

More than 500 Ma of magmatic and tectonic evolution of the Serbo-Macedonian Massif (south Serbia, southwest Bulgaria and east Macedonia)

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The Serbo-Macedonian Massif (SMM) represents a complex crystalline terrane situated between the two diverging branches of the Eastern Mediterranean Alpine orogenic system, the northeast-vergent Carpatho-Balkanides and the southwest-vergent Dinarides and the Hellenides. It can be followed from the Pannonian basin in the north, to the Aegean Sea in the south, along the central and southeastern Serbia, southwestern Bulgaria, eastern Macedonia and southern Greece. It's affiliation to European and/or African plate basement is still questionable due to the lack of reliable geochronological data and a detailed structural investigation. The SMM is the key area for understanding the bipolarity of the Alpine orogenic system, as well as the interaction of the Pannonian and Aegean back-arc extension during the Cenozoic time.

The SMM is generally considered to comprise an Upper (low-grade) and a Lower (medium to high-grade) unit (Dimitrijević, 1959). The protoliths of both units are reported as volcano-sedimentary successions, which have been later intruded by igneous rocks during several magmatic pulses. On our mission to discern the main magmatic episodes and the geodynamic evolution of the SMM we have analysed zircon grains of metamorphic rocks from both units, as well as undeformed igneous rocks. LA-ICP-MS analyses were carried out on zircon grains in order to obtain the protolith ages and geochemical analyses were carried out on the total of nineteen samples from different magmatic rocks.

Our first results reveal the presence of a Permo-Triassic (253±13 Ma) magmatic pulse in the Serbian part of the SMM; additionally, the Ordovician – Silurian (496-416 Ma) and the Ediacaran - early Cambrian (Cadomian ; 595-504 Ma) event complete the Pre-Mesozoic magmatic evolution in the Serbian part of the SMM. The new geochronological constraints, together with the field relationships, allowed us to conclude: a) The Lower SMM consists of a Cadomian (Ediacaran-early Cambrian) volcano-sedimentary sequences and magmatics, which were intruded by Ordovician magmatic rocks; b) The Upper SMM (Vlasina and Morava unit) contains a volcano-sedimentary sequence, which is intruded by the Cadomian magmatic rocks; c) In contrast to the Lower complex, no Ordovician age magmatics were documented in the Upper unit, and d) The Upper SMM is covered by Silurian-Devonian sedimentary sequence.

The youngest magmatic event in the SMM occurred in the late Eocene, it is related to the intrusion of Surdulica granodiorite and subsequent latitic volcanism.

Zircon fission track analysis together with apatite data modelling revealed two distinct cooling events. Late middle-Cretaceous rapid cooling through zircon and apatite closure temperature (300°-60°C) is detected along the lower complex of the SMM. To the east along the Vlasina Complex the rocks have probably followed the same late Cretaceous cooling whereas later they have been heated to the temperatures higher than 120°C (apatite closure temperature) during the Eocene - early Oligocene magmatic activities. The second cooling event in the Cenozoic was related to the formation of the Crnook-Osogovo-Lisets dome and the later, post magmatic, extensional phases.

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Amphibole—a key indicator mineral for petrogenesis of the Vitosha pluton, Western Srednogorie, Bulgaria

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The Vitosha pluton is located in the western part of the Srednogorie tectonic zone. According to Dabovski et al. (1991) this zone developed as an island-arc system in Late Cretaceous and is characterized by a mafic-felsic magmatic association (volcanic, plutonic and dyke rocks). The rocks belong to the normal, subalkaline and alkaline series. Dimitrov (1942) has studied rocks from the Vitosha pluton in detail. According to the latter the pluton consists of 4 intrusive phases: I — gabbroic rocks (gabbro, anorthosite), II — monzonites, III — leuco-syenites, and IV — granosyenites. Pegmatitic dykes cut each of the intrusive phases. Amphibole is one of the main rocks forming minerals in the plutonic rocks and often occurs as secondary mineral in aplites and pegmatites. In the gabbros its modal content reaches 20—22%, in anorthosites — 6.3%, in monzonites and syenites -4%.

According to the classification scheme of Leake et al. (1997) analyzed amphiboles are magnesio-Hbl and actinolites. The amphiboles are formed before or simultaneous with biotite. They are secondary altered to epidote and chlorite.

Major and trace-element composition of magmatic amphiboles from the different phases have been studied. They all contain higher REE than clinopyroxene, and may be important carrier for REE. Most trace elements show also slight preference for amphibole, which is most pronounced for Nb, Ta, U, Th, Rb, Ba and Li. All analyses have significant negative Eu anomalies. The total content of REE decreases with fractionation.

The observed compositional variations of amphibole along with those of biotite, titanite, magnetite, and ilmenite have been tentatively used as indicators of magmatic evolution of the calc-alkaline I-type magma from the Vitosha pluton. Estimated temperatures of crystallization are between 834° and 579°C, based on the Blundy and Holland (1990) geothermometer. The depth of final crystallization of the pluton is considered to be of about 7 km.

The most important process in the evolution of the magma is the fractional crystallization: the total content of REE increases in the rocks from the gabbro to the syenites.

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Oligocene shoshonitic rocks of the Rogozna Mts. (Central Balkan Peninsula): evidence of petrogenetic links to the formation of Pb-Zn-Ag ore deposits

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Abstract

The study focuses on age and evolution of the Oligocene quartzlatite of the Rogozna Mts. (Central Balkan Peninsula), in order to better understand the link between magmatism and formation of Pb-Zn±Ag mineralization. New Ar/Ar biotite and amphibole plateau ages suggest that Rogozna Mts. quartzlatite originated through a continuous volcanic episode from 27.3±0.1 to 29.5±0.1 Ma which was immediately followed by a hydrothermal phase. The quartzlatites are hypocrySTALLINE porphyritic with phenocrysts and microphenocrysts (~60 %vol.) of plagioclase (An₃₇₋₄₉), biotite Mg# [100 × Mg/(Mg + Fe_{tot})] < 50, calcic amphibole, quartz, sanidine clinopyroxene and phlogopite (Mg# = 79 to 84). The rocks display numerous disequilibrium textures, such as: sieved plagioclase phenocrysts, dissolution effects on quartz, phlogopitized biotite and amphibole crystals, and phlogopite microphenocrysts showing effects of incomplete growth (or dissolution?) and biotitization. The Rogozna Mts. quartzlatites are shoshonitic in character having Na₂O/K₂O < 1, high LILE/HFSE ratios, strong depletions at Nb and Ti and K, Pb and U peaks on primitive mantle-normalized diagrams. They are similar to other potassic/ultrapotassic rocks in this region, in particular to those of Veliki Majdan and Rudnik (West Serbia), which are also related to Pb-Zn deposits. The evolution of the Rogozna Mts. quartzlatite is modeled using a trace element binary mixing model adopting a lamproite magma and a dacite-like calc-alkaline melt as end-members. The model implies that a fractionating magma chamber (~4.5–9.5 km) undergoes cooling in the range >860°C- ~720°C and injection of lamproite-like melts. The injection causes increase of temperature and decrease of viscosity of the resulting hybrid magma facilitating its upwelling and triggering pyroclastic eruptions. Addition of new volatiles by lamproitic melts most probably established conditions for hydrothermal phase above the magma chamber that was

previously degassed explosively. This implies that magma mixing processes can be of great importance for the formation of Pb-Zn deposits. Similar processes are likely to have occurred in other areas with economically significant Pb-Zn-Ag±other metals mineralization in the region of Central Balkan Peninsula (Veliki Majdan, Rudnik, Golija, Kopaonik, Avala, etc.).

Au-Ag tellurides and other mineral associations in the Ilovitza Cu-Au deposit

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Within this study were studied mineral associations of the porphyry-type Cu-Au (\pm molybdenum) Ilovitza deposit, located in southeastern Macedonia (17 km northeastern from the Strumica town), hosted in a roughly circular altered intrusion and intrusive breccia complex (probable Tertiary age) emplaced in lower Palaeozoic granite. The Ilovitza Tertiary intrusive complex consists of a central, composite dacitic diatreme breccia body cut by numerous dacitegranodiorite porphyry bodies and minor fine-grained andesite. Drilling demonstrated that dacite/granodiorite porphyry expands at shallow depths into a fairly continuous body, which is itself locally intruded by a late-mineral biotite latite-andesite porphyry.

Within the SCOPEs Project No. IZ73Z0_128089 (Metal transport and ore deposits: The geology, geochemistry and geodynamic setting of mineral resources in Serbia, Macedonia and Bulgaria), funded by the Swiss National Science Foundation, we had a fine opportunity to study in more details the mineral associations from the Ilovitza deposit under the electron microprobe facility located at the ETH-Zurich. Those studies have proven some minerals that were determined for the first time within the Ilovitza deposit. Although gold, silver and tellurium were determined by chemical analysis before, now were certain mineral forms in which they are concentrated. Namely, we have determined presence of hessite (Ag_2Te) with trace to minor values of zinc, as well as presence of unknown Au-Ag-telluride phase with Au:Ag:Te ratio of 3:2:1. Hessite occurs as a fine grained at the contact of a sphalerite-chalcopyrite aggregates within quartz-sulphide veinlet and along rims of sphalerite and chalcopyrite. Hessite aggregates are from 0.03 up to 0.07 mm in size and are showing lamellar composition. The presence of telluride minerals has been interpreted (Afifi et al., 1988; Cooke and McPhail, 1996) to be indicative of a magmatic component for mineralizing fluid.

Also, our efforts to define the mineral paragenesis of the Ilovitza deposit were rewarded with a discovery of native gold irregular grains (0.02 up to 0.03 mm in size). The gold is primary, native, with representative yellow color and high reflection capability, within hessite grain enclosed within a sphalerite matrix. Due to such a mineral setting within the composition of these grains of native gold were determined certain silver concentrations ranging from 13.12 up to 29.25% Ag, which points out that gold and silver experienced a process of forming polymorph series (Frueh, 1959).

