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Българската геология и българските геолози в чужбина

Резюмета на статии в чуждестранни издания, излезли през 2017–2019

2017

Bogdanov, K., J. Kuncheva. 2017. Epithermal gold mineralization in the Krassen deposit, Panagyurishte ore district, Bulgaria. – *Geologica Macedonica*, *31*, 2, 107–116.

Gold mineralization in the Krassen high-sulphidation epithermal deposit, Panagyurishte ore district, Bulgaria, has been studied in respect to mineral assemblages, gold grain size, fineness and trace elements based on EPMA and LA-ICP-MS studies. Part of the gold in the early massive pyrite dominated ores is submicroscopic in size (<0.1 μm) and could be attached to the so called "invisible" gold. Later fracturing of the early massive pyrite, followed the deposition of Cu-pyrite ore bodies enriched in chalcopyrite, enargite, bornite, galena and sphalerite accompanied by deformation and recrystallization is suggested as a reason for Au and Ag migration to cracks and gold grains coarsening. The electrum fineness in individual grains varies between 882 and 998‰. Most commonly observed trace elements in the native gold, electrum grains and gold hosting sulphide minerals are: Cu, Fe, Hg, Sb, Te, Bi, As and Se. The Au content in pyrite varies from 0.35 to 7.83 ppm and in chalcopyrite from 0.97 to 2.78 ppm. BiTe-Se and Ga-Ge-In trace elements signature is characteristic feature of the ore minerals and indicator for Au enrichment.

Cattò, S., W. Cavazza, M. Zattin, A. Okay. 2017. No significant tectonic overprint on the Cimmerian Strandja Massif (SE Bulgaria and NW Turkey). – *Intern. Geol. Review*, 513–529.

We provide the first comprehensive picture of the thermochronometric evolution of the Cimmerian Strandja metamorphic massif of SE Bulgaria and NW Turkey, concluding that the bulk of the massif has escaped significant Alpine-age deformation. Following Late Jurassic heating, the central part of the massif underwent a Kimmeridgian–Berriasian phase of relatively rapid cooling followed by very slow cooling in Cretaceous-to-Early Eocene times. These results are consistent with a Late Jurassic–Early Cretaceous Neocimmerian (palaeo-Alpine) phase of north-verging thrust imbrication and regional metamorphism, followed by slow cooling/exhumation driven by erosion. From a thermochronometric viewpoint, the bulk of the Cimmerian Strandja orogen was largely unaffected by the compressional stress related to the closure of the Vardar-İzmir-Ankara oceanic domain(s) to the south, contrary to the adjacent Rhodopes. Evidence of Alpine-age deformation is recorded only in the northern sector of the Strandja massif, where both basement and sedimentary rocks underwent cooling/exhumation associated with an important phase of shortening of the East Balkan fold-and-thrust belt starting in the Middle–Late Eocene. Such shortening focused in the former Srednogorie rift zone because this area had been rheologically weakened by Late Cretaceous extension.

Georgiev, G., G. Tari. 2017. Salt tectonics in the Carnian evaporite basin of the Eastern Balkan-Forebalkan region of Bulgaria. – In: Soto, J. I., J. Flinch, G. Tari (Eds). *Permo-Triassic Salt Provinces of Europe, North Africa and the Atlantic Margins. Tectonics and Hydrocarbon Potential.* Elsevier.

Moulas, E., F. L. Schenker, J.-P. Burg, D. Kostopoulos. 2017. Metamorphic conditions and structural evolution of the Kesebir-Kardamos dome: Rhodope metamorphic complex (Greece-Bulgaria). – *Intern. J. Earth Sci.*, *106*, 2667–2685; DOI: 10.1007/s00531-017-1452-2.

The synmetamorphic nappe system of the Rhodope Metamorphic Complex has been deformed into dome-and-basin structures attributed to syn- to post-convergent exhumation. We document the deformation style and present new thermobarometric and geochronological constraints for the Kesebir-Kardamos dome in Southern Bulgaria and Northern Greece. The dome consists of a migmatitic core overlain by high-grade thrust sheets. Kinematic indicators indicate a continuum from ductile to brittle conditions during exhumation. Thermodynamic modeling applied to the high-grade, intermediate thrust sheets yielded peak conditions of 1.2 GPa and ca 730 °C. New U-Pb SHRIMP-II dating of zircons from rocks of the same unit revealed Late Jurassic–Early Cretaceous (145 Ma) as the time of metamorphic crystallization; some zircon rims yielded Eocene ages (53 and 44 Ma) interpreted as having been thermally reset owing to coeval granitoid magmatism. The high-grade rocks were covered by Lutetian–Priabonian marine sediments after exhumation. Slumps suggest that sedimentation took place in a tectonically active environment. Our new structural, petrological and geochronological results suggest that the major shear zone in the core of the Kesebir-Kardamos dome is equivalent to the Late Jurassic–Early Cretaceous Nestos Shear Zone. Post-Jurassic metamorphic ages recorded in the Rhodope most likely represent crustal rather than deep subduction geodynamic processes.

Piperov, N. B., R. Atanassova, B. G. Kotzeva, Tz. Iliev. 2017. Reequilibrated fluid inclusions in enargite-luzonite from the Chelopech high-sulfidation Cu-Au epithermal deposit (Bulgaria). – *Neues Jahrbuch für Mineralogie, Abhandlungen*, *194*, 3, 297–310.

