Geochemistry of advanced argillic altered rocks in the area of Breznik, Western Srednogie Unit (Bulgaria)

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Abstract. The distribution and behaviour of major and trace elements in the main zones of hydrothermal alteration (propylite, sericite and advanced argillic) in the area of Breznik Town have been studied, coupled with the chemical composition of alunite group minerals and their isotope geochemistry. The content of Sr decreases in propylite and especially in sericite rocks, and increases significantly in advanced argillic altered (AAA) rocks, which is connected with the formation of aluminium phosphate-sulphate (APS) minerals. Rubidium has high content in sericitic rocks, whereas the element is almost depleted in AAA rocks. The Rb/Sr ratio increases in sericitic rocks and strongly decreases in AAA rocks. Zirconium, Ti, Cr, V, Ga, Hf, Nb, Ta, Th, U and partially Sn and Ba have comparatively inert behaviour during alteration. Manganese, Zn, Ni, Co, Cs and Y are mobile in different degree, with a trend toward complete extraction in the most altered rocks. Arsenium concentrates in AAA rocks, while Li is concentrated only in kaolinite AAA rocks. LREE are comparatively inert in AAA rocks, while MREE and HREE are very mobile, especially in alunite rocks. Alunite has Na-K composition, with permanent admixtures of Ca, Sr, Ba and LREE. APS minerals themselves are woodhouseite and svanbergite-woodhouseite solid solutions (s.s.). Stable isotopes of alunite are characteristic for magmatic-hydrothermal alunite, whereas $\delta^{34}\text{S}$ of jarosite is intermediate between $\delta^{34}\text{S}$ of alunite and sulphides, which confirms its supergene origin. All these features define a high-sulphidation epithermal environment, and a possible porphyry mineralization at deeper part of the system is suggested.

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INTRODUCTION

The formation of hydrothermally altered rocks is commonly connected with ore deposition, and for that reason they both are considered as integral parts of hydrothermal ore deposits. Advanced argillic alteration (Meyer and Hemley, 1967) and metasomatic rocks of the secondary quartzite formation (Zharikov and Omel'yanenko, 1978), which are genetic analogues in the classification of wall rock alteration and the genetic classification of metasomatites (Kanazirski, 2011), are important criteria for prospecting of high-sulphidation epithermal Au deposits (Hedenquist *et al.*, 2000). More than 30 occurrences of advanced argillic alteration (secondary quartzites) are known in Bulgaria (Velinov *et al.*, 2007). They are concen-

trated mainly in the Srednogie Zone and the Central and Eastern Rhodopes. Some of them associate with porphyry copper and epithermal deposits. Similar link between hydrothermal alteration and epithermal mineralization is seen in the area of Breznik, but the ore potential of the magmatic-hydrothermal system has not been clarified completely. Petrological, mineralogical and metallogenic studies have been carried out, but geochemical features of hydrothermal alterations, especially the distribution and behaviour of trace elements, have been considered less well.

The aim of this study is to show the distribution of chemical elements in the alteration zones and to explain their behaviour during advanced argillic alteration and related metasomatic alterations, with special emphasis on trace elements. The study of the distribu-

tion of trace elements in the different alteration types will contribute to complete understanding of advanced argillic alteration, as well as to geochemical discrimination between ore forming and accompanying processes. Finally, the aim is to find geochemical criteria for distinguishing productive from unproductive alteration zones, as well as to find vectors to the mineralizing centre and potentially new ore mineralization.

GEOLOGICAL SETTING

The hydrothermal alteration zone is located in Bardoto area south of Breznik Town. The area belongs to the western part of the Srednogorie Zone (Fig. 1), which is a part of a regional Late Cretaceous island-arc (Boccaletti *et al.*, 1974). The Srednogorie Zone is also considered a part of a regional metallogenic belt with copper specialization (Vassileff and Stanisheva-Vassileva, 1981) or of the Apuseni–Banat–Timok–

Srednogorie (ABTS) magmatic and metallogenic belt (Popov *et al.*, 2002). The Western Srednogorie Unit is well differentiated tectonic unit known also as “Viskyar–Vitosha synclinorium” (Gočev *et al.*, 1970), “Sofia complex trough” (Bončev, 1971) or “Sofia synclinorium” (Vrablyanski, 1971). Upper Cretaceous (Turonian–Maastrichtian) sedimentary, volcano-sedimentary and volcanic rocks predominate. The age of the magmatic activity is Coniacian–Campanian (Dimitrova *et al.*, 1981).

The alteration zone is formed in the central part of the Breznik palaeovolcano (Bajraktarov and Mutafchiev, 1981), Breznik group volcanos (Nachev *et al.*, 1981) or Breznik magmatic centre (Panayotov *et al.*, 1982), which is a part of the Krasava anticline and the upper volcano-sedimentary unit (Campanian) in the Western Srednogorie Unit (Bajraktarov, 1989; Zagorchev *et al.*, 1995; Dabovski *et al.*, 2009). According to Marinova *et al.* (2010), these rocks belong to the Pyroclastic formation and intersect trachybasalts

Fig. 1. Geological sketch map of the Western Srednogorie Unit with the occurrences of the altered rocks (modified from Velinov *et al.*, 2007): 1 – “Tertiary”; 2 – Upper Cretaceous intrusive complex; 3 – Upper Cretaceous effusive complex; 4 – pre-Turonian formations; 5 – faults; occurrences of altered rocks: 6 – contact hydrothermally altered rock (uralitized) andesite lava-breccias, 7 – quartz-sericite-adularia, quartz-adularia and propylite rocks, 8 – propylites, argillites and quartz-sericite rocks, 9 – secondary quartzites (advanced argillic rocks).

and shoshonites from the “Babski Volcanic Complex” of early Campanian age. The host rocks are mainly pyroclastic, rarely lava flows, subvolcanic bodies and dykes. The lava breccias are most abundant, mainly composed of fragments of andesites (Belev, 1967; Dimitrov and Belev, 1970), basaltic andesites and trachybasalts (Velinov, 1967; Bajraktarov, 1989) or alkaline basalts (Marinov and Bajraktarov, 1980). The mineral composition consists of plagioclase, pyroxene $\pm$ olivine, rarely amphibole and volcanic glass groundmass with some primary and secondary minerals.

