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Aluminium phosphate-sulphate minerals in the Chelopech Cu-Au deposit: Spatial development, chemistry and genetic significance

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Abstract. Aluminium phosphate-sulphate (APS) minerals of the svanbergite-woodhouseite (Sv-Wh) solid solution series have been determined in the advanced argillic and sericitic zones of alteration, as well as along with the Cu-As-S ore mineralization in the Chelopech high-sulphidation epithermal deposit. In the advanced argillic zone, Sv-Wh phases are documented down to a depth of 2000 m as known from 2 deep drill-holes. On the Earth surface (elevation 750 m) these minerals are associated with quartz, dickite, kaolinite, alunite, pyrite and anatase. From level 450 m to level 250 m, the alteration assemblage is composed of quartz, dickite, kaolinite, nacrite, pyrite, Sv-Wh and anatase. At deeper levels, diaspore, pyrophyllite, alunite and zunyite occur together with Sv-Wh. The temperature of formation of the advanced argillic alteration assemblages is considered to range from less than 200°C in the upper levels to more than 300°C in the deepest levels of the hydrothermal system. In the sericitic zone, these minerals are associated with quartz, illite, pyrite, halloysite, anatase and apatite. The relationships with apatite indicate that at least a part of Sv-Wh phases are formed by dissolution and replacement of apatite in a low pH environment. As a part of the Cu-As-S ore mineralization, these minerals are closely associated with enargite, pyrite, tennantite, chalcopyrite and barite, which suggest similar Eh-pH conditions of their formation.

The Sv-Wh phases with general formula $(Ca,Sr)Al_3(PO_4,SO_4)_2(OH,H_2O)_6$ range in composition from high Ca- to high Sr-varieties without reaching pure end-member composition. Minor amounts of Ba and K complete their chemistry. The crystals have clear chemical zoning due to substitution among Sr and Ca. Svanbergite-woodhouseite phases and zunyite are described for the first time in the Chelopech Cu-Au deposit.

Key words: APS, svanbergite-woodhouseite, zunyite, advanced argillic alteration, Chelopech Cu-Au deposit
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Резюме. Алуминиеви фосфатно-сулфатни (APS) минерали, съответстващи на сванбергит-вудхаузеитов (Sv-Wh) твърд разтвор бяха установени в интензивно аргилизитовата и серицитовата зона на изменение, както и с Cu-As-S рудна минерализация във високо-сулфидното епитермално находище Челопеч. При интензивно аргилизитовата зона тези минерали се установяват на дълбочина повече от 2000 m под съвременната повърхност. На повърхността (кота 750 m) те асоциират с кварц, дикит, каолинит, алунит, пирит и анатаз. В интервала от кота 450 m до кота 250 m минералната асоциация е кварц, дикит, каолинит, накрит, пирит, Sv-Wh и анатаз. В по-дълбоките нива се установяват още диаспор, пирофилит, алунит и зуниит. Предполага се, че температурата на образуване на интензивно аргилизитовия тип изменение варира от <200°C във високите нива до над 300°C в най-дълбоките нива на хидротермалната система. При серицитовата зона Sv-Wh фази асоциират с кварц, илит, пирит, халуазит, анатаз и апатит. Взаимоотношенията им с апатит показват, че поне част от тях са образувани за сметка на разтварянето и заместването на апатит при ниски стойности на pH. Като част от рудната минерализация Sv-Wh асоциират с енаргит, пирит, тенантит, халкопирит и барит. Близката пространствена връзка на тези минерали с Cu-As-S рудна минерализация предполага сходни Eh-pH условия на образуване.

Sv-Wh фази с обща формула $(Ca,Sr)Al_3(PO_4,SO_4)_2(OH,H_2O)_6$ варират по състав от високо калциеви до високо стронциеви, но чисти крайни членове не са доказани. В химичния им състав са установени ниски съдържания на Ba и K. Установена е ясна химична зоналност на кристалите им, която се дължи на заместването между Sr и Ca. Сванбергит-вудхаузеит и зуниит се описват за първи път в Cu-Au находище Челопеч.

Introduction

The aluminium phosphate-sulphate minerals (APS) refer to the alunite supergroup that consists of three mineral groups (Jambor, 1999), however the subdivisions of the various groups and their naming is still under debate. The supergroup contains more than 40 mineral species the general formula of wich is $DG_3(TO_4)_2(OH,H_2O)_6$, where D is a large cation (Na, U, K, Ag, NH_4, Pb, Ca, Ba, Sr, REE) with a coordination number greater or equal to 9. G sites are occupied by cations (Al, Fe, Cu and Zn) in octahedral coordination, and T is dominated by P, S and As in tetrahedral coordination (Jambor, 1999; Dill, 2001). These minerals have a trigonal symmetry with a space group $R\bar{3}m$, with some exceptions as documented by Jambor (1999).

