# The Influence of Ophiolite Complexes on the Geochemistry and Metallogeny of Tertiary Igneous Rocks in Central Parts of the Balkan Peninsula

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With 2 Figures, 1 Table

### Introduction

Tertiary, mainly Neogene volcanic and intrusive igneous rocks build a NNW-SSE stretching belt in the central part of the Balkan peninsula. They originated from melts of crustal origin, *i. e.* from maymas generated by melting of deep parts of a thickened continental crust in this area (KARAMATA, 1974; KARAMATA & DJORD-JEVIĆ, 1980). These igneous rocks are therefore generally poor in elements related to mafic and ultramafic rocks, especially in Cu, Ni, Co and Cr. Copper ore occurrences related to this magmatism are rare, and these of nickel-cobalt appear only at a few places and are of minor size (KARAMATA, 1974; JANKOVIĆ, 1977).

The low contents of Cu, Ni, Co and Cr in the rocks, as well as the absence of copper-, nickel- and cobalt-mineralizations are not a uniform feature of this belt all along its extension from Srebrnica and Boranja over the Golija Mts. and Rogozna Mts. to the southern Kopaonik, or from Avala, over the Rudnik Mts., the Ibar-Kopaonik area, the Lece volcanic complex and the Surdulica-Besna Kobila area to the Zletovo-Kratovo volcanic complex, but there exist remarkable differences in geochemical respect. These differences are even more evident by crossing the belt from WSW to ENE. In some parts of it the content of the considered elements is higher (e. g. in the igneous rocks of Rudnik or Ibar-Kopaonik area). It is noteworthy that in some areas where the igneous rocks are enriched in Cu, Ni, Co and Cr, copper ore occurrences (Kremići, Lece) and even ore deposits (Bučim) and some nickel-cobalt sulfide occurrences (Kopaonik) are existing.

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## Cu, Ni, Co and Cr Concentrations in Neogene Igneous Rocks

In the central part of the Balkan peninsula the Neogene igneous rocks are represented by quartz-monzonites (Ca-rich granites) to granodiorites as plutonic, mainly shallow intrusive rocks, and by quartz-latites, (K-rich) dacites, andesites (mostly with a high normative quartz), and very rare K-basals as volcanic rocks. The mean chemistry of these rocks corresponds with the low-melting-point of a granitic system, they are as far it concerns the trace elements, characterized by high lead and low copper contents (KARAMATA, 1974).

The study of individual parts of the Neogene igneous rock belt, respectively of some massifs and complexes, has shown that the copper content may vary, and that some rocks have even relatively high Ni, Co and Cr concentrations for granitic rocks. These anomalies cannot be explained without a regional analysis of the geological position of particular complexes. For this purpose the igneous rocks from different areas are compared regarding their position to the main geological units and especially to the main ophiolite belt (Fig. 1):

(1) Areas westwards of the main subduction zone, or at the margin of the suture zone, *i. e.* areas where the ascending Neogene magmas did not meet the rocks of the ophiolite association preserved along the suture zone. Examples for this case are the areas of Golija, Rogozna and Srebrnica-Boranja.

(2) Areas in the central part of the main ophiolite belt-suture zone (Vardar zone) or at its eastern margins, *i. e.* areas where the ascending Neogene magmas passed in the middle to shallow levels through the rocks of the ophiolite zone, compressed and thickened in the upper parts of the suture zone. For this case examples are the Rudnik Mts. and the Kopaonik-Ibar area, as well as the Lece (Radan), Zletovo-Kratovo and Bučim regions.

(3) Areas eastwards of the main subduction zone, *i. e.* areas where the new-born magmas passed the suture zone between two continental blocks only in deep levels, where the ophiolitic rocks mainly were either pulled down into the upper mantle or squeezed out because of intense compression. The example for this position is the area of Surdulica-Kriva Palanka.