HYDROTHERMAL ALTERATION

The zone with hydrothermally altered rocks has been mapped by a geological team (see Velinov, 1967). Regional propylites and locally developed alterations in the tectonic faults have been identified for the re-

gion. The Breznik zone has been referred to the second type and only quartz-sericite facies has been spatially determined, while the other facies are thought to be encountered jointly. The mineralogical and petrological investigations of Velinov (1967) showed a development of propylites (epidote-chlorite-albite, actinolite-epidote-chlorite, quartz-epidote-sericite and quartz-sericite), as well as alunite secondary quartzites (Fig. 2). The alunite quartzites occupy the innermost parts of the altered zone and form positive geomorphological relief. Two bodies of alunite quartzites (both about 0.5 km²) are described. They are composed of quartz, chalcedony, quartzine, alunite, rutile, pyrite, Fe-hydroxides and jarosite. Alunite is fine-grained, with Na-K composition, and gets to 30–40% in the rich sections.

Crummy *et al.* (2001) outlined zonal development of the quartz-kaolinite-alunite, quartz-sericite and propylite alteration types, as well as a later quartz-

Fig. 2. Schematic geological map of the Breznik area (Velinov, 1967; Velinov *et al.*, 2007): 1 – “Tertiary” sediments; Upper Cretaceous; 2 – agglomerate tuffs with trachybasalt clasts, epidote-chlorite-albite alteration, 3 – tuff-marly complex; altered rocks: 4 – alunite quartzites, 5 – quartz-sericite rocks, 6 – quartz-epidote-sericite rocks, 7 – actinolite-epidote-chlorite rocks, 8 – urallite-epidote-chlorite rocks.

sericite-carbonate one. The scarce high-sulphidation (enargite-luzonite) mineralization is developed under and into quartz-kaolinite-alunite and quartz-sericite rocks. The rich gold-bearing quartz-sericite-carbonate mineralization is superimposed on the earlier altered rocks. The authors' opinion is that this low-sulphidation type can be classified as "atypical" epithermal gold manifestation with or without sporadic development of adularia. Moritz *et al.* (2007) discussed juxtaposed high- and low-sulphidation epithermal styles of mineralization, which telescope a porphyry system. Stoykov *et al.* (2007) described ore mineralization that is characteristic for low-temperature epithermal ore deposits. Lerouge *et al.* (2007) proved magmatic-hydrothermal origin of alunite, K-Na zoning of alunite and APS minerals.

Several stages of exploration works were carried out on the Breznik area between 1970 and 2010. Panayotov *et al.* (1982) concluded that the Bardoto ore occurrence is perspective for porphyry copper and base metal mineralizations. Bajraktarov (1989, 1994) defined the Breznik prospective zone with ore occurrences Bardoto (pyrite subformation) and Gorski Dom (pyrolusite-psilomelane-hematite formation). He noted that the zone has potential for prospecting for Au-alunite and Fe-Mn mineralizations, as well as for alunite raw material. As a result of successive exploration work by the company "Trace Resources Ltd", in 2011 the Bardoto occurrence was declared as Milin Kamak ore deposit. At the base case cut-off grade of 2 g/t gold, the inferred resource is 2,439,000 tonnes grading 5.91 g/t Au and 26.78 g/t Ag (Carter, 2011). Sabeva (2015) defined the Milin Kamak ore deposit as Au-Ag intermediate sulphidation type epithermal deposit with local manifestation of high-sulphidation type. She also described limited development of intermediate argillic and transitional propylite-sericite alteration types.

ANALYTICAL METHODS

Representative samples from the main hydrothermal alteration types were collected to characterize the geochemistry of altered rocks from the Breznik area. Detailed study of each sample was carried out to define precisely the alteration type and its place in the altera-

tion zoning. Mineral composition of altered rocks was examined in thin-sections, supported by X-ray diffraction (XRD) and differential-thermal analyses (DTA) at the Geological Institute of BAS, Sofia. Alunite and aluminium-phosphate-sulphate (APS) minerals were analysed by an electron microprobe Camebax SX50 in BRGM (Orléans, France). The analyses were made by EDS system with acceleration voltage 15–20 keV and current beam 2–6 nA. Raman spectrometry was used to characterize alunite and APS minerals. The spectra were performed, using an XY800 DILOR equipped with an Olympus microscope (objx80ULWD), an exciting radiation of 514.5 nm of ionized argon laser (50 mW) in BRGM (Orléans, France).

The whole rocks' chemical composition was studied with X-ray fluorescent (XRF) analysis for the major elements; ICP-EAS for Cr, V, Cu, Zn, Ni, Co, Ag and Ga; atomic absorption (AA) analysis for Li; and LA-ICP-MS for Ba, Zr, Sr, Rb, Pb, Sn, Y, Hf, Ta, Nb, Cs, U, Th, As, Sb, Te, Bi, REE and Au at the Geological Institute (BAS, Sofia). One sample of alunite rock was analysed by ICP-MS at Acme Labs Ltd (Vancouver, Canada). Isotope data on Sr, S, O and H were obtained at the Laboratory of Stable Isotopes and Low Radioactivity of the BRGM (Orléans, France). Oxygen, sulphur and hydrogen isotopes of alunite were analysed, using the analytical methods described by Lerouge *et al.* (2006).

