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## PETROGENESIS OF THE MAGLAJ VOLCANICS, CENTRAL BOSNIA

Salkić Zehra<sup>1</sup>, Babajić Elvir<sup>1</sup>, Babajić Alisa<sup>1</sup>, Pobrić Vedran<sup>2</sup>, Bešić Aldin<sup>1</sup>

<sup>1</sup>*Faculty of Mining, Geology and Civil Engineering, Tuzla, [salkicz@yahoo.com](mailto:salkicz@yahoo.com)*

<sup>2</sup>*A graduate of Geological Sciences at University of Florida*

### ABSTRACT

In Bosnia and Herzegovina, Tertiary volcanic rocks occur within two geotectonically different areas: (1) in northeastern Bosnia, the wider area of Srebrenica and, (2) to a lesser extent in central Bosnia, the wider areas of Maglaj, Teslić and Nemila (Kolići). The major and trace element variations in the rocks surrounding Maglaj indicate their high-K calc-alkaline character, and are consistent with fractionation of the observed phenocryst assemblages (plagioclase, sanidine, biotite and hornblende). The scatter in some graphs cannot be explained by simple crystal fractionation from a common parent magma. More likely, such variations are affected by variable contribution and assimilation of continental crust within the magmas generated in the mantle. The presence of reverse zoned plagioclase phenocrysts, as well as a resorbed rim enclosing the coexisting quartz phenocrysts, can be interpreted by mixing of magmas with different temperatures and compositions.

All analyzed rocks show enrichment of the LILEs over the HFSEs and have significant negative Ta-Nb, P and Ti anomalies, and positive U and Pb anomalies, which are characteristic of subduction-related volcanic rocks generated in (post) collisional zones. Chondrite-normalized REE patterns exhibit enrichment on the LREEs over the HREEs with  $(La/Yb)_{cn}$  ranging from 21.4 to 21.9. All analyzed rocks have small negative Eu anomalies ( $Eu/Eu^* = 0.86-0.89$ ) which suggests that plagioclase fractionation played a minor role in the genesis of the dacites. Ratios of some diagnostic elements versus  $SiO_2$  diagrams are best explained as a result of assimilation of varying degree in the continental crust during magma ascent and continuing fractional crystallization. High values of LILE/HFSE ratios in K/Ti (6.6 to 11.9), K/Zr (124-169), K/Nb (1598-2692) and Ba/Nb (44-65) and negative anomalies of Ti and Nb in the volcanic rocks surrounding Maglaj can be explained as the result of complex processes in the magmatic system originally derived from a mantle wedge.

Keywords: *petrography, geochemistry, geotectonic, Oligocene Volcanic Rocks, Maglaj*

### INTRODUCTION

Volcanic rocks of andesite-dacite origin are common in central Bosnia in the vicinity of Maglaj, Teslić and Nemila, and in northeastern Bosnia in the Srebrenica area. These rocks belong to a volcanic formation of shoshonitic and high-K calc-alkaline rocks Oligocene in age. They occur within Tertiary magmatic formation of Dinarides which were successively arising between 55 and 29 Ma genetically related to the collision of Apulia (Africa) and Tisia (Euroasia) [1]. The rocks of this formation are most common in the Sava-Vardar suture zone [2] and, to a lesser extent, in the neighboring tectonostratigraphic units. Tertiary volcanic rocks from the central and northeastern Bosnia represent,

volumetrically, the most important members of the postorogenic volcanic formations of the SVZ, of the Dinarides and Hellenides [3]. Central Bosnia volcanics have been interpreted to be the oldest Tertiary post-orogenic volcanic rocks of the North Dinarides. Pamić et al. (2000) [4] have dated five samples of volcanic rocks in the area of Maglaj and Srebrenica. They showed that analyzed rocks, with their K-Ar age of 30.4-28.5 Ma, represent the oldest dated postorogenic Tertiary volcanic formations of the North Dinarides.

In this paper mineralogical-petrological and geochemical data on representative volcanic rocks in the area of Maglaj are reported. Geochemical parameters and element ratios were used in order to determine the petrogenesis of the analyzed rocks.

