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Formation Mechanism of Dwarfish Cu–Au Porphyry Deposits of Macedonia

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Regularities in the distribution and formation mechanism of giant Cu porphyry deposits have been discussed by many authors. Most recent works are dedicated to the problem of their formation [1]. The deposits of Macedonia discussed in this communication usually contain up to 150000 t of copper with the Buchim deposits likely being the smallest in the world among similar recently mined deposits. The long-term economically profitable development of the latter refutes the traditional opinion that only Cu porphyry deposits with reserves at least of 2500000 t and Cu content exceeding 0.5% are profitable for exploitation. Therefore, complex study of dwarfish deposits of Macedonia is as important as research into giant deposits of the Pacific ore belt for solving the problem of their formation mechanism and answering the question of how they differ compared to giant deposits.

The Cu porphyry deposits studied belong to the Leche–Shalkidik metallogenic zone located at the transition between the Serbian–Macedonian Massif and the Vardar zone (Fig. 1) and are genetically connected with small Tertiary subvolcanic calc-alkaline stocks such as the Buchim, Tular, and Borov Dol in Macedonia; Vakhi, Gerakaria, and Potokerasia in Greece; and others. Among these massifs, only the Buchim deposit in Macedonia has been mined recently.

The metallogenic features of the southern Balkan Peninsula are determined, on the one hand, by geodynamic evolution of the Tethys–Eurasian metallogenic belt (TEMB), which was defined by Yankovich [2] and, on the other, by old crystalline massifs. The belt was formed during the post-Mesozoic epoch instead of the Jurassic paleoocean Tethys, which was located between the southern continental margin of Eurasia in the north and the African–Arabian and Indian plates in the south. It extends from the Western Mediterranean along the Alps and southeastern Europe via the Lesser Caucasus, Hindu Kush, and Tibetan Plateau up to Burma and northwestern Indonesia, where it joins the western part of the Pacific metallogenic belt. The southern part of the Balkan Peninsula with the Macedonian Republic is one of the segments of the TEMB central part (Fig. 1).

The Jurassic ophiolitic belt extends for hundreds of kilometers through Macedonia and farther for thousands of kilometers through Greece, Turkey, the Caucasus, and Iran to the Himalayas. In Macedonia, the ophiolitic complex is distributed in the Vardar zone (VZ) and the adjacent part of the Serbian–Macedonian Massif (SMM).

Collision between the African and European plates was accompanied by the ocean closure and subduction of the oceanic crust under the Serbian–Macedonian Massif. This process resulted in the formation of arches, dome structures, and a system of grabens [3]. This period was marked by an important metallogenic event: formation of a system of deep faults in the active continental margin in the western part of the massif. The above-mentioned regional structures arranged in parallel with the Vardar zone regulate regional metallogenic zones, ore districts, and fields in the region under consideration (Fig. 1).

Volcanism in this region began in the late Oligocene, while ore mineralization is Miocene in age. Geochronological study by the K-Ar method revealed that andesites of the Damjan and Bobrov Dol fields were formed in the period of 28.0 to 26.5 Ma ago, while andesite stocks of the Buchim ore field appeared between 27.0 and 24.5 Ma ago [4].

The Buchim ore field is located in the northern part of the ore district in the Serbian—Macedonian Massif. A remarkable feature of this ore field is the lack of morphologically expressed structures such as volcanic domes, calderas, and depressions; they have only small ring structures (from several hundreds of meters to 1.5 km across) resulting from intrusion of subvolcanic stocks (Fig. 2). The outer part of these structures is

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Fig. 1. Geological position of Macedonia in the Balkan Peninsula. The inset shows the position of the region under consideration in southeastern Europe. (1) Tertiary volcanic sequences; (2) Tertiary intrusions; (3) Vardar zone; (4) Serbian–Macedonian zone; (5) faults and lineaments; (6) state boundaries; (7) Buchim–Borov Dol ore district.

composed of gneisses, and their central parts are represented by latite stocks.

