Stable isotope (δD , $\delta^{18}O$) data on the structural water of two sericite samples from the Cu-Au high-sulphidation deposit Chelopech, Bulgaria – a tentative study

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Abstract. The epithermal high-sulphidation Cu-Au Chelopech deposit is characterized by a well-developed and well-traceable hydrothermal footprint manifested in the volcanic host rocks. The economic ore mineralization is embedded in the strong silicification, included among the advanced argillic zone of alteration, smoothly transitioning to quartz-sericite alteration that evolves into widespread propylitic. The quartz-sericite alteration zone is accessible for exploration only in underground mining galleries and exploration drillings. The main mineral assemblage in this zone is quartz, sericite, pyrite, minor rutile/anatase and relics of apatite and feldspar. According to XRD data from the studied samples, sericite was defined as illite and muscovite/sericite 2M₁ polytype. The abundance of heavy stable isotopes (D, ^{18}O) in the structural water of two sericite samples is the object of this study. A special attention was paid to the separation of extraneous waters from the structural one by thermal fractionation. The extracted structural water was converted to hydrogen and carbon dioxide before the isotopic measurements. The obtained results, put into a δD vs. $\delta^{18}O$ plot, indicate that sericite structural water is “heavier” than meteoric water, within uncertainty limits.

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INTRODUCTION

The systematic studies on the Chelopech Cu-Au deposit during the last decades (*e.g.*, Petrunov, 1995; Moritz *et al.*, 2003; Georgieva, 2014) classified it as a volcanic-hosted epithermal high-sulphidation deposit (VHED). The summarized data on the formation and the evolution of this type of deposits (Hedenquist and Lowenstern, 1994; Heinrich, 2005) point to the significant participation of magmatic fluids, mainly water, in the wall rock al-

teration, as well as in the ore deposition. The acidic magmatic vapors are commonly absorbed by deeply circulating meteoric waters, and thus become a major factor in the hydrothermal ore formation. The temperature border of $T \approx 300$ °C divides the VHED evolution into two stages: 1) early stage, in which high-oxidation acidic fluids ($pH \leq 3$), at $T > 300$ °C, are responsible for the alteration of the host rocks and the formation of water- (hydroxo-) containing minerals as alunite ($KAl_3(SO_4)_2(OH)_6$), kaolinite ($Al_2Si_2O_5(OH)_4$) and sericite ($KAl_2(AlSi_3O_{10})(OH)_2$);

and 2) hydrothermal stage (at $T \leq 300$ °C), in which ores most often precipitate. The mentioned temperature border is conventional; the formation and the evolution of VHED are determined, most of all, by two factors: redox potential (Eh) and hydrogen potential (pH). Heinrich (2005) combined them to find four pathways for cooling of magmatic fluids. Preserving a relatively high oxidizing potential is specific for the Chelopech type deposits. The environment's acidity is of great importance, however, during the ore stage, it decreases from $\text{pH} \leq 3$ to $\text{pH} \geq 5$, thus supplying an enhanced concentration of HS^- and S^{2-} , needed for sulphide ore deposition.

An increase in pH may be caused by interaction between the acidic volcanic (magmatic?) fluids and the silicate walls of the volcanic channel during the high oxidation stage, by leaching alkalis (Na^+ , K^+). The involvement of deeply circulating hot meteoric water with near to neutral reaction is an alternative. Hedenquist and Lowenstern (1994) considered these waters "critical" for ore deposition. Finally, these authors concluded (*loc. cit.*) that "magmatic fluids are commonly present, but that their signatures may be masked or erased owing to later overprinting by large volumes of meteoric water, which represents >95% of the water ultimately convected during cooling of an intrusion in the shallow crust."

Moritz *et al.* (2003) published data on Sr-O-S isotope systematics in barite formed at the late stage with respect to the ore mineralization. Lerouge *et al.* (2006) studied, by stable isotopes, the origin of alunite from advanced argillic alteration systems, including Chelopech (two samples). Oxygen from SO_4 -groups is used for $\delta^{18}\text{O}$ determination. Later, Piperov *et al.* (2017) analyzed the stable isotopes in water from fluid inclusions in an ore mineral: Chelopech enargite.

