MINERAL COMPOSITION OF THE BREZNIK-BARDOTO AU EPITHERMAL ORE OCCURRENCE (PRELIMINARY DATA)

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ABSTRACT. The Breznik epithermal gold prospect is located in the western part of the Srednogorie zone of the Late Cretaceous Banat-Timok-Srednogorie belt and it is hosted in hydrothermaly altered Late Crateceous volcanic and volcanoclastic rocks of andesitic, trachyandesitic and trachybasaltic composition. The Bardoto prospect involves the central part of the ore occurrence and it is characterised by ore mineralisation typical for the Au epithermal deposits formed at low temperatures. Mineralogical studies found ore minerals pyrite, arsenian pyrite (As content within 7–10 wt. %), chalcopyrite, galena, sphalerite, tennantite, tetrahedrite, native gold, electrum, pyrrhotite, magnetite, hematite, marcasite, covellite, chalcocite, malachite, cerusite and others. paper discussed presence of trace elements in the main ore minerals based on data from quantitative microprobe analyses and preliminary data from fluid inclusion studies.

МИНЕРАЛЕН СЪСТАВ НА AU-ЕПИТЕРМАЛНОТО РУДОПРОЯВЛЕНИЕ БРЕЗНИК-БЪРДОТО (ПРЕДВАРИТЕЛНИ ДАННИ)
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РЕЗЮМЕ. Епитермалното златно рудопроявление Брезник се намира в западната част на Средногорската зона от Апусени- Банат – Тимок – Средногорския пояс и е вместено в хидротермално променени горнокредни вулкански и вулканокластични скали с андезитов, трахиандезитов и трахибазалтов състав. Участък Бърдото обхваща централната част на рудопроявлението и в него се установява рудна минерална асоциация характерна за епитермалните златни находища, образувани при ниски температури. При минераложките изследвания са установени рудните минерали пирит, арсенсъдържащ пирит (със съдържание на As между 7 и 10 тегл. %), халкопирит, галенит, сфалерит, тенантит, тетраедрит, самородно злато, електрум, пиротин, магнетит, хематит, марказит, ковелин, халкозин, куприт, малахит, церуси и др. В работата се разглеждат присъствието на елементи-примеси в главните рудни минрали по данни от количествен рентгеноспектрален анализ и се привеждат получени предварителни данни от изследване на флуидни включения в минералите.

Introduction

The Bardoto prospect is a part of Breznik epithermal gold occurrence, which is located in the Western Srednogorie zone, near the town of Breznik, approximately 35 km west from Sofia. The zone is within the frame of the Late Cretaceous Apuseni-Banat-Timok-Srednogorie belt, which is a major copper and gold metallogenic province in the South-Eastern Europe. This province is characterized mainly by porphyry-Cu and Au-Cu epithermal deposits, which are typically clustered in major mining districts, such as Bor-Madjanpek in Serbia and the Panagyurishte ore district in Bulgaria, separated from each other by segments, in which numerous ore occurrences are known, but no any large ore deposit are found till now.

Geological setting

The Breznik prospect is hosted by Late Cretaceous volcanic and volcanoclastic rocks of andesitic, trachyandesitic and trachybasaltic composition, intruded by porphyry stocks and dikes of gabbrodioritic composition belonging to the Western Srednogorie belt. Basement rocks in the Breznik area consist of Precambrian gneiss and schists, Cambrian-Devonian mafic volcanic rocks, Paleozoic granitic intrusions, Permian-Triassic clastic sedimentary rocks, and Jurassic-Cretaceous limestone, shale and sandstone.

The hydrothermal alterations and data about the ore mineralization have been described by Velinov (1967), Velinov and Kanazirski (1990) and Crummy et al. (2001) (Fig. 1). The altered and mineralized area is EW-oriented and covers an area of approximately 2.5 by 1.5 km. The prospect is subdivided into one northern and one southern mineralized area with distinct types of alteration and metal enrichments.