APS minerals are known from a wide range of environments, including metamorphic, igneous and sedimentary rocks (Stoffregen, Alpers, 1987). They form during hypogene as well as supergene processes. In these conditions complex solid solution series can form. In the igneous environment, these minerals occur mainly in acidic and intermediate pyroclastic, volcanic and subvolcanic rocks that have undergone advanced argillic alteration with or without hydrothermal ore mineralizations (Dill, 2001). They are documented in a large number of epithermal high-sulphidation ore deposits such as Summitville, Colorado (Stoffregen, 1987), Pueblo Viejo, Dominican Republic (Muntean et al., 1990), Nansatsu district, Japan (Hedenquist et al., 1994), and Rodalquilar, Spain (Arribas et al., 1995).

APS minerals of hypogene origin were established also in many Bulgarian occurrences. Svanbergite and alunite are described in the Asarel porphyry-copper deposit, Central Srednogorie (Velinov et al., 1991), within the secondary quartzites of the Bacadjik ore field, Eastern Srednogorie (Kunov, Belivanov, 1996), and in the Spahievo ore field, Eastern Rodopes (Kunov et al., 1986). Svanbergite, woodhouseite, alunite and florencite are found in the advanced argillic type of alteration at Duni, Eastern Srednogorie (Kunov et al., 1996). Svanbergite-woodhouseite, woodhouseite and Na-alunite are reported by Kunov et al. (2000) in the advanced argillic type of alteration of Klissoura, Western Srednogorie. A review of all Bulgarian localities containing APS minerals of hypogene or supergene origin is presented by Kunov (1999).

The presence of svanbergite (?) in the altered rocks of the Chelopech deposit was initially suggested by Chipchakova (unpublished data). More recently, svanbergite-woodhouseite (Sv-Wh) phases were confirmed using electron microprobe analyses by Velinova (Kunov, 1999).

Sv-Wh solid solution series are present in the advanced argillic and sericitic zones of alteration, and in the Cu-As-S ore bodies of the Chelopech deposit. The aim of this study is to provide information on their spatial development and chemical composition. First data of zunyite in this deposit are given as well. The genetic significance of the APS minerals and the corresponding assemblages are discussed.

Materials and methods of study

The samples were collected from present-day surface in the area of Sharlo Dere (easternmost part of the deposit - elevation 750 m) and the underground galleries on the 405 m mine level (300-350 m below the surface). Additional samples from two 2-km deep drill-holes (№ 600 and 600^a at elevations 400 m, 248 m, 193 m, 122 m, -158 m, -400 m and –770 m) were used as well. The samples refer mainly to the advanced argillic and sericitic zones from the central and western sectors of the deposit.

The mineral assemblages and the paragenetic relationship of the APS phases with the other minerals were studied by transmitted and reflected light microscopy. X-ray powder diffraction (Siemens 500 diffractometer) and DTA (MOM – Budapest) methods was used for defining the mineral composition of the rocks in the advanced argillic zone (Geological Institute, BAS). The chemical composition was determined by using a JEOL JSM–35 CF with a TRACOR NORTHERN-TN 2000 microanalyser (Eurotest-Control, Sofia, analyst Chr. Stanchev) and a CAMECA CAMEBAX SX-50 microprobe (University of Lausanne, Switzerland). The chemical zoning of the APS crystals and grains was studied with a JEOL scanning electron microscope (SEM) at the University of Geneva, Switzerland. Representative sample of the investigated material is available in the collections of the Geological Institute under № M.1.2002.10.1.

Geological setting

The Chelopech deposit is a major Cu-Au mine with a past production (since 1954) of 11.5 Mt with 1.0 % Cu, 3.0 g/t Au and remaining resources of 31 Mt with 1.39 % Cu, 3.5 g/t Au (Strashimirov et al., 2002). It is located within the northern part of the Panagyurishte ore region that belongs to the Banat-Srednogorie metallogenic belt.

The genesis of the deposit is related to the Late Cretaceous magmatism (Popov et al., 2000). It is hosted by a Late Cretaceous volcanic and volcano-sedimentary complex, transgressively overlaying Precambrian gneisses, shists and amphibolites and Paleozoic phyllites and shists. The Late Cretaceous rock sequence consists of Turonian sedimentary rocks, Coniacian-Santonian dacite-andesites, sandstones and marls (Chelopech Formation), argillaceous limestones (Mirkovo Formation) and Campanian-Maestrichtian terrigeneous flysh (Chugovitsa Formation) (Moev, Antonov, 1978; Popov, Kovachev, 1996). The Coniacian-Santonian volcanic rock assemblage (Chelopech Formation) is composed of lavas, breccias with volcanic elements and various tuffs. The recent study of Stoykov et al. (2002) defined the igneous rocks dominantly as andesite to trachydacite. Part of this rock assemblage has been intensively altered to an advanced argillic style and hosts the economic Cu-Au ore bodies of the deposit. Sedimentary rocks of the Chelopech-, Mirkovo- and Chugovitsa Formations cover partly the altered volcanic complex and the ore deposit.

The deposit includes more than 20 ore bodies, most of them hosted by breccias. Textural relationships indicate multiple breccia events of different origins – phreatomagmatic and magmatic hydrothermal injection breccias (Moritz et al., 2001; Chambefort et al., 2002). The morphology of the ore bodies is variable, with disseminated, massive, banded and vein-type ore. The vertical development of economic ore is known down to a depth of 600 m below the present-day surface and is open downward.