GEOCHEMISTRY

Geochemistry of alteration zones

The main hydrothermal alteration types were sampled to clarify the geochemical features of advanced argillic altered rocks. The distribution and behaviour of chemical elements with the increasing alteration degree from unaltered volcanic rocks to propylite, sericite (Fig. 3a–c) and advanced argillic altered rocks were studied. Only the most widespread and characteristic epidote-chlorite-albite±carbonate propylitic alteration type was examined. Advanced argillic altered rocks (secondary quartzites) consist of three different types. Besides the known alunite and alunite-kaolinite alterations (Fig. 3d, e), the pyrophyllite-bearing advanced argillic rocks were distinguished during this

Fig. 3. Microphotographs of fresh and altered rocks from the Breznik area: a) plagioclase (Pl) and pyroxene (Px) porphyries in unaltered trachybasalt (crossed polarizers); b) albite (Ab), chlorite (Chl), epidote (Ep) and carbonate (Ct) in propylite rock (plane-polarized light); c) sericite (Ser), quartz (Qtz) and pyrite (Py) in sericite rock (plane-polarized light); d) quartz (Qtz) and alunite (Alu) in alunite advanced argillic rock (crossed polarizers); e) quartz (Qtz) and kaolinite (Kaol) in kaolinite advanced argillic rock (crossed polarizers); f) quartz (Qtz) and pyrophyllite (Pyr) in pyrophyllite advanced argillic rock (crossed polarizers); g) core of APS mineral in alunite (Alu) among quartz (Qtz) (plane-polarized light); h) APS minerals, rutile (Rut) and kaolinite (Kaol) in kaolinite advanced argillic rock (plane-polarized light).

study. These consist of mainly quartz, pyrophyllite and Fe-oxyhydroxides (Fig. 3f). All advanced argillic altered types contain aluminium-phosphate-sulphate (APS) minerals (woodhouseite and svanbergite-woodhouseite s.s.). They usually occur as microscopic pseudocubic crystals, which can form cores of alunite crystals (Figs 3g, h, 4). The composition of mineral water, which springs from the alteration zone, was also analysed.

Statistically unrepresentative “mean value” is used in Table 1 and Fig. 5 to show the main trends of behaviour of chemical elements in advanced argillic rocks. When a single element behaved differently in different advanced argillic alteration types, conclusions were made separately for each alteration type.

New geochemical data confirm the conclusions of Velinov (1967) for gradual extraction of most major elements with increase of the alteration degree (Table 1; Fig. 5a), and even SiO_2 and Al_2O_3 are partly mobile in advanced argillic altered rocks. The contents of K_2O in alunite rocks are close to these in unaltered volcanic rocks; they are considerably higher in sericitic rocks (4.10%), while the element is fully extracted from kaolinite and pyrophyllite altered rocks. Na_2O concentrates in propylite rocks, which is connected with the formation of albite, and decreases in sericite and in advanced argillic rocks, where it can be included only in alunite, APS minerals and probably sericite. CaO and MgO weakly decrease in propylite rocks because of the presence of epidote, carbonate and chlorite and are almost depleted in sericite and advanced argillic rocks.

Concentration of Sr (955 ppm in unaltered volcanic rocks) decreases in propylite (492 ppm) and especially in sericite rocks (31 ppm) and increases significantly in advanced argillic altered rocks (mean

2010 ppm) (Table 1; Fig. 5b). Strontium values are high in all types of advanced argillic alteration, being highest in the kaolinite type (3340 ppm). This high-Sr content is connected with the formation of APS minerals with svanbergite-woodhouseite composition, as well as admixture in alunite whose compositions will be discussed below.

Rubidium content increases in K-bearing sericite rocks (Fig. 5b), while the element is almost depleted in advanced argillic altered rocks, despite the significant K_2O concentration in alunite rocks. The Rb/Sr ratio increases from 0.05 in unaltered rocks to 0.17 in propylite and to 5.56 in sericite rocks and strongly decreases to 0.002 in advanced argillic altered rocks (Fig. 5d).

The elements Ni, Co and Y show different degrees of mobility, with a trend to complete extraction in the most altered rocks, while other elements concentrate in a single zone (e.g., Mn and Zn in propylite and Cs in sericite) and are depleted in the rest of the zones (Fig. 5c, g). Zirconium, Ti, V, Ga, Hf, Nb, Th, U and, to a lesser extent, Cr, Ta, Sn and Ba have comparatively inert behaviour during hydrothermal alteration (Fig. 5e, f). Arsenium concentrates several times in advanced argillic altered rocks, while Li increases only in kaolinite-containing advanced argillic rocks (Fig. 5h). Antimony, Te and Bi tend to concentrate in sericite and advanced argillic rocks, with the highest contents in kaolinite rocks.

The concentrations of Cu and Pb (Fig. 5g) are higher in unaltered volcanic rocks and especially in single altered samples, possibly as a result of the ore mineralization. For that reason, conclusions about their behaviour during hydrothermal alteration cannot be made. Silver has permanent comparatively high contents in all samples (Fig. 5f), while Au is detected

Fig. 4. BSE images of alunite and APS minerals from the Breznik area: a) alunite with K-Na chemical zoning; b) heapings of microscopic pseudocubic APS crystals among alunite and kaolinite.