The northern part displays an advanced argillic alteration with small and shallow zones consisting of quartz, kaolinite and alunite surrounded by an alteration halo with kaolinite and sericite. This part of the prospect shows local anomalies of Mo, Te and Au (locally over 2 g/t).
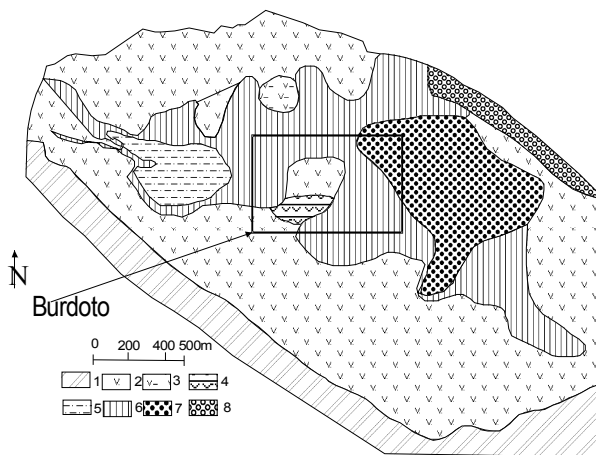
Fig. 1. Schematic geological map of the region south of Breznik (after Velinov, 1967) with additions.
1 – Tuff-marl complex; 2 – Agglomerates, pyroxene and pyroxene-amphibole tuffs, epidote-chlorite facies, 3 – Uralite–epidote-chlorite facies, 4 – actinolite-epidote-chlorite facies, 5 – Quartz-epidote-cericite facies, 6 – Quartz-sericite facies, 7 – Alunite-quartz facies, 8 – Tertiery sediments

Ore mineralogy

Data about the mineral composition of ores in the area are very limited. Previous studies of ore minerals (Crummy et al., 2001) mentioned an interval of 1 m thick in drill hole carried out in the northern part of the prospect relatively rich of ore minerals. The assamblage includes minerals such as enargite, luzonite, tennantite, tetrahedrite, pyrite, chalcopyrite, goldfieldite, arsenosulvanite, colusite, galena-claustalite, Au-Ag tellurides, typical for the high sulphidation type of mineralisations. In the same paper also are mentioned presence of minerals like galena, sphalerite, bournonite, arsenopyrite, marcasite, argentite and Co-Ni-Fe-S phases, native gold and electrum, but no any additional data are provided for their distribution and chemical composition.

The recent study is based on samples from the area Bardoto, which is a part from the mineralised zone of Au-epithermal occurrence Breznik. Followng ore minerals are determined in the samples – pyrite, (also arsenian pyrite) chalcopyrite, galena, sphalerite, tennantite, tetrahedrite, pyrrhotite, native gold, electrum, magnetite, hematite, marcasite, ilmenite, chalcocite, covellite, malachite, cuprite and cerusite.

Pyrite is the most often found ore mineral in the samples studied. It forms mainly semi-euhedral, xenomorphic, euhedral or rarely colloform rounded grains and aggregates within 20 µm up to 2 – 3 sm. Larger aggregates are usually slightly fractured and cemented by gangue or later formed sulphide minerals. On the basis of its textures and chemical composition at least three varieties of pyrite could be distinguished. The first one is related with the pre-ore hydrothermal alteration and it is presented by fine disseminated grains of pyrite without any trace elements over 0.0n wt. % in it. The second one associates with other sulphide minerals which often corroded or cut it (Plate C). In some of its relatively larger aggregates are found fine grains (20–50 µm) with well-expressed anisotropic features, grey-yellowish color and distinct lower reflectivity compared with the normal pyrite. Quantitative microprobe analyses established in this variety significant

content of Cu and lower content of Ni (Table 1, an. # 1). The most unusual is the third variety of pyrite forming rounded colloform aggregates with zonal texture (Plate A, B and D). Their central parts are set up by pyrite containing Cu and As about 0.5 wt.% (Table 1, an.# 2) and they are rimmed by bends of pyrite with extremely high content of As and significant contents of Cu and Sb (Table 1, an. ## 3, 4 and 5). These bends are isotropic but they look distinctly darker compared to the central parts of aggregates. Their color in reflected light is creamy grayish with slight pink tarnish, the reflectivity is lower compared to typical for pyrite (probably about 45 – 48 %). The most outer part of the aggregates comprises very fine crystals of marcasite.