Also, our studies have confirmed numerous minerals characteristic for porphyry Cu-Au (\pm Mo) deposits such are oxide minerals magnetite, rod-like hematite, through the sulfide ones such are pyrite, pyrrhotite and chalcopyrite. Quite often some of the analyzed chalcopyrite aggregates were partially corroded by bornite, chalcocite and covellite. Bornite, chalcocite and covellite were solely determined as secondary products along chalcopyrite, clearly replacing chalcopyrite at following order: chalcopyrite-bornite (with lamellar decay to idaite)-chalcocite-covellite and at such a constellation they encircled and corroded chalcopyrite. Must to mention were molybdenite determinations in form of flake-like aggregates, with dimensions up to 0.5 mm in association with pyrite within quartz-sulphide veins and molybdenites as minute impregnations within altered rocks, but of however limited presence.

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Preliminary data on the age and geochemistry of Mesta volcanic complex and Central Pirin pluton

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Introduction

Mesta volcanic complex (MVC) and Central Pirin pluton (CPP) have been regarded by many authors as a volcano-plutonic association (Arnaudova and Arnaudov, 1982; Zagorchev et al., 1987; Harkovska et al., 1998). In order to verify this concept we carried out: (1) new studies on the mineralogical, geochemical and isotopic composition of 15 whole rock samples and (2) high-precision U-Pb zircon dating of 7 samples from MVC and CPP, complemented by two ⁴⁰Ar/³⁹Ar measurements of sanidine from the volcanic rocks, to constrain the time span of volcanic and plutonic igneous activity..

Geological setting

MVC and CPP are part of the Macedonian-Rhodope-North Aegean Magmatic zone (Harkovska et al. 1998). MVC crops out in an elongated SSE-NNW-oriented graben structure, situated between the western Rhodope block to the east and Pirin horst to the west. Two polygonal calderas (Kremen and Banichan) and two linear volcano-tectonic zones are distinguished within the volcanic complex (Harkovska, 1989). The subvolcanic and volcanic rocks are represented by stocks, domes, dome-flows, cryptodomes, dykes and pyroclastic flows. The volcanic rocks have exclusively felsic compositions, represented by rhyolites (oldest phase in field relations), trachyrhyodacites and rhyolitic ignimbrites. The CPP consists of porphyritic granites and equigranular granodiorites geochemically and isotopically similar to Mesta volcanic rocks.

Analytical techniques

Whole rock samples were analyzed for major and trace element concentrations as well as Sr-Nd-Hf isotopic composition. The major element measurements were obtained at the Institut für Geologie und Mineralogie, Köln on Philips PW 2400 X-ray spectrometer. The Sr-Nd-Hf isotopic compositions were measured at Steinmann-Institut, Bonn on equipment Thermo-Finnigan Neptune MC-ICP-MS. Zircon U-Pb dating as well as trace element content measurements were performed at the Geological Institute of BAS using New Wave UP193FX LA coupled to ELAN DRC-e quadrupole ICP-MS. Sanidine samples were dated by ⁴⁰Ar/³⁹Ar method at the University of Geneva. Cathode-luminescence images of zircon samples and microprobe analyses of feldspars and amphiboles were made in Belgrade University and ETH-Zurich.

Results and conclusions

The zircon ages (34.4-32.61 Ma) of the MVC and CPP suggest a short intrusion time span. The whole rock samples, yielding slightly varying isotopic compositions (⁸⁷Sr/⁸⁶Sr - 0.7108-0.7130; ¹⁴³Nd/¹⁴⁴Nd - 0.512227-0.512285), are consistent with common magma sources. The large number of inherited cores in the studied zircons implies considerable assimilation of varying in age and chemical composition crustal lithologies. Mantle-crust mixed magma source is also predicted by the εNd-εHf model. In conclusion, our new data convincingly confirmed the genetic relations between MVC and CPP.

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Geodynamics, geochronology and Cu-Au hydrothermal ore provinces in the Banat region and Apuseni Mountains

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Introduction

The magmatic-hydrothermal ABTS (Apuseni-Banat-Timok-Srednogorie) belt in southeastern Europe extends from Bulgaria in the east, through Serbia to Romania in the north, where it terminates in the Banat region and Apuseni mountains. ABTS belt hosts some of Europe's largest porphyry Cu deposits and epithermal Cu-Au deposits. Skarn deposits prevail in the Romanian segment. The deposits are associated with predominantly calcalkaline Late Cretaceous magmatism. In the Apuseni mountains an additional younger phase of mineralization is superimposed on the Late Cretaceous metallogenic history. The younger porphyry-type and epithermal Cu-Au-Te deposits are associated with Miocene calcalkaline magmatism. The Late Cretaceous calcalkaline magmatism in the ABTS belt is related to northward subduction of Neotethys ocean. The superimposed Miocene calcalkaline magmatism and the associated Cu-Au-Te deposits were proposed to be related to extensional melting of metasomatized mantle that was previously enriched, probably during Cretaceous subduction (Harris, 2007; Rosu et al., 2004).

Geochemistry and U-Pb isotope geochronology

In the Banat region holocrystalline equigranular intrusive igneous rocks prevail, subvolcanic igneous rocks with porphyritic textures are more common in southern Banat. The medium- to high-K calcalkaline igneous rocks were classified as Granodiorites, Diorites, Gabbros and Syenodiorites. Chondrite-normalized rare earth element (REE) patterns show a moderate light REE enrichment and flat to slightly concave heavy REE. Some samples additionally show a weak Eu anomaly. The igneous rocks are enriched in large ion lithophile elements (LILE) like Rb, K, Pb, Sr and depleted in high field strength elements (HFSE) like Nb, Ta. Only one sample has an adakite-like trace element signature ($Sr/Y \geq 40$, $Y \leq 18$). U-Pb LA-ICP-MS analyses were performed to date the Late Cretaceous igneous rocks from Banat region. First results indicate a time span of magmatism from 75 to 84 Ma. A sample from the Getic basement gave an age of 318 Ma.

Discussion of the results

The trace element patterns of the Late Cretaceous igneous rocks are typical for magmas generated in a subduction setting. The largely missing adakite-like rocks might explain the rare occurrence of porphyry Cu deposits in the Banat region. Former K-Ar age data show a large scatter (110 Ma to 40 Ma) for the Banat region and Apuseni mountains (Ciobanu et al., 2002). New U-Pb ages narrow down the duration of magmatism in Banat region.

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Technogenic deposits in the mine Bucim and their potential economic and ecological effects

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The mine for copper and gold Bucim is in exploitation since 1979th, with a temporary closing in the years 2003-2004. The annual production is around 4.000.000 t ore and 4.500.000 t ore dumping. From this amount of sulfide ore a copper concentrate is gained that amounts 30.000 t, the rest is flotation dumping.

The accumulated ore dumping from 120.000.000 t in the waste rock dump no. 1 with an average content of copper of 0.080% and the accumulation flotation dumping of around 80.000.000 t in the hydro dumping "Topolnica" with an average content of 0.040% Cu, < 0.3 g/t Au, present significant technogene findings and in this work an effort has been made to define their economical productivity and ecological effects on the environment (Serafimovski et al., 2011). The valorization of the copper from the sulfide mine dumping in the waste rock dump no. 1 with the help the hydrometallurgical process with a method of leaching, enables solving the ecology problem with the mining water which drain in the waste rock dump, and at the same time an additional annual production of 2.800 t cathode copper will be added in technological complex for reproduction of the solutions rich with copper located under the postponement no. 1 of the mine Bucim.

From the up to date studies on the flotation tailing dump "Topolnica" it is stated that secondary enrichments of gold appear in some levels, where the content is in the frame of 0.1 - 0.7 g/t. The rhythmical separation of the levels rich with gold is a result of cyclic processing of ore with different content of gold. From the phase analysis turns out that the gold can be found in the pyrite, the rest of the chalcopyrite, and it can also be found as natural small grained disperse, included in the free silica. In the frames of this work results and findings from the performed researches for determining the pollution with heavy metals around the technogene deposits in the mine Bucim are also given, as well as strategies for solving the problems with the pollution. After the analyses and the interpretation of the data the assumptions for increased values of the following heavy metals were confirmed: Cu, Fe, Zn, Pb, Mn, Cd, As and Co. because the mine Bucim is a mine for exploitation of copper, the results of Cu were especially interesting and which reached values of 0.01-704.7 mg/l in the water, 17.8-1734 mg/kg in the soil, 2854 mg/kg in a collective sample of green algae from the Bucim lake and its leak, 55-875 mg/kg in the roots and young branches of acacia. The increased concentration of metal was determined in all the analyzed mediums: water, soil and plants. The increased concentrations of metals are often several times higher than maximum allowed standards.

The increasing of Cu in the water samples is very distinctive nearby the waste rock dump no. 1, today with the beginning of the work of the plant for producing cathode copper that problem with the drainage mining water is solved (). The concentration of the metals in the soil is highest in the surrounding area of the waste rock dump no. 1 and the flotation hydro dumping "Topolnica". This work is focused on the transfer factor (TF) for the system technogene soil-plant in the flotation tailing dump "Topolnica". The plant acacia (lat. *Robina Pseudoacacia*) which is used for biological reclamation of the dam of the hydro dumping and the nearby surrounding of the mine Bucim has a transfer factor that surmounts the hyper accumulation criterion > 1 for Mo (TF = 1.54 – 3.56).

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Transect through the Cenozoic magmatism in WSW Bulgaria and Macedonia from Pirin Mountain to Kozhuf: temporal and isotope geochemistry constraints

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Closing of Vardar Ocean at the Late Cretaceous to Early Cenozoic was followed by collision which caused thickening of the crust under the Morava-Rhodope zone (in Pirin region nowadays it is 49.5–48 km). We present new, preliminary Sr and Nd isotope data and U-Pb zircon ages for Cenozoic magmatic rocks along a NNE–SSW transect through WSW Bulgaria and SE Macedonia, characterized by highly variable crustal thickness. The study is based on U-Pb LA-ICP-MS zircon dating acquired in the Geological institute of BAS and zircon dating and whole-rock $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ and $^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$ ratios obtained in ETH–Zurich using Triton ID–TIMS.