The area of Golija is situated in the Drina-Ivanjica unit westwards of the main suture zone. Here small masses of shallow intrusive granodiorites and quartzmonzonites and subvolcanic quartz-latites and dacites occur. The concentration of the studied trace elements is quoted in Table 1. The concentrations are lower (Cu, Co) or similar (Ni, Cr) to the average contents in analogous rocks.

The area of Rogozna is situated westwards of the ophiolite belt or of the suture zone, *i. e.* in the area where the ophiolitic rocks do not occur. The Neogene igneous rocks are represented by dacito-andesites and quartz-latites consolidated at the subvolcanic to volcanic level. The copper, nickel, colbalt and chromium contents of these rocks are shown at Table 1. They are low compared with the average content of the analogous rocks (Cu, Co) or of similar range (Ni, Cr). The K-basaltic rocks were not considered because of their negligable volume.

The area of Srebrnica-Boranja is situated near or at the Zvornik suture, i. e. at the southwestern side of a northeast dipping zone of melange. In this area volcanic (dacito-andesites and quartz-latites) as well as intrusive (granodiorites and quartz-



Fig. 1. Sketch of the central part of the Balkan peninsula. 1=belts of ophiolite melange, 2=gabbro-diabase complex with copper ore occurrences, 3=Neogene granodiorites and quartz-monzonites, 4=Neogene volcanics (dacito-andesites, latites, quartz-latites and minor K-basalts).

monzonites) rocks occur. The copper, nickel, cobalt and chromium contents of rocks from this area is shown at Table 1. The mean copper concentration in granodioritic rocks is small (5 ppm mean from 5 samples), but much higher in volcanics (17 ppm). Similar enrichments are noticable for nickel and chromium.

The areas of the Rudnik Mts. and of Kopaonik-Ibar are examples for the geological position in the central part of the Vardar zone or of the main ophiolite belt (wide up to 50 km), which represents the upper parts of the suture above the ancient northeastwards diping subduction zone. Here the upper parts of the oceanic plate, the accretion wedge and the oceanic sediments were compressed and have considerable thickness. In these areas the Neogene magmas passed about a tenth of kilometers through a melange with abundant mafic and ultramafic rocks as lenses of blocks of different size. In the Rudnik area mainly andesito-dacites and quartz-latites, associated with minor K-basalts are to be observed. Intrusive rocks, except a few dykes are not exposed. In the Kopaonik-Ibar area large masses of granodiorites to quartz-monzonites and of andesites, latites and quartz-latites occur.

The Cu, Ni, Co and Cr contents in the volcanic rocks of the Rudnik Mts. are showing a wide dispersion of values and for Cu, Ni and Cr they can be grouped into two populations, if the extreme values are neglected. It is noteworthy that among the studied elements no correlation could be found. The contents for the mentioned populations are presented at Table 1. The mean concentration of the first population lies in the range of contents of these elements in analogous rocks, but the second population shows a certain enrichment in Cu, Ni and Cr. Chromium shows even some very high values (1000–1150 ppm).

The volcanic rocks of the Kopaonik-Ibar area are represented by andesites, latites and quartz-latites. Each group has its particular population, but the mean contents for the rock groups are similar and an average concentration for all the volcanics together was calculated. The andesites have the highest contents of all analyzed trace elements, the quartz-latites mostly the lowest. The mean contents are high compared to the mean contents for similar rocks of the Dinarides or in general. All these data are presented at Table 1.

At the eastern margin of the Vardar zone, that is in the melange belt the neogene rocks of Lece (Radan), Zletovo-Kratovo and of Bučim are situated. Here the rising magmas passed through the thickest downpulled zones of the ophiolite-bearing melange. In volcanic rocks of the Lece (Radan) and Zletovo complexes the copper and cobalt contents are only slightly increased compared with the normal values for Dinaride Neogene rocks. The nickel and chromium contents are similar to the average world wide contents (Table 1), but Cu-mineralizations occur in Lece and Zletovo (Zlatica) areas, as well as at Bučim.