In the present study, stable isotope data (D, ^{18}O) on the structural water from two sericite samples, from the quartz-sericite zone of alteration, are presented, and already published data on the stable isotopes of O, H, and S in the Chelopech deposit are also summarized. A sample of contemporary surface meteoric water is additionally analyzed.

GEOLOGICAL SETTING

The epithermal high-sulphidation Cu-Au Chelopech deposit is among the most significant European deposits. Being a part of the Elatsite-Chelopech ore field, it is situated in the Panagyurishte metallogenic district, which falls in the Srednogie tectonic zone. The Panagyurishte metallogenic district

is located in the Central Srednogie Subzone and is characterized by the presence of a cluster of porphyry-Cu and epithermal Cu-Au ore deposits (Fig. 1). Apart from the Chelopech deposit, the Elatsite, Assarel and Medet porphyry-Cu deposits, as well as the Elshitsa and Radka epithermal deposits, are also indicative.

The Cu-Au mineralization of the Chelopech deposit is developed in an Upper Cretaceous volcanic and volcano-sedimentary complex (Popov *et al.*, 1983) (Fig. 2). The basement rocks of the deposit consist of gneisses, amphibolites, schists and phyllites of Neoproterozoic to Paleozoic age (Peytcheva and von Quadt, 2004; Carrigan *et al.*, 2006). The Upper Cretaceous volcanic complex is composed of andesitic, trachydacitic to dacitic rocks of Turonian age (Stoykov *et al.*, 2004). Almost the entire volcanic sequence in the vicinity of the Chelopech deposit was subjected to intensive hydrothermal alteration. The ore mineralization is generally associated with strong silicification areas, included into a zone of advanced argillic alteration and successively passing through the zones of quartz-sericitic and propylitic alteration (Georgieva, 2014) (Fig. 3). The economic ore mineralization is located preferentially among volcanic breccia and/or along intense fracturing and represents massive to stockwork bodies, veins and disseminations. The main Cu and Au-rich mineralization consists of enargite-lusonite, tennantite, chalcopyrite and bornite assemblages. The deposit is characterized by abundant subordinate and rare mineral varieties, such as sulphides, sulphosalts, tellurides and selenides, studied in details by Terziev (1968) and Petrunov (1995).

SAMPLE DESCRIPTION

Two samples from the quartz-sericite alteration zone from two locations in the underground mine level 405 (300–350 m below present-day surface) were selected. The choice among all available samples was made on the base of the sericite amount in the sample and its proportion relative to other mineral components. Sample SP-133 (SER_{133}) was collected from gallery 51, and sample S-178 (SER_{178}) from the Central declined gallery, both galleries situated to the south of exploitation block 18, level 405. Both samples represent altered andesite with preserved porphyritic texture, although the original mineral composition was almost entirely altered to sericite and quartz with minor amounts of anatase. Disseminated pyrite is common in all samples. Orthoclase and apatite are rarely found as a relic of

Fig. 1. a) Major tectonic zones of Bulgaria (after Ivanov, 2017) and location of the Panagyurishte ore district; b) Simplified geological map of the Panagyurishte ore district (after Cheshitev *et al.*, 1995; Moritz *et al.*, 2004).

the parent rock. Single sphalerite grains were observed in thin sections. Sericite replaces both phenocrysts, almost entirely, and the groundmass of the rock, where it is intergrowth with fine-grained quartz (Fig. 4). According to XRD data on the studied samples from the quartz-sericite alteration zone from the Chelopech deposit, sericite is defined as illite and muscovite or sericite $2M_1$ polytype. A quantitative evaluation of the ratio Ser/Qtz in sample S-178 (SER_{178}) was made and, since quartz does not contain alkalis, K(+Na) content reveals the sericite participation is 73.5% of the sample. A sample of contemporary surface meteoric water (Iskar Dam, Bulgaria), labeled MET, was additionally analyzed. The Standard of Mean Ocean Water (SMOW), collected on August 8, 1975, from the central Indian

Ocean, was also used. The latter corresponds to a sealed glass ampoule (ca. 200 ml water), which was donated by the Institute of Oceanography, Academy of Sciences of USSR (Former Soviet Union).

