UPPER CRETACEOUS CONTACT METAMORPHISM AND RELATED MINERALIZATION IN ROMANIA

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The purpose of this plenary lecture is to give a general view over the contact phenomena and mineralization related to the Banatitic Magmatic and Metallogenic Belt (BMMB - see history of the term in BERZA et al. 1998) which represents a series of discontinuous magmatic and metallogenic occurrences of Upper Cretaceous age, which are discordant in respect to mid-Cretaceous nappe structures (CIOFLICA & VLAD, 1973; CIOBANU et al., 2002.) The subvolcanic/plutonic rocks belonging to the BMMB are known under the collective name of "banatites", a term coined by VON COTTA (1864) who described a suite of cogenetic magmatic rocks occurring as either shallow intrusions or subvolcanic bodies, younger than Jurassic and Cretaceous sedimentary formations. Ever since this first description, the name "banatites" has reflected their locus tipicus, that is, Banat and Timok region, covering parts of the south-western Romania and north-eastern Serbia.

During the last few decades, the BMMB has drawn considerable interest in petrology, age, structuraltectonic significance and in the contained skarn, porphyry-copper and hydrothermal ore deposits, with a vast amount of literature published to date. Owing to the space constraints, only selected citations were therefore included in this abstract.



Fig. 1. The extension of the Banatitic Magmatic and Metallogenic Belt over Romania, Eastern Serbia and Bulgaria (with dark gray in the inset and with heavy outline in the map). Simplified after CIOFLICA & VLAD (1973).

Regional extension and geodynamic setting of the BMMB

The BMMB is exposed over approximately 900 km in length and around 30 to 70 km in width. It has a north-east to south-west trend over Apuseni Mts. and Southern Carpathians, it aligns to a north-south direction over eastern Serbia (Timok and Ridanji-Krepoljin zones), and bends widely to the east, through the Srednogorie area, reaching the shores of the Black Sea (Fig. 1). The northern most occurrences of the BMMB in Romania are in Apuseni Mountains where banatites are found both as volcanics in Late Cretaceous Gosau-type basins (e.g., Vlădeasa, Cornițel-Borod, Gilău-Iara, Sălciua-Ocoliş, Vidra, Găina, Roșia) and as dyke swarms or major intrusions, cross-cutting these volcanics or any older formations or tectonic planes (e.g., Gilău, Budureasa, Pietroasa, Băișoara, Valea Seacă, Băița Bihor, Brusturi, Căzănești, Măgureaua Vaței).

South of Mureş Valley, in the Romanian South Carpathians, Late Cretaceous volcanic and plutonic rocks are found in the upper (Supragetic/Getic) and only as tuffs in the lower (Danubian) stacks of basement nappes. BMMB outcrops in the Supragetic/Getic nappes largely consist of dioritic and granodioritic plutons crossed by dyke swarms of andesites, dacites, rhyolites, lamprophyre, as at Hăuzești, Tincova and Ruschița and further south at Bocsa, Ocna de Fier-Dognecea, Surduc, Oravita-Ciclova, Sasca Montană, Moldova Nouă which intersect Upper Paleozoic - Mesozoic covers and underlying crystalline formations of both Getic and Supragetic nappes (BERZA et al., 1998). Eastward of the Bocşa-Moldova Nouă lineament of plutons and of the Late-Carboniferous to Early Cretaceous cover formations, dyke swarms of banatitic rocks are known in the crystalline (metamorphic and granitic) basement of the Getic Nappe or in Late Cretaceous Gosau-type deposits Sopot) and were grouped by **RUSSO-**(at SÅNDULESCU & BERZA (1979) in the Hypabyssal Banatite Zone (HBZ).

In the Supragetic/Getic nappe stack, banatitic volcanics occur on both the northern and southern slopes of Poiana Ruscă Mountains, as well as in the west (Nădrag Basin), in the center (Rusca Montană Basin) and in the east of the massif (Haţeg Basin), associated with Maastrictian continental sediments in volcano-sedimentary formations.

Attempts were made to ascribe such apparently randomly distributed occurrences to several alignments or magmatic trends, with NE-SW orientation (*e.g.*, CIOF-LICA & VLAD, 1980), but geophysics show a different

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trend of larger plutons from beneath (ANDREI et al., 1989).