Table 1
Chemical composition of hydrothermally altered rocks from the area of Breznik

Sample	646	647	648	643	644	645	645A	Mean
Rocks	1	2	3	4(Kaol)	4(Pyr)	4(Al)	4(Al)	4
SiO ₂ , %	51.02	47.95	69.53	62.15	64.39	58.09	54.25	1.16
TiO ₂	0.87	0.70	0.99	1.33	1.15	1.03	1.11	
Al ₂ O ₃	14.62	14.19	14.65	20.04	10.52	15.36	13.04	
Fe ₂ O ₃ ^t	10.55	6.84	1.52	6.23	15.52	1.94	9.47	
MnO	0.14	0.28	0.03	0.007	0.011	0.002	0.003	0.006
MgO	5.49	2.65	0.1	0.06	0.06	0.04	0.08	0.06
CaO	8.72	7.18	0.3	0.42	0.48	0.34	0.73	0.49
Na ₂ O	2.97	4.85	0.65	0.58	0.69	0.55	0.35	0.54
K ₂ O	2.53	2.98	4.1	0.16	0.15	2.37	2.30	1.25
P ₂ O ₅	0.49	0.39	0.11	0.53	0.66	0.41	0.53	0.53
LOI	2.64	12.27	7.7	8.6	7.01	20.33	18.18	
Sum	100.04	100.28	99.68	100.04	100.57	100.42	100.04	
Ba, ppm	498.85	532.01	223.09	196.13	200.08	3266.12	434.6	1024.23
Zr	123.27	120.55	110.20	135.12	109.74	110.91	94.60	112.59
Sr	954.91	491.74	30.94	3339.86	1337.74	1838.91	1526	2010.63
Rb	48.10	85.16	172.16	2.58	2.57	5.66	8.40	4.80
Cr	70.80	7.70	24.40	21.40	45.30	83.70	62.00	53.10
V	208.50	153.60	214.10	244.60	308.40	114.50	201.00	217.13
Cu	119.40	33.60	12.40	476.60	154.40	36.20	51.19	179.60
Zn	113.00	171.30	42.50	49.30	23.70	12.70	9.10	23.70
Pb	16.80	19.87	449.57	301.24	0.13	302.26	413.40	254.26
Ni	35.00	8.60	2.70	6.90	3.50	2.90	1.70	3.75
Co	29.80	16.50	7.80	9.40	9.00	6.80	0.90	6.53
Li	8.00	12.00	5.00	78.00	14.00	6.00	5.00	25.75
Ag	4.50	2.70	3.80	6.90	2.30	3.30	0.27	3.19
Au	<0.06	<0.06	<0.08	0.27	0.08	<0.07	0.05	
Sn	3.41	4.15	2.66	6.82	4.01	13.32	4.50	7.16
Ga	21.80	19.20	19.00	33.10	22.80	13.90	12.76	20.64
Y	23.99	23.72	8.11	12.42	8.76	4.97	3.40	7.39
Hf	3.49	3.04	2.79	3.34	2.74	2.82	1.49	2.60
Ta	1.81	1.13	6.34	5.34	5.08	2.61	0.10	3.28
Nb	7.72	7.95	9.23	10.21	23.78	6.85	2.00	10.71
Cs	0.99	3.45	4.56	0.12	0.14	0.18	0.05	0.12
U	2.48	1.58	2.02	3.17	2.28	1.68	1.50	2.16
Th	7.90	6.71	4.40	7.88	6.22	6.55	4.10	6.19
As	6.19	<8.00	12.80	144.29	166.59	48.65	305.5	166.26
Sb	0.96	2.21	6.44	12.42	5.11	2.80	3.02	5.83
Te	2.61	3.39	4.84	6.97	6.35	5.35		6.22
Bi	0.45	0.64	1.12	7.80	1.68	1.68	1.87	3.26
La	30.99	26.04	12.87	36.71	31.22	18.26	14.60	25.20
Ce	65.04	53.23	26.90	78.00	69.89	36.79	33.42	54.53
Pr	8.36	6.70	3.16	9.89	8.59	4.42	5.30	7.05
Nd	36.10	28.80	14.29	43.42	39.03	18.97	23.00	31.10
Sm	7.38	5.78	2.45	9.42	7.71	3.39	4.10	6.15
Eu	2.10	1.36	0.74	3.27	1.67	1.17	1.00	1.78
Gd	6.14	5.13	2.36	6.55	5.78	1.80	2.50	4.16
Tb	0.90	0.75	0.24	0.55	0.56	0.14	0.20	0.36
Dy	4.80	4.38	1.47	2.39	2.47	0.87	0.90	1.66
Ho	0.86	0.87	0.28	0.46	0.37	0.16	0.10	0.27
Er	2.50	2.42	0.94	1.22	0.91	0.70	0.60	0.86
Tm	0.28	0.33	0.13	0.22	0.16	0.14	0.05	0.14
Yb	2.49	1.99	1.38	1.72	1.13	0.95	0.50	1.08
Lu	0.35	0.32	0.15	0.29	0.19	0.16	0.05	0.17
ΣREE	168.31	138.11	67.35	194.11	169.66	87.94	86.32	134.51
Rb/Sr	0.050	0.173	5.564	0.001	0.002	0.003	0.006	0.002

Rocks: 1 – unaltered trachybasalt; 2 – propylitic; 3 – sericitic; 4 – advanced argillic; 4(Kaol) – kaolinite, 4(Pyr) – pyrophyllite, 4(Al) – alunite.

only in advanced argillic altered rocks, being highest in kaolinite (0.27 ppm) rocks.

The chondrite-normalized REE pattern of propylite rocks is very similar to the unaltered volcanic rocks,

while significant depletion of all REE is seen in sericite rocks (Fig. 6a). REE patterns of pyrophyllite and kaolinite rocks show fractionation of some MREE and all HREE, while LREE are comparatively inert, with slight

Fig. 5. Distribution of some major and trace elements in the zones of hydrothermal alteration from the Breznik area: 1 – unaltered volcanic rocks; 2 – propylitic; 3 – sericitic; 4 – advanced argillic altered rocks.

enrichment (Fig. 6b). REE patterns of alunite rocks are characterized with slight depletion of LREE and strong depletion of MREE and HREE, which is stronger compared to pyrophyllite and kaolinite rocks (Fig. 6b).