ANALYTICAL METHODS

The mineral assemblages and their paragenetic relations in the selected samples were studied by transmitted and reflected light microscopy. X-ray powder diffraction, with a G-670 Guinier camera (Geological Institute, Bulgarian Academy of Sciences) was also carried out to determine the mineral composition and the varieties of micas in the samples from the quartz-sericite alteration zone. The isotope

Fig. 2. Geological map of the Chelopech area (after Moev and Antonov, 1978; Stoykov *et al.*, 2002).

Fig. 3. Hydrothermal alteration zones on underground operating mining level 405, ~350 m below present-day surface in the Chelopech deposit, according to unpublished data of Mutafchiev and Petrunov (1996) with additions after Georgieva (2017). Lithological basis is after Chambeft (2005). The position of the studied samples is marked.

Fig. 4. Photomicrographs of the quartz-sericite zone of alteration developed on andesite in the Chelovech deposit. Ser – sericite, Qz – quartz, Py – pyrite, Ap – apatite.

ratios $R_3 = I_3/I_2$ and $R_{46} = I_{46}/I_{44}$ were measured by a mass-spectrometer: MS10 (AEI – Kratos, UK).

Separation of the surface adsorbed water

It is well known that adsorbed water takes all free surfaces; water molecules can be detected even on the inner walls of high vacuum systems. This is a difficulty, since the water adsorbed on the sample surface may have a different isotope composition than the structural water studied. On that account,

a kinetic investigation was performed, aiming at separation of the surface adsorbed water from the structural one.

Kinetic studies were performed in a specially designed simple vacuum apparatus where a mineral sample was heated gradually (10 ± 2 °C/min) and the increasing water vapor pressure in a constant volume was registered continuously (Fig. 5).

The first derivative demonstrated the existence of two types of water: extraneous, $H_2O(1)$; and structural, $H_2O(2)$. The extraneous water has a

Fig. 5. Kinetics of water release from 11.0 mg of sample S-178 (SER₁₇₈) upon heating up to 650 °C. V – vacuummeter record (pressure in Torr, right ordinate). K – normalized (lineated) V-record, using 24 points (pressure in Pa, left ordinate). The broken line (FD) is the first derivative of K. The squared area represents the water amount evolved as a function of the temperature in arbitrary units (squares). The first peak area (295 sqs), below 170 °C, is considered to cover the extraneous water, whereas the second peak area (2260 sqs), over this temperature, belongs to the structural water in the sample.

maximum evolution rate at $T = 80\text{--}90\text{ }^{\circ}\text{C}$. The main part of this water evolved below $T = 170\text{ }^{\circ}\text{C}$, being surface-adsorbed (O'Neil, 1979). The ratio of the two peak surfaces (below $170\text{ }^{\circ}\text{C}$ and over this temperature helped to calculate graphically the percentage of the extraneous waters in regards to the whole amount of water that evolved below $T = 650\text{ }^{\circ}\text{C}$, which is 11.5%.

Water extraction from solid samples

The low-temperature $\text{H}_2\text{O}(1)$ is most likely meteoric, in equilibrium with the environment. It has to be eliminated before extraction of the structural water, as $\text{H}_2\text{O}(1)$ may interfere with the isotopic signature of the structural water itself.

A sample of 50–80 mg was heated up to $T = 170\text{ }^{\circ}\text{C}$ at continuous pumping out, aiming at removal of the adsorbed $\text{H}_2\text{O}(1)$. Later, by heating up to $650\text{ }^{\circ}\text{C}$, the structural water $\text{H}_2\text{O}(2)$ was evolved and collected (trapped) quantitatively. This temperature is sufficiently high for water extraction from sericite (muscovite), since it breaks down at higher temperatures (O'Neil and Taylor Jr., 1969).

A sericite sample, after water extraction at $650\text{ }^{\circ}\text{C}$, was heated additionally up to $700\text{ }^{\circ}\text{C}$, when no measurable amount of water was found.