The zircon ages support and contribute the idea for general rejuvenation of the Cenozoic magmatism from NNE to SSW. The oldest studied rocks (39.86 ± 0.44 Ma) are the rhyolites of Visoka Elha that crop out to the north-easternmost part of the transect. Further SSW, the volcanic and subvolcanic rocks between the villages of Padesh and Kresna and the granitoides of North Pirin pluton represent a volcano-plutonic system with older plutonic rocks (35.2–34 Ma) and somewhat younger volcanic activity (33.75–31.64 Ma). Further south, the volcanic and subvolcanic rocks near to the villages of Razdol, Krastiltsi and Karnalovo are dated between 31.83–30.80 Ma and to the WSW the subvolcanic bodies and dykes near to Ilovitsa village are in the interval of 30–28 Ma. The volcanic rocks in Kratovo-Zletovo and Buchim–Borov dol areas in Macedonia, located to the WSW, show ages between 31–24.8 Ma and 23.74–23.52 Ma, respectively. The youngest are the south-easternmost situated trachydacites of Kozhuf – 5.64 ± 0.025 Ma. The Kozhuh trachydacites, in Bulgarian territory, yielded age of 12.11 ± 0.57 Ma and represent separate Neogene episode of extensional magmatism.

The magmatic rocks in the transect show considerable isotopic and age variations. The volcanic and subvolcanic rocks near to the villages of Padesh and Kresna, and the granitoides of the North Pirin pluton, which are underlain by the thickest crust (49.5–48 km), exhibit the most radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.71413–0.71558) and least radiogenic $^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$ (0.51220–0.51227) isotopic ratios. Additionally, their zircon populations contain a great number of xeno-grains and inherited cores. Razdol and Karnalovo volcanic and subvolcanic rocks in Bulgaria and, particularly, Ilovitsa, Buchim–Borov Dol and Kratovo–Zletovo volcanic areas in Macedonia, located on progressively thinner continental crust (39–34.5 km) have lower $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ and higher $^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$ ratios suggesting decreasing crustal input. The assimilation of crustal material decreases with the decreasing crustal thickness which reflects on the zircon populations that consist of propagating less number of inherited cores and xeno-grains. The clear correlation between Sr and Nd isotopes and crustal thickness, accompanied by changes in the acid/intermediate rock proportions and decreasing of inherited component suggests that they are most probably formed in post-collisional setting after the main crustal thickening in the area studied. The rhyolites of Visoka Elha have low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.70557) ratio and large population of Cretaceous zircons, suggesting more primitive affinity and assimilation of Upper Cretaceous igneous rocks. The Miocene Kozhuh trachydacite also has low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.70643) which is more likely due to fractionation of a mantle-derived magma with moderate crustal assimilation. The high $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.70904) in the trachydacite of Kozhuf volcano in respect to that of the volcanic rocks of Kratovo-Zletovo (0.70482–0.70835) and Bucim-Borov dol areas (0.7067–0.7073) is most probably related to the metasomatism of the melting substrate due to the magmatism in the Kratovo-Zletovo and Buchim-Borov dol areas.

U-Pb zircon dating and zircon population analyses of the Paleogene magmatic rocks in Kyustendil and Kratovo area

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The investigated Paleogene magmatic rocks crop out mainly in the Serbo-Macedonian Massif and share the eastern part of the Vardar zone. They belong to: (1) the Kyustendil magmatic zone in Bulgaria (Harkovska, 1984) and (2) the northern part of the Kratovo-Zletovo area (Boev, Yanev, 2001 and references therein) in FYR Macedonia.

The Paleogene igneous rocks from the Kyustendil magmatic zone have predominantly acid composition (plot in the field of dacites, rhyolites, trachydacites) and high-K calc-alkaline magmatic seriality. The trace elements contents of these rocks reveal mainly magmatic arc geochemical characteristics (VAG). The REE-normalized patterns show that they are formed in the continental crust.

The studied Paleogene magmatic rocks from the northern part of the Kratovo-Zletovo area are from the Kriva reka valley and from the Bajlovce region – north of Kratovo. The volcanic rocks from the Kriva reka valley are trachyandesites (latites) to trachydacites, while those from Bajlovce region plot only in the field of the trachydacites (norm Q > 20%). The magmatic rocks from both provinces have high-K calc-alkaline magmatic seriality and magmatic arc geochemical signature.

The LA-ICP-MS U-Pb zircon dating of the rocks from Kyustendil area define a time span from 32.5 to 28.9 Ma. The rocks from Bajlovce region yield an average age of 31.25 Ma, while the age of Kriva reka volcanics vary in a narrow range from 28.9 Ma to 27.5 Ma. More interesting picture is outlined by the analyses of the zircon population about the age of the source rocks and their origin. In the zircon population from the dominant volcanic rock variety in the Ruen magmatic zone (the coarse-porphyric by sanidine trachyrhyodacites) one third consists of own magmatic Paleogene zircon crystals and the bigger part of the zircons have old inherited zircon cores. The inherited zircon cores are from two provinces, one with age-range of 220-280 Ma (Middle Triassic-Permian) and the second in the range 400-460 Ma (Lower Devonian – Upper Ordovician) age. The zircons population from the trachydacites of Bajlovce region consists predominantly of own magmatic crystals (2/3 of them) with well-defined magmatic oscillatory zoning and only one third of the grains are xenocrysts with Lower Permian to Upper Devonian ages. The characteristic feature of the zircons from the volcanics of the Kriva reka valley is their random abundance. Zircon xenocrysts are rare and without particular geological significance.

The isotope ages of the old zircon cores and xenocrysts of the Paleogene Kyustendil magmatic rocks (Grozdev et al., 2012) indicated, that these rocks are formed by melting of parts of the Vertiskos Terrane /Ograzhden Unit (Zidarov et al., 2003; Meinhold et al., 2010). In the Paleogene volcanics from the Bajlovce region, the contamination with old rocks was negligible (some Hercynian? materials) and was not a leading process during their formation. The volcanics from the Kriva reka valley are formed from a substrate of basic to intermediate composition.

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Rare earth element (REE) mobility during advanced argillic alteration in Asarel porphyry copper deposit, Central Srednogie, Bulgaria

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The Asarel porphyry copper deposit is located in Panagyurishte ore region, Central Srednogie, part of the Late Cretaceous Apuseni-Banat-Timok-Srednogie (ABTS) magmatic and metallogenic belt defined by intensive magmatic and volcanic activity and formation of many porphyry and epithermal deposits. The volcanic activity in the Asarel magmatic center successively formed andesites to latites, basaltic andesites, andesites to dacites, followed by comagmatic porphyritic plutons (quartz-diorite to quartz-monzodiorite, quartz-monzonite to granodiorite and granite porphyry). Intensive hydrothermal alterations of propylitic, argillic, sericitic and advanced argillic alteration (pyrophyllite, dickite, diaspore and alunite) types had affected volcanic and porphyritic rocks within and around the deposit. K-silicate alteration is weakly developed in the deeper part of the system. Alteration zoning is expressed by successive replacement of advanced argillic alteration, sericitization, argillization and propylitization from the center to the periphery and from the top to the bottom of the deposit.

REE concentration in the unaltered volcanic rocks from the Asarel region is about 110 ppm. Their chondrite-normalized REE patterns are characteristic for island-arc subduction-related magmas with enrichment of LREE in relation to HREE ($(La/Yb)_{cn}$: 7,38–11,5) and comparatively flat HREE patterns ($(Gd/Yb)_{cn}$: 1,58–2). REE patterns of propylitic, weak K-silicate, argillic and sericitic altered rocks are similar to those in fresh volcanic rocks. Visible mobility of MREE and HREE is seen with increasing alteration degree, especially in argillic and sericitic alteration types. LREE do not show differences with respect to parent rocks, only weak mobility is visible in sericitic alteration.

Significant changes in the behaviour of REE are observed in advanced argillic altered zones. REE patterns in pyrophyllite altered rocks show MREE and HREE fractionation, which is stronger in dickite- and diaspore-bearing rocks. REE behaviour in alunitic rocks is very similar to the dickite- and diaspore altered types. LREE are relatively immobile (sometimes with slight enrichment). This is due to the presence of alunite and APS minerals, which contain some amounts of La, Ce and Nd (usually low up to 1%, sometimes with high LREE content). Silicic alteration, which forms small bodies at the top of the alteration zone, is characterized by strong extraction of all REE.

REE concentration in altered rocks from the Asarel deposit show comparatively inert behaviour of REE during the propylitic, intermediate argillic and sericitic alteration of volcanic rocks and slight fractionation with weak mobility of HREE in argillic and sericitic altered types. This is due to the nearly neutral pH of the fluids and the low water/rock ratio during these types of alteration. Starting of mobility in LREE is registered in the sericitic rocks, which is connected to the dissolution of apatite.

During advanced argillic alteration in low-pH environment, high water/rock ratios and high activity of SO_4^{2-} (for the alunitic rocks) or of Cl^- and F^- (for the pyrophyllite, dickite and diaspore rocks) strong fractionation of REE occurs. The mobility of MREE and HREE is connected with the high activity of F^- , low pH of the fluids and their ability to form stable complexes in these conditions (Fulignati et al., 1999). LREE are relatively immobile (with slight enrichment in some samples) due to their entrance in the lattice of appropriate minerals like alunite, APS minerals and clay minerals (Kikawada et al., 2004; Aja, 1998). Decreasing of pH leads to apatite dissolution. Liberated LREE immediately take part in the new-forming APS minerals – mainly svanbergite and woodhouseite. Sometimes florencite-svanbergite solid solutions may form as cores in svanbergite (Hikov et al., 2010). High activity of F^- ions and the lack of new minerals to accommodate REE are the main reasons for their depletion from the silicic altered zones.

S, O and H stable isotope data show that alunite and APS minerals in Asarel are formed from magmatic-hydrothermal fluid between 200 and 300°C with significant dilution (up to 50%) of superficial waters (Hikov et al., 2010). This REE behaviour probably is characteristic of a high-sulphidation style epithermal environment in the upper part of the porphyry copper system and illustrates the main stages in the evolution of the hydrothermal fluids.

The magmatic evolution of the Buchim-Damjan-Borov Dol ore district

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Introduction

This Project explores the Buchim-Damjan-Borov-Dol ore district with a detailed look on the Buchim porphyry Cu-Au deposit (Figure 1). The area, which is about 150 km² in size, is part of the Southern Balkan tectonic system (Serafimovski et al. 2010). The ore district is located in the eastern part of Macedonia, around the contact of the Vardar zone in the east and the Serbo-Macedonian massif in the west (Serafimovski et al. 2010). During Upper Oligocene, a lot of sub- and volcanic activities have occurred in this region resulted in numbers of intrusions with various magmatic compositions and age. The district includes the following intrusions which are specified in this research: Buchim (Central, Vrsnik, Bunarzik), Borov Dol, Damjan and Black Hill. They are dated between 24.5-24.0 Ma with the U-Pb method in Zircon and have an andesitic to trachyandesitic composition. Further most of them consist of various magma generations. This leads to magma mingling and differences in mineralogical features, like phenocryst occurrence and grain size.