## BASIC GEOLOGICAL DATA

Oligocene volcanics of the central Bosnia are situated in the Dinaride Ophiolite Zone (DOZ), southward of the Sava-Vardar Zone (SVZ), within ophiolites, peridotites and genetically related sedimentary formations (ophiolite mélangé) where they occur both as sills and dikes. Dacites and andesites are mainly situated along deep faults which were a predisposition or channels for the emplacement of Tertiary magmas.

The main habitat of the Tertiary volcanic rocks of central Bosnia is in the valley of river Bosnia near Maglaj [5, 6]. A few smaller volcanic bodies occur in the area of several km<sup>2</sup>. The main volcanic body is located near the town of Maglaj (sample M-5), in the contact between ophiolite mélangé and the rocks of the Pogari Formation, Figure 1.

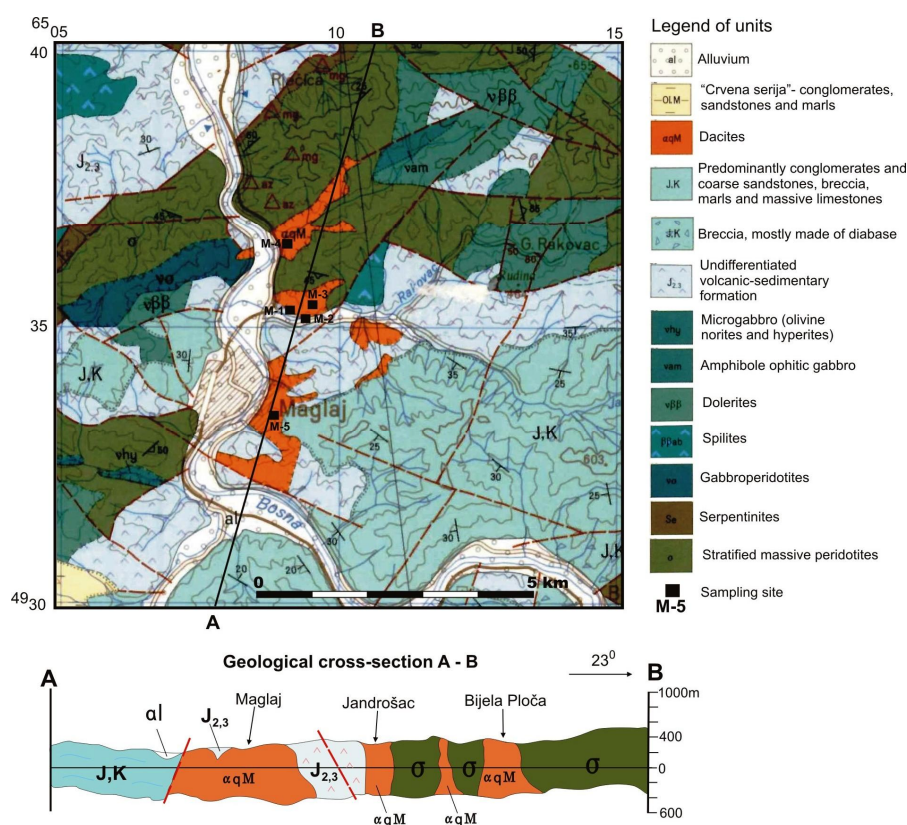


Figure 1. Geological map and cross-section of the Maglaj vicinity (made by OGK JU, 1:100 000, sheet Zavidovići).

In the area of Bijela Ploča and Jandrošac, to the north of Maglaj, there are two smaller occurrences of volcanics. The dacites of Bijela Ploča (sample M-4) occur within peridotites, and volcanic rocks of the Jandrošac quarry (samples M-1, M-2 and M-3) make appearance in the contact between peridotites and the rocks of ophiolite mélangé.

