal veins. This paper comprises the results of the petrographic and microthermometric study of the fluid inclusions associated with both type mineralizations from Bolcana ore deposit. Fluid inclusions from „porphyry" veins are grouped in six main types, respectively (1) – high salinity type enriched in daughter minerals like halite, sylvite, metallic minerals etc., (2) –vapor-rich type, (3) – two-phase liquid+vapor type, (4) – liquid-rich type and (5) - silicate melt inclusions and (6)- sulfide melt inclusions. These inclusions homogenized at T ≥ 370°C, most of them at T ≥ 580°C. Boiling traces are evidenced. Fluid inclusions associated with hydrothermal veins are predominantly liquid-rich type, trapped at temperatures of around 300° C from low salinity solutions. No evidence of boiling is observed in these veins. Thus, the spatial association between porphyry and hydrothermal veins suggests that both belong to the same magmatic-hydrothermal system and a poliascendent evolution of metallogenesis in the Bolcana structure. Results of fluid inclusions study reveal that fluids responsible for the porphyry Cu-Au mineralization have exclusively magmatic origin, high salinity and were enriched in Cu, Fe, Au metallic compounds. Boiling was implied in metallogenesis. The vein mineralization represents tardive metallogenetic events and was induced by the downing of temperature and salinity, caused by the mix of magmatic and meteoric waters.

Keywords: Bolcana, subvolcanic system, porphyry Cu-Au, base metal and gold-silver veins, fluid inclusions, poliascendent evolution.

1. INTRODUCTION

Fluid inclusions represent small quantities of water, gas or a mix of these, which are found trapped in minerals. In metallogeny, the importance of these inclusions derives from the fact that they conserve the physical and chemical properties of the ore-forming solutions.

Bolcana ore deposit is located in the southern part of the Brad-Săcărâmb Metallogenic District (Metaliferi Mts.), at approximately 25 km NE of Deva town. It was discovered in 1972 and was intensely explored by underground mining works, on five levels and also by drilling that covered more than 1200 m in depth. The exploration programs made possible to model an ellipsoidal subvolcanic body, with maximum 750 × 450 m in

extent at the lowermost level (Grimm horizon, + 330 m) and which decreases towards the uppermost level (150 x 100 m). The ore grades are estimated at 0.2% Cu, 0.3 g/t Au and 9,6 g/t Ag in average (Cioacă, 2008). Four breccia columns ("breccia pipes") with richer mineralization were outlined within the Bolcana subvolcano.

The vertical distribution of the gold and copper evidenced two higher-grade zones - one in the uppermost 400 m and another one between 700-1000 m in depth (Cioacă, 2008). The Bolcana ore deposit was mined underground and in a small open pit, but in 2006 the mine was closed.

Brad–Săcărâmb District, like the entire Metaliferi Mts. Subprovince, presents a number of peculiarities, such as: (1) superposition of several magmatic events: Jurassic (ophiolitic), Laramic

(banatitic) and Neogene; (2) presence of Neogene subvolcanic bodies hosting porphyry Cu (Au, Mo) mineralization; (3) presence of Au-Ag tellurides mineralization (Udubaşa et al., 2001); (4) presence of "ring-zoning" disposition of the base metal, respectively Au-Ag epithermal mineralizations around the porphyry copper bodies (Popescu & Neacşu, 2007).

The Bolcana - Troiţa - Măgura volcanic complex is an excellent model of the "ring-zoning" structure type. Another similar zonality is recognized at Bolcana subvolcano scale. Therefore, Bolcana offers a good opportunity to study the evolution of metallogenetic events during the transition from magmatic to hydrothermal processes, to recognize the relationship between porphyry copper and hydrothermal vein mineralization in subvolcanic bodies.

Studies on the fluid inclusions of the porphyry copper deposits from Apuseni Mts. have been published by Pintea (1995, 2001), Nedelcu et al., (2001, 2003), Ivăşcanu et al., (2001), Pettke et al., (2001), André-Mayer et al., (2001) and others. Detailed fluid inclusion researches in these deposits show the earliest fluid phases are characterized by a double immiscibility: firstly between magmatic (glass-bearing) and brine inclusions (silicate magma/saline melts immiscibility and secondly between highly concentrated brine and vapor-rich inclusions (liquid/vapor immiscibility) (Pintea, 2001). The homogenization temperature in silicate glass and associated salt-rich inclusions ranged between 1100 and 920°C, although the brine inclusion microthermometry showed even more large intervals of homogenization temperature between 1100 and 450°C. The salinity values estimated by halite point dissolution temperature ranged between 60-90% (NaCl+KCl).

The sulfides of main porphyry copper and epithermal ore deposits of this region contain a lot of mineral microinclusions as chlorides, sulfides, oxides, sulfates, carbonates, phyllosilicates, silicates and silicates glass (Nedelcu et al., 2001, 2003).

Analytical data on melt and fluid inclusions, using LA-ICP-MS microanalysis was published by Ivăşcanu et al. (2001) for the Bolcana porphyry copper deposit and Pettke et al. (2001) for the volatile and fluid inclusions from Roşia Poieni porphyry copper deposit. In both cases, the inclusions derive from boiling assemblages. All the measurements show a relatively enrichment of Cu and sometime of Au (at Bolcana) and As and Sb (at Roşia Poieni) in volatile phase exolved from magma in early porphyry stages. At Bolcana, only rim inclusions (melt inclusions, salt melt inclusions and hypersaline fluid inclusions) recorded high content in Cu and sometimes Au. In inclusions from core of host quartz,

it is recorded lower or under detection limit content values for Cu and Au, (Ivăşcanu et al., 2001).