The Buchim deposit consists of four ore bodies: Central, Bunardzik, Vrsnik and Cukar. These ore bodies are spread over an area of approximately 10 km² (Čifligance 1993). The Central, Bunardzik and Vrsnik ore bodies are related to andesitic porphyry intrusions, whereas the Cukar ore body consists of a supergene copper mineralization (Čifligance 1993). All four ore bodies lay in different Precambrian Gneisses (Čifligance 1993). The reserves of the Central ore body are 120 Mt with an average Cu content of .34% and an average Au content of .35g/t (Serafimovski et al. 2010). Nevertheless the low ore grade, the mining of the deposit started in 1979 (Serafimovski et al. 2010). A mineralized gneissic xenolith, in the Central porphyry andesite, leads to the conclusion that the current porphyry is an overprinting of an earlier porphyry stock. Further the present intrusion shows some magma mixing features. Crosscut relation at the contact of the Central and Vrsnik porphyry show that Vrsnik body is younger than the Central porphyry bodies. The Vrsnik porphyry contains 4 magmatic events. Two of them show also a magma mingling. The Bunarzik intrusion contains two magma generations.

Results

Zr/Ti vs. Nb/Y (Pierce 1996), Si vs. Zr/Ti (Winchester and Floyd 1977) and Th vs. Co (Hastie et al. 2007) are all indicating the rock composition as andesitic. The only exception is Black Hill. It has a trachytic composition. Based on the Th vs. Co data the rocks further belong to the high K and shoshonitic series. Chondrite-normalized (after Hofmann 1988) rare earth element patterns of the samples are showing enrichment in light REE and depletion in middle REE elements leading to hockeystick geometry. This indicates an early amphibole fractionation. The result is supported by high Sr/Y ratio, which indicates high-pressure magma and/or hydrous magma, in which plagioclase crystallization is suppressed and hornblende saturated (Rohlach and Loucks 2005). Microscopical features are supporting this interpretation of an early amphibole phase and amphibole fractionation. Further N-MORB normalized (after Hofmann 1988) values showing a clear continental arc setting pattern.

Geological Map of the Buchim-Damjan-Borov Dol Ore District

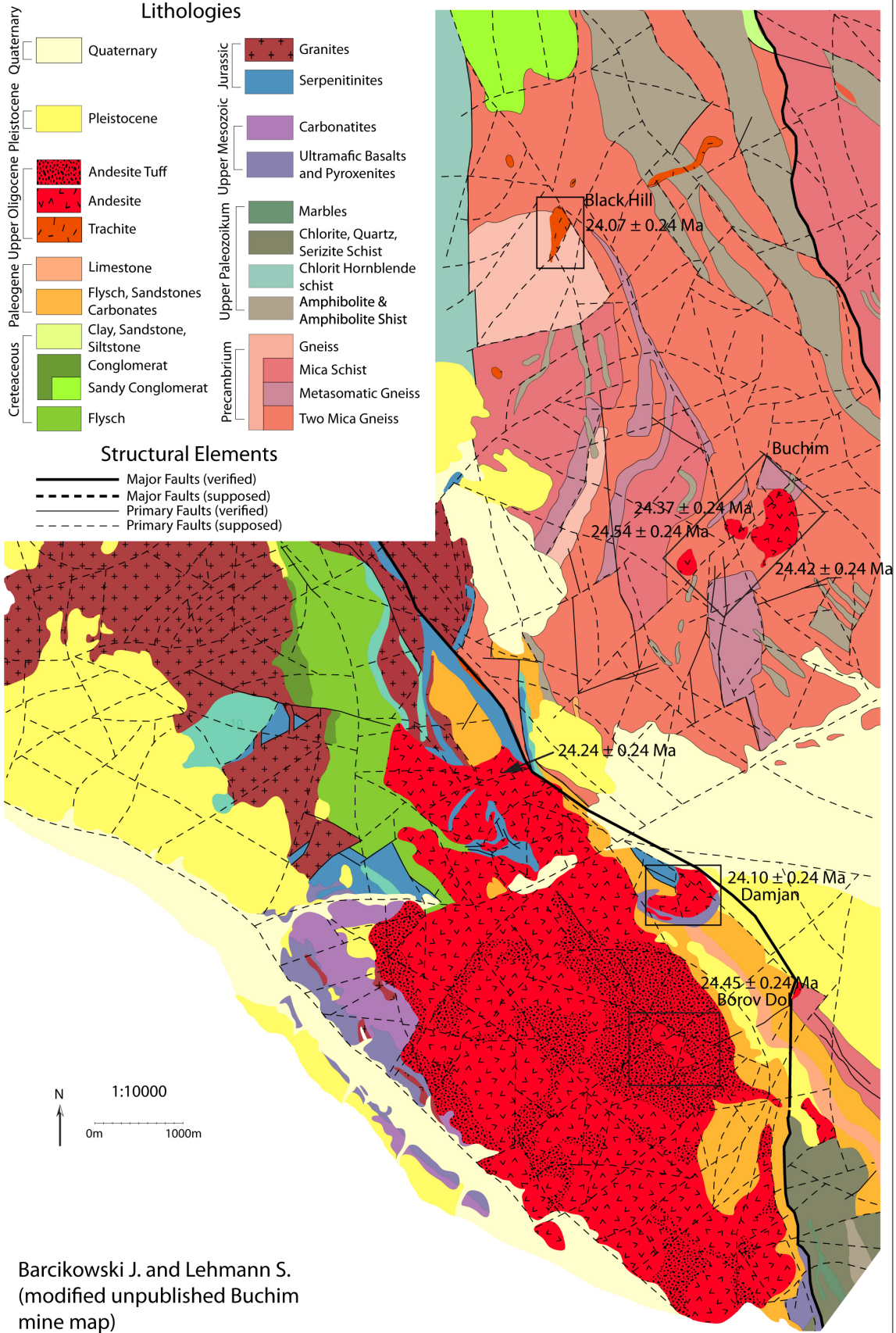


Fig. 1: Geological map of the Buchim-Damjan-Borov Dol ore district

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Time and compositional evolution of the Upper Cretaceous to Miocene magmatism in South Bulgaria, North Greece and Thrace: Implications for the Late Alpine geodynamic evolution of the Balkan Peninsula

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Based on the P-wave tomographic images and modeling for the Eastern Mediterranean region, many recent papers proposed a single, long-lived north-directed subduction zone, starting from Cretaceous or even Jurassic time to recent. However, detailed analyses of the magmatism from Late Cretaceous till Miocene times in the South Bulgaria and North Greece, presented here, require much more complicated model.

Late Cretaceous magmatism covers large areas in the Srednogorie zone, Strandzha and northernmost Rhodopes. It was active from 92 to 67 Ma, showing southward or centroclinal shifting. Magmatic products are represented by intrusive and extrusive rocks of variable composition, typical subduction-related signature and low Sr and Pb and high Nd isotopic compositions. This magmatism is related to N-NE-ward subduction of the Vardar ocean under the Rhodope Massif. The models of slab retreat and rifting can explain the increasing mantle input with time. After a break of ~11 Ma, probably related to continental collision, magmatic activity was renewed in the Kraishte and the Rhodope Massif. The Early-Middle Eocene magmatism (56-40 Ma) is represented by scattered felsic plutons in the Rhodopes and dacitic and rhyodacitic dike swarms in the Kraishte zone. The rocks have subduction-related signature and remarkably similar isotopic compositions, suggesting significant mantle component and uniform crustal thickness throughout the Rhodopes. The missing mafic magmas most probably were underplated to the crustal base, adding crustal material to the previously collision-induced thickening. Contemporaneity and isotopic similarity of this magmatism to the nearby ocean island basalt (OIB)-like basalts in the Eastern Serbia can be interpreted in favor of its origin from asthenospheric OIB source, weakly to moderately influenced by intracrustal contamination and fractionation. The magmatism was followed by 5-7 Ma regional uplift and exhumation of the Upper Cretaceous and Early-MidEocene granitoids and core-complex formation. From 35 to 26 Ma the Rhodope massif and Pirin-Osogovo zone were affected by new episode of magmatism, directly overlying in places the Mid Eocene granitoids. It is represented by volcanic and plutonic rocks and dykes of variable composition, strongly controlled by the crustal thickness. The intrusive and extrusive rocks in Osogovo-Pirin have exceptionally felsic composition and the strongest crustal input. The Central Rhodope magmatism is explosion-dominated, represented by rhyodacite to rhyolite air-fall tuffs and strongly welded rhyolitic ignimbrites, followed by intrusion of dykes and subvolcanic intrusions of latitic to high-K andesitic and monzonitic compositions. The Eastern Rhodope magmas show the most complex compositional variations from basic to acid and calc-alkaline, shoshonitic and rare ultra-K lithologies. Here, the magmatism ended with OIB alkaline basalts and lamprophyres. The geochemistry, Sr and Nd isotopic compositions and zircon populations suggest a strong crustal influence of the magmatism, diminishing from west to east and north to south and with time. We suggest that this magmatism is the result of major orogenic extension, caused by the asthenospheric uplift and asymmetric crustal thinning. The youngest Early-Mid Miocene orogenic magmatism (22-15 Ma) occupies the southernmost (Greek) part of the Rhodope Massif. Its western part is represented by felsic intrusives, whereas the eastern sector is composed of intermediate to acid subduction-related volcano-plutonic associations. Contemporaneous with this magmatism is the OIB basaltic volcanism in the Central Bulgaria, cutting across in a NE-SW strip Srednogorie zone, Balkan zone and Moesian Platform. The orogenic magmatism was post-dated by OIB alkaline basalts (11-7 Ma) in the neighbor Trace basin and Biga Peninsula. The entire Early-Late Miocene magmatic evolution is repetition of the older Late Eocene-Early Oligocene magmatic period and, most probably, is the result of similar geodynamic processes.

