Geochemical features of advanced argillic altered rocks in the area of Breznik town, Western Srednogorie

Геохимични особености на интензивно аргилизираните скали в района на гр. Брезник, Западно Средногорие

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Geological setting

The Bardoto alteration zone near Breznik town is situated in Western Srednogorie zone, part of the Upper Cretaceous Apuseni-Banat-Timok-Srednogorie magmatic and metallogenic belt. The area is built of the Breznik paleovolcano rocks from the Upper volcanogenic-sedimentary unit in Western Srednogorie (Dabovski et al., 2009). The host rocks are mainly pyroclastic, rarely lava flows, subvolcanic bodies and dykes with andesite, basaltic andesite and trachybasalt composition (Velinov, 1967; Dabovski et al., 2009).

Velinov (1967) describes propylites (epidote-chlorite-albite, actinolite-epidote-chlorite, quartz-epidote-sericite and quartz-sericite) and alunite secondary quartzites. Crummy et al. (2001) show a development of quartz-kaolinite-alunite, quartz-sericite and propylytic alteration types as well as the later quartz-sericite-carbonate one. They describe scarce enargite-luzonite and later rich gold-bearing quartz-sericite-carbonate mineralization, which are classified as an “atypical” epithermal gold manifestation. Moritz et al. (2007) discus juxtaposed high- and low-sulphidation epithermal styles of mineralization, which telescope a porphyry system. Lerouge et al. (2007) prove magmatic-hydrothermal origin of alunite, K-Na zoning of alunite and APS minerals. Since 2011 the Bardoto occurrence is known as Milin Kamak ore deposit which Sabeva (2015) define as Au-Ag intermediate sulphidation epithermal deposit.

Geochemical features

The main hydrothermal alteration types are sampled during this study in order to make clear the geochemical features of advanced argillic altered (AAA) rocks. Besides the known alunitic and alunite-kaolinitic varieties the pyrophyllite-bearing AAA rocks are distinguished which consist mainly of quartz, pyrophyllite and Fe-oxyhydroxides. Microscopic pseudocubic crystals of aluminium phosphate-sulphate (APS) minerals are found in all AAA varieties.

New geochemical data confirm the conclusions of Velinov (1967) for gradually extraction of most petrogenic components with the increasing of alteration degree and even SiO_2 and Al_2O_3 are depleted in alunite quartzites. The values of K_2O in alunite rocks are close to these in unaltered volcanics, while they are considerably higher in sericitic rocks (4.10%). The gain of Na_2O is seen in propylitic rocks as a result of formation of albite, while in sericitic and AAA rocks Na_2O, CaO and MgO are almost depleted.

Concentration of Sr decreases in propylitic and especially in sericitic rocks and significant increases in AAA rocks with high content in all varieties. This high Sr content is connected with the formation of APS minerals with svanbergite-woodhouseite composition as well as admixture in alunite. Rb has high content in sericitic rocks while the element is almost depleted in AAA rocks. The Rb/Sr ratio increases from 0.05 in unaltered rocks to 0.17 in propylitic and to 5.56 in sericitic rocks and strongly decreases to 0.002 in AAA rocks, showing the same trend as in other AAA zones in the Srednogorie and Rhodopes regions (Hikov, 2013). Zr, Ti, Cr, V, Ga, Hf, Nb, Ta, Th, U and partially Sn and Ba have comparatively inert behavior during alteration. Mn, Zn, Ni, Co, Cs and Y are mobile in different degree with a trend to complete extraction in the most altered rocks. As concentrates in AAA rocks, while Li – only in kaolinite AAA varieties. The concentrations of Cu and Pb are higher in unaltered rocks and in single altered samples possibly as a result of the ore mineralization. Ag has high contents in all samples, while Au – only in sericitic and alunitic rocks.

The chondrite-normalized REE pattern of propylitic rocks is very similar to the unaltered volcanic rocks, while significant depletion of all REE is seen in sericitic rocks. REE patterns in pyrophyllitic and kaolinitic rocks show strong fractionation of part of MREE and all HREE while LREE are comparatively inert with slight enrichment. REE patterns of alunitic rocks are characterized with slight depletion of LREE and strong depletion of MREE and HREE, which is stronger compare to pyrophyllitic and kaolinitic rocks.