Introducing of liquid samples

The liquid samples (SMOW, MET) were sucked in glass capillaries (spikes), which made possible to control their mass by weighing on a semi-micro balance ($\pm 0.02\text{ mg}$) (Piperov *et al.*, 1977), and sealed. The glass capillaries containing water samples were subjected to the same procedures as solid samples, aiming at reduction of possible inexplicable differences: under continuous pumping the capillary was preheated to $T = 170\text{ }^{\circ}\text{C}$. At $T \approx 420\text{--}450\text{ }^{\circ}\text{C}$, the capillary explodes ("decrepitates") and the water (vapor) is collected by freezing in a cold trap.

Conversion of water to hydrogen or carbon dioxide. Mass-spectrometry

Molecule water is very inconvenient for direct mass-spectrometry. The polar water molecules, even in high-vacuum environment, are strongly adsorbed on the clean inner surfaces of the mass-spectrometer. This favors some fractionation, due to the selective bounding of the heavier molecules (HDO , H_2^{18}O , and especially D_2O) on the metal walls, as well as an inclination for memory-effect. For that reason, the most convenient form is hydrogen for HD/H_2

determination, and carbon dioxide (or O_2), when oxygen isotopes are traced ($^{12}\text{C}^{16}\text{O}^{18}\text{O}/^{12}\text{C}^{16}\text{O}_2$).

We used Zn for the reduction of water to hydrogen (see Friedman, 1953; Tamiya, 1960; Piperov and Penchev, 1982). The synthesis of carbon dioxide, containing the oxygen atoms of the water molecule, proceeds by interaction with an oxygen-free compound: guanidine hydrochloride $[(\text{NH}_2)_2\text{CNH}.\text{HCl}]$ (abbr. GuaHCl)], following the methods of Boyer *et al.* (1961) and Yang *et al.* (1996), with some inessential changes. The conversion of water to hydrogen or carbon dioxide proceeds in sealed glass ampoules.

To identify isotopes and to determine their abundance, atomic masses 2, 3, 16, and 18 were trailed and peak intensities I_2 , I_3 , I_{44} , and I_{46} were registered for the purpose.

RESULTS

The conventional way for presentation of the results is the relative depletion–enrichment ($\delta\text{‰}$) of the heavier isotope, when compared with a universally adopted standard, in this case the Standard Mean Ocean Water (SMOW): $\delta\text{‰} = [(R_x/R_s) - 1] \times 10^3$, where $R_x = R_3 = (I_3/I_2)$ (DH/H_2) or $R_x = R_{46} = (I_{46}/I_{44})$ ($\text{C}^{16}\text{O}^{18}\text{O}/\text{C}^{16}\text{O}_2$), and $R_s = R(\text{SMOW})$ is the corresponding mol ratio for SMOW. Thus, only these ratios are the object of experimental determination. The median is preferred to the average in data processing (Dean and Dixon, 1951). The standard deviation (SD) is calculated using the concise expression $\text{SD} = \pm (w/n^{0.5})$, where w is the range of results and n is the number of measurements (Skoog and West, 1976).

The found ratio $R_{3\text{SMOW}} = (3.08 \pm 0.07) \times 10^{-4}$ corresponds to deuterium concentration $D_{\text{SMOW}} = 0.0154 \pm 0.0004$ atomic percent, well comparable with our earlier data for the same standard ($D_{\text{SMOW}} = 0.0157 \pm 0.0002$ at.%; Piperov and Penchev, 1982), as well as with the concentration $D_{\text{SMOW}} = 0.0158 \pm 0.0002$ at.% proposed by Craig (1961a) and also with the one declared for SMOW-V: $D_{\text{SMOW-V}} = 0.015576$ at.%. The result for ^{18}O -concentration found by $R_{46\text{SMOW}}$ is $^{18}\text{O} = 0.201 \pm 0.004$ at.% and also corresponds to the SMOW-V value: $^{18}\text{O} = 0.20052$ at.%, within the uncertainty limits.