Skarn mineralizations in the Bor ore district: new evidence from study of bornite-chalcopyrite-hematite paragenesis

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Introduction

The Bor ore district is situated in eastern Serbia and it mainly consists of porphyry-copper and related high-sulfidation epithermal deposits. This N-S stretching ore district is hosted by the Timok magmatic complex (TMC) which is predominantly composed of Late Cretaceous andesitic volcanic and plutonic rocks, associated with roughly contemporaneous sedimentary deposits. At the contacts between the magmatic and the surrounding sedimentary rocks, predominantly limestones, marbles and skarns are commonly formed. These contact-metamorphic rocks occur both on the east and west side of the TMC and they frequently contain Cu- and polymetallic mineralizations (Antonijević, 1997). The skarn mineralizations is genetically related to only a few known polymetallic ore bodies in this district, e.g. Tenka and Valja Saka (Antonijević, 1997). However, given that the mineralized marbles and skarns are widespread, such mineralizations could play an important role for discovery of new ore bodies. In this contribution, we summarize the similarities in mineralogical features of the copper mineralization in the andradite skarns of two actual prospects in the TMC.

Results and discussion

The studied skarn mineralization belongs to the two prospects in the east side of the TMC. The first is Kriveljski Kamen near the town of Bor and the second is situated about 25 km northwards, near Majdanpek. Both copper mineralizations are formed along the contacts between volcanic rocks of the TMC generally formed during the first volcanic phase, and surrounding limestones and other sedimentary rocks. These mineralizations, consisted predominately of chalcopyrite, are hosted by hydrothermally altered andesites, skarns and marbles. The skarns of both studied areas show similar mineral assemblage consisting of andradite, quartz, calcite and chalcopyrite-bornite-hematite aggregates. Andradite is predominant mineral in the skarns and it was the first crystallization phase in this assemblage. Other above mentioned minerals are deposited subsequently, during a single mineralization stage when andradite grains were cemented. Chalcopyrite and bornite form typical textures of decomposition of bornite solid solution and replacement of bornite by chalcopyrite. Thus, their precipitation simultaneously started and the deposition of chalcopyrite continued after the deposition of bornite. This typical Cu aggregate consisted of chalcopyrite and bornite contains also hematite that was precipitated simultaneously with and mostly after these copper minerals, along the rims of chalcopyrite. A remarkable feature of these chalcopyrite-bornite-hematite aggregates is the occurrence of carollite exsolutions (up to 50 µm in size). They were found in both studied areas whereas exsolutions of hessite (up to 10 µm in size) were found in the Kriveljski Kamen prospect exclusively. To our knowledge, this is the first evidence of carollite, $\text{Cu}(\text{Co},\text{Ni})_2\text{S}_4$ in the Bor ore district. Hessite, Ag_2Te and other tellurides are economically important minerals as they carry precious metals, silver and gold. Exsolutions of these two minerals in Cu sulfides may indicate occurrence of a typical mineralization in Bor ore district formed from a hydrothermal solution enriched in Co, Ni, Ag, Te. Additionally, this distinctive chalcopyrite-bornite associations suggesting decomposition and replacement processes could indicate the vicinity of a porphyry-copper system.

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Principle metallogenic features of the Sasa Pb-Zn deposit, Republic of Macedonia

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The Sasa Pb-Zn deposit has been localized in northeastern parts of the Republic of Macedonia or within the Serbo-Macedonian metallogenic province. Its formation is related with intrusion of Tertiary volcanics (27-24 Ma) into the crystalline fundament (Precambrian gneisses and Paleozoic schists) of the Serbo-Macedonian massif. Pb-Zn mineralization metasomatically is deposited into cipolins intercalated into the series of quartz-graphite schist. Genesis and spatial displacement of the Pb-Zn mineralization in the Sasa deposits represents a complex polyphase and timely lasting process directly related with the evolution of the Neogene magmatism and hydrothermal solutions in the deposits and its adjacent vicinity (Serafimovski and Aleksandrov, 1995). Magmatic activity started at the end of Eocene and lasted, through few phases, until the Pliocene. The mineralization is formed through several phases during Oligocene-Miocene. The ore mineralization spatially and genetically is related to the fault structures of NNW-SSE, NW-SE direction dipping to SW and its intersections with N-S structures dipping to the west, localized mainly in cipolin-marbles, cipolin-schists within quartz-graphite schists in zones of cataclization (in quartz-graphite schists, gneiss and rarely quartzlatites). Ore-bearing fault structures are of polygene character and its formation is directly related to reactivation of older fault dislocations, regional tectonic tensions under the influence of Neogene magmatic activities, while in the dykes was included influence of contractions due to their cooling.

Mineralization in the deposit is generated as a result of common action of numerous synchronous and consecutive factors that allowed deposit genesis, such are: host rocks conducive to change, grinding-brecciation-abrassion, which have created zones with an increased secondary porosity, intrusion of fluids (gaseous-liquid), common reaction between fluids and adjacent rocks, metasomathosis (thermal change-marbleization and changes with component transfer), formation of calcic skarns (multiple skarn parageneses) and hydrothermal alterations: intermineralizing movements, mineralization-its deposition (polyphase), inter-ore movements and post-ore tectonics.

Genesis of the Svinja Reka deposit (as a synonym of Sasa deposit) was done in three separate phases of which especially is important the skarn phase when have been created condition for deposition of the Pb-Zn mineralization within the hydrothermal stage with additional three phases and few sub-phases (Aleksandrov, 1992). The mineralization has been deposited metasomatically in calcite skarns or by filling of cracks, brecciated zones and faults. In particular parts have been formed impregnation and stockwork-impregnation minerals as a products of polycentric metasomathic processes. The ore bodies have forms of pseudo-layers (tile-like), lenses, layers, oblique ore pillars, followed by impregnation and stockwork-impregnation mineralization in hangingwall and footwall of the ore bodies

Lead-zinc mineralization has been formed in the hydrothermal stage, which have started with manifestation of high-temperature pre-ore alterations of adjacent rocks (skarns), represented by intensive epidotization, chloritization, pyritization, silicification, calcitization that a little bit later continues into first high-temperature ore-bearing sulfide phase. Within that phase have been formed pentlandite, pyrrhotite, pyrite, chalcopyrite, bismuthinite, native bismuth, sphalerite, occasionally galena, bornite, arsenopyrite, hematite, siderite, quartz and calcite. Ore minerals were formed in the temperature range of 400-280°C with simultaneous crystallization of colloidal dispersed solutions. With change of regime of ore-bearing solutions or decrease of temperature (interval of 375-220°C), steep decline of pressure and increase of redox potential, results in deposition of ore minerals from main sulphide phase within hydrothermal stage. In this phase intensively are deposited sphalerite and galena, then chalcopyrite, pyrite, cubanite, valerite, bornite, tennantite, tetrahedrite, freibergite, enargite, altaite etc. With fluid inclusions analyses (in quartz) it was confirmed that this paragenesis was characterized by ore solutions with pH of 6.7 and following composition: 37.42 g/l Cl, 0.57 g/l F, 11.26 g/l SO₄, 11.90 g/l K, 10.68 g/l Na, 0.59 g/l NH₄, 0.46 g/l Mg, 5.24 g/l Ca, SiO-trace and B-trace. This points out that there dominated Ca and Na chlorides, which concentration could easily reach up to 65,00 g/l.

Effusive rocks quite often fill-up the cracks, faults and faulting structures with lower degree of resistivity. The contact parts between effusive and adjacent rocks are usually poorly mineralized, which is probably due to hydrothermal alterations.

The results from up to date numerous studies are pointing out to the fact that the Svinja Reka deposit has been formed at sub-volcanic level, while by the formation conditions it could easily be accounted into the group of skarn-hydrothermal-polymetallic deposits of metasomathic type.

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Timing and Sr-Nd-Hf constraints on the oldest Cenozoic magmatism in Kraishte, W Bulgaria

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Series of Cenozoic subvolcanic bodies and dykes crop out in the Kraishte region forming a NNW (150-160°) trending strip between the Penkyovtsi trust and the Trun-Kosharevo fault zone. Harkovska et al. (2004) pointed out the distinctive character of these rocks, compared with the other Paleogene volcanics in W Bulgaria. They usually form concordant sill-like bodies, which morphology is controlled by the Mid-Cretaceous Penkyovtsi trust and parallel shear zones. Compositionally the rocks are plagioryholites to plagioryhodites with normal calc-alkaline seriality. K-Ar whole-rock dating yielded ages from 42.2±1.6 Ma to 47.4±1.8 Ma, which were interpreted as possible resetting during low-temperature hydrothermal alteration. The authors paid attention on the missing Pb-Zn deposits that are otherwise linked with the Pg magmatic rocks in SW Bulgaria, Serbia and Macedonia.

In the frame of the SCOPES project we sampled and studied dykes and sills that cross-cut the Carboniferous Ruy pluton in Trun region, and some subvolcanic bodies – close to the villages of Erul, Jarlovtsi, Leshnikovtsi and Gorna Glogovitsa. The rocks are fine-porphyric to aphyric. They consist of irregularly hydrothermally altered plagioclase (An₂₆₋₂₉ to An₃₈₋₄₂), biotite, needle amphibole and quartz, whereas K-feldspar is only present in the ground mass, but never as phenocrysts. Accessory minerals are apatite, zircon, monazite (in Gorna Glogovitsa). The major element chemistry is in agreement with published data (Harkovska et al., 2004). Trace element geochemistry defines mainly VAG-affinity. The rocks are enriched in LREE, with Ta-Nb negative anomaly, shallow negative Eu-anomaly and with a sum of REE 70-100 ppm. Moreover, they reveal adakite-like characteristics with Sr/Y ratio >45 (48-71), low Y content <18 (5.9 to 8.3) and La/Yb>20 (30-40).

Sr-Nd isotope data define a mantle dominated source of the plagioryholites and plagiodydites. The initial strontium ratios (⁸⁷Sr/⁸⁶Sr)_i in the least altered samples are consistent around 0.7047, and εNd vary in a narrow range between -0.2 and +2.4. The Hf-isotope system in the zircons are also clearly mantle-influenced and εHf in the magmatic Paleogene zircons and zircons rims are positive – mainly between +4 and +6, but reaches +10 in the Erul volcanics.