## ANALYTICAL TECHNIQUES

Samples collected from the area of Maglaj were analysed by an Olympus C-35AD-4 polarizing microscope and by X-ray powder diffraction analysis (XRD) with Rigaku X-ray diffractometer. Representative samples were analyzed for major elements by X-ray fluorescence (XRF) analysis using an RIX 3000 (Rigaku) X-ray fluorescence spectrometer calibrated against both international and internal rock standards of the appropriate composition. Optical determinations, XRF and XRD analyses were done at the Institute Maden Tetkik ve Arama (MTA) in Ankara, Turkey.

Five of these samples were chosen for the standard trace elements and complete rare earth elements (REE) analysis and were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the Institute Actlabs in Ontario, Canada. The chemical compositions of some rock-forming minerals of the volcanic rocks were performed with Energy Dispersive X-ray Spectroscopy (EDXS), by a JEOL JSM 5800 scanning electron microscope, at the Institute Jožef Stefan in Ljubljana, Slovenia.

## PETROGRAPHY AND MINERAL CHEMISTRY

Macroscopically the rocks are light gray to gray, with a massive texture and porphyritic structure. Samples of the analyzed rocks are relatively fresh, with the exception of the sample of Bijela Ploča which altered to an aggregate of kaolinite, amorphous silica, dolomite and chlorite. According to the prevailing content of ferro-magnesium minerals, the following varieties of rocks can be distinguished: biotite dacites, hornblende-biotite dacites and biotite andesites. The rocks generally have a holocrystalline porphyritic texture with phenocrysts of plagioclase (Figure 2.a), sanidine, quartz, biotite (Figure 2.b) and subordinate amphibole.

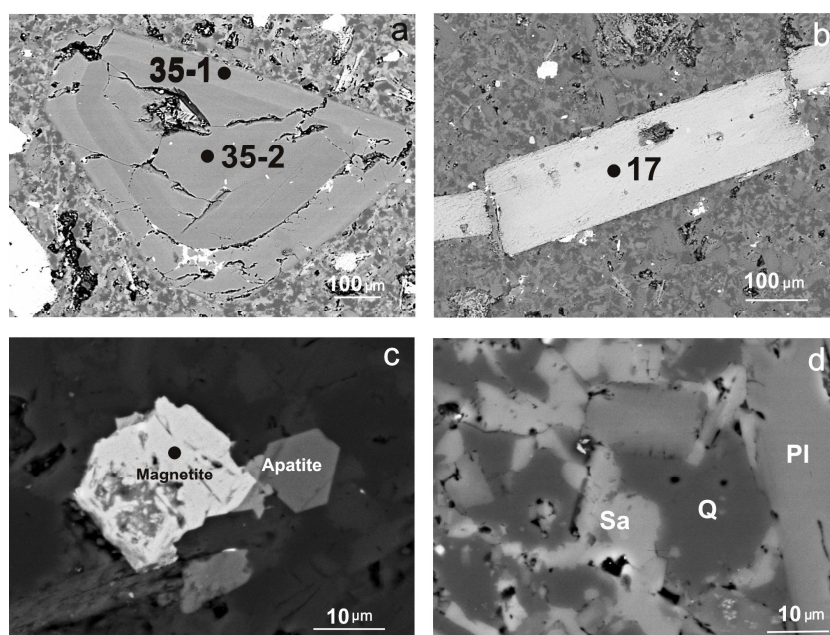


Figure 2. Back-scattered electron images

- a) zonal plagioclase phenocryst surrounded by a matrix consisting of quartz, sanidine and plagioclase. The outer zone is characterized by increased content of anorthite components ( $An_{48}$ ) with respect to the inner zone ( $An_{44}$ ),  
 b) fresh idiomorphic phenocryst of biotite; c) magnetite and apatite embedded in biotites,  
 d) quartz, sanidine and plagioclase in the matrix of Maglaj dacite (sample M-5)

The most abundant ferromagnesian mineral is biotite. It appears as idiomorphic to hypidiomorphic phenocryst and is also found in matrix. Biotite phenocrysts are relatively fresh and show intense brown pleochroism. They contain embedded apatite, rutile and magnetite, Figure 2c, Table 1. In some

samples biotite is moderately chloritized, limonitized and opacitized. Unaltered biotites have Al content of about 1.26 and  $Mg/(Mg+Fe_{tot})$  values of about 43.8, Table 1. Hornblende is almost completely altered in chlorite as well as embedded biotite in clay minerals in all the analyzed samples, but it kept clearly perceptible forms. Pseudomorphisms are idiomorphic to hypidiomorphic and have opacities edge. Hornblende is represented significantly less than biotite.