The ores of the Chelopech high-sulfidation Cu-Au deposit are mineralogically and texturally very complex. Enargite is

a substantial component of the massive, fine-grained sulfide ore. Weak manifestations of luzonite followed enargite, but high-resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) patterns unambiguously reveal numerous luzonite layers in enargite structure, as well as abundant pseudomorphs of luzonite after enargite. Scanning electron microscopy (SEM) and infrared (IR) microscopy were utilized for studying the morphology and occurrence of fluid inclusions in enargite. Microthermometry data, including temperatures of homogenization (Th) and fluid salinity, were also summarized. Crush-leach techniques, followed by atomic absorption spectrometry (AAS) reveal the major cations participation in inclusion solutes (mol %): Na 86.9, K 6.2, Mg 5.6 and Ca 1.4. Molecular species (CO_2, N_2, CH_4), liberated on vacuum crushing, were analyzed by mass spectrometry (MS); H_2O was determined compressometrically. The Th-data processed are mainly a compilation of results already published somewhere in the literature. These temperatures (95–245 °C) are always below the temperature of enargite sta bility (T>270 °C). The occurrence and orientation of the fluid inclusions in the enargite crystals, however, as well as the readings of the empirical Na-K-Ca geothermometer (T≥260 °C) imply inclusion trapping during enargite crystallization. The low Th was ascribed to re-equilibration after deformation (collapse) of the inclusion cavities, caused probably by the polymorphous transition enargite-luzonite on cooling. It is concluded that enargite is deposited at T≥260 °C from solution of low to moderate salinity (ca. 6 wt%). The stable isotopes (δD and $\delta^{18}O$), as well as N_2/Ar ratios point to an ore-forming solution dominated by deeply circulating meteoric water. A pH=5–6, (in eny case over 4) and slightly reducing environment are assumed.

2018

Bonev, N., P. Filipov. 2018. From an ocean floor wrench zone origin to transpressional tectonic emplacement of the Sithonia ophiolite, eastern Vardar Suture Zone, Northern Greece. – *Int. J. Earth Sci*., *107*, 1689–1711.

In the Hellenides of northern Greece, the Sithonia back-arc ophiolite constitute an element of the Vardar suture zone against the Chortiatis island arc magmatic suite, the Melissochori Formation and the Serbo-Macedonian Massif further north at the Mesozoic continental margin of Eurasia. A granodiorite from the Chortiatis island arc magmatic suite crystallized at 160 Ma as derived from new U-Pb zircon geochronology and confirms the end of arc magmatic activity that started at around 173 Ma. Located southerly of the Chortiatis island arc magmatic suite, the Sithonia ophiolite had igneous life from 159 to 149 Ma, and the ophiolite interfinger with clastic-carbonate Kimmeridgian sediments. Magmatic structures (i.e., sheeted dykes) in the ophiolite witness for NE-trending rift axis, while the transform faults and fracture zones sketch NW-SE transcurrent transtension-like propagation of the rift-spreading center at Sithonia that is consistent with a dextral wrench corridor already proposed for the ophiolite origin in the eastern Vardar Zone. The tectonic emplacement of the Sithonia ophiolite involved dextral ENE to SE strike-slip sense of shear and SW and NE reverse thrust sense of shear on mostly steep foliation S_1, subhorizontal lineation L_1 and associated variably inclined F_1 fold axes. This structural grain and kinematics are shared by adjacent Chortiatis island arc magmatic suite and the Melissochori Formation. The coexistence of strike-parallel and thrust components of displacement along discrete dextral strike-slip shear zones and internal deformation of the mentioned units is interpreted to result from a bulk dextral transpressive deformation regime developed in greenschist-facies metamorphic conditions. The back-arc ocean floor previous structural architecture with faults and fracture zones where Kimmeridgian sediments deposited in troughs was used by discrete strike-slip shear zones in which these sediments involved, and the shear zones become the sites for strain partitioning of transpressional deformation. Available biostratigraphic and radiometric age constraints define latest Jurassic–earliest Cretaceous (Tithonian–Berriasian to early Valanginian) time frame for the Sithonia ophiolite northeastward tectonic emplacement accomodated by dextral transpression that led to the ophiolite accretion to the Chortiatis island arc magmatic suite and its trench-fill exposed in the Melissochori Formation and further north toward the Serbo-Macedonian margin of Eurasia.

González-Jiménez, J. M., V. Colás, F. Gervilla, Th. Kerestedjian, I. Sergeeva, A. Casado-González, I. Fanlo. 2018. Metamorphic evolution of sulphide-rich chromitites from the Chernichevo ultramafic massif, SE Bulgaria. – *Ore Geology Reviews*, *101*, 330–348; DOI: 10.1016/j.oregeorev.2018.07.024.

The upper mantle rocks of the metamorphosed ophiolite of Chernichevo, Rhodope Metamorphic Complex in Southern Bulgaria, host small chromite ores with unusual mineralization of base-metal sulphides rich in platinum-group elements. Mineralogical and chemical data indicate that after their formation in the mantle the Chernichevo's chromite ores were modified by the intrusion of an alkaline mafic melt, which resulted in the precipitation of a suite of metasomatic minerals (sulphides, calcite, apatite and ilmenite), accompanied by an increase in FeO, TiO_2, Ga, Zn, Vn, Mn, and especially Ti and Fe_2O_3 contents in the chromite. The degree of chemical modification and abundance of metasomatic minerals are positively correlated and mark the extent of reaction of the chromitite with the intruding melt. Sulphide segregation promoted the concentration of high amounts of PGEs (up to 3661 ppb), particularly Pt and Pd, yielding chromite ores with a typical flat to positive-sloped chondrite-normalized pattern. Subsequently, the chromite ores were deformed and metamorphosed together with their host rocks at ultra-high pressure (UHP) (>2.5 GPa, >1200 °C) to be later retrograded under eclogite and finally hydrous amphibolite-facies conditions, giving rise to three microstructural types. Metamorphism of the most metasomatized (i.e., sulphide-rich) chromitites at temperatures >700 °C within the conditions of UHP and eclogite-facies resulted in the formation of (1) *nonporous recrystallized chromite*, consisting of a granoblastic microstructure made-up of coarse-grained blasts and finer-grained chromite neoblasts. In contrast, hydrous metamorphism on the less metasomatized (i.e., sulphide-poor) chromitite under the conditions of amphibolite-facies (ca. 482–483 °C) resulted in the formation of (2) *partly altered chromite*, characterized by unaltered cores surrounded by Fe^{2+}-rich and Al-depleted porous chromite containing abundant clinochlore, and (3) *porous chromite* corresponding to a chromite that was entirely transformed by the metamorphic alteration to Fe^{2+}-rich and Al-depleted porous chromite. During metamorphism magmatic Ni-Fe-Cu sulphides originally formed during the metasomatic event in the mantle were altered, resulting in a major leaching of Cu-rich sulphides, leading to significant remobilization of Pt and Pd.

