Arsenian marcasite in the barite-ankerite assemblage from the Chiprovtsi deposit, NW Bulgaria

Арсенов марказит в барит-анкеритовата парагенеза от нах. Чипровци, СЗ България

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Introduction

Marcasite is typical late hydrothermal and secondary mineral. It often replaces other primary minerals as pyrrhotite and stannite, and being metastable with respect to pyrite, inverts to pyrite at rates depending on temperature, grain size and concentration of intracrystalline defects. This inversion can be used as indicator of pH and T conditions of deposition (Murowchick, 1992).

Materials and methods

Polished sections were made from samples containing marcasite, collected from barite-ankerite-quartz vein, ~ 10 m long, crosscutting the siderite marble bodies with the main Pb-Ag mineralization, from outcrop at Hlebarska Chuka place, located in Sinya Voda mine section. Microprobe analyses of marcasite were performed by a JEOL Superprobe 733 electron microscope equipped with an ORTEC EDS at the Geological Institute, BAS.

Geological setting of the Chiprovtsi deposit and the barite-ankerite assemblage

The Chiprovtsi Ag-Pb deposit is hosted in low-grade metamorphic rocks (marbles and schists) of the Diabase Phyllitoid Complex (Precambrian – Early Ordovician age) (Carrigan et al., 2003). The formation of the main Ag-Pb metasomatic replacement mineralization is considered to be of Carboniferous age (Amov et al., 1981). The barite-ankerite assemblage is genetically and spatially associated with the second polymetallic assemblage in the Chiprovtsi deposit. Main minerals in the assemblage are barite, quartz, ankerite and calcite. They form veins and veinlet-like bodies within the siderite marbles at the Kamaka, Sinya Voda and Lukina Padina mine sections, crosscutting and over-

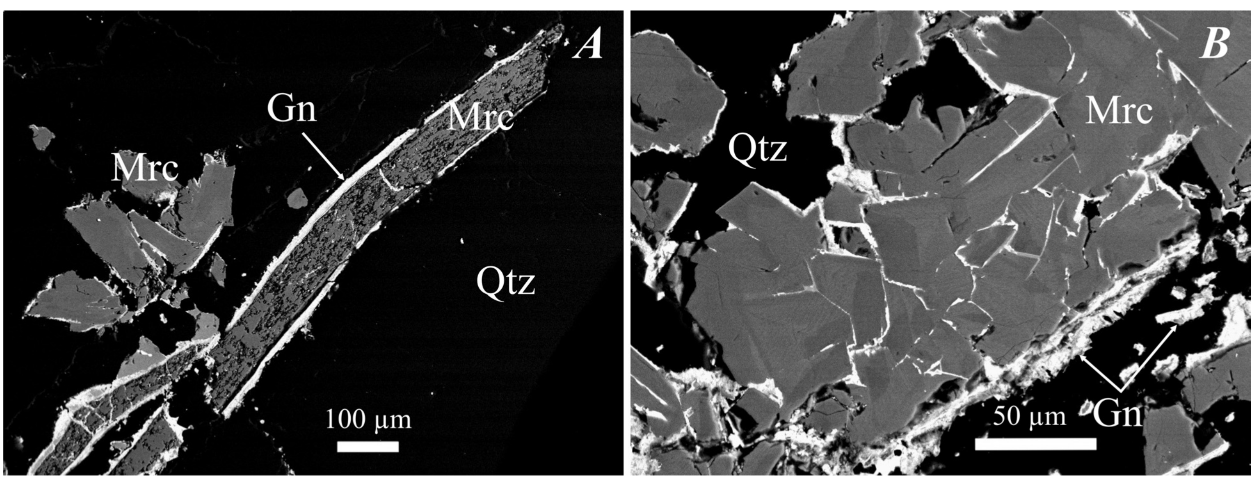

Fig. 1. SEM back-scattered electron images (BSE) of marcasite with high As contents: A, marcasite (Mrc) plate embraced by galena (Gn) in quartz (Qtz); B, marcasite crystals embraced by galena in quartz
Sample ch-340, Sinya Voda mine section, Hlebarska Chuka place

Table 1. Chemical composition of marcasite (wt.%)

№	Fe	Co	Ni	Cu	Sb	As	S	Total	Formula
	wt. %								*apfu*
1.	45.94	0.05	0	0.15	0	0.21	52.96	99.31	$Fe_{0.995}Co_{0.001}Cu_{0.003}As_{0.003}S_{1.998}$
2.	46.27	0.05	0	0.07	0	0.12	53.48	99.99	$Fe_{0.994}Co_{0.001}Cu_{0.001}As_{0.002}S_{2.001}$
3.	45.30	0.22	0	0.13	0	4.83	49.86	100.34	$Fe_{0.999}Co_{0.005}Cu_{0.002}As_{0.079}S_{1.915}$
4.	45.71	0.14	0	0	0	3.50	50.9	100.25	$Fe_{1.000}Co_{0.003}As_{0.057}S_{1.938}$
5.	45.37	0.24	0	0.06	0	6.55	47.01	99.23	$Fe_{1.028}Co_{0.005}Cu_{0.001}As_{0.111}S_{1.855}$
6.	44.55	0.15	0	0	0	10.30	45.00	100.00	$Fe_{1.022}Co_{0.003}As_{0.176}S_{1.798}$
7.	45.15	0.26	0	0.08	0	9.03	45.49	100.01	$Fe_{1.031}Co_{0.006}Cu_{0.002}As_{0.154}S_{1.808}$
8.	44.95	0.28	0	0.02	0	9.35	45.04	99.64	$Fe_{1.032}Co_{0.006}As_{0.160}S_{1.801}$
9.	46.61	0.04	0	0	0	0.14	53.84	100.63	$Fe_{0.995}Co_{0.001}As_{0.002}S_{2.002}$
10.	46.39	0	0	0.07	0	5.23	48.31	100.00	$Fe_{1.035}Cu_{0.001}As_{0.087}S_{1.877}$
11.	45.01	0.21	0	0.11	0	8.83	45.83	99.99	$Fe_{1.025}Co_{0.004}Cu_{0.002}As_{0.150}S_{1.818}$