Plagioclase phenocrysts are the largest and most dominant. They show idiomorphic and hypidiomorphic crystal forms, twinning and minor inverse zonation ( $An_{44}$  with narrow rims reaching  $An_{48}$ , Figure 2a, with the composition, Table 1, corresponding to andesine and labradorite. Sanidine very rarely occurs as a phenocryst. The main mass of sanidine is in the rock matrix. It appears as an allotriomorphic to hypidiomorphic phenocryst, and considerably fresher than plagioclase. Quartz occurs in the form of large phenocrysts (1.5-2.5 mm), which are smaller and less abundant than plagioclase phenocrysts. Characteristically, they are all rounded quartz grains due to magmatic resorption, and some show a thick edge corrosion. It often contains embedded apatite, rutile and/or zircon. A higher percentage of quartz is present in the rock matrix. The matrix is predominantly microcrystalline to cryptocrystalline consisting mainly of leucocratic minerals, Figure 2d, relatively fresh biotite, altered amphibole and accessory minerals. Some of dacites and andesites have hypohyaline matrix with variable amounts of brown volcanic glass.

Table 1. The chemical composition and structural-chemical formulas of plagioclase, biotite and magnetite of Maglaj dacite (sample M-5).

Mineral	Plagioclase		Biotite		Magnetite	
	35-1	35-2	17		40	
Number of grains	35-1	35-2	17		40	
SiO <sub>2</sub>	60.01	60.81	SiO <sub>2</sub>	35.85	TiO <sub>2</sub>	2.57
Al <sub>2</sub> O <sub>3</sub>	25.44	24.87	TiO <sub>2</sub>	4.14	Fe <sub>2</sub> O <sub>3</sub>	61.53
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.00	Al <sub>2</sub> O <sub>3</sub>	13.93	FeO	32.30
CaO	8.93	8.34	Fe <sub>2</sub> O <sub>3</sub>	3.63	Total	96.40
Na <sub>2</sub> O	5.07	5.42	FeO	18.51	Ti	0.077
K <sub>2</sub> O	0.55	0.56	MnO	0.39	Fe <sup>3+</sup>	1.846
Total	100.00	100.00	MgO	9.51	Fe <sup>2+</sup>	1.077
Si	2.670	2.701	BaO	0.00	Total	3.000
Al	1.334	1.302	Na <sub>2</sub> O	0.00		
Fe <sup>3+</sup>	0.000	0.000	K <sub>2</sub> O	10.13		
Ca	0.426	0.397	H <sub>2</sub> O	3.90		
Na	0.437	0.467	Total	99.99		
K	0.031	0.032	Si	2.756		
Total	4.898	4.898	Ti	0.239		
Or	3.5	3.5	Al	1.262		
Ab	48.9	52.1	Fe <sup>3+</sup>	0.210		
An	47.6	44.3	Fe <sup>2+</sup>	1.190		
Total	100.0	100.0	Mn	0.025		
			Mg	1.090		
			Ba	0.000		
			Na	0.000		
			K	0.993		
			Total	7.766		
			Mg <sub>value</sub>	43.8		
			Mg#	47.8		

$$Mg_{value} = 100 * Mg / (Mg + Fe^{2+} + Fe^{3+})$$

$$Mg\# = 1000 * Mg / (Mg + Fe^{2+})$$

## GEOCHEMISTRY

The SiO<sub>2</sub> concentration of the volcanics in the area of Maglaj is moving in a narrow range of 60.21 to 63.51 %. The rocks are enriched in alkalis (K<sub>2</sub>O+Na<sub>2</sub>O = 6.25–6.88 %) with ascendant potassium (K<sub>2</sub>O/Na<sub>2</sub>O = 0.87–1.20). Major element variations, using silica variation diagrams [7], show decreasing FeO\*, MgO, CaO and TiO<sub>2</sub> with increasing SiO<sub>2</sub>, while Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O and Na<sub>2</sub>O show slight positive correlation with SiO<sub>2</sub> with some scatter.