Jovanović, D., V. Cvetković, S. Erić, B. Kostić, I. Peytcheva, K. Šarić. 2018. Variscan granitoids of the East Serbian Carpatho-Balkanides: new insight inferred from U-Pb zircon ages and geochemical data. – *Swiss J. Geosci*., *112*, 121–142; DOI: 10.1007/s00015-018-0325-4.

The study reports and discusses new LA-ICP-MS zircon U–Pb data and major and trace element analyses for 16 samples from

nine different plutons intruding the Getic (Brnjica, Neresnica, Ziman, Gornjane-Tanda-Blizna), and the Danubian (Aldinac, Janja, Ravno Bučje, Plavna and Suvodol) units of the East Serbian Carpatho-Balkanides (ESCB). Within the entire ESCB belt predominate slightly peraluminous granitoids, ranging in composition from biotite–hornblende tonalite through granodiorite to monzogranite. They contain mafic enclaves and are often cut by lamprophyre shallow intrusions and show gradual transitions to, or are cut by muscovite-bearing granitoids. All the above mentioned rocks formed under post-collisional conditions with some of them displaying evidence of post-emplacement shearing and recrystallization. By contrast, the garnet-bearing muscovite granite of Ziman (Getic unit) is distinctively peraluminous and shows evidence of syn-collisional emplacement and crystallization. The most reliable U-Pb zircon ages on the post-collisional granitoids show an age range between ~323 and ~290 Ma. The granitoids of the Getic unit reveal better concordia ages suggesting that Variscan magmatism lasted longer than previously thought, i.e., even until Permian times. On the other hand, the concordia age of 325.8±1.2 Ma for the syn-collisional Ziman granitoid likely represents a minimum age for the collision event in this part of the Variscan belt. The ages of the Danubian plutons at least allow for discussing still open questions, such as (1) whether the Danubian intrusives are systematically older than those intruding the Getic basement, (2) if Variscan syn-collisional plutons do exist in the Danubian unit, and (3) what role the Variscan magmatism played in the formation of uranium mineralization in the area.

Nikolov, T. 2018. Science versus fear: Global problems and global responsibilities. – *Intern. J. Organizational Innovation*, *11*, 2, N.-York, 10–30.

According to many political analysts fear has become an integral part of the present day political processes. The dynamics of nowadays development and the flow of negative information which pervades society require that scientists, devoted to their studies, spend adequate time for making their scientific results popular, for fighting against pseudo-science, for explaining the regional and global problems which our society faces today. The present-day era is totally different from the previous stages of humankind history.

The main characteristic features of the present day are at least four: the dynamic development of science and technologies, the existence of weapons of mass destruction, the horrifying environmental pollution and growth in population. All these characteristic features of the present have a global character. In the time of globalization people should unite because they have a common destiny on Earth – theco-existence or non-existence. Global problems require global responsibilities. It isscientists who should be among the first to form new horizons for humankind.

Kostov, K. S., N. Dobrev, J. Stemberk, M. Briestenský, P. Ivanov. 2018. Monitoring of microdisplacements in Golyamata Tsepnatina cave, Madara Plateau, NE Bulgaria. – *Acta Carsologica*, *47*, 1, 69–81.

The only early medieval rock bas-relief in Europe Madara Horseman is included in UNESCO World Heritage List. This article presents the results from an in situ monitoring of microdisplacements across fissure forming the Golyamata Tsepnatina Cave located at the edge of Madara Plateau above the Horseman, NE Bulgaria. Additionally, we studied movements along cracks behind the plateau edge, which are related to the dynamics of peripheral plateau parts and shaped the rock slices. Monitoring involves the use of a 3D extensometer model TM-71 installed in the cave as well as five sets of pin marks installed across the cracks behind the plateau edge. The results obtained since 1990 indicate formation of a new rock slice from the cliff due to the gravitational extension of rock massif. The established horizontal microdisplacements of the rock slice to SSE imply the existence of a possible active fault with left-lateral component of movements at the base of the plateau. We established influences from near and distant earthquakes with epicenters in NE Bulgaria (Provadia), Romania (Vrancea), and Turkey (Izmit). The graphs of established movements mark continuously ongoing process of shear processes along the slice forming cracks.

Stanimirova, Ts. 2018. Exchange reactions of zinc hydroxide-sulfate minerals in halide solutions. – *Applied Clay Sci.*, *168*, 386–408.

The possibilities of exchange reactions in two types of layer Zn-hydroxy sulfate minerals with neutral and negatively charged hydroxide layer-namuwite ($Zn_4(OH)_6(SO_4)\cdot 4H_2O$) and gordaite ($NaZn_4(OH)_6(SO_4)Cl\cdot 6H_2O$) were studied. As starting materials, synthetic analogs of these minerals are used. Through direct synthesis, besides the known namuwite, gordaite, and its Ca^{2+} form, a series of new cationic (K^+, NH^{4+}) and anionic (Cl^- and Br^-) gordaite forms were synthesized. The K^+, NH^{4+} content is respectively about 1/3 and 2/3 of the nominal compositions. The determined characteristics of Br-forms showed similarity with corresponding chloride forms. The results of the experimental study of the interaction between gordaites and namuwite and various halide solutions showed the realization of three types of solid-state exchange reactions: cation exchange, simultaneous cation-anion exchange, and water molecule-halide anion exchange. All samples were characterized by powder XRD and EDS chemical analysis, and the transformation mechanism was monitored by SEM investigation. By cation exchange, the all cationic gordaite forms were formed, and in addition, Sr^{2+}-form was also obtained. Mutual conversions between the isovalent cations Na^+-K^+, Ca^{2+}-Sr^{2+}, and between all possible combinations of heterovalent cation pairs were established. Regardless of the charge of the hydroxide layer-neutral (namuwite) or negatively charged (gordaites), due to the stronger interaction of halide anion with the interlayer cations than that with the hydroxide layer's tetra-hedral Zn^{2+} cation, the anion exit together with the leaving cations was observed, causing the simultaneous cation-anion exchange or mutual substitution of H_2O molecules and halide anions. In the first case, the gordaite Br-forms from chloride one are formed. However, under treatment of the all various gordaite forms with iodide solutions, no exchange was observed. The big size of I^- anion probably prevents its occupation of the apical position of hydroxide layer's Zn-tetrahedron and provokes the formation of new pure Zn-hydroxy-sulfate-hydrate phase with unknown specific structure. In the second case, the solid-state mutual substitution of H_2O molecules and halide anions halide in the apex of the Zn-tetrahedron resulted in the formation of different Zn-hydroxy-sulfate-hydrates, depending on the treating water amount. The reversible reaction caused a formation of different cationic gordaite forms under treatment of namuwite with chloride solutions of Na^+, K^+, NH^{4+}, Ca^{2+}, and Sr^{2+}. The treatment of gordaites and namuwite with chloride solutions of some of the other alkaline and alkaline earth metals Li^+, Mg^{2+}, and Ba^{2+} resulted in gordaite dissolution and subsequent pseudomorphic simonkolleite crystallization. The simonkolleite formation is probably due to geometric difficulties for Li^+ and Mg^{2+} interlayer incorporation caused by their great hydration capability and for Ba^{2+} due to its ability to form insoluble barite.