Hydrothermal alteration and ore assemblages

Mutafchiev and Chipchakova (1969) described the alteration products in the Chelopech deposit as secondary quartzites, which include alunite, kaolinite and sericite facies to quartz-sericite alteration imposed on earlier propylitically altered rocks. M. Kanazirski (in Popov et al., 2000) distinguished propylitic, propylitic-sericite, sericitic, sericitic-advanced argillic and advanced argillic pre-ore alteration types.

On the mine level 405, three main

Table 1. *Mineral composition of rocks from the advanced argillic zone, determined by X-ray powder diffraction and DTA, wt. %*

Таблица 1. *Минерален състав на скали от интензивно аргилизитовата зона, определен чрез прахова рентгенова дифракция и диференциално-термичен анализ, тегл. %*

№	Level, m	D/Kl	Q	Py	Sv-Wh	Pyr	Al	Ser	Crb
60	750	43	41	7	3	2	2	1	-
7		37	39	18	-	2	2	-	-
PS39	400	63	3	16	3	10	3	-	-
43		51	3	37	2	3	3	-	-
B56	248	30	46	15	-	-	7	-	-
B25	122	29	51	7	-	-	11	-	-
B32	-158	38	40	8	-	-	10	-	2

D/Kl - dickite/kaolinite, Q - quartz, Py - pyrite, Sv-Wh – svanbergite-woodhouseite, Pyr - pyrophyllite, Al - alunite, Ser - sericite, Crb - cristobalite

D/Kl – дикит/каолинит, Q – кварц, Py – пирит, Sv-Wh – сванбергит-вудхаузеит, Pyr – пирофилит, Al – алунит, Ser – серицит, Crb – кристобалит

alteration types are distinguished laterally with distance from the ore bodies (Simova et al., 2001). The innermost part consists of advanced argillic zone with “vuggy” silica and massive silica localities. This zone is spatially followed of sericitic and an external propylitic zones of alteration. Two deep drill-holes reveal that the advanced argillic alteration is developed in the volcanic rocks down to a depth of more than 2000 m. A vertical variation of the mineral composition is observed with development of diaspore, pyrophyllite and zunyite at depth.

Three successive stages of the ore-mineralizing process have been recognized (Petrunov, 1994, 1995): (1) Fe-S, with disseminated and massive pyrite of banded texture (considered to be of hydrothermal sedimentary-diagenetic origin); (2) Cu-As-S with enargite and tennantite and (3) Pb-Zn-S. The predominant minerals are pyrite, enargite, tennantite, chalcopyrite, bornite and barite. A large number of subordinate and rare minerals associate with the Cu-As-S main economic ore stage, including sulphides, sulphosalts, tellurides, selenides and native metals. These minerals refer to a large geochemical association: Cu, Fe, S, As, Sb, Te, Bi, Se, Sn, Mo, Ge, Au, Ag, Pb, Zn, Hg, and Ga (Terziev, 1968; Petrunov, 1994, 1995; Simova, 2000 etc.).

Results

The Sv-Wh phases occur in the advanced argillic and sericitic zones of alteration. They are most abundant in the advanced argillic zone and associate with quartz, dickite, kaolinite, pyrite, alunite, pyrophyllite, diaspore and rarely zunyite and anatase The quantitative ratio of the mineral alteration assemblage is shown in Table 1. In the area of Sharlo Dere, where advanced argillic zone crop out, these minerals associate with abundant alunite, quartz, dickite, kaolinite, pyrite and anatase. Commonly they are present as zonal grains with an irregular shape, enclosed in bladed alunite crystals (Fig. 1). This is an earlier formed solid solution series, which is partly dissolved and replaced by alunite. The chemical composition of alunite is shown in Table 2. A characteristic feature of the studied samples is the high Na_2O content, that reach up to 4.88 wt. %. A clear zoning in the alunite crystals is established with the BSEI images. This zoning demonstrates variations in the K and Na content.

Table 2. *Representative microprobe analyses of alunite from the advanced argillic zone, wt. %*
Таблица 2. *Представителни микросондови анализи на алунит от интензивно аргилизитовата зона, тегл. %*

	PS56/8	PS56/12	PS56/14	PS56/15	PS56/16	PS56/18
Sample	Sharlo Dere, present-day surface, level 750 m					
K_2O	5.25	3.52	4.54	6.14	5.32	4.45
Na_2O	3.46	4.88	4.08	2.43	3.57	4.28
SrO	0.23	0.18	0.10	0.42	0.21	0.13
CaO	0.03	0.05	-	0.40	0.06	0.03
BaO	0.02	0.11	0.14	0.68	0.16	0.17
Al_2O_3	38.96	38.54	38.55	37.31	38.30	38.19
SO_3	39.04	40.07	39.62	38.26	40.16	38.75
P_2O_5	0.02	0.11	0.11	1.23	0.10	0.08
H_2O*	12.88	12.26	12.62	12.98	11.95	13.67
	O = 14					
K	0.45	0.30	0.39	0.53	0.46	0.38
Na	0.45	0.64	0.53	0.32	0.47	0.56
Sr	0.10	0.01	-	0.02	0.01	-
Ca	-	-	-	0.03	-	-
Ba	-	-	-	0.02	-	-
Al	3.11	3.07	3.07	3.00	3.07	3.03
S	1.98	2.03	2.01	1.96	2.05	1.96
P	-	0.01	0.01	0.07	-	-
OH	5.81	5.53	5,69	5.90	5.43	6.13