The data obtained for sericite samples SP-133 (SER_{133}) and S-178 (SER_{178}) were plotted in coordinates δD vs. $\delta^{18}\text{O}$, together with the results for the meteoric water (MET) (Fig. 6). The points of two samples of Chelopech alunite (Lerouge *et al.*, 2006) are also presented in the same diagram, as

Fig. 6. δD vs. $\delta^{18}O$ diagram. The meteoric water line (MWL) fits Craig's (1961b) equation. The field of primary magmatic water (PMW) is after White (1974) and Viglino *et al.* (1985); the fields of crustal felsic magmas (CFM), arc magmas (AM) and subduction-related volcanic vapor (SDVV) cover the vision of Hedenquist and Lowenstern (1994, fig. 3a). ALU_{3C} and ALU_7 denote the samples of Chelopech alunites, respectively (Lerouge *et al.*, 2006). ENA_{FI} marks the location of water from Chelopech enargite hosted fluid inclusions (Piperov *et al.*, 2017). MET is the point of a sample of extant surface meteoric water (Iskar Dam, Bulgaria). The isotope fractionation reveals D-rich primordial waters (empty hexagons).

well as the result from the isotope analysis of the enargite trapped fluid inclusions from the same deposit (Piperov *et al.*, 2017).

The δD values of both sericite samples show relatively similar results. Sample S-178 (SER_{178}) shows $\delta D_{178} = -14 \pm 23\text{‰}$, whereas sample SP-133 (SER_{133}) shows $\delta D_{133} = -28 \pm 22\text{‰}$. The respective $\delta^{18}O$ values for these samples are: $\delta^{18}O_{178} = -1 \pm 10\text{‰}$ and $\delta^{18}O_{133} = +11 \pm 7\text{‰}$. The δD and $\delta^{18}O$ data for meteoric water (MET), collected from the Iskar Dam, are $\delta D_{MET} = -93 \pm 23\text{‰}$ and $\delta^{18}O_{MET} = -14 \pm 9\text{‰}$, and show significant similarity with the data on surface waters in the area of the Assarel deposit studied by Lerouge *et al.* (2006).

DISCUSSION AND CONCLUSIONS

The stable isotope signatures of H and O are favorable tools for investigation of the characteristics and origin of fluids involved in and responsible for hydrothermal processes in mineral deposits. The isotopic composition of the alteration and/or ore minerals should give a feedback about the parental fluid

composition. Generally, the major sources of fluids participating in the formation of alteration haloes in the host rocks of epithermal deposits represent magmatic, meteoric and also sea or intra-basin waters. Normally, their isotopic signatures are particular. Caution is needed when different factors could influence and obscure the original isotopic signature. The most important factor could be the fluid-wall rock isotopic exchanges caused during fluid circulation and interaction.

The δD and $\delta^{18}O$ values obtained from sericite samples from the quartz-sericite alteration zone in the Chelopech deposit are consistent with precipitation from fluids dominated by volcanic derivatives with some tendency towards lower $\delta^{18}O$, especially in sample S-178 (SER_{178}), which indicates dilution with surficial waters. The δD and $\delta^{18}O$ values for SP-133 (SER_{133}) are statistically indistinct from the points of the two samples of Chelopech alunites studied by Lerouge *et al.* (2006).

Moritz *et al.* (2003) investigated primary fluid inclusions in enargite and isotope signatures of barite crystallized during the late stage of mineral formation in the deposit. According to enargite

fluid inclusion data, the fluid responsible for the precipitation of the most important mineral in the economic mineralization is a mixing of a hot and saline end-member, likely a magmatic brine, and a lower temperature and dilute fluid, which could be heated groundwater of meteoric or seawater origin, or condensed magmatic vapor. The isotope signature of barite (Sr, O, S) also supports mixing of a magmatic fluid with a dilute fluid during late ore formation stage, but the data do not allow discriminating accurately if this dilute end-member could be of meteoric or of seawater origin.

The isotopic signatures of H, O and S from alunite (Lerouge *et al.*, 2006) revealed that it crystallized in the frame of the advanced argillic alteration zone of the deposit, but also exhibited characteristics of mixing between magmatic fluids and an external component. The latter was identified as seawater-derived fluid or meteoric water in the vicinity of a sea, but the magmatic fluid was deemed dominant. The data obtained by Piperov *et al.* (2017), also concerning enargite hosted fluid inclusions, indicated that the enargite from the Chelopech deposit is a product of the late hydrothermal stage and it was deposited from solution dominated by deeply circulating meteoric water.