Tarassov, M., E. Tarassova. 2018. Modes of occurrence of tungsten in oxidized ores of the Grantcharitsa tungsten deposit (Western Rhodopes, Bulgaria). – In: *17th Serbian Geological Congress, Book of Abstracts*. Vrnjačka Banja, Serbia, 82–85.

It is shown that modes of occurrence of tungsten in the oxidation zone of the vein-type scheelite deposit Grantcharitsa (Bulgaria) are very manifold and controlled by the high values of oxidation potential Eh and with a very high role of Fe^{3+} during the scheelite destruction and the chemical and structural evolution of tungsten in the deposit. The following W minerals and W-bearing minerals are established in the oxidized ores: hypogene minerals – scheelite (intact and relic – most common), supergene minerals: iron-containing meymacite (important), tungstite, hydrotungstite, iron-containing hydrokenoelsmoreite (ferritungstite), stolzite (rare), colloform supergene scheelite (rare), undefined amorphous $WO_3.xFe_2O_3.nH_2O$ gels; mineral bearers of tungsten: goethite (most widespread), hematite, undefined amorphous $SiO_2.xAl_2O_3.yFe_2O_3.nH_2O$ gels. Physicochemical conditions and some ecological consequences of the evolution of various forms of tungsten in the oxidation zone of deposit are discussed.

2019

Bonev, N., R. Moritz, M. Borisova, P. Filipov. 2019. Therma-Volvi-Gomati complex of the Serbo-Macedonian Massif, Northern Greece: A Middle Triassic continental margin ophiolite of Neotethyan origin. – *J. Geol. Soc. London*, *176*, 931–944; DOI: https://doi.org/10.1144/jgs2017-130.

We present field, chemical and U-Pb age data for metamafic-ultramafic bodies of the Triassic rift-related Therma-Volvi-Gomati (TVG) complex of the Serbo-Macedonian Massif (SMM) in the northern Aegean region. The TVG rocks record igneous textures overprinted by Alpine metamorphism and deformation. The high-Ti Volvi body transformed into amphibolites which also rim a low-Ti Gomati and Nea Roda bodies. The compositions are compatible with N- and E-MORB and weak OIB signatures of high-Ti rocks, while the low-Ti rocks are depleted with respect to MORB suggesting melt extraction from a mantle source. U-Pb geochronology reveals Triassic crystallization of the Volvi body at 240 Ma. Ordovician to Carboniferous xenocrystic zircons were found in Stratoni body of the TVG complex, which were sampled from the SMM basement. The Triassic Arnea riftrelated metagranite intrudes the Volvi body. Comparison of the compositions of the Volvi body and the Arnea metagranite from the SMM, with Triassic metagranite of the Rhodope Massif (RM) supports the presence of a regional bimodal rift suite. The location of the TVG complex at the SMMRM margin of Eurasia confirms its origin as a Middle Triassic rift suite, and its nature as a continental margin ophiolite representing an ocean-continent transition of the propagating Neotethys.

Bonev, N., P. Filipov, R. Raicheva, R. Moritz. 2019. Timing and tectonic significance of Paleozoic magmatism in the Sakar unit of the Sakar-Strandzha Zone, SE Bulgaria. – *Intern. Geol. Rev.*, *61*, 1957–1975*;* DOI: 10.1080/00206814.2019.1575090.

Palaeozoic granitoids and meta-granitoids dominate the metamorphic basement of the Sakar unit of the Sakar-Strandzha Zone (SASTZ) in southeast Bulgaria. In this article, we present new whole-rock geochemical data and U-Pb zircon geochronology for the Sakar unit granitoids. The igneous minerals and textures are preserved, except the meta-granitoids that experienced a weak amphibolite-facies overprint. Geochemistry reveals compositions of peraluminous high-K calc-alkaline I- to S-type granitoids of volcanic arc origin. A major group of LILE-LREE-enriched granitoids and meta-granitoids and a single HFSE-HREE-enriched meta-granitoid are distinguished. U-Pb geochronology has yielded crystallization ages between 305 and 295 Ma for the major group granitoids and a ca. 462 Ma crystallization age of HFSE-HREE-enriched meta-granitoid. Late Palaeozoic granitoids of the Sakar unit show similar compositions and a similar tectonic setting when compared to other granitoids of the SASTZ, confirming a uniform region-wide tectono-magmatic event. As the Late Carboniferous–Permian magmatic arc components extend across the SASTZ, they trace the time-correspondent active continental margin along the Eurasian plate during subduction of the Palaeotethys oceanic lithosphere. The late Palaeozoic Eurasian active continental margin magmatic arc evolution of the SASTZ can be extended into the Serbo-Macedonian-Rhodope zones to the west, where time equivalent meta-granitoids support the same geodynamic context.

Delcheva, Z., Ts. Stanimirova, N. Petrova, E. Tacheva. 2019. Thermal decomposition of bromine gordaite: $NaZn_4(OH)_6(SO_4)Br{\cdot}6H_2O$. – *J. Thermal Analysis and Calorimetry*; DOI: 10.1007/s10973-019-08217-5 (in press).