The Neogene igneous rocks of the Surdulica-Kriva Palanka area are characterized by low to very low contents of Cu, Ni, Co and Cr (Table 1). These igneous rocks crystallized from magmas which had not passed through any wider zone with ophiolitic rocks. The magmas rose through the zone of maximal compression between the Pelagonian/Drina-Ivanjica blocks and the Serbo-Mazedonian massif, where the rocks of the ophiolite association were thinned, downpulled or squeezed out, or even reworked by the Lower Cretaceous granitic magmas.

Magmatic complex	Cu ppm	Ni ppm	Co ppm	Cr ppm Re	ference
Neogene magmatic rocks of the Dinarides	$\bar{x}_{99} = 8 \ (1-50)$				1
Volcanics and shallow intru- sions (granitic to grano- dioritic) of Golija	$\bar{x}_{61} = 6,7$	$\bar{x}_{59} = 10$	$\bar{x}_{61} = 2,7$	$\bar{x}_{61} = 21$	2
Volcanics of the Srebrnica area	$\bar{x}_{20} = 17$	$\bar{x}_{20} = 29$	$\bar{x}_{21} = 4,3$	$\bar{x}_{20} = 31$	2
Intrusive rocks (granitic to granodioritic) of the Borania area	ž.=5				1
Volcanics (rhyodacites to dacites) of the Rogozna area	$\bar{x}_{23} = 5$	$\bar{\mathbf{x}}_{22} = 11$	$\bar{x}_{21} = 3,4$	$\bar{x}_{18} = 25$	2
Volcanics of the Rudnik area (rhyodacites to K-basalts)					
1st population	$\bar{x}_{143} = 8,5 \ (1-25)$	$\bar{x}_{141} = 17 \ (1-35)$	$\bar{x}_{169} = 5,5 \ (1-26)$	$\bar{x}_{136} = 44 \ (7 - 150)$	2,3
2nd population	$\bar{\mathbf{x}}_7 \!=\! 52 \; (32 \!-\! 70)$	$\bar{x}_{10} = 102 (40-180)$ some scattered anomalous con- tents (over 200 ppm) were not considered	some scattered values (over 30 ppm) were not considered	$\bar{x}_6 = 340 (260-400)$ three values are 1000 ppm and mor	• <b>3</b> e
	Remark-the concentrations of Cu, Ni, Co and Cr are not correlable				
Volcanics					
of the Kopaonik-Ibar area	$\bar{x}_{78} = 17$	$\bar{\mathbf{x}}_{78} = 15$	$\bar{x}_{78} = 15$	$\bar{x}_{78} = 29$	4
Andesites only	$\bar{x}_{29} = 26$	$\bar{\mathbf{x}}_{29} = 20$	$\bar{x}_{29} = 20$	$\bar{x}_{29} = 44$	4

# Table 1. Cu, Ni, Co and Cr concentrations in some Neogene magmatic complexes of Dinarides

Magmatic complex	Cuppm	Ni ppm	Coppm	Crppm	Reference
Latites only	$\bar{x}_{12} = 17$	$\bar{x}_{12} = 9$	$\bar{x}_{12} = 15$	$\bar{\mathbf{x}}_{12} = 20$	4
Quartz-latites only	$\bar{x}_{37} = 10$	$\bar{x}_{37} = 12,5$	$\bar{x}_{37} = 10$	$\bar{x}_{37} = 20$	4
Andesites of Radan (Lece)	$\bar{x}_{50} = 10$	$\bar{x}_{53} = 9$	$\bar{x}_{53} = 6, 6$	$\bar{x}_{52} = 20$	<b>2</b>
Volcanics (andesites to rhyodacites) of the Zletovo-Kratovo area	$\bar{x}_{309} = 17$	$\bar{x}_{310} = 7$	$\bar{x}_{310} = 5,5$	$\bar{x}_{310} = 21$	2
Volcanics of the Surdulica- Kriva Palanka area	$\bar{x}_{56} = 9$	$\bar{x}_{63} = 6$	$\bar{x}_{61} = 3,5$	$\bar{x}_{62} = 12$	2
Granodiorites of Surdulica	$\bar{x}_3 = 2,5$	$\bar{\mathbf{x}}_2 = 4$	$\bar{x}_2 = 2,5$	$\bar{\mathbf{x}}_2 = 6$	5
Mean contents for granites and similar rocks after VINOGRADOV (1962)	20	8	5	25	
Mean contents for Ca-rich granitic rocks after TUREKIAN and WEDEPOHL					
(1961)	<b>3</b> 0	15 ·	7	22	