The subvolcanic rocks are dated more precisely using U-Pb method on zircons and monazite and two techniques - LA-ICP-MS and ID-TIMS. Leshnikovtsi plagioryholite is dated at 43.58±0.56 Ma (LA-ICP-MS data on zircons). ID-TIMS of chemically abraded zircons of the Erul body yield an age of 45.71±0.08 Ma – this is the youngest of four concordant zircons, whereas the other three define ages between 47.99±0.03 Ma and 45.71±0.04 Ma. In the Gorna Glogovitsa body Paleogene zircons are sparse and concordant between 43 and 45, the majority being around 44 Ma, and monazites are slightly younger – mainly between 42-43 Ma. Considerable amount of inherited zircons and cores are present in the zircon population of all dated samples, ranging from 330 to more than 1000 Ma. The εHf of these zircons define crustal source for their protoliths.

The new data for the Paleogenic subvolcanic rocks confirm their formation in Pre-Preabonian (Lutecian) time between 43 and 45.8 Ma. The older concordant zircon ages are possibly related to negligible lead inheritance from xeno- and antecrysts, whereas slightly younger monazite ages of 42 Ma might be reset by hydrothermal fluids. The mantle Sr-Nd-Hf isotope and trace-element characteristics infer subduction or post-collisional tectonic setting. Adakite-like characteristics are described in many old tonalitic (TTG) rocks, and also in the Upper Cretaceous Timok and Ridanj-Krepolin belts in Serbia. They do not necessarily infer subduction and slab melting and could be explained by high-pressure amphibole fractionation in the lower crust. Adakite-like magmas are usually fertile; consequently the new data may provide evidence for a new perspective ore-bearing region in W Bulgaria.

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Types of hydrothermal alteration within the Ilovitza deposit, Republic of Macedonia

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As a result of the recent detailed explorations, made by the company *Phelps Dodge*, and today, extended from the company *EuroMax*, Ilovitza deposit is separated to the polymetallic Cu-Au-Mo porphyry deposit, located within Tertiary intrusive complex, whose mineralization is closely related to intensive hydrothermal alterations of surrounding rocks. It is located in southeastern part of Republic of Macedonia, more precisely on Ograzden mountain, at about 17 km at a distance from Strumica city, near Ilovitza village. In the Republic of Macedonia even and broader, "Ilovitza" deposit represents one of the more significant porphyry deposits of *Cu-Au-Mo*. This deposit represents a part of several porphyry systems in eastern Macedonia and northern Greece, which are in association with igneous complexes and is one of deposits of the type of the deposit Bucovik-Kadiica in Macedonia and Scurries in Greece. In view of the regional geotectonic position, "Ilovitza" deposit belongs to Serbian-Macedonian Massif (*Zagorchev et al., 2008*) and the Serbian-Macedonian Metallogenic Zone (*Jankovic, 1977; Serafimovski, 1990*), in belt, in whose geological construction participate late Proterozoic to Palaeozoic metasediments and granitoids. The processes that took place in the frame of the SMM have caused structure of the volcanic apparatus, domes and regional dislocations, as the Tupal dislocation and dislocation Besna Kobila-Osogovo (*Serafimovski, 1990; Aleksandrov, 1992*). Actually, creation and spatial distribution of the magmatism and the ore are in function of the structural factor of a control or disjunctive-depth structures that are present in the Ograzden granite massif and have direction along the borders of the basic geotectonic units: Serbian-Macedonian Massif and the Vardar Zone (*Serafimovski, 1990*). Hydrothermal alterations, as a special mark of the deposit, with our laboratory examinations, which consisted of X-ray and microscopic examinations of the samples, were determined as an alteration that characterizes porphyry systems (*Rogozareva, 2010*). They are allocated on the basis of the typomorphic and characteristic follow minerals. Between them can be separated the following types of hydrothermal alterations: supergene sulphide alteration, weak propylitic alteration, advanced argillic alteration, quartz-sericite-pyrite ("phyllitic") alteration and potassium metasomatism with the presence of intermediate argillic alteration. In addition, in view of the mineralization especially are interesting deeper parts of the deposit, especially zones and their contact parts where the quartz-sericite-pyrite alteration is developed and potassium metasomatism with the presence of intermediate argillic alteration.

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New LA-ICP-MS U/Pb zircon data on various granitoids from the European side of the Tethyan Mesozoic suture

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Modern radiometric age determinations of many geological events of the Serbian part of the Balkan Peninsula are still poor. Most age constraints are still based on superpositional relationships of the distinguished geological units. New LA-ICP-MS U/Pb zircon age determinations obtained within the SCOPES Project provided a good basis for re-visiting and/or refining the interpretations of some geodynamic events. This contribution is an interim report of the so far acquired data which focused on two granitoid suites: in the Eastern Serbian Carpatho-Balkanides and along the East Vardar Zone.

Presumably Variscan granitoids and associated intermediate rocks occur at several localities within the East Serbian Carpatho-Balkanides: the Plavna mass intruded green complex of the Vrška Čuka terrane, Gornjani, Tanda and Blizna magmatites penetrate the Inovo series of the Stara Planina-Poreč terrane, while Neresnica and Blizna masses are intruded into Proterozoic Osanica gneisses and Proterozoic-Early Cambrian Green Complex within the Kučaj terrane. Petrographically, these rocks correspond to syenites, syenodiorites, granodiorites and granites. All of them are mainly reported as I-type intrusives formed in the late stage or after the amalgamation of the East Serbian terranes. The mean ages done by LA-ICP-MS U/Pb zircon method for Brnjica massive are in range of 292.5 ± 7.5 to 293.4 ± 5.0 Ma, Gornjane 302.3 ± 4.5 to 303.7 ± 5.5 Ma, Blizna 298.6 ± 7.2 Ma, Tanda 290.4 ± 3.4 to 305.7 ± 3.4 Ma, Neresnica 289.4 ± 6.5 to 295.8 ± 4.9 Ma and Plavna 267 ± 16 to 290.5 ± 8.1 Ma.

The second group comprises calc-alkaline granitoids and related rocks intruded into the Mesozoic ophiolitic complexes of the East Vardar zone in Serbia (Ždraljica and Kuršumljia areas). They appear as small isolated, and strictly intra-ophiolitic magmatic bodies. On the basis of petrochemical characteristics they were divided as (i) intermediate rocks, (ii) low- Sr_i granites and (iii) high- Sr_i granites. The age of all occurrences was determined by the fact that the intrusives cut Mesozoic ophiolites and that the ophiolites themselves are covered by an Upper Jurassic overstep sequence. Zircon ages acquired by TIMS (unpublished) on diorite (ZD-703/2) and low- Sr_i granite (V-306/6) have an intercept on the age of 170.16 ± 0.44 Ma, while low- Sr_i granite (KS-214) shows an age of around 90 Ma. New LA-ICP-MS U/Pb zircon data partly confirm the Jurassic age of the low- Sr_i granite (KS-205) and high- Sr_i granite (KS-226B) with 151.6 ± 5.7 Ma and 152 ± 16 Ma, respectively. However, data for zircons from low- Sr_i granite (KS-209) gave an age of 31.83 ± 0.84 Ma. These distinctively younger ages suggest that the origin and evolution of calc-alkaline intrusives within the East Vardar zone ophiolites must be reinterpreted. They should not be considered as Mesozoic magmas formed during subduction or obduction processes. There is a possibility that some of the existed bodies (around 30 Ma) represent small satellitic bodies as counterparts of the Oligocene Jastrebac granitoid. The age of 90 Ma cannot be related to any known igneous event in the close vicinity, but igneous rocks similar in age indeed occur in the northern part of the Vardar zone near Belgrade. Although geodynamic significance of this Upper Cretaceous age remains to be elucidated, it is fairly possible that it indicates the southward continuation of the narrow belt of Late Cretaceous ophiolite, known as the Sava zone.