This study aims to add new data about the properties of the solutions responsible for the porphyry copper mineralization of Metaliferi Mts. and the evolution of these solutions, using Bolcana ore deposit as a case study.

2. GEOLOGICAL SETTING

Bolcana ore deposit is spatially associated with Bolcana – Troiţa – Măgura volcanic complex, where an important hydrothermal metallogenetic activity was developed and generated numerous mineralized structures in a small area (about 8 km^2). The geology of this area is represented by the Mesozoic ophiolitic basement (basaltic andesites and basalts) overlain by Paleocene sedimentary formation (Almaşul Mare Gravel) with gravel, sands, clays and silty clays. Băiţa rhyolites are developed underneath the Almaşul Mare Formation. The age of these rhyolites was considered as Upper Helvetian (Cioflica et al., 1966), but radiometric dating shows a Lower Cretaceous age (Roşu et al., 1997).

Neogene volcanic products are the most developed in this area, occurring as intrusions, lava flow and piroclastic adesites. Andesitic stocks outcrop on some peaks, such as Făerag, Măgura, Teascu, Lelii, Mialu, Bolcana, Piţiguş, Sântana, Dumbrava, Sasu, Măceş and Dumbrăviţa. Most of them are surrounded by explosive breccia mantles composed of andesites, ophiolites and clasts of sedimentary rocks. Bolcana structure has a central position in this magmatic complex (Fig. 1).

The Hondol – Făerag andesites are the most extended in the Bolcana – Troiţa – Măgura area, having porphyric structure, with green hornblende and plagioclase phenocrysts. In the unaltered samples these andesites are grey, but commonly they are extensively propylitized and the color is changed in green.

In according with K-Ar radiometric dating, the Neogene volcanic activity from Metaliferi Mts. took place between Kossovian and Pannonian (14.7-1.6 Ma). The age of the Făerag-Hondol andesites vary in the range of 14.2 ± 0.9 to 10.8±0.6 Ma (Roşu et al., 1997, 2001). The age of the mineralization from Bolcana was investigated by Cardon et al., (2008) using Re-Os isotopic system applied to pyrite, obtaining an age of 11.8 +0.51/–2.8 Ma on pyrite and chalcopyrite-pyrite assemblage.

Regarding the genesis and evolution of the Neogene magmatic activity from Metaliferi Mts., on the basis of paleomagnetic data in correlation with geochemical and age data, two magmatic events with distinct evolution were identified (Roşu et al.,

2001, 2004). During the first event (14.5-11 Ma) magma had a normal calc-alkaline character, with significant crustal contamination, controlled by the tensional regime associated with the clockwise rotation of Tisia block (including the basement of Apuseni Mts.). During the second event (12.6-7.4 Ma), the rotation stopped. The volcanic products cover a larger area and the magma has adakite-like calc-alkaline features. Most of the mineralized structures appear after the clockwise rotation stopped, when the structural context permitted to small subvolcanic stocks to ascend along a deep-seated transtensional fault system. In the upper part of these structures, porphyry systems were generated, enveloped by epithermal veins (Bolcana-Troiţa, Valea Morii etc.) (Roşu et al., 2001, 2004).

3. PETROGRAPHY

The petrography of Bolcana subvolcano is an amphibole-bearing andesite/microdioritic rocks named Bolcana andesites/microdiorites. It has a porphyric-holocrystaline or microcrystalline-porphyric structure, where the phenocrysts are represented by plagioclase (ca. 65%) and hornblende enclosed in a microcrystalline quartz-feldspar groundmass. The rock has grey color varying to dark grey (when it has more secondary biotite in composition), to green (when it is intensely chloritized) and whitish when it is sericitized and/or argillized. The Bolcana andesites are calc-alkaline character but some geochemical characteristics of this are common with adakites ($SiO_2 \geq 56\%$, $Al_2O_3 \geq 15\%$, $MgO < 3\%$, Sr > 300 ppm, Y < 15 ppm). On the Sr/Y vs. Y diagram, Bolcana is placed in proximity of the adakitic field (Cioacă & Popescu, 2006).

4. HYDROTHERMAL ALTERATION AND MINERALIZATION

Four alteration types were distinguished: potassic, phyllic (less developed), argillic and propylitic. The alteration assemblages are typical for porphyry ore deposit, but overlappings of the alteration zones are present, showing a complex evolution of the hydrothermal processes at Bolcana. Around the epithermal veins, phyllic and argillic alterations were recognized (Milu & Pintea, 2001; Milu et al., 2003). The sulfidation (anhydrite) and carbonation (calcite) is large developed at Bolcana (Milu et al., 2003).

Bolcana structure is characterized by the association of the following two types of mineralization: (1) *the porphyry copper mineralization,* with two zones: (1a) The inner part of

the mineralization is characterized by the assemblage chalcopyrite – magnetite (hematite) - pyrite ± bornite ± molybdenite ± native gold (mainly as inclusions in chalcopyrite), which occurs as microveins forming stockwork and impregnations, superimposed on the potassic alteration zone. Abundance of the magnetite as monomineral centimetric veins and impregnations it is another peculiarity of this porphyry deposit. (1b) pyrite ± chalcopyrite (covellite) ± magnetite (hematite), dominant towards the upper and marginal parts associated with the intensely argillized zones of the mineralized body; the porphyry-type economic mineralization is developed only within the intrusion of Bolcana.

(2) *The hydrothermal mineralization* (low sulfidation type) contains sphalerite, galena, pyrite, chalcopyrite, tetrahedrite, bournonite, marcasite, pyrrothite, native gold etc. as metallic mineral assemblage. It forms thin veins (< 0,5 m) developed on short distance and with N-S direction. These veins could crosscut the subvolcano body or only the andesitic rocks.