Table 1 (Continuation). Cu, Ni, Co and Cr concentrations in some Neogene magmatic complexes of Dinarides

In the index of the mean value is given the number of analysis used for mean value calculation, and in the brackets the range of values.

References: 1=KARAMATA, 1974; 2=ANTONOVIĆ and FILIPOVIĆ, 1977; 3=MAKSIMOVIĆ and TERZIĆ, 1965; 4=MAKSIMOVIĆ and MIĆIĆ, 1978; 5=MAKSIMOVIĆ et al., 1964.



Fig. 2. Cu, Ni, Co and Cr concentrations in igneous rocks of selected areas or complexes of Neogene age (upper part), and their geotectonic position at Neogene (lower part). Explanation of abbreviations and signs: EXD = continental crust of outer Dinarides, DIB = continental crust of the Drina-Ivanjica block, SMM = continental crust of the Serbo-Mazedonian massif, 1=ophiolitic melange, 2=zone of origin of Tertiary magmas, 3=rise direction of Tertiary magmas; 4=area of consolidation of Tertiary (mainly Neogene) magmas: intrusive and volcanic rocks, 5=ore occurrence, 6=ore deposit, 7=mean concentration of trace element, 8=mean concentration for particular population, 9=mean concentrations of Cu, Ni, Ca and Cr in Ca-rich granitic rocks after TUREKIAN and WEDEPOHL, 1961, and in granitic rocks ("acid rocks") after VINOGRADOV, 1962. B and S = data for the Boranja granodiorites and Srebrnica volcanics respectively, I and V = data for the granodiorites of Surdulica and volcanics of the Surdulica-Kriva Palanka area respectively.

#### Conclusion

The before mentioned data on the concentrations of Cu, Ni, Co and Cr in Neogene igneous rocks shall be considered together with the following for further conclusions:

- small copper ore occurrences (Kremići) and nickel-cobalt sulfides veinlets and impregnations occur in the area of Kopaonik;

- copper ore occurrences (Lece, Zlatica) and the copper ore deposit Bučim are situated along the eastern margin of the ophiolite belt or in the suture zone (Vardar zone), where because of the northeast directed subduction the ophiolite-bearing melange was thickened and pulled down and the magmas having passed through the melange, along the greatest distance.

All these informations are summarized at Fig. 2. Synthesizing all this the following may be concluded:

(1) The Neogene granitic to granodioritic magmas of continental crustal origin were contaminated by metals related to mafic and ultramafic rocks (Cu, Ni, Co, Cr) when they crossed the ophiolite-bearing complexes (mainly the melange) during their rise towards the surface.

(2) The degree of contamination of these magmas depends on the duration of passing through the ophiolitic melange, *i. e.* mainly on the thickness of the melange and the depth where they meet it on their way. This is evident for the Neogene magmatites of the Rudnik Mts. and Kopaonik-Ibar, and even more of the zone Lece-Zlatica-Bučim, where they had to pass the thickest melange pile, here the enrichment in copper became so high that copper ore occurrences originated. The origin of the ore deposit Bučim may be related to mobilization of copper from the copper ore occurrences in the gabbro-diabase massif of Dren which underlies this area. Copper ore occurrences are known in the exposed parts of the Dren massif and similar exist probably in the covered parts too.