H_2O* - by difference to 100%; FeO, As_2O_5, Ce_2O_3 and SiO_2 are bellow 0.10 wt. %
H_2O* - по разликата до 100%; FeO, As_2O_5, Ce_2O_3 и SiO_2 - под 0.10 тегл. %

From level 450 m to level 250 m, the mineral alteration assemblage is composed of quartz, dickite, kaolinite, Sv-Wh phases, nacrite, pyrite and anatase (Fig. 2a). In these levels Sv-Wh phases are generally intergrown with clay minerals, pyrite, and Cu-As-S ore minerals also, including enargite, tennantite, chalcopyrite and barite (Fig. 2b). We do not have representative Sv-Wh microprobe analyses from this association, but we expect the presence of As in their chemical composition because of the high activity of this element in the ore-forming process.

Mainly, Sv-Wh phases form clusters, bands or isolated 5-150 μm pseudocubic crystals (Fig. 3a). Clear zoning can be observed in some grains (Fig. 3b). Within fine tuffs, composed of clay minerals, crystal clasts and banded massive pyrite, these minerals occur as bands of fine-grained mass or as separate 10-100 μm pseudocubic zonal crystals.

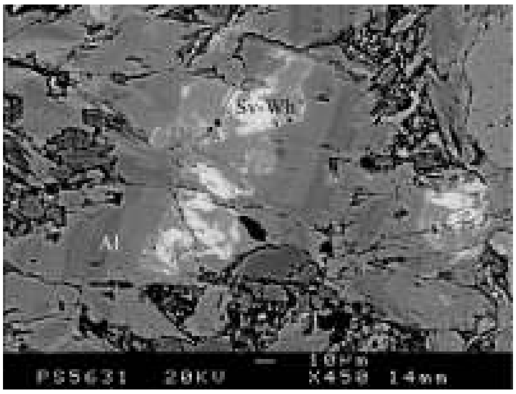
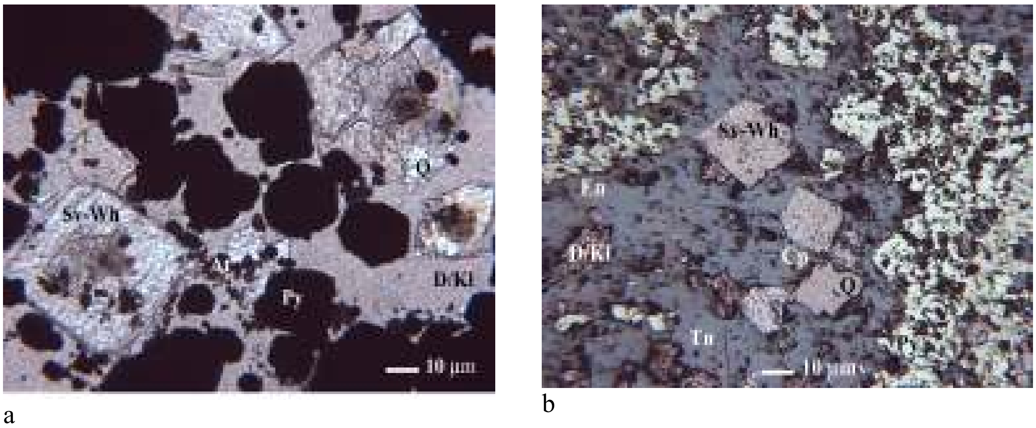


Fig. 1. BSEI microphotograph of alunite (Al) in advanced argillic zone. The central parts of the alunite are composed of turbid Sv-Wh grains with irregular shapes. Sample PS56, Earth surface. Sharlo Dere

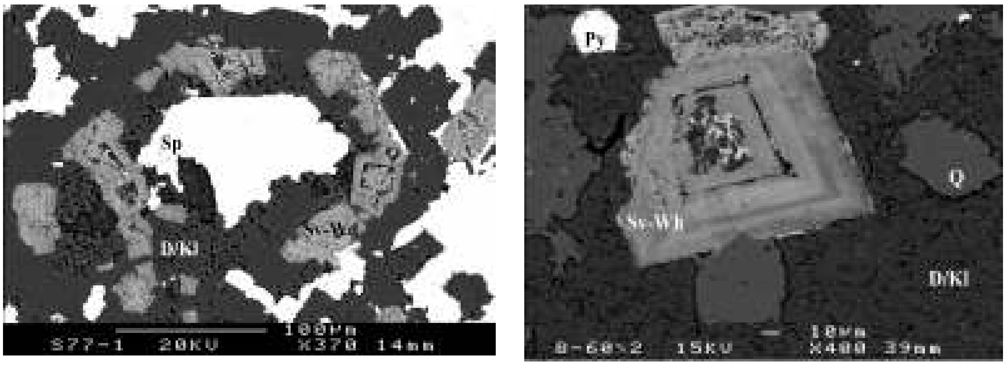
Фиг. 1. BSEI изображение на алунит (Al) в интензивно аргилизитовата зона. Централните части на алунита са съставени от Sv-Wh с неправилна форма. Образец PS56, съвременна повърхност. Шарло дере