3D GEOCAD modelling shows a homogenous 3D zonality of the Au and Pb-Zn deposits centered on the porphyry; Pb-Zn deposits are closer to the porphyry and located deeper compared to the Au veins, which are more distal from the porphyry and closer to the surface (Cardon et al., 2005).

The local zonality of mineralization is superimposed on a regional zonality. Spatial superposition of the two types of mineralization and also the circular disposition of the volcanic bodies and hydrothermal vein systems around Bolcana subvolcano is explained by a multistadial evolution of a calderan-type system who developed the so called „ring-zoning" of copper, polymetallic and gold-silver mineralizations (Cioacă & Popescu, 2006).

5. ANALYTICAL METHODS

Microthermometry is a non-destructive method that makes possible the determination of several parameters of fluid inclusions (temperature, density and composition). The heating and freezing experiments were done at the Mineralogy Department of the Geology and Geophysics Faculty (Bucharest University) using the Linkham TMSG600 system. The distribution and general features of the fluid inclusions were examined under the Nikon E400 microscope in double-polished thin sections. Linkham TMS G600 uses a measurement range between -196°C to +600°C and T gradient between 0.1°C – 30°C/min. In practice, all measurements temperatures were restricted at most 580°C.
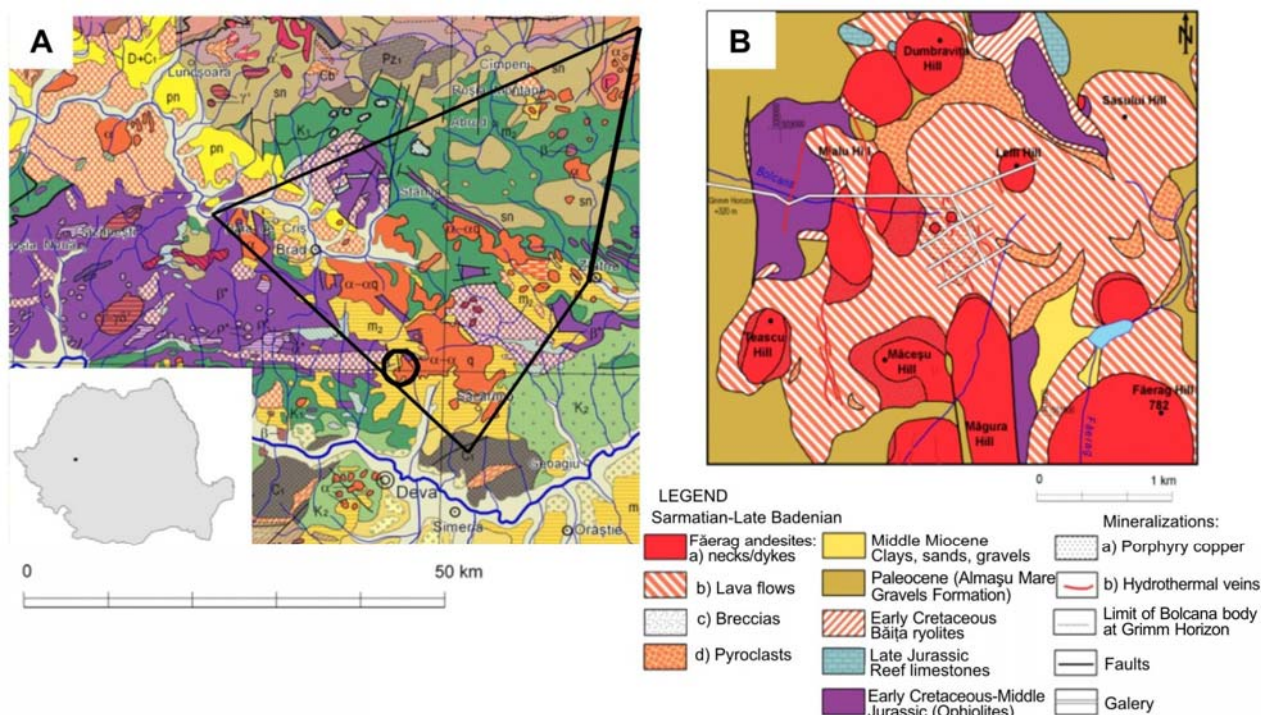
Figure 1. A) Geological map of Metaliferi Mts. with Gold Quadrangle and Troiţa-Măgura area marked on the map (using Geological Map of Romania, Săndulescu et al., 1978; drawn by Gheuca I.). B. Detalied map of Troiţa-Măgura area (after Milu & Pintea, 2001; Cioflica et al., 1966).