The Buchim deposit is known from ancient times, although it was explored in detail only in the 1970s. The deposit reserves are 120 000 000 t of ores with average Cu and Au contents of 0.34% and 0.35 g/t, respectively. The deposit has been developed since 1979. By now, approximately 80 000 000 t of ores have been mined with an annual production of 4 000 000 t. Recently, the respective average contents of Cu, Au, and Ag in ores produced were as high as 0.21%, 0.2 g/t, and 0.8 g/t.

The Damjan ore field is located in the central part of the ore district in the Vardar zone 5 km southwest of the Buchim mine (Fig. 2). It is spatially controlled by NW-trending faults, and its Tertiary volcanism is represented by andesite dikes and sills. The ore field is crossed by dominant latitudinal faults. The recent relief is marked by distinct Neogene arcuate and ring fractures (Fig. 2). Mineralization associates with calcareous scarns formed around subvolcanic dikes and sills due to metasomatic alteration of limestone interbeds in Paleogene flysch sequences. The main ore minerals are magnetite and hematite occurring in equal proportions. The important metallogenic feature of this ore district is the lack of economically significant Cu and Au concentrations in scarns of the Damjan deposit. The reserves of the latter are approximately 10 000 000 t of ores with an average iron content of 35%. The deposit was mined in the period of 1968–1992.

The Borov Dol ore field is located in the southern part of the ore district in the Vardar zone. The volcanic caldera hosting this deposit is 5 km across being well developed in the district morphostructure (Fig. 2). The caldera is complicated by several domes and depressions (1.0–1.5 km in diameter), one of which hosts the Borov Dol deposit. The ore field is crossed by NW-extending faults with associated Neogene latite to quartz–latite dikes, necks, and lava extrusions. Ore-enclosing volcanics are altered by hydrothermal processes. The Borov Dol deposit, which serves as a



Fig. 2. Morphostructural map of the Buchim–Borov Dol ore district. (1) Fluvial sediments; (2) river terrace; (3) proluvium; (4) Pliocene–Quaternary sediments; (5) latites, andseites, and quartz latites; (6) pyroclastic sequences; (7) Paleogene flysch; (8) Cretaceous flysch; (9) granites; (10) serpentinites; (11) scarns; (12) limy–shaly sediments; (13) muscovite schists; (14) gneisses; (15) main faults; (16) second-order faults; (17) local faults; (18) volcanic centers; (19) secondary volcanic centers; (20) volcanic necks; (21) relicts of calderas, ring structures; (22) positive ring structures; (23) negative ring structures. Tectonic blocks: (A) Buchim, (B) Damjan, (C) Shtip, (D) Radovich, (E) Radovich graben.

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Fig. 3. Spider diagram demonstrating the distribution of MORB-normalized trace elements in volcanics of the Buchim–Borov Dol ore district. (1-3) Latites corresponding to 1, 2, 6 in Table 1; (4-7) trachyte: (4, 5, 6) corresponding to 3, 4, 5 and (7) corresponding to 8 in Table 1.

reserve for the Buchim mine, was discovered in 1930, when boreholes recovered mineralization with Cu contents of 0.2-0.7%. The ore reserves of the deposit were estimated by thorough systemic exploration in 1973–1977 to be 40 000 000 t with average Cu and Au concentrations of 0.3% and 0.28 g/t, respectively.

In addition to the above-mentioned deposits, the northern part of the district hosts numerous ore occurrences with Cu porphyry mineralization: Vranjak, Orljak, Crn–Vrv–Kalapetrivci, Kosevo, Kosevska Reaka, and others.

Volcanics of the district represent derivatives of intermediate—acid magmas with relatively high alkali contents, which are highly differentiated from basic to highly acidic and calc-alkaline varieties. They belong to the high-potassic series being represented by andesites, latites, trachytes, rhyolites, and transitional rocks [5].