According to the total alkali-silica (TAS) diagram, analyzed rocks are dacites, and only a sample from quarry Jandrošac plots in the field of andesite. In the SiO<sub>2</sub> versus K<sub>2</sub>O diagram all the samples are dacites and belong to a high-K calc-alkaline series. According to this data the rocks are not members of shoshonite series [7]. The difference between the classification based on the content of major elements and classification according to content of immobile elements, Figure 3a is reflected in the allocation of trachyandesite as moderately alkaline rocks. Belonging to shoshonitic series of rocks in Ce/Yb-Ta/Yb diagram, Figure 3b can be explained by the increased content of Ta and Ce in the analyzed volcanics [8].

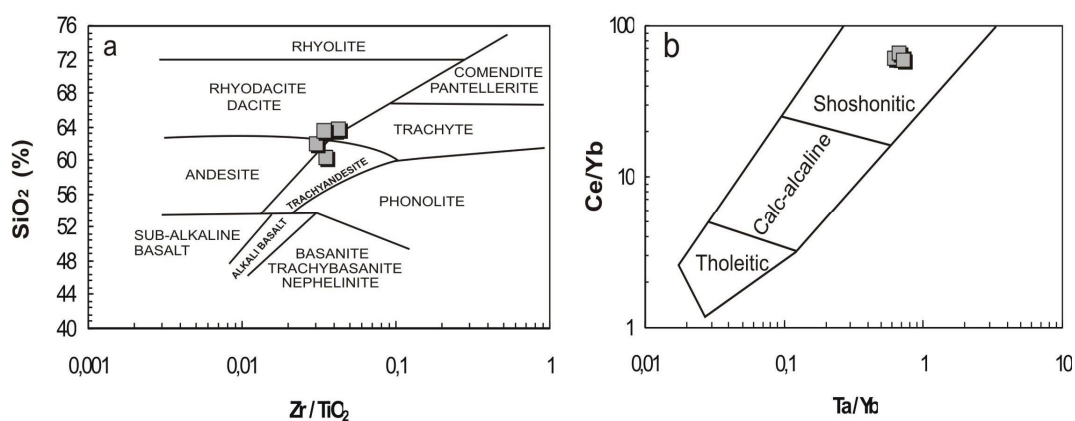


Figure 3. a) SiO<sub>2</sub>-Zr/TiO<sub>2</sub> diagram [10] and b) Ce/Yb-Ta/Yb diagram for classification of Tertiary volcanics from the Maglaj environment

Enrichment of the Maglaj volcanics with K, Cs, Rb, Ba, Sr, Pb, Th, U, Zr, Hf, Nb, Ta, La and Y (in comparison to the composition of the continental crust [9]) is characteristic of high-K magmas. In the trace elements variation diagrams Rb, Ba and Cu display positive correlation, while Sr, Th, U, Hf, Ta, V, La, Y and Yb have negative correlation with SiO<sub>2</sub> [7]. With respect to the narrow span of the SiO<sub>2</sub> content, such compositional variations are typical for an evolving magmatic suite.

The trace element concentrations of the Maglaj area volcanic rocks are shown in spider diagrams [7] show enrichment of the LILEs over the HFSEs, and display significant negative Ta-Nb, P and Ti anomalies, and also negative Ba anomaly. They also show positive U and Pb, and less markedly La and Sr anomalies. Such geochemical characteristics are distinctive for the magmatic rocks which arise in subduction-related or collisional zones. Chondrite-normalized REE patterns of the Maglaj volcanic rocks exhibit a significant enrichment of the LREEs over the HREEs with (La/Yb)<sub>n</sub> ranging from 21.4 to 21.9. These patterns are similar to those observed in the subductional-collisional regime. Oligocene volcanic rocks in the area of Maglaj have similar geochemical characteristics to volcanic rocks from Kolići and Teslić [10].