Numerous models have been published in the last decades to explain the formation and the geodynamic significance of the BMMB. *Subduction models* have used the two major ocean sutures within the Carpathian-Balkan orogen: the Vardar Ocean with its Mureş Zone (and Transylvanian?) extension, and the Severin Ocean with remnants preserved in Măgura, Ceahlău, Severin and Trojan nappes. Both the dominant calc-alkaline geochemical trend of the igneous rocks and the metal-logenic features of the associated ore deposits were extensively used supporting the subduction models. However, major disagreement exists among these models, especially in what concerns the direction and timing of subduction.

Comprehensive overviews of such subduction related models are given by BERZA *et al.* (1998), CIO-BANU *et al.* (2002) and ZIMMERMANN *et al.* (2008) and will be summarized during the lecture.

Authors such as POPOV *et al.* (2000), BERZA *et al.* (1998) and NEUBAUER (2002) have considered that the banatitic magmas where generated in an *extensional regime* during Late Cretaceous – documented by Gosautype basins – caused by orogenic collapse affecting the upper crust. Mantle delamination due to slab break-off in the Late Cretaceous has followed the Jurassic and Lower Cretaceous northwards directed subduction Vardar Ocean.

Slab-rollback models postulate that in the Late Cretaceous, the subducting Vardar oceanic slab began to roll back and steepened, thus leading to extension in the upper crustal block and favouring the access of melts to high crustal levels, ultimately leading to volcanism. The slab-tear model (NEUBAUER, 2002, NEUBAUER *et al.*, 2003) predicts that in a post-subduction, postcollisional regime, the subducting slab breaks from its continental counterpart and initiates asthenospheric upwelling into the slab window created as the tectonic units separate.

Based on the paleomagnetic data from the Carpathian and Pannonian areas, PANAIOTU *et al.* (2005) suggested a two-step rotation model, to explain the up to 90° declinations measured on banatites in the Apuseni Mountains and in the Southern Carpathians. The Late Cretaceous paleoaltitude calculated for banatites by PANAIOTU *et al.* (2005) is $24^{\circ}N \pm 4^{\circ}$. At the time of their emplacement, the banatites of the BMMB had an east-west spatial trend, and continued to the east with the alignments of the Western and Eastern Pontides (Fig. 2).

Petrology and geochronological summary of the banatites

The BMMB is characterized by an extreme petrographic diversity, and many of the individual outcropping massifs encompass a significant part of this variety. Thus, a detailed petrographic inventory of each banatite occurrence in the Romanian part of BMMB would be far beyond the scope of this lecture.

Effusive banatites encompass a wide range of compositions from rhyolites (Vlădeasa), to alkali basalts (Poiana Ruscă Mountains), but medium and high-K andesites and dacites prevail in all volcanic complexes of the Romanian portion of the BMMB. Intrusive banatites range from gabbros to leucogranites, but the most widespread are (quartz) diorites, granodiorites and (quartz) monzodiorites (BERZA *et al.*, 1998, POPOV *et al.*, 2000). Numerous satellite dykes contain basalts, andesites, dacites, rhyolites and relatively diverse lamprophyres. A general characteristic of banatitic intrusions is the large quantity of the mafic microgranular enclaves, frequently porphyric and incorporating crystals from the host, thus testifying for magma mingling.

A compilation of radiometric dating for banatites was published by CIOBANU *et al.* (2002), pointing to K-Ar age spans between 49.5–77 Ma in Apuseni Mountains, 47.2–110 Ma in Poiana Ruscă Mountains, 67–89 Ma in Banat, 38–93 Ma in Serbia and 67–94 Ma in Bulgaria, respectively. Maximum of K-Ar age frequencies occur in the 65–95 Ma interval (Turonian–Maastrichtian), a shorter time span, confirmed by recent Ar-Ar, U-Pb and Re-Os dating (*e.g.*, POLLER *et al.* 2001; VON QUADT *et al.*, 2001).



Fig. 2. The position of banatites (BN), western Pontides (WP) and eastern Pontides (EP) on the basis of paleomagnetic data, compared with the paleogeographic reconstructions of NEUBAUER et al. (2003); (after PANAIOTU et al., 2005).