The problem of isomorphic form of presence of As, Cu and Sb in pyrite is one of the most discussed in literature about chemistry of this mineral. The described findings with high As content could be nominated as arsenian pyrite according Chvileva et al. (1988) which mentioned that As content in this variety could reach 14.5 % and Sb up to 2 %. Colloform textures are very typical for it as it is in this case.

Low concentrations of As in pyrite as trace element are found in numerous deposits in Bulgaria, especially in copper deposits from the Srednogorie zone. Higher content of As (4.08 wt.%) is reported for pyrite in the Sedmochislenitzi low-temperature (teletermal) Pb-Zn-(Cu) deposit (Vratza ore region, Western Stara Planina) by Shadlun et al. (1975). Petrunov (1994) mentioned high content of As in pyrite from Chelopech Au-Cu deposit from the Central Srednogorie zone.

Chalcopyrite associates with pyrite as irregular aggregates cutting early formed pyrite (Plate C) or fine nests among large pyrite aggregates (Plate E). Typical is the association of chalcopyrite with tennatite (Plate F). In some cases tennatite rims chalcopyrite (Plate C) and in the other marginal parts are set up by chalcopyrite and it seams that tennantite replace it. The most probable is that both minerals are formed in narrow interval of mineralisation process and both relations between them are available. Marginal part of chalcopyrite from upper levels is replaced by secondary copper minerals such as chalcocite and covellite. Fine chalcopyrite emulsion is rarely found in larger sphalerite grains.

Quantitative microprobe analysis of chalcopyrite established also significant a high content of As and low presence of Sb (Table 1, an. # 6). Such high content of As is not typical for chalcopyrite and additional analyses are obvious for precise determination of chemical composition of this mineral.

Galena presents as fine isometric slightly rounded inclusions in pyrite (Plate D) and as irregular shaped inclusions rarely in chalcopyrite (Plate C). Inclusions found in pyrite do not contain any trace elements while these found in chalcopyrite are characterized by presence of Se and Ag (Table 1, an. # 7 and 8).