The correct discussion on the water origin needs also conformance to the isotope fractionation. The isotope signature of the structural water of a given mineral does not copy the isotope composition of the water that participates in the mineral formation, since the crystal lattice selectively incorporates water molecules of “preferred” isotopic composition. This effect is known as isotope fractionation: $\Delta = 10^3 \ln \alpha_{M-W} \approx \delta_M - \delta_W$, where α_{M-W} is the fractionation factor for the corresponding mineral and water (Sheppard *et al.*, 1971).

In the case of sericite (muscovite)–water equilibrium, the hydrogen isotope fractionation at $T \leq 450$ °C is evaluated as $\Delta = -23.7\text{‰}$ (Suzuoki and Epstein, 1976), and for oxygen isotopes it is $\Delta = +2\text{‰}$ (O’Neil and Taylor, Jr., 1969).

The large uncertainty field of our results is due entirely to the limitations of the mass-spectrometer used. Unfortunately, the isotope fractionation dur-

ing sericite crystallization, as well as the isotope exchange on the extraction heating (*i.e.*, silicate-water interactions with $\Delta^{18}\text{O} \leq 10\text{‰}$), cannot be revealed, since the δ -variations lie entirely in the field of uncertainty. Nevertheless, it may be concluded that the isotope signature of the structural water of the examined sericites clearly differs from contemporary surface meteoric water, as well as from the ancient hydrothermal inclusion fluid, which also seems to be dominated by meteoric water. This finding minimizes the possibility for participation of meteoric water in sericite crystallization (see above).

Considering the data obtained from various studies on the origin of hydrothermal fluids responsible for the formation of economic mineralization in the Chelopech deposit, a main conclusion can be drawn. The study of stable isotope signatures in various minerals from different hydrothermal alteration zones – advanced argillic (alunite), quartz-sericite (sericite), economic mineralization (fluid inclusions in enargite), late stage of mineralization (barite) – regardless of the different methodology, unequivocally prove that the deposit was formed by the precipitation from fluids of magmatic and external origin, most probably sea water. The uncertainty in determining the origin of the external fluid could be explained with the role of interaction of the wall rock and the possible mixing between different fluid members with undefinable impact. However, the isotope signature in sericite from the quartz-sericite alteration zone complements the study and unequivocally confirms the continuity of the hydrothermal ore formation process developed in successive stages in time and space, and the significant participation of magmatic fluid in the system.

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REFERENCES

- Boyer, P.D., Graves, D.J., Suelter, C.H., Dempsey, M.E. 1961. Simple procedure for conversion of oxygen of orthophosphate or water to carbon dioxide for oxygen-18 determination. *Analytical Chemistry* 33 (13), 1906–1909, <https://doi.org/10.1021/ac50154a036>.
- Carrigan, C., Mukasa, S., Haydutov, I., Kolcheva, K. 2006. Neoproterozoic magmatism and Carboniferous high-grade metamorphism in the Sredna Gora Zone, Bulgaria: An extension of the Gondwana-derived Avalonian-Cadomian belt?. *Precambrian Research* 147 (3–4), 404–416, <https://doi.org/10.1016/j.precamres.2006.01.026>.
- Chambefort, I. 2005. *The Cu-Au Chelopech Deposit, Panagyurishte District, Bulgaria: Volcanic Setting, Hydrothermal Evolution, and Tectonic Overprint of a Late Cretaceous*