A new compound, $NaZn_4(OH)_6(SO_4)Br{\cdot}6H_2O$ named "Br-gordaite", was obtained by mixing of ZnO with a solution of $ZnSO_4$ and NaBr. The Br^- ion occupies the Cl^- ion tetrahedral position of the brucite-like layer of the gordaite structure without any other changes relating to the structure and chemical composition. The thermal decomposition of the new phase was studied by DSC-TG(DTG)-MS in regard to the thermal events and mass loss during volatile releasing, while phase composition and chemical composition of the initial and heating products were studied by XRD and SEM-EDAX, respectively. All processes are endothermic: (1) dehydration (20–185 °C), (2) dehydroxylation (185–320 °C), (3) evolving of bromine (400–600 °C) and (4) evolving of SO_3 (770–1165 °C). One-stage releasing of bromine from the "Br-gordaite" was observed at 400–600 °C. Bromine-containing intermediate crystalline phases were not detected by XRD during the "Br-gordaite" decomposition. The presence of bromine in the solid residue at 340 °C was established by chemical analysis, while after 600 °C the bromine was no longer present. The final products of the thermal decomposition of "Br-gordaite" are ZnO and traces of $Na_2Zn(SO_4)_2$. The thermal behavior and the obtained thermal decomposition products of the "Br-gordaite" were compared with other minerals with Zn octahedral–tetrahedral hydroxide layer.

Dyulgerov, M., R. Oberti, B. Platvoet, M. Kadiyski, **V. Rusanov**. 2019. Potassic-magnesio-arfvedsonite – $KNa_2(MgFe^{2+}Fe^{3+})_5Si_8O_{22}(OH)_2$: mineral description and crystal chemistry. – *Mineral. Mag.*; DOI: 10.1180/mgm.2018.135 (in press).

The complete mineral description of potassic-magnesio-arfvedsonite, a recently approved (IMA-CNMNC 2016-083) new species of the amphibole supergroup is provided using electron microprobe and LA-ICP-MS analysis, single-crystal structure refinement, Mössbauer and Raman spectroscopy as well as measurement of optical and physical properties. The holotype material was found in syenitic and granitic dyke rocks in association with quartz, potassium feldspar and aegirine-augite from the Buhovo-Seslavtsi pluton (Bulgaria). Potassic-magnesio-arfvedsonite is monoclinic *C2/m*, with unit-cell parameters: a=9.9804(11), b=18.0127(19), c=5.2971(6) Å, β=104.341(2)°, V=922.61 Å^3. In transmitted plane-polarized light (λ=590 cm^{-1}), potassic-magnesio-arfvedsonite is pleo-

chroic (X yellow pale-green, Y green, Z dark-violet brown). It is biaxial (-), α=1.645(2), β=1.655(2), γ=1.660(2) and 2V (meas): 70°. The empirical unit formula obtained from EMP analysis and structure refinement is $^{A}(K_{0.86}Na0_{\cdot 0.08})_{0.94}{}^{B}(Na_{1.74}Ca_{0.25}Mn^{2+}{}_{0.01})_{2.00}{}^{C}(Mg_{2.67}Fe^{2+}{}_{1.42}Fe^{3+}{}_{0.76}Ti_{0.12}Mn^{2+}{}_{0.03})_{5.00}{}^{T}Si_{8}O_{22}{}^{W}(OH_{1.58}F_{0.2}O_{0.20})_{2.00}$. The Fe^{3+}/Fe_{tot} ratio (0.35) is coherent with both the Mössbauer spectra and the single-crystal structure refinement. The 10 strongest X-ray powder reflections [*d* values (in Å), *I*, (hkl)] are: 8.519, 80.5, (110); 3.402, 67.3, (131); 3.295, 41.0, (240); 3.173, 65.0, (310); 2.752, 35.6, ($\bar{3}$31); 2.715, 100.0 (151); 2.591, 44.1, (061); 2.542, 73.2, ($\bar{2}$02); 2.348, 38.5, ($\bar{3}$51); 2.174, 42.0, (261). Potassic-magnesio-arfvedsonite is the product of strongly peralkaline and potassic (perpotassic) magma compositions. Trace-elements analysis shows that this amphibole did not exert significant control on trace elements distribution in the crystallizing peralkaline magma.

Caucia, F., L. Marinoni, G. Bruni. 2019. Investigation on the gemological, physical and compositional properties of some green opals from Eastern Rhodopes, Bulgaria. – *Rendiconti Lincei. Scienze Fisiche e Naturali*; DOI: https://doi.org/10.1007/s12210-019-00855-z

The physical and compositional properties of some common opals from Eastern Rhodopes, Bulgaria have been investigated through several methodologies such as optical and gemological equipments, X-Ray Powder Diffraction (XRPD), Scanning Electron Microscopy (SEM), Raman Spectroscopy and Laser Ablation Microprobe (LA-ICP-MS). The investigated opals show different colors such as light-apple and yellowish green; the diaphaneity is opaque or opaque/translucent with luster waxy/dull/greasy. They are inert to the long and short wavelength UV radiation (366–254 nm). Refractive index and specific gravity values are between 1.445–1.470 and 1.96–2.09 g/cm^3, respectively. XRPD analyses show the opals are CT type and in some cases contain quartz and clay minerals (saponite). Fe and, subordinately, V appear the main chromophores that determine the green-yellowish color, while Ni is responsible for the apple and light green. Other detected trace elements are Al, Ca, K, Mg, Na, B, Zn, Rb. SEM analysis shows three types of structures already observed in the CT opals like randomly distributed nanograins and lepispheres, mammillary structure, channels structure made up by bundles of fibers. Raman spectra confirm the samples are made up by para-crystalline CT-opal, generally considered of volcanic origin, with significative content of saponite.

Georgieva, H., R. Nedyalkov, I. Krumov. 2019. Hydrothermal amphiboles from Na-Ca and Na-Ca-K-silicate alterations: An example from Elatsite porphyry copper–gold deposit, Bulgaria. – *Geologica Carpathica*, *70*, 9–11, 65–68.

The progression of exploitation and new prospection get to the discovery of Na-Ca and transitional Na-Ca-K-silicate alterations (transitional between Na-Ca and K-silicate alteration) in the deeper parts of the Elatsite porphyry copper–gold deposit (PCGD). The study of these new for the deposit alterations reveal the presence of different in morphology, distribution and chemistry hydrothermal amphiboles.