a b

Fig. 2. Microphotograph of Sv-Wh crystals: (a) in advanced argillic zone, associating with pyrite (Py), dickite/kaolinite (D/Kl), quartz (Q), and anatase (At). The cores of the crystals are filled with dickite/ kaolinite. Sample P5, level 400 m. Transmitted light, N //; (b) Sv-Wh crystals included in tennantite (Tn), enargite (En), chalcopyrite (Cp), pyrite, quartz and dickite/kaolinite. Sample C103, level 405 m. Transmitted/reflected light, N //

Фиг. 2. Микроскопска снимка на Sv-Wh кристали: (a) в интензивно аргилизитовата зона, асоцииращи с пирит (Py), дикит/каолинит (D/Kl), кварц (Q) и анатаз (At). Централните части на кристалите са запълнени с дикит/каолинит. Образец P5, кота 400 m. Проходяща светлина, N //; (b) включени в тенантит (Tn), енаргит (En), халкопирит (Cp), пирит, кварц и дикит/каолинит. Образец C103, хор. 405 m. Проходяща/отразена светлина, N //



a b

Fig. 3. BSEI microphotograph of Sv-Wh crystals in advanced argillic zone: (a) associating with dickite/kaolinite (D/Kl) and sphalerite (Sp). Sample S77 – level 395 m; (b) zonal Sv-Wh crystal, associating with dickite/kaolinite, quartz (Q) and pyrite (Py) The core of the crystal is filled with dickite/kaolinite. Sample B60 – level 193 m

Фиг. 3. BSEI изображение на Sv-Wh кристали в интензивно аргилизитовата зона: (a) асоцииращи с дикит/каолинит (D/Kl) и сфалерит (Sp). Образец S77 – хор. 395 m; (b) зонален Sv-Wh кристал, асоцииращ с дикит/каолинит, кварц (Q) и пирит (Py). Централните части на кристала са запълнени с дикит/каолинит. Образец B60 – кота 193 m

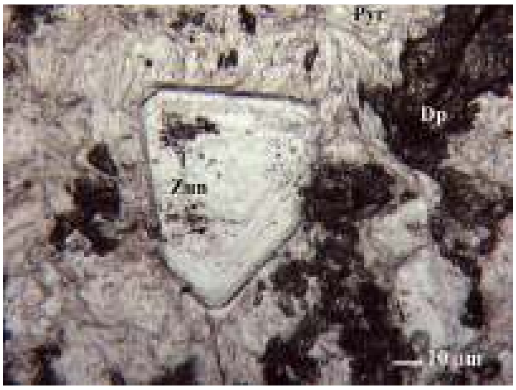


Fig. 4. Microphotograph of zunyite (Zun) in advanced argillic zone, associated with pyrophyllite (Pyr) and diaspore (Dp). Sample B36, level –400 m. Transmitted light, N //
Фиг. 4. Микроскопска снимка на зуниит (Zun) в интензивно аргилизитовата зона, асоцииращ с пирофилит (Pyr) и диаспор (Dp). Образец B36, кота –400 m. Проходяща светлина, N //

At levels lower than 250 m, diaspore, pyrophyllite, alunite and zunyite occur together with Sv-Wh phases. Zunyite is described for a first time in the deposit (Fig. 4; Table 3). It is a characteristic mineral for the advanced argillic alteration assemblage along with APS minerals, diaspore and pyrophyllite.

Table 3. *Representative microprobe analyses of zunyite, $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$, from the deep levels (-400 m) in advanced argillic zone, wt. %*
Таблица 3. *Представителни микросондови анализи на зуниит, $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$, от дълбоките нива (-400 m) на интензивно аргилизитовата зона, тегл. %*

Sample	B36/3	B36/5	B36/6c	B36/6c1
Al_2O_3	57.87	57.49	56.31	54.94
SiO_2	25.10	24.26	24.77	25.41
Na_2O	-	0.28	-	-
K_2O	-	-	0.09	-
Fe_2O_3	0.14	-	-	-
Cl	3.16	3.23	3.23	3.16
H_2O,F	13.73	14.74	15.60	16.49

Fig. 5. Microphotograph of pseudocubic Sv-Wh crystals in sericitic zone associated with quartz (Q), illite (Ill) and pyrite (Py). Central parts are filled with illite and quartz. Sample S25, level 405 m. Transmitted light, N //
Фиг. 5. Микроскопска снимка на псевдокубични Sv-Wh кристали в серицитовата зона, асоцииращи с кварц (Q), илит (Ill) и пирит (Py). Централните им части са запълнени с илит и кварц. Образец S25, хор. 405 m. Проходяща светлина, N //

In the sericitic zone, Sv-Wh phases associate with quartz, illite, pyrite, halloysite and anatase. Relics of primary magmatic apatite can also be observed. In this assemblage, these minerals form 10-50 µm pseudocubic crystals with clearly developed rims. Their central parts are filled with illite and quartz (Fig. 5). The minor apatite crystals are generally enclosed in grains of Sv-Wh. This relationship suggests that at least a part of these minerals was formed by dissolution and replacement of apatite in a low pH environment, as proposed by Stoffregen and Alpers (1987).