printing the earlier Pb-Ag polymetallic assemblage. Small amounts of marcasite, pyrite, galena and chalcopyrite also occur in the quartz-barite veins.

Results and conclusions

Marcasite in the barite-ankerite assemblage is observed as: *1)* small irregular inclusions (~5–10 μm) in elongated plates of porous pyrite with size from ~ 200 μm to 1.5 cm (Fig. 1*A*) and *2)* prismatic crystals and irregular grains with size from 20 μm to ~ 200 μm (Fig. 1*B*). The small marcasite inclusions in pyrite are considered as relics of bigger marcasite plate pervasively replaced by pyrite. Small galena inclusions in the porous pyrite plates are also determined. The marcasite crystals and grains are usually orientated almost perpendicularly to the pyrite plates, forming layer on both sides of the plates, or are observed separately in quartz. Pyrite crystals are also found forming a layer almost parallel to the pyrite plates. Pyrite plates and marcasite crystals and grains are embraced by thin galena coating, forming a "core" in rosette-like quartz aggregates infilling cracks and cavities in the siderite marbles.

SEM study of marcasite crystals and grains show clear inhomogeneity in their chemical composition, represented by zones and sectors in the crystals, enriched in arsenic (light grey coloured zones and sectors in the crystals, Fig. 1*B*). The microprobe analyses of the zones and sectors revealed arsenic content, varying in wide range, between 3.50 wt.% and 10. 30 wt.%, but usually 5–6 wt.% (Table 1). Such high contents of arsenic (0.150–0.176 *apfu*) can define the marcasite as arsenian. The calculated crystal chemical formula is in the range $Fe_{1.000}Co_{0.003}As_{0.057}S_{1.938}$ – $Fe_{1.022}Co_{0.003}As_{0.176}S_{1.798}$. On the other hand, the small marcasite inclusions in the pyrite plates as well as pyrite show very low arsenic content (up to 0.21 wt.%).

According to Reich and Becker (2006) marcasite and pyrite can contain arsenic up to 6 wt.% as a solid solution $Fe(S,As)_2$ before unmixing into (pyrite or marcasite) + arsenopyrite. The high and varying arsenic contents suggest the presence of submicron to nanoscale arsenopyrite domains or inclusions similarly to those reported by Palenik et al. (2004) and Deditius et al. (2009). The low arsenic contents in marcasite replaced by pyrite in the elongated plates indicate that arsenic was probably extracted during the replacement and galena deposition. Most likely, marcasite was formed at temperatures below 240 °C (Murowchick, 1992), which is confirmed by the measured homogenization temperatures (*Th*) of primary fluid inclusions in the surrounding quartz (210 °C).

References

Amov, B., V. Arnaudov, M. Pavlova, P. Dragov, Ts. Baldjieva, S. Evstatieva. 1981. Lead isotope data on the Paleozoic granitoids and ore mineralizations from the Western Balkan Mountains and the Tran district (West Bulgaria). I. Isotopic ratios and geochronology. – *Geologica Balc.*, *11*, 2, 3–26.

Atanassov, V., I. Pavlov. 1983, Notes about mineralogy and paragenetic zoning of minerals deposits in Chiprovtsi ore region. – *Ann. Ecol. Sup. Min. Geol.*, *28*, 2, 159–178 (in Bulgarian).

Carrigan, C. W., S. B. Mukasa, I. Haydoutov, K. Kolcheva. 2003. Ion microprobe U-Pb zircon ages of pre-Alpine rocks in the Balkan, Sredna Gora and Rhodope Terranes of Bulgaria: Constraints on Neoproterozoic and Variscan tectonic evolution. – *J. Czech. Geo. Soc.*, *48*, 32–33.

Deditius, A. P., S. Utsunomiya, R. C. Ewing, S. E. Kesler. 2009. Nanoscale "liquid" inclusions of As-Fe-S in arsenian pyrite. – *Amer. Mineral.*, *94*, 391–394.

Murowchick, J. B. 1992. Marcasite inversion and the petrographic determination of pyrite ancestry. – *Econ. Geol.*, *87*, 1141–1152.

Palenik, C. S., S. Utsonomiya, M. Reich, S. E. Kesler, E. C. Ewing. 2004. "Invisible" gold revealed: direct imaging of gold nanoparticles in a Carlin-type deposit. – *Amer. Mineral.*, *89*, 1359–1366.

Reich, M., U. Becker. 2006. First-principles calculations of the thermodynamic mixing properties of arsenic incorporation into pyrite and marcasite. – *Chem. Geol.*, *225*, 3–4, 278–290.