- High-sulphidation Epithermal Deposit*. PhD thesis, Université de Genève, Terre et Environnement, 173 pp.
- Cheshitev, G., Milanova, V., Sapunov, I., Tchoumatchenko, P. 1995. *Explanatory notes to the geological map of Bulgaria in scale 1:100 000, Teteven map sheet*. Avers, Sofia, 94 pp. (in Bulgarian, with English summary).
- Craig, H. 1961a. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* 133 (3467), 1833–1834, <https://doi.org/10.1126/science.133.3467.1833>.
- Craig, H. 1961b. Isotopic variations in meteoric waters. *Science* 133 (3465), 1702–1703, <https://doi.org/10.1126/science.133.3465.1702>.
- Dean, R.B., Dixon, W.J. 1951. Simplified statistics for small numbers of observations. *Analytical Chemistry* 23 (4), 636–638, <https://doi.org/10.1021/ac60052a025>.
- Friedman, I. 1953. Deuterium content of natural waters and other substances. *Geochimica et Cosmochimica Acta* 4 (1–2), 89–103, [https://doi.org/10.1016/0016-7037\(53\)90066-0](https://doi.org/10.1016/0016-7037(53)90066-0).
- Georgieva, S. 2014. *Mineralogy and zonal development of the hydrothermal alterations in the Chelopech deposit and their relation to mineralizations*. PhD thesis, Geological Institute, Bulgarian Academy of Sciences, Sofia, 49 pp.
- Georgieva, S. 2017. Mineral associations and their distribution in hydrothermal alteration zones of the Chelopech high-sulphidation deposit, Bulgaria. *Geologica Balcanica* 46 (2), 11–16.
- Hedenquist, J.W., Lowenstern, J.B. 1994. The role of magmas in the formation of hydrothermal ore deposits. *Nature* 370, 519–527, <https://doi.org/10.1038/370519a0>.
- Heinrich, C.A. 2005. The physical and chemical evolution of low-salinity magmatic fluids at the porphyry to epithermal transition: a thermodynamic study. *Mineralium Deposita* 39, 864–889, <https://doi.org/10.1007/s00126-004-0461-9>.
- Ivanov, Z. 2017. *Tectonics of Bulgaria*. Sofia University Press, Sofia, 331 pp. (in Bulgarian).
- Lerouge, C., Kunov, A., Fléhoc, C., Georgieva, S., Hikov, A., Lescuyer, J.L., Petrunov, R., Velinova, N. 2006. Constraints of stable isotopes on the origin of alunite from advanced argillic alteration systems in Bulgaria. *Journal of Geochemical Exploration* 90 (3), 166–182, <https://doi.org/10.1016/j.gexplo.2005.11.001>.
- Moev, M., Antonov, M. 1978. Stratigraphy of the Upper Cretaceous in the eastern part of Strelcha-Chelopech line. *Annual of the University of Mining and Geology* 23 (2), 7–27 (in Bulgarian).
- Moritz, R., Jacquat, S., Chambefort, I., Fontignie, D., Petrunov, R., Georgieva, S. 2003. Control on ore formation at the high-sulphidation Cu-Au Chelopech deposit, Bulgaria: Evidence from infrared fluid inclusion microthermometry of enargite and isotope systematics of barite. In: Eliopoulos, D.G., et al. (Eds), *Mineral Exploration and Sustainable Development*. Millpress, Rotterdam, 1173–1176.
- Moritz, R., Kouzmanov, K., Petrunov, R. 2004. Upper Cretaceous Cu-Au epithermal deposits of the Panagyurishte district, Srednogie zone, Bulgaria. *Swiss Bulletin of Mineralogy and Petrology* 84, 79–99.
- Mutafchiev, I., Petrunov, R. 1996. *Geological Genetic Models of Ore-deposit Formation in the Panagyurishte-Etropole Ore Region*. Unpublished report for Chelopech LTD, 69 pp.
- O'Neil, J.R. 1979. Stable isotope geochemistry of rocks and minerals. In: Jäger, E., Hunziker, J.C. (Eds), *Lectures in Isotope Geology*, Springer, Berlin, Heidelberg, 235–263, https://doi.org/10.1007/978-3-642-67161-6_21.
- O'Neil, J.R., Taylor Jr., H.P. 1969. Oxygen isotope equilibrium between muscovite and water. *Journal of Geophysical Research* 74 (25), 6012–6022, <https://doi.org/10.1029/JB074i025p06012>.