(Nb/Zr)<sub>n</sub> represents the quotient of normalized values of Nb and Zr [11,12,13]. On the (Nb/Zr)<sub>n</sub>-Zr diagram, Figure 4, it may be noted that in the rocks surrounding Maglaj this ratio is approximately constant. The rocks from the Maglaj area lie in the field B indicating geochemical similarity with the rocks originated in a collisional zone.

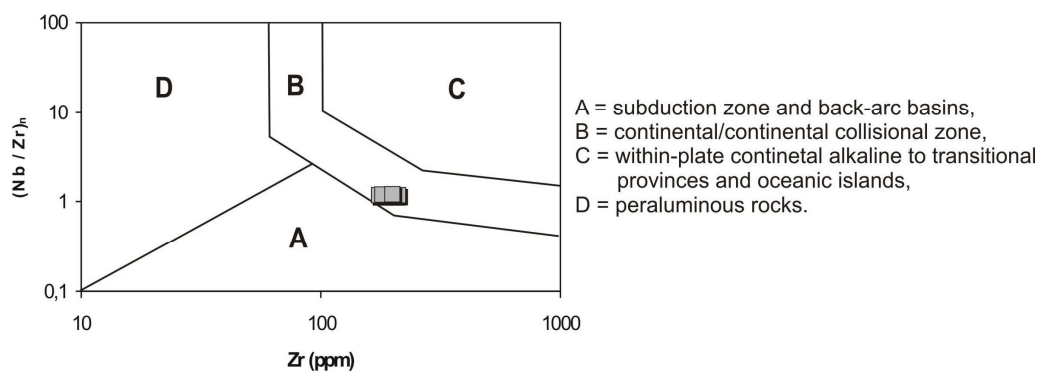
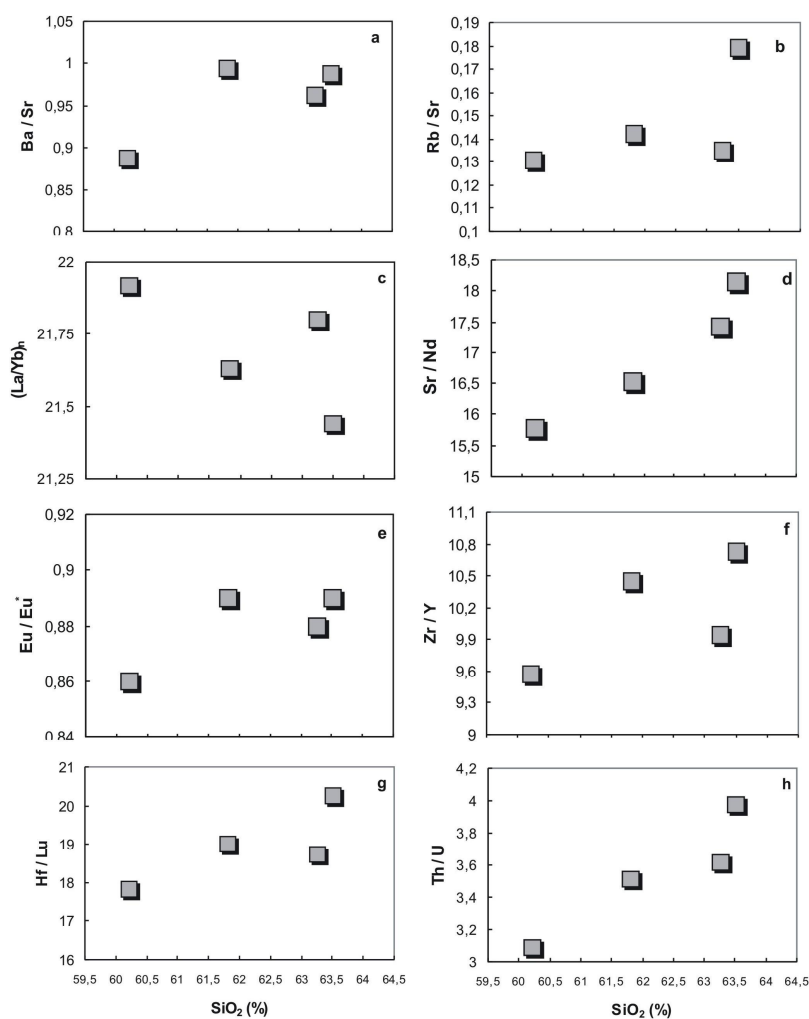