Previously, it was thought [6] that the parental magma of the volcanogenic—intrusive complex in the Serbian—Macedonian metallogenic zone resulted from partial melting of the continental crust in response to deep collision of continental blocks, which was intruded through a deep-seated fault into higher formations.

The subsequent analysis of 87 Sr/ 86 Sr isotope ratios (0.706633–0.706928) and distribution of minor elements revealed that volcanic rocks of the study area resulted from mixing of material originating from the continental crust and upper mantle [7, 8]. In addition, it was shown [7] that by the concentrations of minor and trace elements the volcanics of the area are similar to their counterparts from active continental margins.

The original data (Table 1, Fig. 3) indicate that differentiation of the magmatic melt yielded conditions favorable for different interactions between mineral components. Concentrations of trace and accessory elements (Table 1) imply fractionation of minerals during magmatic evolution. The spider diagram demonstrates distinct positive Th and Y anomalies and insignificant negative Nb and TiO₂ anomalies; anomalously high K₂O, Rb, Nb, and Sc contents characteristic of subduction-related magmas are established for Sample 5 (Fig. 3).

Thus, the geochemical study of minor elements indicates that igneous rocks of the deposits under consideration were most likely formed in the transitional zone between the continental crust and the upper mantle.

The study of stable isotopes is now used for obtaining more accurate information on the genesis of ore metals. The S isotope composition for the Buchim deposit was studied in 10 pyrite samples (Table 2). As follows from the table, the S isotope composition in pyrite varies in narrow limits (+0.16 to +2.53%) averaging +1.06% in all three orebodies of the deposit with insignificant enrichment in the heavy isotope relative to meteorite sulfur. According to classification in [9], such a composition of S isotopes allows the Buchim deposit to be attributed to the category associated with felsite volcanics. As follows from these data, sulfur of the Buchim deposit is either of magmatic origin or was mobilized from sulfides of volcanic rocks. At the same time, the S isotope composition in the Borov Dol deposit is characterized by the dominant light S isotope ranging from 0 to -7% [10]. Such a difference in the isotope composition of sulfur from closely spaced deposits may be explained by their different geological structures. As was mentioned, the Buchim deposit is located in the Serbian-Macedonian Massif, while the Borov Dol deposit is confined to the Vardar zone. It is conceivable that sulfur of the Borov Dol deposit partly originates from host sedimentary rocks.

The study of ¹³C/¹²C and ¹⁸O/¹⁶O values in calcite from ores of the Buchim deposit demonstrates that water of the ore-forming fluid originates from several sources, including mainly meteoritic [10]. This inference needs, however, further verification.

The composition of fluid inclusions in quartz from the Buchim deposit indicates that ore-forming hydrothermal solutions were of the chlorite—sodium type with concentrations of salts varying from 10 to 25 wt %/equiv. The NaCl and mineralization temperatures ranged from 490 to 200°C. Ore components were transported in the form of complex ions, which contained Na and K chlorides and less common sulfates and carbonates [10].

In conclusion, an important metallogenic fact should be noted for the Buchim–Borov Dol ore district: lack of economically significant copper mineralization in magnetite–hematite scarns of the Damjan

Sample	1	2	3	4	5	6	7	8
Cr*	65	38	29	29	64	26	60	50
Li*	18	9	12	4	4	3	9	9
Rb*	54	46	57	61	271	46	3	42
Nb	10	11	10	8	16	12	9	10
Y	26	26	23	25	33	28	26	27
Sr	1227	1501	1349	1491	926	1702	1327	1633
U	5	3	4	<2	9	6	6	<2
Th	21	30	25	31	37	37	27	23
Pb	51	67*	60	65	72	43	26	71
Ga	19	19	18	19	20	18	17	19
Zn	170*	69	75	67	33	49	66	60
Cu	43	51	70	323*	8	32	11	52
Ni	9	7	8	6	6	9	6	6
Co	16	13	14	13	5	16	6	11
Nd	46	59	50	48	_	59	50	52
La	65	76	88	69	61	84	74	98
S	51	_	_	96	27	_	90	28
Hf	9	7	11	13	10	11	14	9
Sc	11	14	11	10	<2	12	16	14
As	8	4	6	<3	14	<3	8	3