Due to the relatively minor size of analyzed grains, the contents of Fe and part of Cu registered in them are probably a result of influence of the chalciopyrite matrix. That is why crystallochemical formulas are calculated taking into acount the contamination of chalcopyrite and excluding Fe and corresponding Cu from analyses.
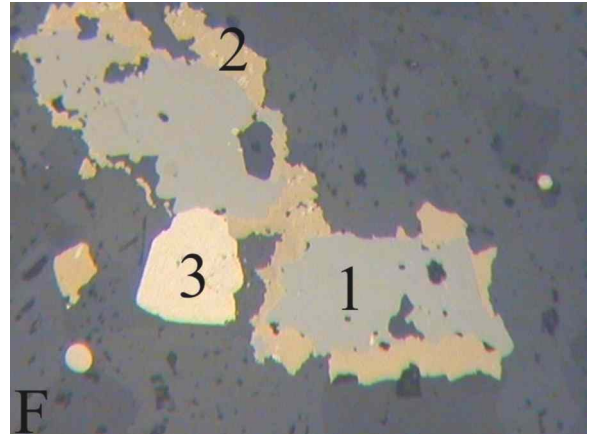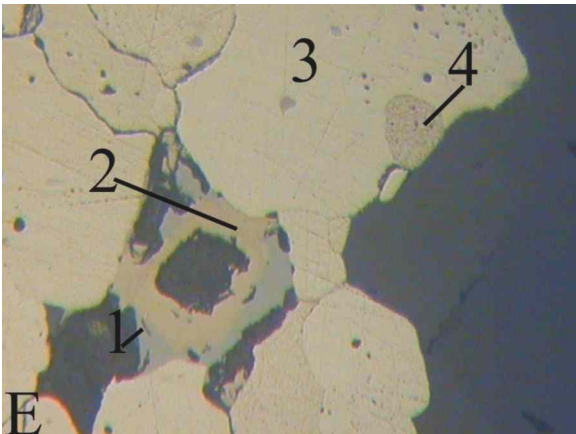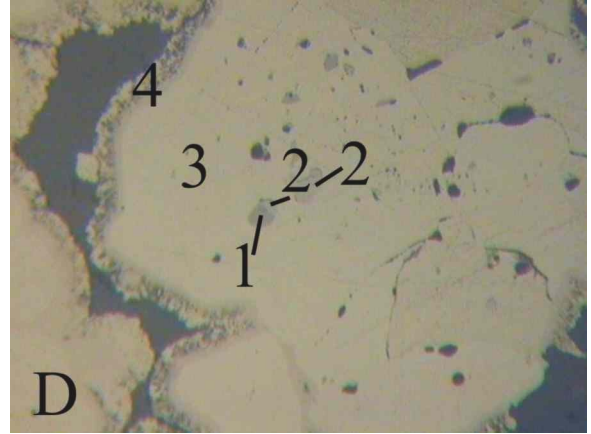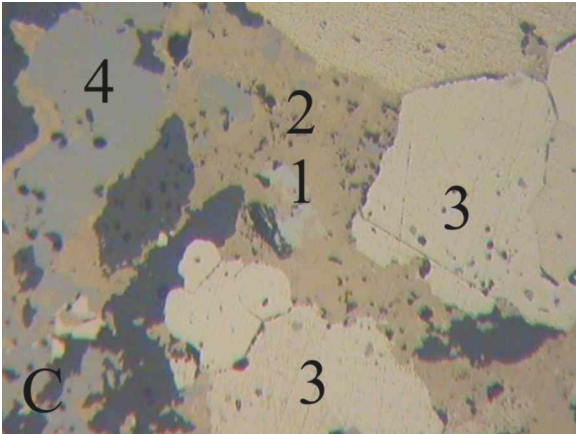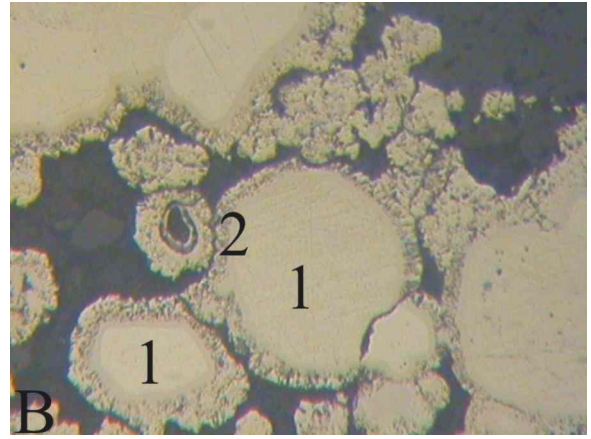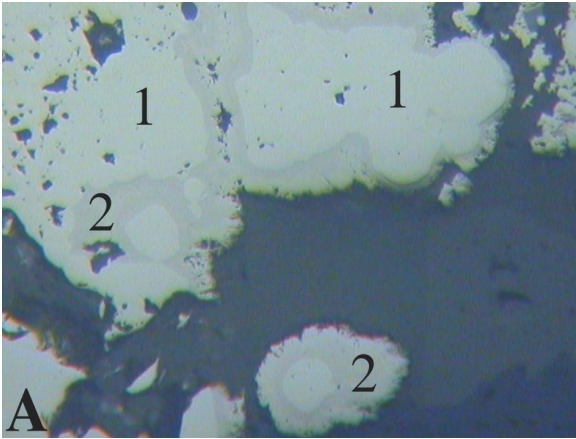
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Plate A. Pyrite (1) rimmed by As-pyrite containing (2) As between 7 – 10 wt.%, II N, (Size of the observation field of all plates = 320 μm).