Analyzed alunites from Breznik have Na-K composition with K/Na ratio between 4.6 and 1. Permanent admixtures of 2- and 3-valent cations reach to (*apfu*): Ca 0.245, Sr 0.076, Ba 0.047, Ce 0.019, La 0.004, Nd 0.009 as well as F 0.049 and Cl 0.008. Phosphorous usually is <0.132 *apfu* but sometimes gets to 0.450 *apfu* in mixed alunite-APS phases where admixtures of Ca, Sr, Ba and LREE are highest and K/Na ratio decreases. APS minerals themselves are woodhouseite and svanbergite-woodhouseite solid solutions. Calcium predominates over Sr and Ca/Sr ratio varies from 5.21 to 2.06. The highest Sr content gets to 0.246 *apfu* (5.67% SrO). P/S ratio usually is <1 but in some cases is >1. Permanent admixtures reach to (*apfu*): K 0.246, Na 0.243, Ba 0.076, La 0.016, Ce 0.025, Nd 0.009, F 0.046, Cl 0.010. Jarosite is another mineral from the alunite supergroup and is often seen as supergene product in the region. Its composition is characterized with lack of admixtures except a bit Ba and Al.

The isotopic study of Lerouge et al. (2007) shows very close $^{87}Sr/^{86}Sr$ ratio of alunite (0.704861) and jarosite (0.704858) which correspond to the range of $^{87}Sr/^{86}Sr$ for the volcanic rocks of the Srednogorie zone. Stable isotopes for alunite are: $\delta^{34}S$ = 18.9–24.1‰, $\delta^{18}O$ = 13.7–14.4‰, δD = –29‰ are characteristic of magmatic-hydrothermal alunite such as other alunite deposits from the Srednogorie zone. $\delta^{34}S$ of jarosite (12.9‰) is intermediate between $\delta^{34}S$ of alunite and sulfides which confirmed its supergene origin.

Discussion and conclusions

Geochemical study of hydrothermally altered rocks in the area of Breznik town shows a number of similar features with the same AAA zones in the Srednogorie belt. Advanced argillic altered rocks are characterized with concentration of Sr and As, extraction of Rb, characteristic REE patterns, magmatic-hydrothermal origin of alunite, typical presence of APS minerals with woodhouseite and svanbergite-woodhouseite composition, concentration of Li in kaolinitic AAA rocks, etc. (Lerouge et al., 2007; Hikov, 2013). All these features define a high sulphidation epithermal environment. Milin Kamak ore deposit is situated on the periphery of AAA zone and is described as Au-Ag intermediate sulphidation epithermal deposit with local development of high sulphidation epithermal type (Sabeva, 2015). Probably the erosion level does not allow rich high sulphidation ore concentrations to be found. On the other hand the idea of Moritz et al. (2007) for development of porphyry system at depth should not be rejected and need to be tested.

References

Crummy, J., I. Mutafchiev, I. Velinov, R. Petrunov. 2001. The Breznik epithermal Au occcurence, Western Srednogorie – Bulgaria: an "atypical" (?) low-sulphidation hydrothermal system. – In: Piestrzynski, A. et al. (Eds.). *Mineral Deposits at the Beginning of the 21st Centuty. Proc. of the Joint Sixth Biennial SGA-SEG Meeting*. Krakow, 723–726.

Dabovski, Ch., B. Kamenov, E. Vasilev, I. Bairaktarov. 2009. Upper Cretaceous Geology. – In: Zagorchev, I., Ch. Dabovski, T. Nikolov (Eds.). *Geology of Bulgaria. Volume II. Part 5. Mesozoic Geology*. Sofia, Prof. Marin Drinov Academic Publishing House, 423–553 (in Bulgarian with an English summary).

Hikov, A. 2013. *Geochemistry of Advanced Argillic Alteration Zones of Deposits from Srednogorie and Rhodopes Regions*. Abstract of PhD Thesis. Sofia, Geol. Ins., BAS, 62 p. (in Bulgarian).

Lerouge, C., A. Hikov, C. Beny, C. Flehoc, C. Guerrot, A. Kunov, Y. Yanev. 2007. Constraints of stable isotopes, Raman spectrometry on the formation of the advanced argillic alteration of the Breznik epithermal Au occurrence in Bulgaria – impact of weathering. – In: *Proc. of the 9th Biennial SGA Meeting*. Dublin, 885–888.

Moritz, R., R. Petrunov, S. Stoykov, J. Todorov, S. Strashimirov. 2007. The Breznik gold prospect, Late Cretaceous Srednegorie belt, Bulgaria: evidence for an epithermal system telescoping a porphyry environment. – In: *Proc. of the 9th Biennial SGA Meeting*. Dublin, 193–196.

Sabeva, R. 2015. *Milin Kamak Gold Deposit, Western Srednogorie: Hydrothermal Alteration, Mineral Composition, Genesis*. Unpublished PhD thesis. Sofia University, 180 p. (in Bulgarian).

Velinov, I. 1967. Propylites and alunite quartzites in the area of Breznik. – *Bull. Geol. Inst., Ser. Geochem., Mineral. and Petrogr.*, 16, 205–220 (in Bulgarian with an English abstract).