Gervilla, F., M. P. Asta, l. Fanlo, D. Grolimund, D. F. Sanchez, V. A. Samson, D. Hunziker, V. Colás, J. M. González-Jiménez, Th. Kerestedjian, I. Sergeeva. 2019. Diffusion pathways of Fe^{2+} and Fe^{3+} during the formation of ferrian chromite: a µXANES study. – *Contrib. Mineral. and Petrol.*, *174*(8); DOI: 10.1007/s00410-019-1605-3.

The alteration of chromian spinel is a key process during serpentinization and metamorphism of ultramafic rocks controlled by oxygen fugacity (f_{O_2}) and $Fe^{2+}\leftrightarrow Fe^{3+}$ exchange during fluid–rock interaction. Chromian spinel alteration is better recorded in less permeable chromitite than in peridotites where extensive fluid–rock interaction frequently overprints the record of earlier stages of alteration. To shed light on that process we have studied the distribution of Fe^{2+} and Fe^{3+} in variably altered chromian spinel grains from a set of chromitite samples from the same mining district using synchrotron-based microscopic chemical imaging and spatially resolved X-ray absorption near edge structure spectroscopy. Our results show that early stages of alteration do not involve changes in Cr^{3+} and Fe^{2+} contents or in Fe speciation but only depletion in Al^{3+} and Mg^{2+} resulting in the formation of porous chromite. With ongoing alteration Fe^{3+} migrates into porous chromite mainly along fracture walls and fracture zones as well as along grain boundaries. Sheared-type chromitites record the maximum rates of fluid–rock interaction because in these chromitite-types the accommodation of deformation on porous chromite allowed higher rates of diffusion of Fe^{3+} and Fe^{2+} (a magnetite component with Fe^{3+}/Fe_{total} = 0.66) into the newly formed neoblasts. In porous chromite-type texture (all the original chromite grains fully transformed to porous chromite) the deformation and accompanying diffusion processes result in the formation of homogenous ferrian chromite grains. In contrast, in partly altered-type texture (chromite grains with original cores surrounded by porous chromite), such processes are only restricted to the porous rims, giving rise to zoned chromian spinel-ferrian chromite grains.

Gorinova, Ts., N. Georgiev, Z. Cherneva, K. Naydenov, V. Grozdev, A. Lazarova. 2019. Kinematics and time of emplacement of the Upper Allochthon of the Rhodope Metamorphic Complex: evidence from the Rila Mountains, Bulgaria. – *Intern. J. Earth Sci.*, *108*, 2129–2152; DOI: 10.1007/s00531-019-01754-2.

The Rhodope Metamorphic Complex is a nappe pile of four large allochthonous megaunits, referred to as Lower, Middle, Upper, and Uppermost Allochthons. These were originally derived from different paleogeographic provinces and were stacked on top of each other in the course of convergent processes along the European continental margin between the Late Jurassic and the Late Eocene. The direction and age of thrusting as well as the degree and age of Alpine metamorphism vary between individual allochthons and are altogether controversial. The affiliation of individual tectonic units to allochthons is often unclear. However, for the area of the Eastern Rhodope Mountains, there is agreement that the thrusting of the Upper Allochthon onto the Middle Allochthon happened before ca. 68–70 Ma, since Upper Cretaceous magmatic bodies crosscut the metamorphic fabric of the rocks. For the northwestern parts of the Rhodope Metamorphic Complex (Rila Mountains), the age of thrusting was considered to predate the Late Cretaceous. Here, we present the results of mapping, structural observations, and LA-ICP-MS dating of zircons and monazites from the Northwest Rila Mountains and revise the tectonic architecture and history of the area. There the boundary between the Upper and Middle allochthons is the Dodov Vrah Shear Zone. This regional-scale structure represents a top-to-the-southeast amphibolite-facies thrust, along which numerous syn-kinematic intrusive bodies were emplaced. U–Pb LA-ICP-MS zircon and monazite dating of the latter, as well as dating of pre- and post-kinematic plutonic rocks from the study area showed that the time of activity of the Dodov Vrah Shear Zone can be bracketed between ca. 58 Ma and 50–48 Ma. Thus, at least for the northwestern parts of the Rhodope Metamorphic Complex, the thrusting of

the Upper onto the Middle Allochthon happened after the latest Paleocene and before the end of the Lower Eocene.

Hantsche, A. L., K. Kouzmanov, A. Dini, R. Vassileva, O. Laurent. 2019. District-scale geochemical signatures of calc-silicate skarn minerals from the Pb-Zn (±Ag, Cu) distal skarn deposits in Madan, Bulgaria. – In: *Conference SGA 2019*, Glasgow.

The distal skarn bodies of the Madan ore field provide a unique case study on the chemical evolution of a metasomatic mineralizing system at the regional scale. Despite the lack of a known causative intrusive body, skarn formation in the Madan ore field is accompanied by chemical zonation at the district scale, suggesting more proximal metasomatic replacement and mineralization towards the south. Hosted in marble lenses of the basement rocks, skarn pyroxene crystals show an increase in Fe/Mn ratio by an order of magnitude over a 15 km N-S transect. Despite the regional trend, pyroxene compositions exhibit a wide range of concentrations at the deposit scale, where the Fe/Mn ratio is controlled by sequential crystallization during skarn formation. These trends correspond with local shifts in grain size and Fe/Mg ratio, and are observed at sample locations across the entire district. Epidote and other Al-bearing alteration phases, hosted primarily in gneiss, can be sorted into two distinct groups based on major element geochemistry. One phase, Al-rich clinozoisite, maintains the major element chemical signature of the aluminous host rocks, while the second, ferriepidote, forms in veins that cut across the former. Previous work suggests that the secondary epidote may be the coeval metasomatic product of the calc-silicate skarn which formed in the marble, providing additional information for the regional scale chemical patterns.

Hristov, V., N. Stoyanov, S. Valtchev, S. Kolev, A. Benderev. 2019. Utilization of low enthalpy geothermal energy in Bulgaria. – In: *IOP Conf. Ser.: Earth Environ. Sci.*, *249*, 012035; DOI: 10.1088/1755-1315/249/1/012035.