Plate C. Irregular inclusion of Se-bearing galena (1) in chalcopyrite (2) crosscutting pyrite (3) aggregate. (4) – tennantite, II N.

Plate E. A rim of tennnatite (1) around chalcopyrite (2) as fine nest among larger pyrite aggregate (3). (4) – inclusion of slightly rounded Cu-rich anisotropic pyrite in matrix of normal pyrite, II N.

Plate B. Atol-like textures of pyrite (1) aggregates rimmed by marcasite and As-pyrite (2), II N.

Plate D. Inclusions of tetrahedrite (1) and galena (2) in pyrite (3) rimmed by marcasite and As-pyrite (4), II N.

Plate F. Tennantite (1) replacing central part of chalcopyrite (2) aggregate. (3) – semi-euhedral pyrite grain, II N.

Table 1
Results from quantitative microprobe analyses (Breznik, # 16276, drill hole 525, level – 169 m)

No	element wt. %) mineral	Ag	Ni	Sb	Fe	Cu	Zn	Pb	As	Se	Mn	S	Total
1	pyrite	0.0	0.22	0.0	46.09	0.56	0.0	0.0	0.0	0.0	0.0	53.00	99.85
2	pyrite	0.0	0.0	0.0	45.88	0.67	0.0	0.0	0.45	0.0	0.0	52.51	99.50
3	As-pyrite	0.0	0.16	2.92	39.53	1.97	0.0	0.0	8.92	0.0	0.0	46.91	100.41
4	As-pyrite	0.0	0.0	2.09	39.40	1.75	0.0	0.0	9.38	0.0	0.0	46.44	99.05
5	As-pyrite	0.0	0.15	1.26	39.40	1.75	0.0	0.0	10.96	0.0	0.0	46.14	99.06
6	chalcopyrite	0.0	0.0	0.20	26.49	36.28	0.0	0.0	4.19	0.0	0.0	32.00	99.15
7	galena+Se	1.16	0.0	1.81	1.26	3.06	0.18	78.28	0.0	0.62	0.0	13.39	99.76
8	galena+Se	0.92	0.0	0.62	1.90	3.65	0.0	77.72	0.0	1.80	0.0	13.40	100.01
9	tennantite	0.30	0.0	0.57	5.94	40.05	0.0	0.0	23.69	0.0	1.95	27.59	100.09
10	tennantite	0.88	0.0	0.75	3.82	40.86	0.0	0.0	23.67	0.0	2.87	27.06	99.90
11	tennantite	0.76	0.0	0.95	4.94	41.02	0.0	0.0	22.51	0.0	2.57	27.20	99.83
12	tetrahedrite	2.04	0.0	20.81	2.67	37.23	6.00	0.0	8.14	0.0	0.0	23.34	100.23

Crystallochemical formulae:

1. $(Fe_{0.99}Cu_{0.01}Ni_{0.01})_{0.01}S_{1.99}$
2. $(Fe_{0.99}Cu_{0.01})_{1.00}(S_{1.98}As_{0.01})_{1.99}$
3. $(Fe_{0.91}Cu_{0.04})_{0.95}(S_{1.97}As_{0.15}Sb_{0.03})_{2.05}$
4. $(Fe_{0.91}Cu_{0.04})_{0.95}(S_{1.97}As_{0.16}Sb_{0.03})_{2.05}$
5. $(Fe_{0.92}Cu_{0.02})_{0.94}(S_{1.85}As_{0.19}Sb_{0.01})_{2.05}$
6. $Cu_{1.09}Fe_{0.90}(S_{1.90}As_{0.11})_{2.01}$
7. $(Pb_{0.86}Cu_{0.11}Sb_{0.03}Ag_{0.03})_{1.03}(S_{0.95}Se_{0.02})_{0.97}$
8. $(Pb_{0.85}Cu_{0.13}Ag_{0.02}Sb_{0.01})_{1.01}(S_{0.94}Se_{0.05})_{0.95}$
9. $(Cu_{9.34}Fe_{1.58}Mn_{0.53}Ag_{0.04})_{11.49}(As_{4.69}Sb_{0.07})_{4.76}S_{12.76}$
10. $(Cu_{9.62}Fe_{1.02}Mn_{0.78}Ag_{0.12})_{11.54}(As_{4.73}Sb_{0.09})_{4.82}S_{12.63}$
11. $(Cu_{9.63}Fe_{1.32}Mn_{0.70}Ag_{0.10})_{11.75}(As_{4.48}Sb_{0.12})_{1.60}S_{12.65}$
12. $(Cu_{9.70}Zn_{1.52}Fe_{0.79}Ag_{0.31})_{12.32}(Sb_{2.83}As_{1.80})_{4.63}S_{12.05}$