- Peytcheva, I., von Quadt, A. 2004. The Palaeozoic protoliths of Central Srednogie, Bulgaria: records in zircons from basement rocks and Cretaceous magmatites. *Proceedings of the Fifth International Symposium on the Eastern Mediterranean Geology*, 14–20 April 2004, Thessaloniki, Greece, 392–395.
- Petrunov, R. 1995. Ore mineral paragenesis and zoning in the deposit of Chelopech. *Geochemistry, Mineralogy and Petrology* 30, 89–98 (in Bulgarian, with English abstract).
- Piperov, N.B., Penchev, N.P. 1982. Deuterium content of the inclusion water from hydrothermal galenas, Madan, Bulgaria. Preliminary investigation. *Economic Geology* 77 (1), 195–197, <https://doi.org/10.2113/gsecongeo.77.1.195>.
- Piperov, N.B., Penchev, N.B., Bonev, I.K. 1977. Primary fluid inclusions in galena crystals. II. Chemical composition of the liquid and gas phase. *Mineralium Deposita* 12, 77–89, <https://doi.org/10.1007/BF00204506>.
- Piperov, N.B., Atanassova, R., Kotzeva, B.G., Iliev, T. 2017. Reequilibrated fluid inclusions in enargite-luzonite from the Chelopech high-sulphidation Cu-Au epithermal deposit (Bulgaria). *Neues Jahrbuch für Mineralogie, Abhandlungen* 194 (3), 297–310, <https://doi.org/10.1127/njma/2017/0023>.
- Popov, P., Vladimirov, V., Bakardjiev, S. 1983. Structural model of the polyformational Chelopech copper field (Bulgaria). *Geologia Rudnih Mestorojdeniya* 25 (5), 3–11 (in Russian).
- Sheppard, S.M.F., Nielsen, R.L., Taylor Jr., H.P. 1971. Hydrogen and oxygen isotope ratios in minerals from porphyry copper deposits. *Economic Geology* 66 (4), 515–542, <https://doi.org/10.2113/gsecongeo.66.4.515>.
- Skoog, D.A., West, D.M. 1976. *Fundamentals of Analytical Chemistry (3rd Edition)*. Holt, Rinehart and Winston, New York, 804 pp.
- Stoykov, S., Yanev, Y., Moritz, R., Katona, I. 2002. Geological structure and petrology of the late Cretaceous Chelopech volcano, Srednogie magmatic zone. *Geochemistry, Mineralogy and Petrology* 39, 27–38.
- Stoykov, S., Peytcheva, I., von Quadt, A., Moritz, R., Frank, M., Fontignie, D. 2004. Timing and magma evolution of the Chelopech volcanic complex (Bulgaria). *Schweizerische Mineralogische und Petrographische Mitteilungen* 84, 101–117.
- Suzuoki, T., Epstein, S. 1976. Hydrogen isotope fractionation between OH-bearing minerals and water. *Geochimica et Cosmochimica Acta* 40 (10), 1229–1240, [https://doi.org/10.1016/0016-7037\(76\)90158-7](https://doi.org/10.1016/0016-7037(76)90158-7).
- Tamiya, N. 1960. Determination of deuterium in water and organic compounds. *Analytical Chemistry* 32 (6), 724–725, <https://doi.org/10.1021/ac60162a051>.
- Terziev, G. 1968. Mineral composition and genesis of the Chelopech ore deposit. *Bulletin of the Geological Institute, Series Geochemistry, Mineralogy and Petrography* 17, 123–187 (in Bulgarian, with English abstract).
- Vigliano, J.A., Harmon, R.S., Borthwick, J., Nehring, N.L., Motyka, R.J., White, L.D., Johnston, D.A. 1985. Stable-isotope evidence for a magmatic component in fumarole condensates from Augustine Volcano, Cook Inlet, Alaska, U.S.A. In: Kitano, I. (Ed), *Water-Rock Interaction, International Symposium on Water-Rock Interaction*, 4, Misasa,

- Japan, Aug. 29-Sept. 8, 1983, *Chemical Geology* 49 (1–3), 141–157, [https://doi.org/10.1016/0009-2541\(85\)90152-4](https://doi.org/10.1016/0009-2541(85)90152-4).
- White, D.E. 1974. Diverse origins of hydrothermal ore fluids. *Economic Geology* 69 (6), 954–973, <https://doi.org/10.2113/gsecongeo.69.6.954>.
- Yang, W., Roy Krouse, H., Spencer, R.J. 1996. Improved techniques for stable isotope analyses of microlitre quantities of water from fluid inclusions in halite and concentrated brines. *Chemical Geology* 130 (1–2), 139–145, [https://doi.org/10.1016/0009-2541\(96\)00013-7](https://doi.org/10.1016/0009-2541(96)00013-7).