Figure 2. Fluid inclusions hosted by one quartz crystal in Bolcana porphyry ore deposits (at 25° C). a – general aspects of boiling, b – different aspect of V type inclusions; c – V type inclusion with chalcopyrite (Ccp) as mineral daughter and B2 type inclusion with halite (H), gas (V) and unidentified small transparent crystal; d – B1 type inclusion with halite (H), anhydrite (Anh), mica? (M), gas (V) and chalcopyrite? (Ccp).
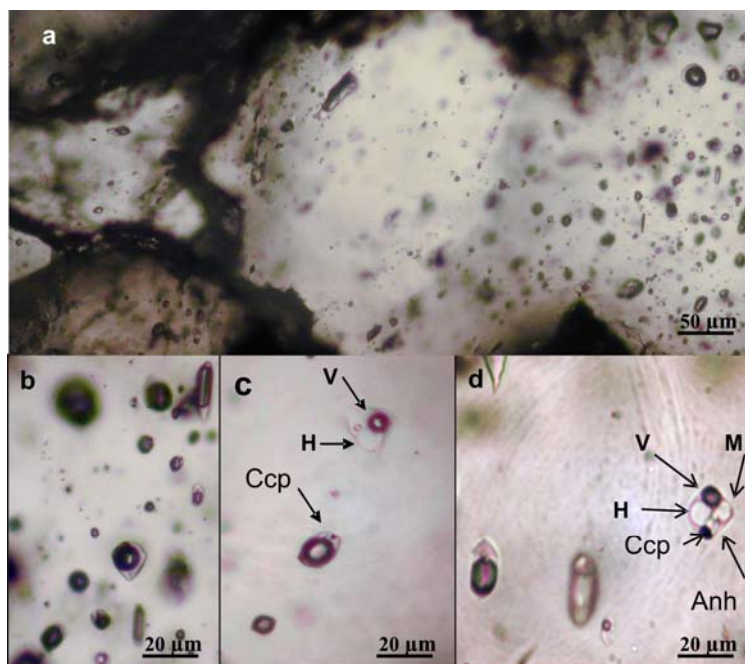
6. RESULTS

6.1. Fluid inclusions from porphyry copper mineralization.

Samples were selected from different levels of Bolcana ore deposit. Six main types of fluid inclusions were recognized based on component phases and their ratios: (1) high salinity type, (2) vapor-rich type, (3) two-phase liquid+vapor type, (4) liquid-rich type and (5) silicate melt inclusions and (6) sulfide melt inclusions. The values of the homogenization temperature of fluid inclusions are presented in table 1 and their distribution histogram are given in figure 3.

Table 1. Microthermometrical data on the fluid inclusions associated with the porphyry copper mineralization (fluid inclusions with total or partial homogenization temperature below 580°C only)

Probe no.	Samples description	Host crystal	FI type	Genetic type	L/G/S	n	Th_{L-V}	Tm NaCl	Homogenization mode	Tms
F1/ 1066	Quartz vein in porphyry rock having a weak impregnation with magnetit	Q1	B2	1	40/20/40	3	454	541	L	
		Q1	B2	1	40/20/40	6	377	393	L	466
		Q1	B1	1	10/40/50	3	495	>580	L	
		Q1	V	1	30/60	5	>580			
		Q1	V	1	80/20	8	>580			
		Q2	B2	1	30/10/60	3	509	>580		
		Q2	B2	1	30/10/60	2	>580	414		435
		Q3	I	2	90/10	5	424		L	
		Q4	B2	1	40/10/50	4	455	524	L	
		Q4	B2	2	40/10/50	4	505	>580	L	
		Q4	B2	1	40/10/50	5	>580	450		
200 - 640S	Quartz vein with chalcopyrite, pyrite, magnetite and bornite	Q1	I	2	90/10	2	411		L	
		Q1	I	1	90/10	4	420		L	
		Q2	I	1	90/10	2	408		L	
		Q3	I	2	90/10	3	493		L	
		Q3	I	?	90/10	1	560		L	
		Q4	I	1	90/10	8	393			
		Q4	I	1	90/10	2	439		L	
		Q2	I	1	90/10	2	467		L	
Bo-F1/ 884	Quartz vein in porphyry rock with magnetite, pyrite and chalcopyrite	Q1	B2	1	30/20/50	1	>580	514	L	580
		Q2	B3	1	80/20	1	527		L	
Bo-F1/ 302,5	Mineralized quartz vein with chalcopyrite, pyrite and magnetite.	Q1	I	2	70/30	4	418		L	

1 = primary inclusions; 2 = secondary inclusions; ~2 - pseudosecondary inclusions; L/G/S - phases ratio (liquid, gas, salt); n – number of measured inclusions; Th_{V-L} – the homogenization temperature of gas

(1) High salinity fluid inclusions (B type = brine) are characterized by the presence of halite crystals plus a liquid (10-60 vol. %) and vapor (20-50 vol. %.). In some cases liquid or vapor can be missing. Beside halite, other daughter minerals were found, such as sylvite, anhydrite, chalcopyrite, hematite and others unidentified crystals. One inclusion contained one or more solid phases. Chalcopyrite was recognized by triangular shape and hematite by its red crystals. Anhydrite and magnetite as daughter minerals seem to be a special feature of these types of inclusions in the growth zones of coarse grain quartz from the veinlet network at Bolcana (Milu & Pintea, 2001). Using the ratio between the phases, the B-type inclusions were subdivided into four subtypes:

B1 subtype groups the inclusions where the solid phases and the vapor occupied most of the fluid inclusion volume. The liquid is minor or absent. These inclusions have always metallic minerals as daughter crystals (Fig. 2d). The homogenization temperatures of these inclusions are high. Either halite or vapor does not change their phase below 580°C.

B2 subtype inclusions contain the same components with B1 subtype, but the liquid phase proportions are more than 20 vol. % (Fig. 2c). This subtype is the most frequent. Just a few inclusions of this type had homogenization temperatures in the range 400° - 580° C; for the other inclusions, T > 580°C. The final homogenization is represented either as salt dissolution (Tm_{NaCl}) or gas bubble dissolution in the liquid phase (Th_{V-L}); the first case is more frequent.

B3 subtype rarely appears. The inclusions have no gas in their composition, but only liquid

and daughter crystals. It is possible that B3 subtype forms by loss of gas component from the B2 subtype, when the walls of inclusions were microfractured.

B4 subtype is also rare and contains just halite and gas phases. The homogenization temperature is in excess of 580°C.