Fig. 6. Chondrite-normalized REE patterns of fresh and altered volcanic rocks from the Breznik area: *volc* – unaltered volcanic rocks; *prop* – propylitic; *ser* – sericitic; advanced argillic altered rocks: *kaol* – kaolinite, *pyr* – pyrophyllite, *alu* – alunite.

Geochemistry of alunite group minerals

Alunite is the main mineral of alunite quartzites in the area of Breznik. Electron microprobe analyses of alunite provide evidence of K/Na ratio between 4.6 and 1 (Table 2; Fig. 7). Chemical K-Na zoning in alunite is often seen (Fig. 4a), which is also well documented with Raman spectroscopy (Fig. 8). 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 is usually <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.

Aluminium phosphate-sulphate minerals are permanent admixtures in all advanced argillic altered types, usually as microscopic pseudocubic crystals. APS minerals often form the cores of alunite crystals (Fig. 4b), but the different phases are well identified by Raman spectroscopy (Fig. 8). The composition of APS minerals shows that they are mainly woodhouseite and svanbergite-woodhouseite s.s. (Table 2; Figs 7, 9). Calcium predominates over strontium and Ca/Sr ratio varies from 5.21 to 2.06. The highest Sr content reaches up to 0.246 *apfu* (5.67% SrO). Phosphorus/sulphur ratio is usually <1 but in some cases is >1 (Fig. 9). 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 that is often seen as supergene product in the region. Its composition is characterized by lack of admixtures, except for small contents of Ba and Al (Table 2; Fig. 7a).

Fig. 7. D position diagrams of alunite and APS minerals: a) K–Na–(Ca+Sr+Ba+REE); b) (K+Na)–(Ca+Sr+Ba)–REE.

Table 2
Electron microprobe analyses (wt.%) of alunite, APS minerals and jarosite from the area of Breznik

Sample	52	53	63	91	92	65	57	58	88	93	94	96	97	98	99	100	116
Mineral	Alu	Alu	Alu	Alu	Alu-APS s.s.	Alu-APS s.s.	Alu-APS s.s.	APS s.s.	APS s.s.	APS s.s.	APS s.s.	Wh	Wh	Wh	Wh	Wh	Jar
K ₂ O	5.79	7.16	6.46	5.44	2.47	3.63	5.22	2.81	1.27	1.34	1.57	1.00	0.61	1.05	0.51	0.90	8.79
Na ₂ O	2.05	1.61	2.48	1.76	0.59	2.34	1.41	1.70	0.54	1.02	0.69	0.63	0.53	0.76	0.29	0.50	—
CaO	1.45	0.96	0.50	0.40	2.79	2.63	3.15	4.91	5.90	5.27	5.70	6.53	6.83	7.35	6.32	6.36	—
SrO	0.38	0.30	0.17	0.13	1.59	1.51	0.89	1.75	2.97	3.66	2.76	4.22	4.54	2.61	5.67	3.92	—
BaO	0.35	0.81	0.69	—	0.87	0.93	1.42	2.18	0.96	2.56	0.92	0.92	1.93	1.44	2.16	1.45	0.49
La ₂ O ₃	—	—	—	—	0.01	—	0.16	0.15	—	0.09	0.43	—	0.32	—	0.60	—	—
Ce ₂ O ₃	0.08	0.14	0.08	—	0.41	0.45	0.31	0.47	0.73	0.79	0.19	0.71	0.90	0.34	0.58	0.64	—
Nd ₂ O ₃	0.09	—	—	—	—	—	—	—	0.19	—	0.04	—	—	—	0.35	—	—
Al ₂ O ₃	34.44	33.90	35.44	41.47	36.82	32.96	32.96	33.16	36.54	35.91	35.71	34.53	33.71	35.18	34.04	34.62	0.14
Fe ₂ O ₃	0.30	0.71	0.03	0.10	0.02	0.68	1.11	0.48	—	0.01	0.05	0.21	—	—	0.11	—	44.64
SO ₃	35.20	35.30	37.92	39.47	29.45	31.16	31.57	25.12	20.90	19.64	22.52	19.82	16.39	19.05	16.13	18.66	27.56
P ₂ O ₅	2.16	1.75	0.87	0.57	7.34	5.88	5.54	10.81	13.42	13.68	13.58	14.42	17.43	16.66	17.93	16.50	—
Cl	—	0.04	—	—	0.07	0.03	0.05	—	0.02	0.07	0.05	0.08	0.04	0.02	0.04	0.078	—
F	0.20	—	—	—	—	—	—	—	—	—	0.11	—	0.06	0.20	0.04	0.13	—
Total	82.49	82.66	84.64	89.33	82.43	82.21	83.76	83.52	83.42	84.04	84.32	83.06	83.27	84.68	84.75	83.74	81.66
Structural formulae calculated on the basis of 11 Ox.																	
K	0.53	0.66	0.58	0.45	0.23	0.34	0.48	0.26	0.12	0.13	0.14	0.09	0.06	0.10	0.05	0.08	1.08
Na	0.29	0.23	0.34	0.22	0.08	0.33	0.20	0.24	0.08	0.15	0.09	0.09	0.08	0.11	0.04	0.07	—
Ca	0.11	0.07	0.04	0.03	0.21	0.21	0.25	0.39	0.46	0.42	0.42	0.50	0.55	0.57	0.51	0.50	—
Sr	0.02	0.01	0.01	0.00	0.07	0.06	0.04	0.07	0.13	0.16	0.11	0.18	0.20	0.11	0.25	0.17	—
Ba	0.01	0.02	0.02	—	0.02	0.03	0.04	0.06	0.03	0.07	0.02	0.03	0.06	0.04	0.06	0.04	0.02
La	—	—	—	—	0.00	—	0.00	0.00	—	0.00	0.01	—	0.01	—	0.02	—	—
Ce	0.00	0.00	0.00	—	0.01	0.01	0.01	0.01	0.02	0.02	0.00	0.02	0.02	0.01	0.02	0.02	—
Nd	0.00	—	—	—	—	—	—	—	0.00	—	0.00	—	—	—	0.01	—	—
Al	2.92	2.89	2.91	3.18	3.10	2.84	2.82	2.88	3.15	3.14	2.90	2.91	2.97	2.99	3.00	3.00	0.02
Fe	0.02	0.04	0.00	0.01	0.00	0.04	0.06	0.03	—	0.00	0.00	0.01	—	—	0.01	—	3.40
S	1.90	1.92	1.99	1.93	1.58	1.71	1.72	1.39	1.15	1.09	1.16	1.06	0.92	1.03	0.91	1.03	2.00
P	0.13	0.11	0.05	0.03	0.44	0.36	0.34	0.67	0.83	0.86	0.79	0.87	1.10	1.02	1.14	1.03	—
Cl	—	0.005	—	—	0.01	0.004	0.006	—	0.002	0.01	0.01	0.01	0.005	0.002	0.005	0.01	—
F	0.05	—	—	—	—	—	—	—	—	—	0.02	—	0.01	0.05	0.01	0.03	—