The chemical microprobe analyses show that the APS minerals belong mainly to the svanbergite-woodhouseite solid solution series: $(Ca,Sr)Al_3(PO_4,SO_4)_2(OH,H_2O)_6$. Their composition ranges from Ca-rich to Sr-rich phases without reaching the pure end-members. In addition minor amounts of Ba and K are also present (Tables 4 and 5).

The clear chemical zoning revealed by BSEI is a characteristic feature of the Sv-Wh grains and crystals of (Fig. 3b). This explained by the substitution among Sr and Ca. BaO is present in minor amounts in each sample with a maximum of 3.67 wt. %. Low concentrations of K_2O exist in some of the samples and range from 0.07 to 0.81 wt. %.

Table 4. *Representative microprobe analyses of Sv-Wh phases from the sericitic and advanced argillic zones, wt. %*
Таблица 4. *Представителни микросондови анализи на Sv-Wh фази от серицитовата и интензивно аргилизитовата зона, тегл. %*

Sample	S25/6	S25/7	S30	PS39/3	B56/1		B56/3			B56/4	
					periphery	centre	periphery	middle	centre	periphery	centre
Level	405 m				248 m						
Zone	sericitic zone		advanced argillic zone								
SrO	14.99	15.24	12.38	8.70	2.84	5.33	2.51	8.11	8.05	3.96	8.53
CaO	3.18	3.82	2.79	6.78	8.02	3.32	8.38	6.45	6.46	7.98	6.30
BaO	0.63	0.26	1.32	0.77	3.01	3.67	2.40	1.04	0.81	2.46	1.16
K_2O	0.69	0.07	0.81	-	-	0.35	0.26	0.60	0.40	0.42	0.58
FeO_{tot}	-	-	-	-	-	0.28	0.27	0.34	-	-	-
Al_2O_3	32.96	33.89	32.02	34.72	35.78	33.16	35.80	34.83	34.97	35.50	34.67
P_2O_5	19.55	19.46	17.04	18.00	19.41	19.11	18.06	18.47	17.23	16.51	17.17
SO_3	14.52	15.09	20.40	17.52	18.99	22.20	20.65	18.10	19.70	21.05	19.35
H_2O*	13.46	12.21	13.21	13.49	11.95	12.58	11.67	12.50	12.38	12.12	12.24
	O = 14										
Sr	0.64	0.66	0.52	0.36	0.12	0.22	0.10	0.34	0.30	0.16	0.36
Ca	0.25	0.30	0.22	0.50	0.61	0.25	0.63	0.50	0.50	0.61	0.49
Ba	0.02	0.01	0.04	0.02	0.10	0.10	0.07	0.03	0.02	0.07	0.03
K	0.06	0.01	0.08	-	-	0.03	0.02	0.01	0.04	0.04	0.05
Fe	-	-	-	-	-	0.02	0.02	0.02	-	-	-
Al	2.90	2.96	2.72	2.91	2.98	2.74	2.97	2.94	2.94	2.96	2.94
P	1.20	1.20	1.04	1.09	1.16	1.14	1.08	1.12	1.04	0.99	1.05
S	0.80	0.84	1.10	0.90	1.00	1.17	1.09	0.97	1.05	1.12	1.05
OH	6.60	6.00	6.36	6.40	5.63	5.89	5.48	5.97	5.90	5.73	5.87

H_2O* - by difference to 100%
H_2O* - по разликата до 100%

The phosphate/sulphate molar ratio is close to a 1:1 in the predominant number of analyses, which is the expected value for stoichiometric svanbergite or woodhouseite. Slight enrich-ment of PO_4^{3-} is established in some samples of the deeper levels, to a maximum ratio of 1.3:0.7 (Fig. 6). An abrupt increase of content of P_2O_5 up to 25.59 wt. % and of CaO up to 11.63 wt. % was observed in the central parts of some crystals. Thus the chemical composition of the studied samples approaches that of the crandallite [$CaAl_3(PO_4)_2(OH,H_2O)_6$] (Fig. 7).

Clear enrichment in SrO to a maximum value of 8.53 wt. % was documented in the central parts of the zonal Sv-Wh crystals in the samples of the advanced argillic alteration zone. In the peripheral parts of the crystals CaO is predominant and reach a maximum value of 8.38 wt. % (Fig. 8). A significant increase of the SrO content up to 17.19 wt. % was observed with some exceptions in the grains from the deeper levels, as well as in these from the sericitic alteration zone (Fig. 9).