Sphalerite is also in minor quantity but relatively much often found compared to galena. It forms fine xenomorphic nests in association with the rest of sulphide minerals. It is observed as well fine veinlets in fractures of pyrite aggregates. Some of its grains are rimmed by tennantite. Chalcopyrite dissemination in it is not typical although it is observed in some cases. The size of its grains and aggregates usually is below 1 mm.

Tennantite is often found in association mainly with chalcopyrite (Plate C). It forms thin rims around it (Plate E) or it replaces larger chalcopyrite aggregates (Plate F). Chemical composition of tennantite studied by quantitative microprobe analyses show constant presence of trace elements such as Ag, Fe and Mn. A very low Sb content determines the phases very close to the end-member of tennantite-tetrahedrite serie. Relatively high Fe content nominate it as feroan tennantite according classification offered by Chvileva et al. (1988) where maximal iron content in tennantite established is mentioned as 7 wt. %. Very high is also Mn content which normally is typical one for tetrahedrite. It should be mentioned that the most tennantite phases analyzed in samples from deposits in the Central Srednogorie contain Zn, an element which is not detected in this case. The silver content is relatively low but taking into account the presence of tennantite in ores it should be registered as potential carrier of this element.

Tetrahedrite has a very rare distribution in samples studied. It is found only as small rounded inclusions in pyrite (Plate D) in association with galena. Their size is within 10 – 30 µm. Analyzed grain is characterized by relatively high As content (up to 8.17 wt.%, Table 1, an. # 12) so it could be concluded that the most phases from tennantite-tetrahedrite serie found in this ore occurrence are much more belonging to the As rich and intermediate sector of the row. Zn content is high and the phase could be nominated as Zn-rich tetrahedrite. Compared with described above tennantite this phase has relatively higher Ag content (up to 2 wt. %).

Pyrrhotite forms single slightly rounded inclusions with minor size in larger pyrite aggregates. It is very rare in samples studied.

Native gold is not observed in the samples studied but in prospecting reports it is reported as presenting as fine inclusions within 10 – 100 µm. Four microprobe analyses of gold inclusions established native gold (Au 935 ‰) as well as electrum (Au 730 – 740‰).

Magnetite observed in the mineralization probably is a relict from the accessory minerals of the host rock and it is also formed at the beginning of the ore mineralization stage as fine grains in quartz. Its distribution in samples is very rare.

Hematite is a result of martitisation of magnetite during the changes of oxi-reductional potential of the environment. It is observed the most often as fine veinlets in the marginal parts of magnetite grains. In some cases itergrowths with ilmenite also presents.

Secondary copper minerals (chalcocite, covellite, cuprite and malachite) are formed as result of supergenic destruction of chalcopyrite. Chalcocite and covellte are developed as fine veinlets and rims along the periphery of chalcopyrite grains. Malachite and cuprite are observed as fine veinlets in quartz. All of them have rare distribution at the upper part of the mineralised zone.

Cerusite has a very rare distribution as a rim around galena grains.

Gangue minerals are presented mainly by quartz dveloped in 4 generations. The first one is related to the pre-ore metasomatic alterations and it associates with fine-grained pyrite. The rest three generations form fine veinlets and veins within several mm up to 15–20 cm. The most outern part is formed by chalcedony-like quartz.