Bulgaria is relatively rich in geothermal water of temperature in the range of 25 °C–100 °C and the total flow-rate exceeds 3000 L/s. Generally, there are more than 170 geothermal fields: 102 of them are state-owned and the rest of them – belong to some municipalities. Up to 72% of the total known flow-rate from the reservoirs has a comparatively low temperature – up to 50 ºC. Flow-rates for individual sources vary within 1–20 L/s for most of the reservoirs. The highest temperature (approximately 100 ºC) is measured at the surface in Sapareva Banya near Rila Mountain. TDS (total dissolved solids) vary between 0.1 g/L and 1.0 g/L for most of the reservoirs in S. Bulgaria, while in N. Bulgaria it is significantly higher – the maximum is up to 150 g/L. The installed capacity amounts to about 97.5 MWt (for 2017), excluding the low grade energy use by ground source heat pumps (GSHP). Geothermal energy has only direct utilization – in balneology, heating of buildings, air-conditioning, greenhouses, geothermal ground source heat pumps, direct thermal water supply for industrial processes. Geothermal water is also used for bottling of potable water and soft drinks. Most of the hydrothermal sites are developed as mountainous or sea resorts. Electricity generation from geothermal water is not currently available in the country

Hristov, V., B. Deneva, S. Valchev, A. Benderev. 2019. Geothermal energy use, country update for Bulgaria (2014–2018). – In: *European Geothermal Congress 2019*, EGEC. Den Haag, The Netherlands, 11–14.

The main objective of this paper is to provide an update for the development of geothermal energy use in Bulgaria by comparing the periods 2009–2013 and 2014–2018. The temperature of geothermal water (natural springs and wells) in Bulgaria varies in the range 25–100 ºC and the total flow rate is up to about 3000 L/s. More than 170 geothermal fields are located all over the country: 102 of them are state-owned, the rest were conceded to several municipalities for a period of 25 years. About 72% of the total resources are of comparatively low temperature – up to 50 ºC at the surface. Flow rates of most of the sources vary from 1 L/s to 20 L/s. Total dissolved solids (TDS) are in the range between 0.1 g/L and 1.0 g/L for most geothermal sources in Southern Bulgaria, while in Northern Bulgaria TDS is significantly higher – the maximum measured is up to 150 g/L. The installed capacity increased to 99.37 MWt in 2018 from 83.10 MWt in 2014 (Bojatgieva et al., 2015), excluding the low grade energy utilization by ground source heat pumps (GSHP). Geothermal energy has only direct use – in water supply, balneology, heating of buildings (including spa-centres), air conditioning, greenhouses etc. In the last more than 40 years, some geothermal (also called mineral) water sources have been used for bottling of potable water and soft drinks. Some of the hydrothermal sites are developed as mountainous or sea resorts. Electricity generation from geothermal water is not currently available in the country due to the relatively low temperatures of geothermal water.

Ivanov, V., M. Dyulgerov, R. Oberti. 2019. Polarized Raman spectroscopy and lattice dynamics of potassic-magnesio-arfvedsonite – *Physics, Chem. Miner.*, *46*, 2, 181–91; DOI: org/10.1007/s 00269-018-0996-4.

We report polarized Raman spectra from potassic-magnesio-arfvedsonite in all informative scattering configurations. On the basis of the polarization selection rules, several A_g vibrational modes have been identified. The B_g modes, however, are below the detection limits of the Raman spectrometer. The OH stretching band is situated between 3630 and 3750 cm^{-1}, and its spectral shape is typical of amphiboles with high occupancy of the A site. It is composed of seven overlapping but resolvable subbands, which stem from occupied A-site configurations M(1)M(1)M(3)–OH–^{A}(K/Na)–^{W}OH and M(1)M(1)M(3)–OH–^{A}(K/Na)–^{W}F, as well as from vacant A-site configurations M(1)M(1)M(3)–OH–$^{A}\square$–^{W}OH, with different Mg and Fe occupancy of the M(1) and M(3) sites. The experimental Raman spectra are compared with the results of theoretical calculations based on a shell-model force-field and a bond polarizability model. The simulated partial Raman spectra allowed us to assign many low-frequency Raman bands to stretching vibrations involving specific cation-oxygen bonds, as well as the higher-frequency modes of the Si–O skeleton. On the basis of our calculations we hypothesize that the Raman bands at 467, 540 and 589 cm^{-1} are related to a superposition of $^{M(2)}Fe^{3+}$–O bond stretching and Si–O–Si bending vibrations.

Ivanova, K., Z. Stojanovska, B. Kunovska, N. Chobanova, V. Badulin, A. Benderev. 2019. Analysis of the spatial variation of indoor radon concentrations (national survey in Bulgaria). – *Environm. Sci. and Pollution Res.*; DOI: 10.1007/s11356-019-04163-9 (in press)

This paper presents the methodology and results of the national radon survey in Bulgaria and its spatial variability. The measurements were carried out in 2778 dwellings using CR-39 track detectors over two successive 9 and 3-month periods

from April 2015 to March 2016. The arithmetic (AM) and geometric (GM) means of annual indoor radon concentration were 111 ± 105 Bq/m^3 and 81 Bq/m^3 (GSD = 2.15), respectively. The distribution of data has been accepted to be lognormal. Two hypotheses have been investigated in the paper. The first one was a spatial variation of indoor radon concentration and the second was spatiality of the factor that influences radon variation. The indoor radon concentrations in the 28 districts have been significantly different, which prove the first hypothesis. The influence of the factors, geology (geotectonic unit, type of rock, and faults distance of the measuring site), type of the region, and the presence of the basement in the building on radon spatial variation, was examined. The analyses have been shown that they significantly affect radon variations but with a relatively small contribution in comparison to the radon variation between district. Furthermore, the significance and contribution of the investigated factors were different in each district, which confirmed the second hypothesis for their spatiality.

Kotelnikov, A. R., N. I. Suk, Z. A. Kotelnikova, Y. Yanev, S. Encheva, V. V. Ananiev. 2019. Liquid immiscibility in fluid-magmatic systems: an experimental study. – *Petrology*, *27*, 2, 206–224; DOI: https://doi.org/10.31857/S0869-5903272206-224 (също на руски).