Correlation of tectonic units from the Alps to Western Turkey

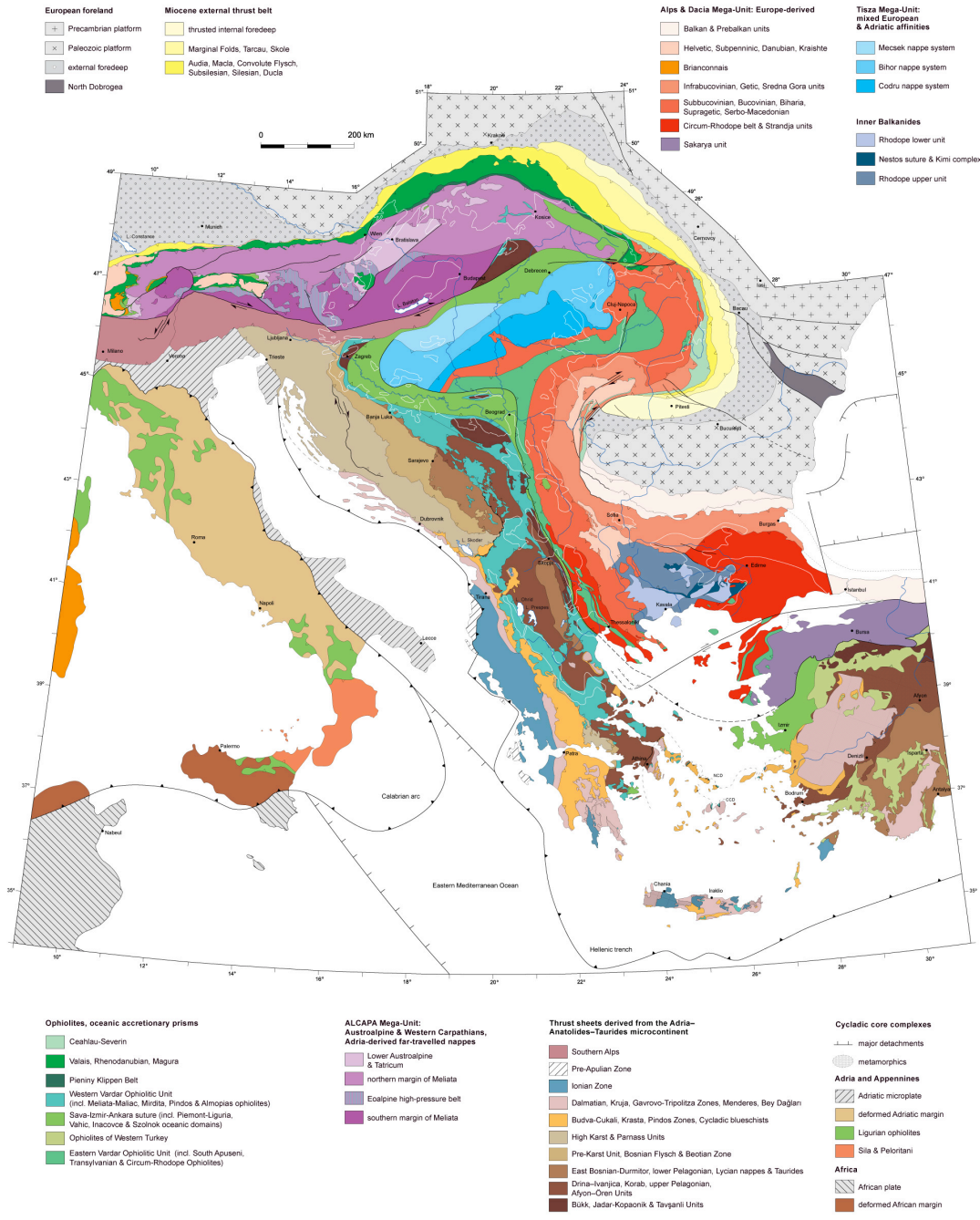
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We compiled a new map correlating tectonic units across several circum-Mediterranean orogen strands between Alps, Carpathians, Balkan Peninsula, the Aegean and Western Turkey, which allows discussing fundamental along-strike similarities and differences. One first-order difference is that Dinarides-Hellenides, Anatolides and Taurides represent orogens of opposite subduction polarity and age with respect to the Alps and Carpathians. The internal Dinarides are linked to the Alps and Western Carpathians along the Mid-Hungarian fault zone, a suspected former trench-trench transform fault, whose lithospheric root was obliterated during Neogene back-arc extension that formed the Pannonian Basin. Dinarides and Hellenides alike consist of far-travelled nappes detached from the Adriatic continental margin along decollement horizons in Paleozoic or younger stratigraphic levels during Cretaceous and Cenozoic orogeny. The more internal nappes (i.e. Drina-Ivanjica, Pelagonian units) are composite nappes whereby the allochthonous Adriatic margin sequences passively carry ophiolites (Western Vardar Ophiolitic Unit) obducted during the latest Jurassic-earliest Cretaceous. Hence, such obducted ophiolitic units root in one single Neotethys ocean that started to close with the initiation of obduction in the latest Jurassic; final suturing occurred during Cretaceous times, terminating with the formation of the Sava-Izmir-Ankara suture in the latest Cretaceous. Ophiolitic “massifs” found SW or S of the Sava-Izmir-Ankara suture zone do not mark oceanic sutures, nor do the Drina-Ivanjica and Pelagonian “massifs” represent independent continental fragments (terranes). The same logic applies to Western Turkey with the difference that the ophiolites overlying the Tavsanlı zone, Ören-Afyon zone and the Lycian composite nappes were obducted in Late Cretaceous rather than Late Jurassic times. The widespread existence of obducted ophiolites between the Dinarides and Western Turkey thus represents another first-order difference to the Alps and Carpathians, where oceanic units occur invariably within accretionary prisms. Important lateral changes are also observed when comparing the present-day lithospheric configuration of the Dinarides with that of the Hellenides. While in the Dinarides the Adriatic lithospheric slab can only be traced down to a depth of c. 200 km, where its deeper parts broke off, an over 2100 km long slab is still preserved below the Aegean part of the Hellenides, indicating long-lasting subduction of a coherent lithospheric slab that initiated during the onset of closure of Neotethys (early Cretaceous?). According to crustal-scale retro-deformations, c. 1100 km of the total of 2200 km plate convergence since 120 Ma occurred after the closure of Neotethys and formation of the Sava-Izmir-Ankara suture zone some 65 Ma ago.

TECTONIC UNITS OF THE ALPINE COLLISION ZONE BETWEEN EASTERN ALPS AND WESTERN TURKEY

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Major Alpine ore districts at the territory of the Republic of Macedonia

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In accordance to the basic principles and major factors of the metallogenic analysis (structural-morphostructural, magmatic and mineralizing), at the territory of the Republic of Macedonia were determined few major Alpine ore districts: Kratovo-Zletovo, Damjan-Buchim-Borov Dol, Sasa-Toranica, Pehcevo-Ograzden and Kozuf. All of them are enclosed within the Serbo-Macedonian metallogenetic province defined by Jankovic (1967), or more precisely, in metallogenetic zones Lece-Chalkidiki and Besna Kobila-Osogovo-Tasos defined by Serafimovski (1990, 1993).

All defined Alpine ore districts at the territory of the Republic of Macedonia are characterized by polymetallic mineralization related to the Tertiary magmatism and representative structural-morphostructural forms. Scale of the defined Alpine ore districts at the territory of the Republic of Macedonia are in function of surface manifestations of Tertiary magmatism. Very often in those ore districts has been determined zonal distribution of ore mineralization, laterally and vertically.

From up to date studies it was determined that the biggest ore district is Kratovo-Zletovo that occupies an area of approximately 400 km², which has been determined in the most eastern parts of the well-known Kratovo-Zletovo volcanic area, whose surface manifestations defined an area of around 1200 km². Lead-zinc mineralizations are the main Alpine ores in this ore district mainly localized at sub-volcanic levels within the famous Zletovo Pb-Zn deposit. There the Pb-Zn mineralization is of vein type. Along these mineralizations within this ore district were determined porphyry Cu-Au mineralizations in the Plavica deposit, localized in old, partially deformed volcanic calderas. Morphostructural studies in this region have shown that there are typical collapse calderas in central parts while "parasite" volcanic centers dominate on the peripheral parts. On the peripheral parts were determined uranium mineralizations localized in hydrothermally altered and brecciated volcanics in Zletovska Reka deposit.

Ore district Buchim-Damjan-Borov Dol occupies an area of around 150 km² and it is characterized by skarn iron mineralizations in its central parts as well as with productive copper and gold mineralization in its peripheral parts (Buchim and Borov Dol deposits). At the most peripheral parts in this ore district were registered even narrow Pb-Zn veins. The well-known porphyry copper deposit Buchim is localized in the northern parts of this ore district, within the Precambrian metamorphic complex intruded by andesite-latite dykes (27.5-24 Ma), around which has been localized porphyry copper mineralization.

Kozuf ore district has been localized in the southern parts of the territory of the Republic of Macedonia close to the national border with Republic of Greece. Opposite to the other ore districts its determination was based on surface manifestations of Pliocene magmatism (6-1.8 Ma) and representative Sb-As-Tl-Au-Cu-Pb-Zn mineral associations. Two deposits are of special interest there, the Alshar and the Dudica deposits. The famous Alshar deposit is divided in three particular parts: northern part where dominates thallium mineralization, central part with prevailing Sb-As mineralizations with interesting gold contents and southern parts that was defined as characteristic Carlin gold type of mineralization. At the Dudica deposit prevails copper mineralization ± gold and Pb-Zn.

In eastern parts of the Republic of Macedonia, or more precisely, within the Besna Kobila-Osogovo-Tasos metallogenetic zone are located Sasa-Toranica ore district, where prevail lead-zinc mineralizations in Sasa deposit and Toranica deposit, and Pehcevo-Ograzden ore district where prevail copper or copper-gold mineralization, as it is case with the Ilovitza deposit. These ore districts are characterized by specific structural-morphostructural composition, which has direct reflection to the genesis and distribution of polymetallic mineralizations in these areas.

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Miocene-Quaternary basalts from East Carpathian volcanic chain, Romania: a mineral chemistry and melt inclusion study

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Călimani-Gurghiu-North Harghita (CGNH hereafter) volcanic chain, known for its diminishing age and volume southwards at 10-3.9 Ma marks the end of calc-alkaline magmatism along the post-collision front of the European convergent plate margin. The rocks show $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.7035-0.7120 and a linear trend in the Th/Y vs Nb/Y diagram that reflects a common mantle source considered to be the metasomatized lithospheric mantle wedge. Fractionation or AFC are characteristic for each main volcanic area, suggestive of lower to middle crust magma chamber processes (Mason et al., 1995, 1996; Seghedi et al., 2004).

The South Harghita volcanic area is at the continuation of the CGNH volcanic chain. Here at ca. 3 Ma following a time-gap, magma compositions changed to adakite-like calc-alkaline and continued until recent times (< 0.03 Ma). This volcanism was interrupted at 1.6-1.2 Ma by simultaneous generation of Na- and K-alkalic varieties in nearby areas, suggestive of various sources and melting mechanisms. The specific geochemistry is revealed by higher Nb/Y and Th/Y ratios and lower $^{87}\text{Sr}/^{86}\text{Sr}$ as compared to the CGNH chain.

Identification of primitive magmas has been difficult despite the fact that this volcanic chain, i.e., Călimani Mountains, contains more basalts than any other in the Carpathian-Pannonian region (Mason et al., 1996, Seghedi et al., 2005). Since the most primitive rocks represent the best opportunity to identify the trace element composition of the mantle source beneath the East Carpathian volcanic chain we use mineral and melt inclusions in olivine and composition of the most primitive clinopyroxene to estimate the source composition. The results show extremely diverse olivine compositions (Fo_{90-65}) in single rocks indicative of extensive mixing and back-mixing processes during fractionation. The most forsteritic olivines (Fo_{80-90}) contain either Al_2O_3 rich spinels (25-40%), with low Cr/(Cr+Al) ratio (0.2-0.4), or low Al_2O_3 spinels (25-40%), but with high Cr/(Cr+Al) ratio (0.6-0.8).

Trace element concentrations of melt inclusions in the most forsteritic olivines give a snapshot of early and hence primitive magma chemistry. The data suggests that the whole rocks geochemistry does not define the source region being an average of various melt components and further fractionation processes. The study of the most primitive basaltic rocks in the East Carpathians suggest two distinct mantle components: a variably metasomatized lithospheric mantle and slightly modified asthenosphere which support slab breakoff (CGNH) and slab-pull and tearing models (SH) (Mason et al., 1998, Seghedi et al., 2011).