(2) V type is a vapor – rich inclusion. The gas bubble occupies 60-95% of the inclusion volume. These inclusions have a great diversity of shapes and dimensions. The vapor phase is represented by water and/or CO_2. The liquid could be water and exceptionally CO_2 liquid. Opaque minerals and different others transparent crystal daughters can be present as well (Fig. 2a-d). The homogenization of inclusions takes place around 580°C when the gas bubbles (water vapor) disappears in the liquid phase; the CO_2-rich inclusions homogenization does not occur below 580°C. V type inclusions are a constant presence in the entire porphyry type ore deposits.

(3) Two phase liquid - vapor inclusions (I type) are contain two components under the standard conditions - liquid (60-90 vol. %) and vapor, but no halite crystals.

These inclusions are small, have irregular shapes and rarely occur at the periphery of hosting crystals, probably having secondary origin or being trapped during late events. Homogenization temperatures cover a wide range of values (between 390° and 560°C).

(4) Liquid-rich type (L type) contains just water as liquid phase and appears as small inclusions in association with other inclusion types, but is relatively scarce.

They are more frequent in tardive quartz veins from the argillized top of the porphyry zone. Because they are very small, they could not be measured microthermometrically.

(5) Silicate melt inclusions (IM) are associated with the B and V type inclusions. IM inclusions are small, with negative-crystal, rounded or irregular shapes. Sometimes, an incipient crystallization can be observed.

(6) Sulfide melt inclusions (SM) are presented frequently as irregular inclusions with different sizes, trapped as clusters in the some quartz grains, mostly in the peripheral zones of these. They appear in association with the brine, vapor-rich and silicate melt inclusions.

6.2. Fluid inclusions from hydrothermal veins

Fluid inclusions were studied in samples from both external and internal veins. The vein mineralization consists of sphalerite, galena, tetrahedrite, pyrite and chalcopyrite, mostly in quartz gangue.

Table 2. Microthermometrical data on fluid inclusions associated with the hydrothermal veins

Probe no.	Mineralization	Host crystal	Inclusion type	Genetic type	L/G	n	Th_{L-V}	Homogenization type
M 516	Sphalerite, galena, tetrahedrite	Q1	I	1	0.90-0.95	5	300	L
		Q1	V	~2?	0.05	3		
		Q1	I	?	0.8-0.6	7	350	L
		Q1	I	1	0.9	5	318	L
				1	0.9	1	390	L
		Q2	I	1	0.8-0.9	7	370	L
		Q2	I	~2?	0.9	11	345	L
		Q3	I	1	0.9	8	342	L
		Q3	I	~2?	0.9	2	372	L
		Q3		1	0.9	4	400	L
F2-567	Sphalerite, galena	Ca 1	I	1	0.8	2	378	L
		Ca 1	I	1	0.8	2	374	L
		Ca 1	I	1	0.8	1	453	L
F22-801	Sphalerite, galena, pyrite, chalcopyrite	Q1	I	2	0.8	7	380	L
		Q1	I	2	3	2	420	L

1 - primary inclusions; 2 - secondary inclusions; ~2 - pseudosecondary inclusions; L/G - phases ratio (liquid, gas, salt); n – number of measured inclusions; Th_{V-L} - homogenization temperature of gas.

One sample contains sphalerite and galena in a calcite-dominated small vein. In all samples, the fluid inclusions are of the liquid-rich type, with 10-20% gas and no daughter minerals. These inclusions are small (<20μm) and have irregular shapes. Commonly, the inclusions were clustered in the core, rarely in the external growing zone of hosting crystal. They are also present as secondary or pseudo-secondary inclusions, localized in the cracks of the hosting quartz. When the inclusions are hosted by calcite, they are located on the cleavages and at the intersections of cleavages (ex. probe F2-567). The homogenization of the gas and liquid phases occurs at temperatures between 300° and 453°C (Table 2). A histogram of the homogenization temperatures of the fluid inclusions associated with base metal and Au-Ag veins is given in figure 4.

7. DISCUSSIONS

The quartz stockwork veins from Bolcana ore deposit hosted numerous fluid inclusions, most of them having primary origin. These inclusions vary broadly with regard to the vapor–liquid ratio, daughter crystals mineralogy, range of homogenization temperatures, and the shapes of inclusions. Co-existence of the high salinity type, vapor rich type and silicate melt type within the same fluid inclusions assemblages suggests a primary origin of these and the development of boiling processes (Beane & Bodnar, 1995; Pintea, 1995, 2001). This aspect also implies the immiscibility of a silicate melt; sulfide melt and a hypersaline melt in the water-saturated magmatic chamber. The high salinity of these solutions is proven by the presence of halite and sylvite crystals captured during inclusions trapping or as „daughter" crystals.

Homogenization temperature of gas-liquid (Th_{V-L}) and the dissolution temperature of halite (Tm_{NaCl}) for B type inclusions show values in the range 370°C to > 580°C. Only a few B2 type inclusions homogenized totally or partially at temperatures < 580°C (Table 1). The large variation range of Th_{V-L} and Tm_{NaCl} could have been caused by heterogeneous trapping, were the vapor-salt ratio was very different. Most inclusions that homogenized at temperatures below 580°C recorded $Th_{V-L} < Tm_{NaCl}$, which means that the fluid was NaCl supersaturated at the moment of trapping. For the inclusions having $Th_{V-L} > Tm_{NaCl}$, it is proposed that the solutions were undersaturated in halite, and the saturation was attained by cooling, after the trapping of the inclusions. The daughter minerals of fluid inclusions and mineral microinclusions hosted reveals the role played by Cl and S as complex ligand components during the magmatic-hydrothermal fluid evolution.