Re-Os ages published by ZIMMERMAN *et al.* (2008) for 50 banatite (molybdenite bearing) samples, from throughout the BMMB (Romania, Serbia, Bulgaria), indicate 20 My time interval, *i.e.*, 72.2–92.4 Ma, in good agreement with the zircon U-Pb ages and overlapping with median zone of the much more scattered

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K-Ar or Rb-Sr data. The Re-Os ages measured on molybdenite bearing samples by ZIMMERMANN *et al.* (2008) for various segments of the BMMB, distribute as follows: Apuseni Mountains (Băița Bihor): 78.7– 80.6 Ma; Poiana Ruscă (Calova, Valea Căprișoara, Tincova): 72.2–76.6 Ma; Banat (Ocna de Fier, Bocşa, Oravița, Ciclova, Moldova Nouă): 72.4–82.7 Ma; Timok (Majdanpek, Crni Vrh, Veliki Krivelj, Bor): 80.7– 87.9; Panagyurishte (Elatsite, Chelopech, Medet, Assarel, Vlaykov Vruh-Elshitsa): 86.8–92.4 Ma.

Contact metamorphism related to BMMB

The main effect of the banatitic emplacement was the thermal and metasomatic transformation of the surrounding rocks. Often, the metasomatic processes had an endomorphous character, affecting to different degrees the intrusive bodies themselves. In the majority of igneous occurrences in the BMMB, the contact metamorphism extended over the pre-intrusion host formations, including crystalline schists, detrital sedimentary and carbonate rocks, leading to the formation of structurally and mineralogically complex contact aureoles.

Isochemical transformations include recrystallization, prograde reactions without major implication of fluid phases, combinations of both, and subordinately, irreversible devolatilization (pyrolysis). The later process is often responsible for the discoloration of recrystallized carbonate rocks in the close vicinity of magmatic sources (*e.g.*, Dognecea – VLAD, 1974), followed by the removal of organic carbon traces.

Recrystallization products are widespread within the contact aureoles, especially in areas where pure carbonate rocks prevail: calcitic or dolomitic marbles, often zoned, with rougher textures in the vicinity of the magmatic bodies (VLAD, 1974; IONESCU, 1996b). Carbonate rocks with silicate alloclasts, argillaceous or arenaceous limestones, marls, detrital rocks or crystalline schists are also transformed under the heat flow and may result in "hardening", "hornfelsing", "softening" of the rocks - as named by various authors, or in textural transformations leading to obliteration of initial stratification or schistosity. Recrystallization commonly resulted in micro- or mesoblastic calcic or dolomitic marbles and relatively homogeneous, medium-grained calcsilicate hornfels with grossular + calcite or diopside + calcite. Siliceous and aluminous hornfels with biotite- or quartz-dominant assemblages or with andalusite + cordierite \pm corundum and actinolite + chlorite + epidote \pm zoisite are also present, yet at least in part, their mineralogical composition might point as well to superposed hydrothermal alteration.

Prograde reaction products are much more diversified and reflect the complex nature of the premetamorphic rocks. Various criteria have been used to classify hornfels: (1) texture or overall macroscopic appearance; (2) mineralogical composition; (3) chemical composition; (4) metamorphic "facies" or the nature of premetamorphic rock. In some cases, the prograde reactions are weak and only singular metamorphic mineral phases are identified against an unchanged background (*e.g.*, "biotite in gneisses", "cordierite in porphyritic rocks", "andalusite in biotite-bearing gneisses"). Sometimes, the thermal effects are inferred from *the loss* of certain mineral phases from the initial paragenesis (*e.g.*, loss of biotite from thermally affected gneisses).

The most typical products of *allochemical transformations* in the contact aureoles of banatites are skarns and hydrothermal alterations. Cases of large scale Ca \Leftrightarrow Mg transfer reactions resulting in dolomitization of limestones (*e.g.*, Ocna de Fier-Dognecea – VLAD, 1974) or in dedolomitization (*e.g.*, Antoniu metasomatic body, Băița Bihor – CIOFLICA *et al.*, 1992) have also been recorded.

Skarns have also been classified or referred to according to a multitude of criteria: (1) dominant chemical character ("calcic skarns", "magnesian skarns"); (2) mineralogical composition (skarns with various Ca, Mg, Al silicates); (3) the nature of the carbonate paleosome ("skarns formed on limestones", "skarns formed on dolostones"; (4) the passive or active role of the paleosome vs. the mineralizing fluids ("exoskarns", "endoskarns", "periskarns"); (5) position with regard to the magmatic contact ("proximal skarns", "distal skarns"); (6) evolution stage of magmatic bodies ("magmatic skarns", "post-magmatic skarns"); (7) thermal character of fluids ("pyro-metasomatites", "hydrometasomatites", "pseudo skarns").