Discussion

The formation of the APS minerals together with the alteration assemblage is related to the replacement of andesites to trachydacites. The deep, endogene acid and oxidized hydrothermal fluids, enriched in S, Sr and P, reacted with the host environment and decomposed magmatic apatite, which provided additional amounts of P and Ca to form APS minerals belonging to the woodhouseite and crandallite solid solution:

$$Ca_5(PO_4)_3(OH) + 4^1/_2Al(OH)_4 + 11^1/_2H^+ = 1^1/_2CaAl_3(PO_4)_2(OH,H_2O)_6 + 3^1/_2Ca^{2+} + 10H_2O.$$

According to Ripp et al. (1998), APS minerals form in conditions of high activity of PO_4^{3-} ions, high oxygen potential and a large pH interval, that is from strong acid to neutral (pH 3-8) solutions. In the Chelopech deposit, these minerals occur mainly in the advanced argillic altered rocks, where the pH conditions during the formation are considered as acid rather than neutral.

Table 5. *Representative microprobe analyses of Sv-Wh phases from the advanced argillic zone, wt. %*
Таблица 5. *Представителни микросондови анализи на Sv-Wh фази от интензивно аргилизитовата зона, тегл. %*

	B56/1	B56/5	B36/1a	B36/1b	B36/2a	B36/4	B36/9	B36/9a	B42/2b	B42/3
	level 248 m		level -400 m						level -770 m	
SrO	4.53	7.42	17.05	16.44	5.49	15.39	17.19	14.33	5.25	14.38
CaO	8.32	7.16	2.29	3.12	8.17	0.42	1.06	2.53	9.59	4.13
BaO	1.35	1.37	0.36	0.95	2.98	-	0.20	0.42	0.40	0.39
K_2O	-	-	0.07	-	0.12	0.14	-	0.07	-	-
FeO_{tot}	0.11	-	-	-	-	-	-	-	0.20	-
Al_2O_3	37.74	35.11	32.82	33.08	34.74	33.84	33.08	34.12	35.81	34.29
P_2O_5	19.68	18.04	18.76	22.57	18.07	15.36	16.75	16.90	20.34	21.56
SO_3	15.59	18.06	17.44	12.81	19.35	22.29	20.61	20.16	16.34	13.31
H_2O*	12.68	12.84	11.21	11.03	11.08	12.56	11.11	11.47	12.07	11.94
					O = 14					
Sr	0.19	0.31	0.74	0.72	0.23	0.64	0.74	0.61	0.22	0.62
Ca	0.63	0.55	0.18	0.25	0.63	0.03	0.08	0.20	0.73	0.33
Ba	0.04	0.04	0.01	0.03	0.08	-	0.01	0.01	0.01	0.01
K	-	-	0.01	-	0.01	0.01	-	0.01	-	-
Fe	0.01	-	-	-	-	-	-	-	0.01	-
Al	3.15	2.95	2.91	2.95	2.97	2.88	2.90	2.95	3.00	3.01
P	1.18	1.09	1.19	1.45	1.10	0.94	1.05	1.05	1.22	1,36
S	0.83	0.97	0.98	0.73	1.05	1.20	1.15	1.10	0.87	0.74
OH	5.98	6.10	5.62	5.57	5.35	6.05	5.50	5.61	5.73	5.78

H_2O* - by difference to 100% (по разликата до 100%)

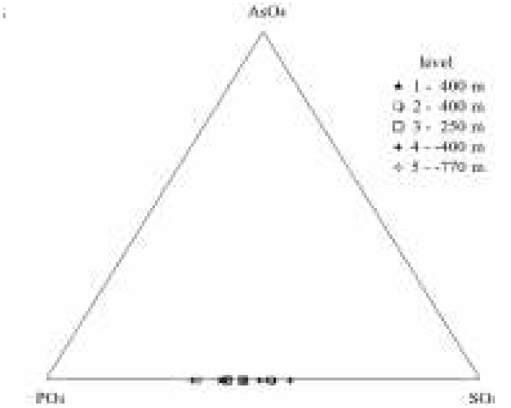


Fig. 6. Anion composition in the T sites of Sv-Wh phases from the sericitic zone (1) and advanced argillic zone (2-5)
Фиг. 6. Анионен състав в Т позициите на Sv-Wh фази от серицитовата зона (1) и интензивно аргилизитовата зона (2-5)

APS minerals are stable up to a temperature of 400°C at a moderately high fluid pressure of up to 1 kbar (Dill, 2001). The predominance of dickite and kaolinite in the upper level mineral assemblage in the Chelopech deposit suggests a temperature of formation of the APS minerals around 200°C, as proposed Corbett and Leach (1998) for the temperature of formation of dickite and kaolinite. At a greater depth, where diaspore, pyrophyllite and zunyite appear, the temperature augments. There are different suggestions according to several authors. According to Corbett and Leach (1998) pyrophyllite forms below 200-250°C. Papezik and Keats (1976) proposed that in the presence of acid conditions, pyrophyllite forms at temperatures around 260-280°C under a presure of 2 kbar or less and that temperatures very likely did not exceed 300°C. After Berman (1988) the presence of zunyite, pyrophyllite and dickite constrains the upper temperature limit of formation to 375°C. Thus, the temperature of formation of the advanced argillic alteration assemblage might be considered in a range from 200°C in the upper levels to more than 300°C in the deeper levels of the hydrothermal alteration system.