In most of the B-type inclusions, the halite crystals extend in the gas bubbles (when the bubble occupies more than 20% from inclusion volume). This aspect proposes that halite crystallized after the sealing of the inclusions. The presence of sulfides and sulfates shows an important activity of sulfur in the magmatic fluids and also the presence of chloride (at least halite and sylvite) certifies an important role of Cl in metal transport in the hydrothermal solutions. The anhydrite and magnetite minerals also are a clue of the oxidizing character of the mineralizing solutions.
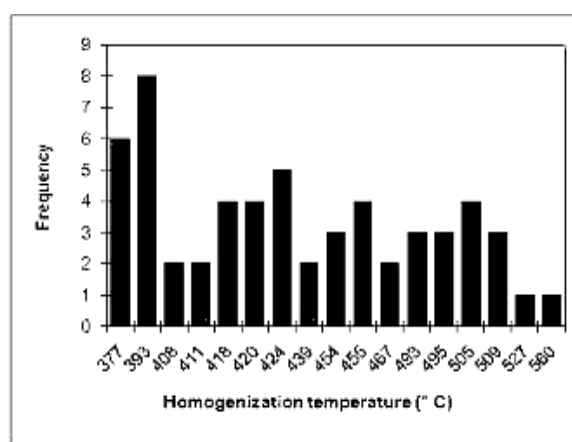

Figure 3. Histogram of the homogenization temperatures of the fluid inclusions associated with porphyry copper mineralization
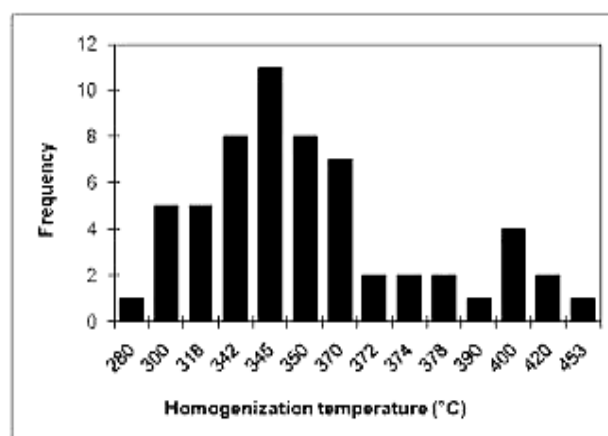

Figure 4. Histogram of the homogenization temperature of the fluid inclusions associated with hydrothermal mineralization

Chalcopyrite presence as daughter mineral in the B-type and V-type inclusions suggests that copper and reduced sulfur in hosted vapor inclusions was higher in the moment of trapping.

Regarding gold and copper behavior, it can be remarked a positive correlation of these elements at Bolcana ore deposit (Popescu & Cioacă, 2006). LA-ICP-MS measurements of the melt and fluid inclusions show high content in gold and copper at Bolcana (Ivăşcanu et al., 2001). Therefore, it is accepted a common magmatic origin, enrichment process and the same conditions of precipitation of these metals.

Halite-bearing fluid inclusions trapped in a boiling system are common in many geologic environments, including magmatic-hydrothermal ore deposits associated with siliceous magmas (Bodnar, 2003). Assuming that the hypersaline inclusions consisted initially only of liquid phase in an immiscible fluid system, the composition of the inclusion is determined at the temperature of halite dissolution, and the trapping temperature is equal to the homogenization temperature. The salinity of the brine inclusions could not be exactly determined, because Th is higher than 580° C, but could be estimated using temperature-salinity diagram of H_2O-NaCl system (Bodnar, 2003). According to this author, the salinity corresponding to Th above 600°C is > 70 wt % NaCl equiv. The complete range of P-T conditions over which immiscibility may occur in the H2O-NaCl system is unknown. For any composition, the two - phase region extends to temperatures at least as high as the critical temperature (Bodnar, 2003).

The variable shapes of the fluid inclusions from irregular, negative-crystal, round or long in the same host quartz crystal could indicate variations of the lithostatic pressure in time (Bodnar, 2003). Pintea (2001) suggested the minimum trapping pressure (inferred from H_2O-NaCl system phase equilibrium) range between 0.5 and 1 kb. This pressure corresponds to high trapping temperatures of fluids having salinity about 60-80 % NaCl equiv. In the case of boiling, volatile pressure is more relevant for the development of the hydrothermal processes. High salinity fluid inclusions having homogenization temperatures > 600°C are present in a wide range of depths (from 300 m to more than 1000 m deep), being found in veins associated with potassic alteration and also with propylitic alteration. This fact could signify that the hydrostatic pressure of the hypersaline magmatic solutions was high enough to provoke a significant brecciation of the solidified intrusion across a large depth interval and the magmatic solutions had a rapid ascent along the cracks. As an effect of the dramatic depressurization, boiling took place and the silicate melt, hypersaline hydrous liquid and vapors separated.

The fluid inclusions from the hydrothermal vein mineralization recorded homogenization temperatures within the 350°- 453°C interval. This could indicate that the vein-type mineralization from Bolcana was precipitated in a high-temperature hydrothermal environment (hypothermal range). No evidence of boiling was found. Because they are very small, the ice melting temperature could not be measured during the freezing stage, therefore, the salinity of these inclusions could not by accurately determinate. The absence of halite indicates a low salinity range, (< 20 wt. % NaCl equiv.).

The genesis of the low-sulfidation hydrothermal mineralization is linked in generally by the dilution and cooling of the hypersaline magmatic solutions, by additions of meteoric water that flowed along the faults. The contribution of the meteoric water became dominant during the last stages of evolution of the hydrothermal system (Heinrich, 2005). The mixing of waters induced significant changes of the physico-chemical parameters of the hydrothermal solutions (chemical composition, pH, Eh, fS_2 etc.) that provoke the precipitation of base metal and gold-silver mineralization and also hydrothermal alterations (sericitization, argillization, carbonation, silicification).