Calcic skarns prevail in all banatite occurrences located nearby carbonate sedimentary formations. Subordinately, in several massifs from Bihor and Banat, magnesian skarns occur, with assemblages including forsterite + chondrodite + diopside \pm phlogopite (clinochlore) + tremolite. At Băița Bihor, Budureasa, Pietroasa, Cacova Ierii, Ocna de Fier, skarns contain endogenous borates, such as ludwigite, kotoite, suanite or szaibélyite (e.g., IONESCU, 1996a,b; MARINCEA, 2006). Other chemical types may also be present, such as Mn-rich skarns at Dognecea (e.g., VLAD, 1974). Skarns unusually rich in aluminum occur in Valea Tiganilor, Ciclova and at Sasca Montană. The main Al-rich phase is vesuvianite which forms monomineralic concentrations, with crystals reaching up to 5-10 cm. Commonly, vesuvianite replaces diopside, wollastonite and garnet and points rather to a significant Al-mobility towards the late phases of metamorphism than to an Al-rich host rock.

Exoskarns are predominant in the banatitic contact aureoles, but well developed endoskarn assemblages have also been described. At Ciclova, the outer parts of a monzodiorite body have been transformed in endoskarns with grossular + vesuvianite + Fe-diopside + phlogopite, locally accompanied by periskarns with Feaugite + orthoclase + titanite + grossular (CIOFLICA *et al.*, 1980). At Surduc, MARINCEA & RUSSO-SĂNDULESCU (1996) described calcic endoskarns with prehnite + andradite + Ca-rich plagioclase + diopside, formed on bodies of basic magmatites of the Coniacian – Maastrichtian cycle.

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High-temperature skarn assemblages with spurritetilleyite-gehlenite, or diopside-gehlenite occur at Cornet Hill-Măgureaua Vaței, Apuseni Mountains (MARINCEA *et al.*, 2001; PASCAL *et al.*, 2001) and Ogașul Crișenilor-Oravița (CONSTANTINESCU *et al.*, 1988b; KATONA *et al.*, 2003) where they are related to quartz monzonite-monzodiorites, or diorite-gabbros.

Skarns related to BMMB in Romanian have been examined and classified also with respect to regional structural relationships with surrounding rocks. Three main types have been distinguished (CIOFLICA & VLAD, 1973; VLAD, 1997), (1) the Băița Bihor type, (2) the Ocna de Fier type and (3) the Moldova Nouă type.

- The *Băița Bihor type* skarns may develop along magmatic-sedimentary contacts, but more often they form distal bodies along fractures or thrust planes, or highly brecciated metasomatic columns.

- The Ocna de Fier type skarns are controlled by the contact of the Ocna de Fier-Dognecea pluton with carbonate rocks and form discontinuous bands, irregularor tabular-shaped bodies and metasomatic veins. A relatively homogeneous carbonate paleosome favoured diffusion, rather than infiltrative exchange as the major metasomatic process involved. Metasomatic asymmetrical zoning is obvious: an inner zone with andraditedominant assemblages, locally rimmed by wollastonitites and an outer zone with pyroxenic skarns – diopside at Ocna de Fier and Mn-hedenbergite at Dognecea (VLAD, 1974).

- The *Moldova Nouă type* skarns develop at Moldova Nouă, Sasca Montană and partially at Oravița-Ciclova, where they are controlled mainly by contact zones between subvolcanic bodies and carbonate rocks. They occur commonly as lenses with branching apophyses in the vicinity of igneous apices. Skarns of this type display no striking mineral zoning.

A continuum between skarns and hydrothermal alterations is specific to all skarns occurrences in BMMB, but the effects of hydro-metasomatism are usually extended beyond the limits of skarn zones.

Hydrothermal retrograde reactions affecting garnets and vesuvianite, commonly result in epidote + chlorite \pm carbonates, quartz whereas pyroxenes breakdown to form tremolite - actinolite + serpentine + talc. High temperature hydrothermal assemblages with tourmaline + quartz \pm orthoclase, magnetite were described in relation to porphyritic granodiorite intrusions from Oravița and from Sasca Montană (CONSTANTINESCU, 1980).