Alu – alunite; APS s.s. – aluminium phosphate-sulphate solid solutions; Wh – woodhouseite; Jar – jarosite

Fig. 8. Raman spectra of pseudocubic grains of APS mineral and of zoned tabular alunite (K-rich and Na-rich).

Chemistry of mineral water

Mineral water was sampled in the source crosscutting the zone of hydrothermal alteration. The water is orange, due to its high iron concentration. The pH in the source was measured at 3. The chemical analysis of

water also shows significant concentration of Ca, Mg, SO_4^{2-} , Sr and Rb (Table 3).

The low pH may be due to the weathering of sulphides, but also to the equilibration of water with advanced argillic alteration. The water chemistry results from the weathering of fresh and hydrothermally altered volcanic rocks. This is the present-day acid-sulphate alteration at low temperatures. The high concentrations of Fe, Ca, Mg, Sr and Rb are a result of leaching of propylite and sericite altered rocks and correspond to our data for the zones of hydrothermal alteration in Breznik area and in the Srednogie Zone (Hikov, 2013). On the other hand, the low concentrations of PO_4^{3-} , K and Na could be partly explained by the secondary deposition of APS minerals, alunite and jarosite.

Table 3
Chemical composition of water of Breznik (mg/l)

Ca	Cl	Fe*	K	Mg	Na	PO_4	SO_4	Rb	Sr
430	8	550	5	239	11	0.3	4218	19	314

* after Vladeva *et al.* (2001)

Fig. 9. Composition of alunite and APS minerals from the Breznik area.

Isotope geochemistry

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of alunite (0.704861) from Breznik area (Table 4) is quite close to the range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that characterize the magmatism of the Timok–Srednogorie belt [0.7039–0.7061 after 85–90 Ma correction (von Quadt *et al.*, 2003; Kouzmanov *et al.*, 2009)]. This data confirm the magmatic-hydrothermal origin of the alunite of Breznik (Lerouge *et al.*, 2006). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of jarosite (0.704858) is close to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of alunite, suggesting a common source of strontium for both sulphates. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the water (0.705459) is slightly higher than

Table 4

Strontium, sulfur, oxygen and hydrogen isotopic composition of water, alunite (Alu) and jarosite (Jar) from the area of Breznik

Isotopic signature	water	alunite rocks
$^{87}\text{Sr}/^{86}\text{Sr}$ water	0.705459	
$^{87}\text{Sr}/^{86}\text{Sr}$ Alu		0.704861
$^{87}\text{Sr}/^{86}\text{Sr}$ Jar		0.704858
$\delta^{34}\text{S}_{\text{SO}_4}$ (CDT)	+3.6‰	
$\delta^{34}\text{S}$ Alu		24.1–18.9‰
$\delta^{34}\text{S}$ Jar		12.9‰
$\delta^{18}\text{O}_{\text{water}}$ (V-SMOW)	–10.6‰	
$\delta^{18}\text{O}_{\text{SO}_4}$	–4.7‰	
$\delta^{18}\text{O}$ Alu		13.7–14.4‰
$\delta^{18}\text{O}$ Jar		11.3‰
$\delta\text{D}_{\text{water}}$ (V-SMOW)	–71‰	
δD Alu		–29‰

the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of alunite and jarosite, but remains in the range of the volcanism of the Timok–Srednogorie belt.

The $\delta^{34}\text{S}$ of sulphates in water at +3.6‰ is slightly higher than the $\delta^{34}\text{S}$ of sulphides of magmatic origin from the porphyry copper and epithermal deposits from the Panagyurishte District (Kouzmanov *et al.*, 2003; Lerouge *et al.*, 2006) and from the Timok District (Lerouge *et al.*, 2005), as well as from the Milin Kamak epithermal Au–Ag deposit (Sabeva, 2015). The $\delta^{34}\text{S}$ values (18.9–24.1‰) of alunite from Breznik area are characteristic of magmatic hydrothermal alunite (Rye *et al.*, 1992), while the $\delta^{18}\text{O}$ (13.7–14.4‰) and δD (–29‰) of alunite show precipitation of magmatic fluids with meteoric waters (Lerouge *et al.*, 2006). These data are very similar to the other alunite manifestations from the Srednogorie Zone (Lerouge *et al.*, 2006). The $\delta^{34}\text{S}$ of jarosite (12.9‰) is intermediate between $\delta^{34}\text{S}$ of sulphides and $\delta^{34}\text{S}$ of alunite. That could suggest a preferential mobilization of sulphides

during the weathering, but also a slight destabilization of alunite.