Figure 4. (Nb/Zr) vs. Zr diagram for discriminating calc-alkaline rocks of different geotectonic position

## PETROGENESIS OF THE MAGLAJ VOLCANICS

Geochemical variations of trace elements and trace element ratios versus  $\text{SiO}_2$  indicate that the rocks vicinity of Maglaj formed during the process of combining the assimilation-fractional crystallization, crustal contamination and magma mixing. To a varying extent, alteration processes influenced the chemistry of the rocks.



Slika 5. Variations of the ratio between some diagnostic elements versus  $\text{SiO}_2$  for Tertiary volcanic rocks surrounding Maglaj.

### Fractional crystallization

Variations of major elements in relation to the increase of SiO<sub>2</sub> suggest that crystal fractionation was an important process in controlling chemistry of Maglaj volcanics. Trace elements Hf, Y and Yb are incorporated in the lattice of zircon and titanium oxide minerals. Patterns of relative concentrations in the spider diagrams do not support the idea of crucial importance of zircon during fractionation. Negative anomalies of the relative concentrations of Ti and P in spider diagrams are consistent with crystallization of magnetite, ilmenite, rutile, monazite and apatite. Trace elements Rb and Cu show a positive correlation, and the elements U, Ta, La and Yb have a negative correlation with SiO<sub>2</sub> content.

HFS elements except Ti in Ti-magnetite, ilmenite and rutile cannot be incorporated easily in important rock forming minerals. As a result, they are positively correlated with each other, such as Nb with Zr. A positive linear correlation between K and Rb in Tertiary volcanic rocks surrounding Maglaj points to the fact that they are highly enriched in these elements in the residual melt [7]. The processes of crystal fractionation in volcanic rocks surrounding Maglaj are indicated by a positive correlation between Ba/Sr and Rb/Sr ratios with SiO<sub>2</sub>, Figure 5a and 5b. (La/Yb)<sub>n</sub> ratio decreases with increasing SiO<sub>2</sub> content that cannot be explained solely as a result of the process of fractional crystallization, Figure 5c.

### Crustal contamination and AFC processes

LILEs such as K, Rb and Ba can be not only useful indicators of the degree of fractionation, but may indicate whether the magma producing volcanic rocks were contaminated with crustal material [14, 15]. Varying ratios K<sub>2</sub>O/Na<sub>2</sub>O versus SiO<sub>2</sub> in terms of sanidine fractionation may be the result of assimilation of crustal rocks rich in potassium. The high content of Sr and variations in its content (549-763 ppm) suggests that crystal fractionation of plagioclase was not the dominant and exclusive process responsible for these variations. In addition, all the analyzed rocks have a small negative Eu-anomaly (Eu/Eu\* = 0.86-0.89), which again supports the idea that the fractionation of plagioclase has not played a crucial role in the genesis of dacite.

Further evidence that supports this hypothesis includes an increase in the value of the ratio of Sr/Nd and the absence of pronounced correlation between the ratio of Eu/Eu\* and SiO<sub>2</sub> content, Figure 5d and 5e. Part of the REE pattern from Sm to Yb with value ratio (Sm/Yb)<sub>n</sub> from 4.7 to 5.0 indicates the enrichment of a medium heavy REE which excludes amphibole fractionation in the early stages of magma differentiation [5]. Also, the value of the Zr/Y and Hf/Lu ratios (9.5 to 10.7, respectively, from 17.8 to 20.2), which increase with increasing SiO<sub>2</sub>, Figure 5f and 5g, tells against the fractionation of substantial amounts of amphibole and zircon.