More abundant are the hydrothermal assemblages containing a) K-feldspar + biotite \pm quartz, muscovite (potassic alteration), b) epidote + actinolite + chlorite + quartz + calcite (propylitic alteration), and c) illite + quartz \pm chlorite, calcite, pyrite (phyllic alteration) which are frequently related to ore deposits. Rich epithermal alteration with zeolites (laumontite, stilbite, thomsonite, chabazite, etc.), gypsum, anhydrite, and cryptocrystalline silica are also present.

Types of mineral deposits in the BMMB

The studies of VON COTTA (1864) upon the Fe-Cu-Pb-Zn skarn deposits of Dognecea, Ocna de Fier and other mines in Banat are the first widely cited papers to define a class of "contact-deposits" found at the contact of igneous intrusions and limestones. Since then, more than 50 mineral deposits have been discovered, and pending of a given historical epoch, they were of some economic interest. The mineralization related to the BMMB is represented mainly by porphyry copper, massive sulphide, skarn and vein (epithermal and mesothermal) deposits (BERZA *et al.*, 1998).

Copper metallogeny is predominant and distinguishes the BMMB in the context of the larger Alpine-Balkan-Carpathian-Dinarides belt (CIOBANU et al., 2002). Copper ores are commonly associated with Pb-Zn, Au-Ag, and subordinately with Mo, Bi, W, Fe, Co, Ni and B. Mineral deposits within the BMMB are strongly differentiated with respect to host rock types and depth of magma emplacement. Shallower hypabyssal bodies are hosts for porphyry copper ores with Cu \pm Au, Ag, Mo: e.g., Moldova Nouă, Majdanpek, Cerovo, Veliki Krivelj, Bor (Timok Massif, Serbia), Elatsite, Chelopech, Assarel (Panagyurishte district, Bulgaria). High-sulphidation epithermal deposits are sometimes spatially associated with larger porphyry copper systems (e.g., at Bor and Majdanpek - CIOBANU et al., 2002). Subeconomic porphyry copper (± Mo) accumulations are also present at Oravita, but hydrothermal alteration is far less pervasive than at Moldova Nouă. Large shallow porphyry-style systems with pyrite halos (and/or skarn halos) extend only south of Poiana Ruscă but they lack economic mineralization: e.g., Tincova-Ruschita, Sopot-Teregova-Lăpușnicel areas.

Copper and base metal skarn deposits form the most widespread metal accumulations across the BMMB. Some occurrences are set apart by prominent Fe metallogeny (e.g., Ocna de Fier, Masca Băisoara). Ocna de Fier is considered typical for fluid plume mineralization in a proximal skarn setting (COOK & CIOBANU, 2001). Forsterite skarns host a magnetite-chalcopyritebornite mineralization which represents the inner Cu-Fe core of the deposit (COOK & CIOBANU, 2001). Scheelite forms significant concentrations in the Cu-Mo mineralization of Băița Bihor and Oravița. Bismuth sulphosalts are minor but ubiquitous components of many skarn deposits. Extremely rich and diverse bismuth sulphosalt assemblages have been described at Băița Bihor, Valea Seacă, Ocna de Fier and Oravița-Ciclova.

Regional zoning of skarn deposits in correlation with Upper Cretaceous subduction settings was summarized by VLAD (in BERZA *et al.* 1998; VLAD & BERZA 2003) who distinguished two major metallogenic segments within the BMMB (Apuseni Mountains and Southern Carpathians), each one still amenable of division into further units (sub-belts, zones and districts). Local zoning is well expressed for numerous ore environments in the BMMB. At Băița Bihor, the areas closest to the magmatic sources are enriched in molybdenite. Towards the external zones, Mo-rich ores grade into Mo-W-Bi-Te (in calcic skarns) or Cu-W-Bi (in magnesian skarns), Pb-Zn (in magnesian skarns and sedimentary schists) and finally into boron mineralization overlapping dedolomitization zones. At Dognecea-Ocna de Fier, CIOBANU & COOK (2000) described a Cu-Fe \rightarrow Fe \rightarrow Pb-Zn metal zoning around a single granodiorite core in the deepest part of the deposit.