DISCUSSION

The Upper Cretaceous volcanic rocks from the Breznik area were affected by intensive hydrothermal alteration of propylite, sericite and advanced argillic types. Alunite, kaolinite and pyrophyllite advanced argillic rocks have been distinguished. Advanced argillic alteration results from extremely acid (pH <2), rich in volatiles (CO_3^{2-} , F^- , Cl^- , SO_4^{2-}) magmatic-hydrothermal fluids of temperature mostly between 200 °C and 300 °C (Meyer and Hemley, 1967; Hemley *et al.*, 1980; Zharikov *et al.*, 1998; Velinov *et al.*, 2007). During hydrothermal alteration, a significant to complete change of mineral and chemical composition of the parent rocks occurred.

The distribution and behaviour of main and trace elements in advanced argillic altered rocks and accompanying hydrothermal alterations in the area of Breznik show several common features with similar hydrothermal alteration zones from the Central and Western Srednogorie and from the Rhodopes (Hikov, 2013). Most characteristic is the behaviour of Sr. The element is depleted from the outer propylite and sericite alteration zones and is accumulated in the inner zones of advanced argillic alteration. The concentration of Sr is connected with the formation of new strontium minerals. These are aluminium phosphate-sulphate (APS) minerals: woodhouseite and svanbergite-woodhouseite s.s. APS minerals form in a broad interval of pH (3–8) and high activity of PO_4^{3-} (Stoffregen and Alpers, 1987; Ripp *et al.*, 1998; Schwab *et al.*, 2005). The presence of phosphate anion PO_4^{3-} (after apatite dissolution) is crucially important. Apatite is fully preserved in propylitic, partially dissolved in sericitic and completely dissolved in advanced argillic rocks in a low-pH environment (Stoffregen and Alpers, 1987). The liberated PO_4^{3-} and Ca^{2+} do not move out with the solutions but, together with added Sr^{2+} and SO_4^{2-} from fluids, form new APS minerals. According to Stoffregen and Alpers (1987), APS minerals can coexist with alunite and kaolinite at 250 °C and with pyrophyllite between 270 °C and 350 °C. Part of the strontium is also included in alunite and alunite–APS s.s. (Kashkai, 1970; Hikov, 2004; Hikov *et al.*, 2010; Chang *et al.*, 2011; Georgieva and Velinova, 2012). Similar Sr behaviour has been established in advanced argillic alteration zones from Asarel, Pesovets, Petelovo, Chelopech, Klisura and Spahievo deposits from the Srednogorie Zone and the Rhodopes (Hikov, 2004; Georgieva and Hikov, 2016) and also in other porphyry copper and high-sulphidation epithermal deposits (Schwartz, 1981; Bove and Hon, 1990; Arribas *et al.*, 1995). Permanent presence of APS minerals in the zones of advanced argillic alteration has been documented (Stoffregen and Alpers, 1987; Aoki

et al., 1993; Hedenquist *et al.*, 1994; Dill, 2001; Georgieva *et al.*, 2002; Kunov *et al.*, 2006; Khashgerel *et al.*, 2008; Hikov *et al.*, 2010; Voudouris and Melfos, 2013). The distribution and behaviour of Sr in altered rocks in the area of Breznik confirms the hypothesis that “the accumulation of Sr is a characteristic feature of the process of advanced argillic alteration of volcanic rocks” (Hikov, 2002) and is probably a widespread phenomenon. High concentrations of strontium should be expected everywhere where advanced argillic alteration occurs, because it leads to strontium re-distribution and accumulation. This may be an additional tool in geochemical mapping of advanced argillic alteration zones.

Several elements, such as Rb, Cs, Mn, Ni, Co, Y, HREE, etc., are very mobile and are depleted in advanced argillic zones. Rubidium, in contrast to the other elements, is accumulated in sericite rocks, being fully depleted in advanced argillic altered rocks. The behaviour of Rb is opposite to that of Sr, which leads to high Rb/Sr ratio in sericite rocks and extremely low Rb/Sr ratio in advanced argillic altered rocks, as in other advanced argillic altered zones from the Srednogie Zone and the Rhodopes (Hikov, 2004). Thus, the Rb/Sr ratio should be recommended for geochemical prospecting. Anomalously low values of Rb/Sr ratio are typical for advanced argillic zones and suggest high-sulphidation epithermal system, while high values are characteristic for sericite rocks and could be perspective for prospecting of porphyry copper or low-sulphidation epithermal mineralization (Armbrust *et al.*, 1977; Arribas *et al.*, 1995; Hikov, 2004).

Low mobility of LREE and pronounced mobility of MREE and HREE have been registered in advanced argillic alteration zones from Breznik area, which is characteristic for advanced argillic zones from the Central Srednogie Unit (Hikov, 2014; Georgieva and Hikov, 2016). The mobility of MREE and HREE is connected with the high activity of F⁻, low pH of the fluids, high water/rock ratio and their ability to form stable complexes in these conditions (Lottermoser, 1992; Fulignati *et al.*, 1999). LREE are relatively immobile (with slight enrichment in kaolinite and pyrophyllite rocks), due to their entrance in the lattice of appropriate minerals like alunite, APS minerals and clay minerals (Aja, 1998; Fulignati *et al.*, 1999; Kikawada *et al.*, 2004; Hikov *et al.*, 2010). APS minerals are usually vanbergite-woodhouseite s.s., but locally florencite may form (Hikov *et al.*, 2010; Georgieva and Velinova, 2014). The slight depletion of LREE in alunite rocks from Breznik area is probably due to the prolonged influence of extremely acid fluids, which have not allowed all LREE to include in the newly forming minerals.