Other gangue minerals observed in the zone are calcite, hydromica, chlorite, barite and gypsum.

The gold content in the analyzed samples from the Bardoto prospect is a part of Breznik epithermal gold occurrence varies from 1.99 to 12.17 ppm. The Au ones from 11.6 to 46.7 ppm, the Cu one from 231 to 231.

Table 2
Chemical composition of representative samples (trace elements)

Elements (in ppm)	1	2	3	4	5
As	1189	1832	2974	549	1251
Bi	<10	<10	39	21	<10
Cd	<10	24	22	<10	14
Co	<10	<10	28	10	<10
Cr	50	35	48	65	71
Cu	647	231	1179	231	713
Mo	<10	<10	<10	<10	<10
Ni	13	26	24	22	13
Pb	4926	1270	2278	1134	1387
Sb	16	259	40	41	143
Sn	79	<20	<20	<20	<20
Se	<10	49	16	12	10
Te	12	<10	21	<10	17
Ag	22.4	46.7	44.6	13.7	11.6
Au	6.69	11.02	12.17	1.99	7.18

Fluid inclusion studies

Fluid inclusion studies are provided on 4 samples and they should be accepted as preliminary. The first sample icludes quartz from breccia consisting of altered granodioritic fragments in a zoned matrix with crustification containing magmatic quartz in the intermost bands, surrounded by intergroun fine-grained silica, chalcedony and euhedral quartz. The intermost magmatic quartz has trapped coexisting assamblages of vapour-rich and liquid rich inclusions. The salinity of the liquid rich inclusions is within 20.7–26.6 wt. % NaCl eqv. One of the liquid inclusion show salinity within 0.5–3.2 wt. % NaCl eqv. Homogenization temperature is high – about 400^0 C for both types of inclusions. Coexsistance of these two types suggests possibility of development of boiling events during this stage of the process. The intermost magmatic quartz is separated from the typical hydrothermal quartz by a zone of fine grained silica, deposited as silica gel. Such textural relationship is similar to the recognized for magmatic-hydrothermal systems as it is described for instance in Refugio district of the Maricunga belt (Chile) where it is interpreted as being the result of a sudden pressure drop (Muntean and Einaudi, 2000). The later formed hydrothermal quartz post-dating the fine-grained silica gel event only contains single phase, vapour rich inclusions with traces of CO_2 as detected by Raman spectroscopy occurring typically along growth zones. This indicates that after the sudden pressure drop deposition of hydrothermal minerals occurred in vapour-dominated environment.

Late stage fluids are recognized in paragenetically late dolomite and Mn-rich carbonate in samples from drill cores from northern and southern part of the prospected area. Inclusions occur along well-defined growth zones and they have high liquid to vapour rich ratio at room temperature. The inclusions have homogenization temperature within 58–76^0 C with exception of one inclusion that has salinity of 10 wt. % NaCl eqv. These inclusions are interpreted as a late low temperature brune with moderate salinity reflected a basinal brine or possibly condenses-absorbed magmatic fluid in groundwater.

Conclusions

Data obtained show some differences in mineral composition of ores reported by Crummy et al. (2001) for the northern part of the area. Mineral association reported by mentioned above authors is much more typical for high to intermediate sulphidation type of copper-gold deposits. The absence of enargite, luzonite, arsensulvanite, colusite and other minerals usually found in the high sulphidation type here are not observed. Arsenium presents in high quantity in arsenian pyrite, which is one of the rare findings of this variety for the country. It is registred also in chalcopyrite and As-rich members of tennantite-tetrahedrite serie distinctly dominate in the samples studied. From this point of view misevaluation should be nominated as transitional type between intermediate to low sulphidation type of Au epithermal deposits.

Evidences of boiling and relatively high temperatures of homogenisation of inclusions found in quartz, which is probably of magmatic origin, support the presumption of development of a porphyry system in depth below the gold mineralization.

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