The polyascendant character of skarn deposits in the BMMB has either been asserted (*e.g.*, POPESCU & CONSTANTINESCU, 1977; CIOFLICA & VLAD, 1981) or argued against (ILINCA, 1998). Extensive sampling and detailed investigation of ore paragenesis over numerous skarn deposits in the BMMB, plead for coeval and isochronous mineralization, most probably formed from the differentiation of a single fluid. Moreover, apart from several cases of prominent metallogeny (*e.g.*, Fe at Ocna de Fier), the overall paragenetic sequence for virtually all mineral deposits in the BMMB is roughly the same, both as mineral phases and deposition sequence. ILINCA (1998) separated the following ore deposition sequences:

- Stage 1 ("siderophile" – Fe \pm Co, Ni, As, Mn) – iron oxides and sulphides, Co, Ni, Fe arsenides and sulpharsenides, with subordinate Fe-Mn calcic silicates. The stage signifies the highest deposition temperatures and a continuous decrease of oxygen fugacity (*e.g.*, hematite \rightarrow magnetite, magnesioferrite) vs. increase of sulphur fugacity (pyrrhotite \rightarrow pyrite). At Băi ța Bihor, Ocna de Fier, Oravița, Ciclova and Sasca Montană, early iron sulphides are accompanied by nickeline, rammelsbergite, cobaltite, gersdorffite (ILINCA, 1998), Co-pentlandite (COOK & CIOBANU, 2001), linnaeite, bravoite, siegenite, millerite.

- Stage 2 (Pb, Zn \pm Ag, Bi, Fe) – forms the bulk of the mineralization in numerous occurrences across the BMMB. The stage is represented by galena (with up to 10 mol% matildite) and sphalerite usually with 14– 15 mol% FeS). Invariably, the direct contact between galena and siderophiles, shows the late character of the Pb-Zn phases.

- Stage 3 (Pb, Bi \pm Ag, Sb, Te, Cu) – contains Pb-(Ag)/Bi sulphosalts (lillianite homologues (heyrovskýite, lillianite, vikingite), cosalite, cannizzarite, galenobismutite. Some Pb-Bi sulphosalts are formed on older galena, most probably belonging to the previous stage. Stage 3 members often substitute siderophile sulphides likely to belong to stage 1. The same stage witnesses the deposition of Bi (\pm Pb) tellurides: joséite-A, joséite-B, protojoséite, and rarely native bismuth. Cosalite represents a late deposition within this stage. It contains small amounts of Cu and replaces heyrovskýite, lillianite and cannizzarite. In Sasca Montană and Moldova Nouă, stage 3 assemblages are mostly represented by Sb (\pm As) sulphosalts: geocronite, boulangerite and zinkenite, often formed on older galena.

- Stage 4 ("copper metasomatosis" (CM) – Cu, Bi \pm Pb, Ag, Fe, Sb, Te, As, Zn, Au, Mo, W) – is distin-

guished by an increase of Cu content in sulphides and sulphosalts. Massive deposition of chalcopyrite, cubanite and bornite takes place in this stage. Fahlore minerals (tetrahedrite-tennantite, enargite, luzonite) occur also now, most frequently on Fe, Zn, Sb, As phases of earlier stages. At Băița Bihor, Oravița and Ciclova, chalcopyrite and cubanite are often pseudomorphs after pyrite and replace Co and Fe sulpharsenides. "Chalcopyrite disease" phenomena, *i.e.* chalcopyrite (± bornite, mackinawite) blebs in sphalerite are widespread and represent yet another facet of CM. Bi-sulphosalts are particularly sensitive to CM transformations. First Bi phases show an increased Bi₂S₃/PbS ratio compared to previous stages and grade towards decreasing Bi/Cu. Such minerals form directly or by replacing older Pb-Bi sulphosalts (especially cannizzarite and galenobismutite): proudite, lillianite (with up to 2.9 at% Cu), felbertalite, (high Cu) cosalite, cupronevite, junoite. The sequence continues with nuffieldite and massive deposition of bismuthinite derivatives, covering the entire range between bismuthinite and aikinite. In antimonydominated assemblages, bournonite is formed. The highest Cu contents are embodied by makovickyitecupromakovickyite, paděraite, hodrushite and kupčíkite and finally by pure Cu-Bi sulphosalts such as emplectite and wittichenite.

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