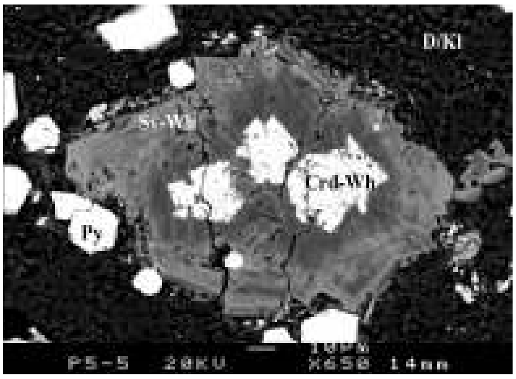


Fig. 7. BSEI microphotograph of zonal Sv-Wh intergrowth crystals in advanced argillic zone, associated with dickite/kaolinite (D/Kl) and pyrite (Py). The chemical composition of the white cores of the crystals are distinguished by a sharp increase of P_2O_5 and CaO, a crandallite (?)-woodhouseite phase (Crd-Wh). Sample P5, level 400 m
Фиг. 7. BSEI изображение на срастък от зонални Sv-Wh кристали в интензивно аргилизитовата зона, асоцииращи с дикит/каолинит (D/Kl) и пирит (Py). Химичният състав на централните части (бяло) се различава с рязко нарастване на P_2O_5 и CaO – крандалит (?)-вудхаузеит (Crd-Wh). Образец P5, кота 400 m

The temperature range of the Cu-As-S ore-forming process is between more than 300°C to 214-183°C as shown by Petrunov (1994) and Moritz et al. (2002). The ore-accompanying development of APS minerals confirms similar to lower temperature for the main ore mineralization in the Chelopech deposit.

Conclusions

Three spatially separate zones of altered rocks are distinguished laterally from the ore bodies in the deposit. The innermost zone consists of advanced argillic zone with "vuggy" silica and massive silica localities, which is spatially followed by sericitic zone and an outer propylitic zone of alteration.

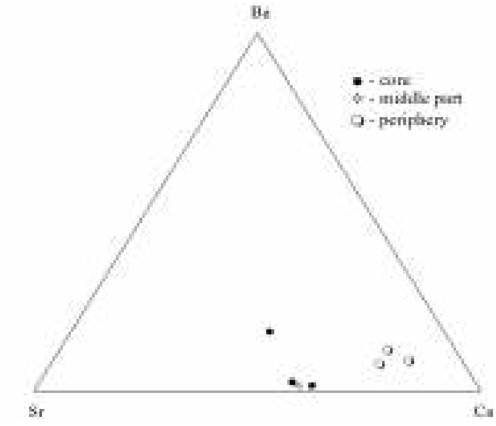


Fig. 8. Cation composition in the D sites of zonal Sv-Wh phases from the advanced argillic zone
Фиг. 8. Катионен състав в D позициите на зонални Sv-Wh фази от интензивно аргилизитовата зона

APS phases occur within the advanced argillic and sericitic zone and within the Cu-As-S ore bodies as gangue minerals. They belong to the svanbergite-woodhouseite solid solution series and range in composition from Ca-rich to Sr-rich varieties without reaching pure end-member compositions.

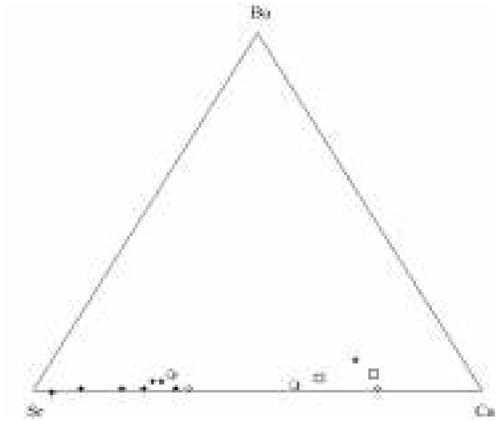


Fig. 9. Cation composition in the D sites of Sv-Wh phases from the advanced argillic zone. Symbols, as in Fig. 6
Фиг. 9. Катионен състав в D позициите на Sv-Wh фази от интензивно аргилизитовата зона. Означенията са като на фиг. 6

The temperature of formation of the advanced argillic alteration assemblages is considered to range from less than 200°C in the upper levels to more than 300°C in the deeper levels of the hydrothermal system. The relationships with apatite indicate that at least a part of the Sv-Wh phases are formed by dissolution and replacement of apatite in a low pH environment.

The pre-ore hydrothermal alteration and the ore mineral assemblage of the Chelopech deposit are typical of high-sulphidation epithermal systems, including a locally developed early stage of banded massive pyrite that is typically described in hydrothermal sedimentary-diagenetic environments.

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