A similar model it is proposed by André-Mayer et al., (2001) at Valea Morii porphyry Cu-Au ore deposit (Metaliferi Mts.). The authors published the results of isotopic composition of sulfur in the both porphyry and low-sulfidation epithermal type (Au) of mineralization. The all values of $\delta^{34}S$ are in range of 0,2-3,3‰, that indicate a magmatic source for both type of mineralisation. Microthermometric and petrographic data show temperatures between 400–450°C, pressures between 200 and 400 bars and indicate boiling events for porphyry system. In the epithermal veins are obtained temperatures from 250 to 290°C and pressures from 55 to 95 bars. Based on these data, the authors proposed a telescoping or a superimposition phenomenon between these types of mineralization. The epithermal mineralization is favored by meteoric fluids that migrate along the fractures. The authors consider the telescoping is more probable, linked by an erosion phenomenon during hydrothermal activity or due to collapse of the upper part of the system.

As shown by Alderton & Fallick (2000), in some cases of base metal and gold-silver (tellurium) vein deposits from Metaliferi Mts, (e.g. Măgura, Săcărâmb, Coranda, Bocşa and Băiaga), O-H, S and C isotope compositions indicate a limited contribution of meteoric waters, although other characteristics (such as genesis at moderate

temperatures and the low salinity) are similar with the classical low-sulfidation volcanic-hosted ore deposits. The authors consider that these deposits could be formed in a hydrothermal system dominated by magmatic water, derived from the crystallization of deep plutons, with low salinity (<10 wt % NaCl equiv), which carried base and precious metals, Te, S, and C. The main stage of mineralization took place from metal-enriched fluids, at temperatures of 200-300°C, depths of about 500-1000 m and near-neutral pH. Meteoric fluids were present just in the last stage of mineralization (barite and some carbonates). Măgura and Bolcana are part of the same major metallogenetic field superimposed on caldereantype magmato-volcanic system (Troiţa-Măgura area), but Bolcana vein mineralization was generated in a particular metallogenetic event, linked to the subvolcano body. In the case of Bolcana deposit, an assessment of the importance of meteoric fluid in the formation of the base metal (with subordinated Au and Ag) mineralization needs O-H isotopic investigations.

8. CONCLUSIONS

The Bolcana porphyry Cu-Au deposit is associated with an adakite-like microdioriticandesitic subvolcanic body. This deposit is located in the center of a concentrically-zoned metallogenic complex were two type of mineralization are associated: porphyry and low sulfidation vein type. Both mineralization processes could have o common source and the fluid inclusions could derived from the same magmatic fluid.

Petrographic and microthermometric data on the fluid inclusions associated with the porphyry copper mineralization and the hydrothermal veins indicate the following conclusions:

1. The genesis of Bolcana structure is characterized by the complex polyascendent evolution into magmatic-hydrothermal system, evidenced by the superimposed mineralizations and alterations and characteristics of the fluid inclusions.

2. Primary boiling is the most important process recognized in the Bolcana ore deposit. The boiling was repetitive at high temperature (from 400°C to more than 600°C). The traces of these events are recognized in the potassic and propylitic alterations on a large depth interval.

3. The boiling is also responsible for the extraction of the metals from the magma, as complexes with Cl or/and S and for the precipitation of metallic minerals, as an effect of the changes in the geochemical and thermodynamic conditions.

Therefore, the porphyry Cu-Au mineralization was controlled by residual magmatic fluids, enriched in vapors, chloride and sulfide compounds that was derived from crystallization of the host subvolcano. The presence of metallic minerals such as chalcopyrite, hematite etc. in inclusions supports a magmatic source of the metals. These minerals precipitated at elevated temperature (>500 C) and pressure (>500 bar).

4. In the latest metallogenetic events, base metal (Au, Ag) mineralization was developed along the fractures. These metals solubility could down when the derived-magma fluid cooled and was changed its chemical composition, as effect of the contact with hosted rock and possibly mixing with meteoric waters. In the last stages, in some veins, only pyrite and/or argillaceous minerals precipitated.

REFERENCES

André-Mayer A.S., Leroy J.L., Marcoux E. & Lerouge C., 2001. *Inclusions fluides et isotopes du soufre du gisement Cu–Au de Valea Morii (Monts Apuseni, Roumanie): un télescopage porphyre–épithermal neutre.* Earth and Planetary Science Letters 333, 121–128.

Alderton D. H. M. & Fallick A. E., 2000. *The Nature and Genesis of Gold-Silver-Tellurium Mineralization in the Metaliferi Mountains of Western Romani*a, Economic Geology, Vol. 95, pp. 495–516.

Beane R. E. & Bodnar R. J., 1995. *Hydrothermal fluids and hydrothermal alteration in porphyry cooper deposits*. In Pierce F.W. and Bohm J.G., "Porphyry Copper Deposits of the American Cordillera". Arizona Geological Society Digest 20, Tucson, AZ, p. 83-93.

Bodnar R. J., 2003. *Introduction to aqueous-electrolyte fluid inclusions*. In I. Samson, A. Anderson, & D. Marshall, eds. Fluid Inclusions: Analysis and Interpretation. Chapter 4. Mineral. Assoc. Canada, Short Course 32, 81-99.

Cardon O., Andre-Mayer A. S., Sausse J., Milu V.,

Chauvet A., Leroy J. L., Lespinasse M. & Udubaşa S., 2005. *Connexion poprphyre cuprifere-epithermaux de type low-sulfidation: analyse structurale et represntation 3D du secteur de Bolcana, Monts Apuseni, Roumanie* – C.R. Geosience, 337, 824-831.