 Table 1. Trace elements in volcanic rocks (ppm)

Note: (*) Samples studied by the atomic absorption method (Sophia), other analyses by X-ray spectroscopy (Swiss). (1, 2) Latite from southern Pamukluk; (3) trachyte from southern Pamukluk; (4) trachyte from Damjan; (5) alkali trachyte from Crkviste; (6) latite from Borov Dol; (7, 8) latites from Daman.

deposit, although they were formed at the contact between carbonate flysch rocks and subvolcanic andesites compositionally similar and coeval with rocks constituting stocks of the Buchim and Borov Dol deposits. It is quite conceivable that the upper part of the orebody with copper mineralization is eroded in the Damjan deposit. This is evident from the study of similar polymetallic scarn deposits in Karamazar [11], which demonstrate distinctly zoned patterns: the upper levels of these deposits host polymetallic mineralization, which is replaced downward by hematitemagnetite ores. This observation confirms the inference by Cifliganes [4], who believed, proceeding from metasomatic zoning, that the Buchim deposit was eroded up to its medium level and no erosion was characteristic of the Borov Dol deposit.

It is conceivable that a primary intrusive center served as a source of copper for the deposits under consideration. At the same time, subvolcanic intrusive bodies of these deposits are insufficiently large for mobilization of a quantity of copper from them by the hydrothermal convective system to provide its presentday content in orebodies. Consequently, the magmatic source of copper was likely located at deeper levels and represented a relatively large intrusive body (Fig. 4). It may be suggested that the significant volume of orebearing magma that formed the intrusive bode at a deep level could yield copper for a relatively large porphyry deposit, although the latter is missing in the entire Leche–Shalkidik metallogenic zone, the district under consideration included.

 Table 2. Sulfur isotope composition in pyrite from the Buchim deposit

Orebody	Horizon, m	$^{32}S/^{34}S$	δ ³⁴ S, ‰
Cukar	630	22.164	+2.53
	630	22.216	+0.16
	630	22.197	+1.02
Central	605	22.186	+1.52
	605	22.211	+0.42
	605	22.205	+0.70
Vrsnjak	650	22.220	+0.00
	650	22.212	+0.38
	650	22.180	+0.80
	650	22.174	+2.09

Note: Analyses were performed at aInstitute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, analyst L.P. Nosik.



Fig. 4. Model of the magmatic system in the Buchim–Borov Dol ore district. (1) Pliocene–Quaternary sediments; (2) volcanic; (3) subvolcanic bodies; (4) granitoids; (5) rocks of the Vardar zone (ultramafics, granitoids, Cretaceous and Paleogene rocks); (6) rocks of the Serbian–Macedonian Massif (gneisses, muscovite schists, amphibolites); (7) faults.

It is possible that some copper could have been mobilized from ultramafics occurring both in the Serbian-Macedonian Massif (amphibolites) and Vardar zone (peridotites and serpentinites), which were intruded by the Cenozoic magmatic complex. Such a possibility is more real since the Neogene calc-alkaline magmatic complex in the Serbian–Macedonian province is depleted in copper as compared with Cretaceous igneous rocks in the Bor area [6]. The hypothesis of copper remobilization from serpentinites and ultramafics of the Vardar zone or massive sulfide deposits of the Cyprus type is also supported by insignificant reserves and low concentrations of ore elements in the studied Cu porphyry deposits, which is characteristic of regenerated deposits [12]. This likely represents the main feature, owing to which formation of dwarfish deposits differs from that of their giant counterparts.

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