Liquid immiscibility was studied in melting experiments in the system trachyrhyolite–water + salt (NaF, Na_2CO_3) conducted at parameters imitating those of the volcanic process. The indicator components were La, Nb, Sr, W, Mo, Cr, Fe, Rb, and Cs. The experimental runs were carried out in a high gas pressure apparatus. At 1200 °C and 5 kbar, melting, homogenization, and melt saturation with fluid components occurred. A decrease in the P-T parameters to 1000 °C and 1 kbar led to the onset of liquid immiscibility in the form of droplets in the melt matrix. The composition of the droplets is similar to that of the melt matrix and differs from the latter only in concentrations of water, indicator components, and proportions of alkaline and alkali-earth elements. In the presence of salt (NaF), the melt exsolved into immiscible silicate and salt melts. No liquid immiscibility was detected when Na carbonate was added to the melt, but its agpaitic coefficient increased.

Lihareva, N., L. Dimowa, O. Petrov, Y. Tzvetanova, S. Vladimirova. 2019. Study of the kinetics and mechanism of Sr^{2+} sorption by clinoptilolite. – *J. Radioanalytical and Nuclear Chem*.; DOI: 10.1007/s10967-019-06574-x (in press).

The parameters of kinetics of Sr^{2+} sorption by natural clinoptilolite were investigated. The overall rate constants were determined by application of pseudo-first and pseudo-second order kinetic models. The actual sorption mechanism was studied by application of both intraparticle and surface film diffusion models. The application of Rietveld structure refinement shows the preferable sites of strontium ion exchange in the clinoptilolite structure and their diffusion through cationic sites with time, as well as indicates the positions occupied by Sr^{2+} ions at the start of the exchange process and the positions where Sr^{2+} accumulates in subsequent ion exchange stages.

Túri, M., M. Molnár, T. Orehova, A. Toteva, V. Hristov, A. Benderev, A. Horváth, L. Palcsu. 2019. Tracing groundwater recharge conditions based on environmental isotopes and noble gases, Lom depression, Bulgaria. – *J. Hydrology: Regional Studies*, *24*; DOI: 10.1016/j.ejrh.2019.100611.

A multi-tracer investigation was applied to identify the recharge conditions and isotope hydrological character of four aquifers in the Lom depression (Northwest Bulgaria) using environmental isotopes ($\delta^{18}O$, δ^2H, $\delta^{13}C$, ^3H, ^{14}C) and noble gases. The radiocarbon age model of Ingerson and Pearson was used to estimate the mean residence time of groundwater samples from four aquifers (Dacian, Pontian, Meotian, Sarmatian). Our study focuses on the study of recharge conditions and provides an additional information to hydrodynamic understanding of the four aquifers. New hydrological insights for the region: The mean residence time of groundwater samples represent the last twelve thousand years. In addition to a recently recharged groundwater sample, some samples represent the early Holocene and samples closely correspond to the Late Pleistocene or the transition time between the Early Holocene–Late Pleistocene. The lower noble-gas recharge temperature values may indicate that the recharge occurred during the Late Glacial–Holocene climatic transition. These data can also be used to verify the existence of paleowater from the Pontian and Sarmatian quifers on a trend of the mean residence time of older water heading north away from the study area. Besides the paleoclimatological investigation, it was determined that the Pontian aquifer has no hydraulic connection with the Danube River. The sandy layers and lenses forming the Dacian aquifer are apparently hydraulically isolated and therefore have high degree of heterogeneity.

Zdravkov, A., G. Ajdanlijsky, D. Gross, A. Bechtel. 2019. Organic petrological and geochemical properties of jet from the Middle Triassic Mogila Formation, West Bulgaria. – *Geologica Carpath.*, *70*, 1, 62–74.

The paper presents the results of the petrographic and organic geochemical studies of a jet sample recovered from a mid-Triassic carbonate succession from the West Balkan tectonic zone in Bulgaria. Total organic carbon contents (TOC = 92% daf) and high vitrinite reflectance (R_o = 1.9%) indicate semi-anthracite coalification rank. Very high T_{max} (577 °C) and low HI (~10 mg HC/g TOC) further support the overmature organic matter. Extractable organic matter is characterized by high portions of NSO compounds and asphaltenes (>75%). Hydrocarbons constitute about 20% and are characterized by the predominance of the saturated hydrocarbons over the aromatics. n-Alkanes distribution, dominated by short-chain compounds (n-$C_{17–18}$), is consistent with the woody origin of the jet and the thermal maturity of the organic matter. The predominance of PAHs with condensed structure over their alkylated isomers is considered to be a result of the complex reaction occurring within the organic matrix during the catagenesis, rather than to the presence of combustion-derived organic matter. Based on the distribution of the diterpenoids, a tentative identification of a possible Voltziales conifer family source is identified. Low P_r/Ph ratio (0.88) and aryl isoprenoids outline anoxic conditions of jet formation, whereas the presence of organic sulfur compounds and tri-MTTchroman suggest marine depositional environment with normal salinity.

Zdravkov, A., G. Ajdanlijsky, M. Stefanova, D. Groß, Y. Dintchev. 2019. First lithological and organic geochemical characterization of organic-rich mudstones from Shavar Formation, southeast Bulgaria. – *Energy Sources. Part A – Energy Sources, Part A Recover. Util. Environ. Eff.*, 1–14; DOI: 10.1080/15567036.2019.1649749.

The paper reports the first results of the organic geochemical characterization of mudstones from the Shavar Fm (Eastern Rhodopes Mt., Bulgaria). The rock matrix is unevenly impreg-

nated by amorphous organic matter at the onset of the oil generation (T_{max} ~ 445 °C; PI 0.1–0.2). High total organic carbon contents (avg. TOC – 5.9 wt%) and HI (~720 mg HC/g TOC) argue for oil-prone source-rocks with very good hydrocarbon potential. The n-alkane distributions with maxima in the range n-C20-25 are consistent with organic matter origin from submerged plants. Additionally, sterane distributions dominated by C28-30 4-methyl steranes, indicate dinoflagellate contribution. High pristane/phytane ratio (Pr/Ph=2–4) argue for deposition under oxic conditions.