(3) This synthesis seems to be very plausible by correlation of the afore described Neogene magmatites with different enrichment in the studied trace elements and the position of copper ore occurrences (see the schematic geological cross demonstrated Fig. 2).

(4) Special interest deserves the different behavior of copper, nickel, cobalt and chromium. The first three elements were primary present in sulfides or in silicates of mafic and ultramafic rocks, and were leached by Neogene magmas and transported as dissolved compounds. Chromium was primary only partly contained in silicates, but mainly in chromite. The transport of chromium by rising melts was therefore minor as a dissolved compound, but mostly minute grains of chromite were carried up by the melt. In this way it is possible to explain the very different chromium concentrations in the volcanics of the Rudnik Mts.

In most of the mentioned cases the mobilization of Cu, Ni, Co and Cr was minor, but anyway important as indication that some elements can be mobilized from older rocks by heating and penetration by younger magmas. This process of mobilization begins with slight increase of concentrations of some elements, and is followed by their enrichment, and may finally lead to formation of ore occurrences or even deposits.

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#### References

- ANTONOVIĆ, A., FILIPOVIĆ, V. (1977): Some aspects of geology, petrology, geochemistry and ore mineralization of kainotype volcanites of Yugoslavia. – Radovi, Inst. for Geol. and Min. Exploration and Investigation of Nuclear and oth. Mineral Raw Materials, Vol. 11., 1–25, Belgrade.
- JANKOVIĆ, S. (1977): Major Alpine Metallogenic units in the Northeastern Mediterranean and concepts of plate Tectonics. Plate Tectonics in Northeastern Mediterranean. – Fac. of Min. and Geol., University of Belgrade-UNESCO: Correlation project No. 3, JANKOVIĆ, S. (ed.), 21–105, Belgrade.
- KARAMATA, S. (1974): Geochemical, Petrologie and Metallogenetic provinces on the Balkan Peninsula and in Asia Minor. – Serbian Academy of Sci. and Arts, Vol. CDLXXV, monographs. Section for nat. and math. sci., 1–55, Belgrade.
- KARAMATA, S. (1975): Geologic Evolution of Yugoslavian area from Triassic to Quaternary. Radovi, Inst. for Geol. and Min. Exploration and Investigation of Nuclear and oth. Mineral Raw Materials, Vol. 10, 1–15, Belgrade.
- KARAMATA, S., DJORDJEVIĆ, P. (1980): Origin of the Upper Cretaceous and Tertiary magmas in the Eastern parts of Yugoslavia. – Bull. de l'Acad. Serbe des Sci. et des Arts, Classe des Sci. Nat. et Math., No. 20, 99–108, Belgrade.
- MAKSIMOVIĆ, Z., BRABEC, D., NIKOLIĆ, V. (1964): Geochemical prospecting for molybdenum in Mačkatica area (East Serbia). – Glas de l'Acad. Serbe des Sci. et des Arts, Classe des Sci. Nat. et Math., No. 25, 1–28, Belgrade.
- MAKSIMOVIĆ, Z., TERZIĆ, M. (1965): Geochemistry of volcanic rocks from Rudnik Mountain area. – I. Geochemical Simposium, Serbian Geological Society, 221–242, Belgrade.
- MAKSIMOVIĆ, Z., DANGIĆ, A., MIĆIĆ, I. (1978): Geochemical study of the volcanics rocks of the Kopaonik Mountain Area (Yugoslavia). – Zbornik radova, IX. Kongres geologa Jugoslavije, 282–291, Sarajevo.
- TUREKIAN, K. K., WEDEPOHL, K. H. (1961): Distribution of the elements in some major units of the Earth's crust. Bull. geol. soc. America, No. 72, 175-191.
- VINOGRADOV, A.R. (1962): Srednie soderžania himičeskih elementov v glavnyh tipah izverženyh gornih porod Zemnoj kory. – Geohimia, No. 7, 555–571.