The study offers a better insight on melting processes during post-collisional processes of an anomalous mantle potentially affected by previous subduction metasomatism and triggered by the asthenospheric upwelling.

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Ilovitsa porphyry Cu-Au deposit: sequence of vein formation and sulfide deposition

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Introduction

Ilovitsa porphyry Cu (Au) deposit is located in south-eastern Macedonia, 30 km from the town of Strumitsa. It is hosted in the Serbo-Macedonian Massif. Formation of Ilovitsa deposit is related to the intrusion of multiple Tertiary porphyry intrusions and dykes (predominantly granodioritic in composition, also mingling enclaves are observed) hosted in granites, intruded into metamorphic rocks of Vertiskos-Ograzhden Unit. The main goal of the present study is to distinguish the relative timing of different dykes, vein types, vein minerals and ore deposition, and related hydrothermal alteration. For that purpose 7 drill holes were sampled and around 80 samples containing various vein and alteration types were collected for laboratory analyses. Cross-cutting relationships were used to distinguish the relative timing of vein formation. Scanning electron microscope cathodoluminescence (SEM-CL) petrography was then used for identification and textural correlation between successive quartz types and sulfide distribution. Hydrothermal veins were named according to mineral assemblages and quartz textures.

Time relations of veins and mineralization

We have distinguished several successive vein types: an early quartz-magnetite; barren quartz veins; magnetite-bornite-chalcopryrite; pyrite-chalcopryrite; quartz-molybdenite; quartz-pyrite; quartz-galena-sphalerite and quartz-carbonate. *Magnetite or quartz-magnetite veinlets* are up to few cm thick with potassic alteration (mostly biotite and less K-feldspar). Quartz, where present, is granular with homogeneous CL-gray luminosity. *Barren quartz veins* are divided into two subtypes: granular quartz veinlets and crystalline quartz veins. Granular quartz veinlets are thin, with irregular walls and are related to potassic alteration. The quartz grains are anhedral with CL-dark luminescence. Crystalline quartz veins are composed of subhedral to euhedral quartz crystals, oriented perpendicular to straight vein walls. The crystals have oscillatory zoning ranging in luminosity from CL-gray to CL-bright. Vein centers may have open spaces. Often the veins are reopened and filled with pyrite and chalcopryrite in the central parts. *Magnetite-bornite-chalcopryrite veinlets* are rare in Ilovitsa. They are thin and have irregular walls. *Pyrite-chalcopryrite±hematite* form thin veinlets cutting the earlier vein types. These veins typically contain only minor amount of CL-dark luminescent quartz. *Quartz-molybdenite veins* commonly contain open spaces lined by euhedral quartz crystals overgrowing a more granular zone along the vein walls. Often symmetric lines of molybdenite flakes, growing adjacent to the vein walls, are observed in these veins. Molybdenite forms also thin veinlets that cut crystalline quartz veins. *Quartz-pyrite veins* with sericitic alteration cut all of the above described veins. Often they are observed in the central parts of earlier formed veins. These veins contain only small amounts of CL-dark luminescent quartz and pyrite. *Quartz-galena-sphalerite (±pyrite, chalcopryrite) veins* are widely spread in Ilovitsa. Quartz forms idiomorphic crystals with oscillatory zoning. *Quartz-carbonate veins* are formed during a post-ore stage. Carbonates are found in thin veinlets as well as in voids of earlier formed veins. In some of these quartz generations different fluid inclusion types were distinguished and described, and several fluid inclusion assemblages were analyzed by microthermometry and LA-ICP-MS. It is necessary to study additional fluid inclusions in order to determine the P-T-X evolution of hydrothermal fluids during the different mineralization stages. Such analyses are currently performed in our group.

New data of fluid inclusions studies of the Bukovik-Kadiica deposit, Republic of Macedonia

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Bukovik-Kadiica deposit is located in the eastern part of the Republic of Macedonia in a hilly region close to the border with Bulgaria and 2 km northeast of the town Pehcevo. The deposit can be described as one of a number of dacite plugs of Neogene origin that exist within the Serbo-Macedonian Massif and that the volcanic complex is intruded into Palaeozoic sediments, andesites and gabbros. On a larger scale the Kadiica region is underlain by metamorphic rocks (metadiabases, schists, gabbro, diorite and younger granitoids) of Upper Proterozoic to Palaeozoic age. Having the intention to reveal the metallogenetic features of deposit through the determination of temperatures and nature of mineralizing fluids and if there were multiple stages of mineralization we have performed thermobarogeochemical study of fluid inclusions. There were studied numerous transparent polished wafers (23 samples with up to 450 analyzed separate fluid inclusions), where have been analyzed primary fluid inclusions (8–16µm in size) in quartz from fresh volcanics as well as occasional calcites. The pressure of heterogeneous fluids has been determined using method of sections of isochors and isotherms. Studied fluid inclusions were divided into three main types: 1. Fluid inclusions of chloride brines with air bubble, liquid solution, one or more isotropic crystals and sometimes opaque ore mineral; 2. Mainly gaseous fluid inclusions characterized by narrow rim filled with liquid solution (sometimes with isotropic cube crystal); and 3. Two phases fluid inclusions, gas-liquid, fluid inclusions with unsaturated solutions. The results of thermo and cryometric studies have shown that hydrothermal solutions consisted mainly of chlorides of Na, Ca and K (±Mg), which was concluded by chloride eutectics of solutions within temperature intervals from –42 to –25°C and from –60 to –48°C, as well as from the presence of daughter halite, identified by the similarity of the refractive index of the daughter cubic crystal to quartz and its transition into hydrohalite upon freezing of the inclusion solutions.

A complete homogenization of brine inclusions was attained at 501–326°C, with salinities of 45.6–32.4 wt % NaCl equiv. Pressure estimated from inclusions of saturated brines was 1620 bar at 383°C while the fluid density varied from 1.16 to 0.90 g/cm³. Gas-dominated fluid inclusions homogenized into gas at 497–438°C and contained fluid with salinity of 16.3–6.3 wt% NaCl equiv., and were defined pressures of 630–390 bar. Two-phase gas–liquid fluid inclusions of diluted solutions homogenize into liquid at 627–360°C, and the eutectic temperature varies from –60 to –25°C, indicating their chloride composition and the presence of Ca, Na, and Mg ions. The salinity of these inclusions is 24.3–3.2 wt % NaCl equiv., and the fluid density varies from 0.58 to 0.72 g/cm³. Appearance of high salinity inclusions, beside existing low salinity ones, points out that at particular geological periods of the existence of the Bukovik-Kadiica magmatic-hydrothermal system there was a yield of brine fluids from deeper reservoirs. The salinities ranges of 3.2 up to 45.6 wt% NaCl equiv. (gap between 23–30 wt% NaCl equiv. is probably due to boiling process), pointed out that ore components probably were transported as Cl-complexes. Relatively high salinity (up to 46wt% NaCl), probably had its influence to the polymetallic character of the deposit, because chloride complexes are effective way of transport for basic metals (Barnes, 1979). Noted was the high percentage of solid phases both daughter (halite and occasionally sylvite) and opaque phases (ore minerals) that were found within all of the samples. Evidence from study of fluid inclusions suggests that at some point Kadiica has experienced boiling (fluid inclusions that are gas rich and contain bubbles that occupy at least 60% of the inclusions and had homogenization temperatures between 360–530°C; Grancea et al., 2002), which in association with additional data such are those for salinity was used as a marker to interpret the depth of the system (Sheperd et al., 1985) that has been extrapolated to reveal a paleodepth of mineralization of approximately 800 m.

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Placer gold prospecting around the Tertiary occurrences in the Republic of Macedonia

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Exploration of gold as a mineral resource in Macedonia has a long history. There are more than 30 occurrences, but now gold is obtained only from the Buchim mine (Bogoevski, K., 1998). This paper presents the chemical characteristics of gold which was researched by schlich prospecting in several localities related to the Tertiary magmatism.- Borovic, Borov Dol, Plavica and Alshar. The localities selected belong to two major geotectonic units - the Vardar zone (ore deposits Borov Dol, Alshar and ore occurrence Borovic) and the Serbo-Macedonian massif (Plavica ore deposit). The Tertiary magmatism of calc-alkaline type is most important for ore-forming processes in the region. The host rocks of the localities are mostly presented by volcanic sediments and volcanic and subvolcanic facies of latite, quartzlatite, andesite, basalt and their pyroclastics (ignimbrites, tuffs and breccias)

Ore mineralization, in general, has been represented by copper sulphide minerals except in the Alshar deposit, where the main ore mineral is arsenic and antimony. In the Borov Dol deposit are dominated chalcopyrite (Stefanova et al, 2004^b), while in the Plavica deposit beside the chalcopyrite, enargite is of essential significance. In the Borovic occurrence, pyrite is more common sulphide mineral than chalcopyrite.

Gold paining sampling on the territory of the Borov Dol deposit and Plavica and Borovic occurrences shows the presence of placer gold. On the Alshar deposit area, gold was not established by this method. The sampled gold aggregates – 64 from the Borovic occurrence, 44 from the Plavica occurrence and 37 from the Borov Dol deposit were studied for chemical composition and morphology.

The performed investigation reveals that the gold in the all localities are of high-grade type. The most high-grade gold is found in the Borovic followed by the Plavica and the Borov Dol.

The analyzed 11 gold grains from the Borovic occurrence were characterized with very high degree of fineness ranging between 977 and 999. The other admixtures in the gold are copper and iron.

The placer gold from the Borov Dol deposit territory (there were analysed 13 grains) belongs to a group of high grain gold (900-950) that in this deposit ranges from 834 to 981.

The gold of the Plavica is with fineness of 842-994 from analysed 13 grains (Stefanova et al, 2007).

The size of the gold ranges from 150 µm to 1 mm in the Borov Dol, from 50 to 200 µm in the Plavica and from 30 to 150 µm in the Borovic. The gold occurs as elongated, globular, scaly, isometric, randomly shaped and dendritic grains. The gold of isometric morphology prevails in the Borov Dol. In the Plavica along the isometric morphology of the gold, elongated and dendritic forms are commonly encountered too. Isometric, randomly shaped gold grains prevail in the Borovic occurrence. It should be noted that in the all three localities, the most typical morphology of the gold grains is isometric or randomly shaped one – a characteristic that indicates that the gold studied had not suffered significant deformation.

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