The volcanic rocks of Maglaj have a relatively low content of U (3.72-4.92 ppm) and a relatively large value of the ratio of Th/U (3.6 to 4.5), which increases with increasing SiO<sub>2</sub> content, indicating a reduced assimilation of crustal materials in more differentiated rocks, Figure 63h. The values of the ratios Hf/Ta (3.6 to 4.2) and Zr/Rb (1.7-1.9) are generally low indicating crustal contamination, i.e. the crustal contribution to Rb and Ta-enriched rock material in the magma ascent.

### Magma mixing

A reaction edge on many, mainly alioyomorphic phenocrysts of quartz, indicates magma mixing in the formation of the Tertiary volcanic rocks surrounding Maglaj [16]. This means that the larger quartz grains were exposed to magmatic corrosion and resorption, or were not in chemical equilibrium with the liquid phase in a new environment. The amount of individual magma mixing cannot be determined without a precise analysis of the isotopic composition of the rocks. The existence of the inverse zonal plagioclase phenocrysts in the same samples containing resorbed phenocrysts of quartz is in favor of the conclusion supporting magma mixing under different thermal conditions and chemical composition.

### Characteristics of the source region

The spider diagrams show enrichment in LILEs, especially in U, Pb and to a lesser extent in La and Sr in relation to HFS elements. Such geochemical features are typical for igneous rocks of magmatic arc origin that generally occur in subduction zones, collision of continental plates and in zones of postcollisional extensions in a former, deeply eroded orogen. Increased content of Cs (10.1 to 14.5 ppm) is characteristic of crustal rocks in the area of volcanic arcs. REE patterns show a strong enrichment in light REEs relative to heavy REEs, with ratios (La/Yb)<sub>n</sub> between 21.4 and 21.9, which is typical of volcanic rocks formed in subduction geotectonic regimes. The concentration of immobile HFS elements in rocks may reflect chemistry of original substrate that is partially melted and is still controlled with processes of fractional crystallization. LILEs, unlike HFSEs, are concentrated in the continental crust and can also be an indicator of crustal contamination of the magmas with a source in the mantle. The value of the Zr/Nb ratio of 13.3 to 13.6 is characteristic of high-potassium island arc rocks [17] and rocks of continental margins [18].

### CONCLUSIONS

Volcanic rocks surrounding Maglaj belong to the Oligocene volcanic formation of the shoshonitic and high-K calc-alkaline rocks. Given that there are no large differences in the chemical and mineral composition among the volcanic rocks surrounding Maglaj and those from other areas in central Bosnia, one can assume the same source and a relatively short period of their effusion.

Tertiary volcanic rocks of Maglaj with high-fractionated LREEs, low-fractionated HREEs, and a small negative Eu-anomaly can be compared with a high-potassium calc-alkaline rocks from volcanic arcs around the edges of continents (Andean type subduction). It appears that from the petrographic and chemical characteristics it can be concluded that the magma mixing played an important role in the evolution of the volcanic rocks surrounding Maglaj. Characteristics of quartz phenocrysts may indicate that they are xenocrysts involved in magma from the surrounding crustal rock, or that they are fractionated from an acidic magma that mixed with less acidic magma in common, homogeneous magma in which earlier fractionated stages may become unstable. High values of LILE/HFSE ratios in K/Ti (6.6 to 11.9), K/Zr (124-169), K/Nb (1598-2692) and Ba/Nb (44-65) and negative anomalies of Ti and Nb in the volcanic rocks surrounding Maglaj can be considered as the result of complex processes in the magmatic system that was originally derived from the mantle wedge. Such characteristics may not be related to subduction, but at the same time characteristics can be inherited during geologically ancient subduction. These characteristics can be further emphasized by the assimilation of crustal rocks.

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