Cardon O., Reisberg L., Andre-Mayer A. S., Leroy J. L., Sausse J., Milu V. & Zimmermann C., 2008. *Re-Os systematics of pyrite from the Bolcana porphyry copper deposit, Apuseni Mountains, Romania.* Economic Geology*, 103, 8, 1695-1702.*

Cioacă M. E. & Popescu Gh., 2006. *Porphyry copper mineralization from Bolcana, Metaliferi Mts; petrochemical and geochemical aspects.* Romanian Journal of Mineral Deposit and Romanian Journal of Mineralogy, 82 (joint volume), 57-60.

Cioacă M. E., 2008. *The study of the copper and gold "porphyry" type mineralisation at Bolcana, Metaliferi Mts.* PhD thesis, Univ. Bucharest (In Romanian).

Cioflica G., Jude R. & Udubaşa G., 1966. The s*tructural and mineralogical features of the Măgura–Troiţa vein systems (Metaliferi Mts.)* Revue Romaine de géologie, géophysique et géographie, Serie de Geologie, 10, 2, 389-401 (In Romanian).

Heinrich C.A., 2005. *The physical and chemical evolution of low-salinity magmatic fluids at the porphyry to epithermal transition: a thermodynamic study.* Mineralium Deposita, 39, 864-889.

Ivăşcanu P. M., Pettke T., Heinrich C. A., Roşu E., Nedelcu L. & Pintea I. (2001). *Magmatic hydrothermal transition in porphyry environment, South Apuseni Mountains, Romania. Outline from single inclusion LA-ICP-MS analyses.* Romanian Journal of Mineral Deposits, 79, suppl. 2. Abstracts vol., 111-112.

Milu V. & Pintea I., 2001. *Bolcana porphyry ore deposit stop 1.* Romanian Journal of Mineral Deposit, 79, suppl. 2. Guidebook. 68-69.

Milu V., Leroy J. L. & Piantone P., 2003. *The Bolcana Cu-Au ore deposit (Metaliferi Mts, Romania) first data on the alteration and related mineralisation.* C.R. Geoscience 335, 671-680, Elsevier.

Nedelcu L., Roşu E. & Costea C., 2001. *Mineral microinclusions hosted in sulfides of main neogene porphyry copper and epithermal ore deposits of the south Apuseni Mountains, Romania.* Romanian Journal of Mineral Deposit, 79, suppl. 2. Abstracts vol., 72-73.

Nedelcu L., Roşu E. & Costea C. M., 2003. M*ineral microinclusions hosted in sulfides of main neogene porphyry copper and epithermal ore deposits of the*

South Apuseni Mountains, Romania; Acta Mineralogica-Petrographica, Abstract Series 1, 78.

Pettke T., Halter W. E., MacIntosh I. & Heinrich C., 2001. *The porphyry to epithermal link: preliminary fluid chemical results from Roşia Poieni, Romania, and Famatina, Argentina.* Romanian Journal of Mineral Deposit, 79, suppl. 2. Abstracts vol., 81-82.

Pintea I., 1995. *The study of fluid inclusions with special regard on immiscibility of the fluids phases associated with the genesis of the porphyry copper ore deposit from Metaliferi Mts.* PhD thesis, Univ. of Bucharest (In Romanian).

Pintea I., 2001. *Melt and fluide inclusions study in neogene porphyry Cu-Au (Mo) from Metaliferi Mountains* Romanian Journal of Mineral Deposit, vol 79, suppl. 2. p. 28-29, Field Guidebook.

Popescu Gh. & Cioacă M., 2006. *Preliminary data concerning the Cu, Au, Ag distribution in the Bolcana ore deposit, Metaliferi Mts., Romania.* Acta Mineralogica – Petrographica, Abstracts series 5, 95.

Popescu Gh. & Neacşu A., 2007. *Relationship between gold and copper metallogenesis in the Metaliferi Mts.* Analele Ştiinţifice ale Univ. ”Al. I. Cuza”, Iaşi. Geologie. Tome LIII, 71-78.

Roşu E, Pecskay Z, Stefan A., Popescu G., Panaiotu C. & Panaiotu C. E. (1997) - *The evolution of the Neogene volcanism in the Apuseni Mountains, Romania, constrain from new K-Ar data.* Geologica Carpathica 48, 353-359.

Roşu E., Szakacs A, Downes H., Seghedi I. & Peckskay Z., 2001. *The origin of neogene calc-alkaline magmas in the Apuseni Mountains, Romania: the adakite connection.* Romanian Journal of Mineral Deposit 72, suppl. 2, 3-23.

Roşu E, Seghedi I., Downes H., Alderton D., Szakacs A., Pecskay Z., Panaiotu C., Panaiotu C. E. & Nedelcu l., 2004. *Extention related Miocene calc-alkaline magmatism in the Apuseni Mountains, Romania: origin of magmas.* Scheizerische Mineralogische und Petrographiche Mitteilungen 84, 153-172.

Săndulescu M., Kräutner H., Borcoş M., Năstăseanu S., Patrulius D., Ghenea C., Lupu M., Savu H., Bercia I. & Marinescu F., 1978. *Geological Map of Romania, scale 1: 1000000.* Geological Atlas, 1th sheet. Institute of Geology and Geophysics.

Udubaşa G, Roşu E. & Seghedi I., 2001. *The „Golden Quadrangle” in the Metaliferi Mts., Romania: what does this really mean?* Romanian Journal of Mineral Deposit, 79, suppl. 2. Abstracts volume, 24-35.