Comparatively inert behaviour during hydrothermal alteration have Zr, Ti, V, Ga, Hf, Nb, Th, U and, to a lesser extent, Cr, Ta, Sn and Ba. This is due to the relative stability of their minerals (titanite, zircon, apatite) in the outer propylite and sericite alteration

zones. During advanced argillic alteration, these minerals are dissolved, the majority of MREE and HREE are liberated and migrate, having high mobility under these conditions. The elements Ti, V and Zr do not migrate, and form new mineral phases: rutile and microscopic zirconium phases [zircon and/or baddeleyite (Hikov, 2013)], which concentrate Ti, V, Sn, Nb, Ta, Zr, Hf, partially U, Th, etc. LREE and other inert elements take part in alunite and APS minerals. Alunite and APS minerals are characteristic for advanced argillic alteration and high-sulphidation epithermal deposits (Sillitoe and Hedenquist, 2003) but also control the geochemistry of a number of chemical elements, which concentrate or are immobile in advanced argillic zones (Hikov, 2013). These are K, Na, Ca, Sr, Ba, P, La, Ce, Nd and, partly, Pb (Chang *et al.*, 2011; Hikov, 2013), in some cases Ga (Boriskin, 1967; Ryktuba *et al.*, 2003), Sc and V (Kashkai, 1970), U and Th (Khashgerel *et al.*, 2008).

Arsenium concentrates several times in advanced argillic altered rocks, which, together with the higher contents of Sb, Te and Bi, is indication of high-sulphidation epithermal environment (Hedenquist *et al.*, 2000). Increased concentration of Li is documented only in kaolinite-containing advanced argillic rocks, where Li is possibly included in the crystal lattice of kaolinite (Starkey, 1982). The same behaviour of Li has been registered in other hydrothermal alteration zones from the Srednogie Zone and the Rhodopes (Hikov, 2013).

The isotope data show magmatic-hydrothermal origin of alunite, as well as the volcanic host rocks as a source for Sr (von Quadt *et al.*, 2003; Lerouge *et al.*, 2006; Kouzmanov *et al.*, 2009). This confirms the assumption of Sr redistribution during advanced argillic alteration and related alteration types without support from any outer source (Hikov, 2004, 2013). It is not excluded that some APS minerals have supergene origin, but most of them are formed during advanced argillic alteration close to, together or just later than the alunite. Despite of the variable compositions of alunite and APS minerals, their formation can be associated with a single fluid with the gradual depletion of its individual components (Figs 7a, 9). APS minerals occur in the alunite zone, but also in kaolinite and in pyrophyllite advanced argillic rocks. Their presence in pyrophyllite zone strongly suggests that APS minerals are formed at temperatures about or over 300 °C (Hemley *et al.*, 1980; Stoffregen and Alpers, 1987).

Nowadays, as a result of pyrite oxidation during weathering, acid-sulphate environment is created, which leads to leaching of Fe, Ca, Mg, Sr and Rb from volcanic rocks and zones of propylitization and sericitization. New minerals as jarosite and possibly APS minerals are formed, which are stable in these conditions. There are not registered admixtures of Sr in jarosite, so the accumulation of Sr in advanced argillic rocks does not realize in supergene conditions

and dissolved Sr migrates with surficial waters. The formation of jarosite during weathering of pyrite-rich rocks requires more extreme acidity and more oxidizing conditions than alunite (Stoffregen *et al.*, 2000). It is supposed that the formation of alunite and APS minerals, as well as the participation of 2- and 3-valent cations in the alunite group minerals, in these conditions is very limited.

The development of advanced argillic altered rocks as a part of a hydrothermally altered zone near Breznik and their mineral and chemical composition (concentration of Sr and As, depletion of Rb, typical distribution of REE, magmatic-hydrothermal alunite, permanent presence of APS minerals, etc.) define a high-sulphidation epithermal environment (White and Hedenquist, 1990; Hedenquist *et al.*, 1996). Milin Kamak ore deposit is situated at the periphery of advanced argillic altered zone and is described as Au-Ag intermediate sulphidation epithermal deposit with local development of high-sulphidation epithermal type (Sabeva, 2015). According to Crummy *et al.* (2001), the erosional level is around 250–300 m, which does not allow rich high-sulphidation ore concentrations to be found. On the other hand, the presence of high-temperature pyrophyllite advanced argillic rocks and actinolite containing propylite rocks, as well as the data for temperatures of ~400 °C from fluid inclusions (Moritz *et al.*, 2007), suggest the presence of magmatic source under the advanced argillic zone. For that reason, the idea for development of porphyry system at depth (Moritz *et al.*, 2007) should not be rejected and needs to be assessed.

Increased contents of elements such as As, Sb, Te, Bi and Li are characteristic for advanced argillic zones in the upper epithermal parts of porphyry copper systems (Halley *et al.*, 2015). A more detailed geochemical study of the indicator elements in the area of Breznik can outline the centre of the magmatic-hydrothermal system, as well as point to potentially porphyry ore mineralization.

CONCLUSIONS

The present geochemical studies of the hydrothermally altered rocks in the area of Breznik confirm that they belong to the epithermal part of a magmatic-hydrothermal system. Discovering of epithermal Au-Ag mineralizations, which are in spatial and genetic connection with hydrothermally altered rocks in the area of Breznik and both are part of the same magmatic-hydrothermal system, hold out new prospective for additional exploration works in the region, especially for potentially porphyry ore mineralization. Metallogenic re-evaluation should be made of the whole Western Srednogie Unit, which until recently was not considered prospective for new ore deposits (Vassileff and Stanisheva-Vassileva, 1989), in spite of its location between the rich Panagyurishte and Timok ore regions.

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