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# GEOLOGICA MACEDONICA



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| --- | --- | --- | --- | --- |
| Geologica Macedonica | Год. | Број | стр. | Штип |

# TABLE OF CONTENTS

| Geologica Macedonica | Vol. 38 | No. 1 | pp. 1–80 | Štip 2024 |
|---|---|---|---|---|
| Geologica Macedonica | Год. | Број | стр. | Штип |

# СОДРЖИНА

| Geologica Macedonica | Vol. | No. | pp. | Štip |
| --- | --- | --- | --- | --- |
| | **38** | 1 | 1–80 | 2024 |
| Geologica Macedonica | Год. | Број | стр. | Штип |

# GEOLOGICA MACEDONICA

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(Makreski et al., 2004): Makreski, P.; Jovanovski, G.; Stafilov, T.; Boev, B. (2004): Minerals from Macedonia, XII. The dependence of quartz and opal color on trace element composition – AAS, FT IR and micro Raman-spectrocsopy study. *Bull. Chem. Technol. Macedonia,* **23,** 2, 65–212 (2004).

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405
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*Original scientific paper*

# AGE OF THE VOLCANOCLASTIC SEDIMENTARY ROCKS OF THE VITAČEVO VOLCANIC PLATEAU (KOŽUF MOUNTAIN), NORTH MACEDONIA

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A b s t r a c t: The paper presents the results of the petrological, geochemical and isotopic investigations of the age of the volcanoclastic sedimentary rocks from the Vitačevo volcanic plateau. The volcanoclastic sedimentary rocks overlie the Upper Pliocene lacustrine sediments of the Tikveš basin and occur at an elevation of about 450 meters above sea level through the upper parts of the lacustrine sediments which are represented by clays and a small horizon of limestones. The volcanoclastic sediments are represented by lacustrine tuffs in which there are rounded pieces of stratified volcanic rocks, which by their character represent intermediate rocks from the group of latites and trachytes. The isotopic age of these rocks is 5.8 million years and corresponds to the Lower Pliocene.

**Key words**: volcanoclastic sedimentary rocks, latite-trahite

## INTRODUCTION

The Kožuf volcanic area encompasses numerous volcanic eruptive centers and pyroclastic sediments distributed across the Tikveš and Mariovo basins to the north, as well as in Meglensko and Thessaloniki to the south, extending into Greece (Boev, 1988; Vougioukalakis, 2002). Extensive geological surveys have been conducted on both sides of the national border, dating volcanic activity between 6.5 to 1.8 million years ago (Kolios et al., 1980; Boev, 1988; Janković et al., 1997). Distinct classifications of volcanic rocks have been established for the Macedonian and Greek regions (see Figure 1). On the Macedonian side, two primary groups have been identified: a high-Mg shoshonitic to trachydacite group and an andesite-dacite-rhyolite group (Boev & Yanev, 2001). Conversely, the Greek side is characterized by an east-central, western, and southwestern group (Eleftheriadis et al., 2003; Eleftheriadis and Vougioukalakis, 2006). Further insights into the volcanic rocks of Kožuf Mountain are available in studies by Yanev et al. (2008a, 2008b) and Karamata et al. (1992).

However, no correlation of sedimentary formations between the two sides has been established thus.

Despite extensive geological research, there remains a lack of geochemical and geochronologic-al data on volcanoclastic sediments in the Mariovo and Tikveš basins. Previous studies have outlined their distribution and basic petrological characteristics as part of geological mapping efforts (Dumurdžanov et al., 1981; Rakičević and Pendžerkovski, 1970; Rakičević et al., 1973; Hristov et al., 1973). While more detailed profiles are available on the eastern side (e.g., Boev, 1988; Janković et al., 1997), western side data primarily stem from research related to coal deposits (e.g., Institute for Mineral and Raw Materials Research, 1978). Geochronological data on volcanoclastic sediments are confined to tuffs from Vitačevo (Lippolt and Fuhrmann, 1986; Neubauer et al., 2009). Additionally, studies on the evolution of Neogene-Quarternary basins in Macedonia have explored the occurrence of volcanoclastic sediments and utilized them for dating sedimentary formations by comparing them with the age of the Kožuf volcanic area (Dumurdžanov et al., 2003, 2004, 2005).

This study aims to address existing gaps in the geochronology and geochemistry of volcanoclastic sediments in the Mariovo and Tikveš basins. We present new comprehensive geochemical whole-rock data complemented by K-Ar geochronology to enhance understanding of the origin and timing of these lava formations.

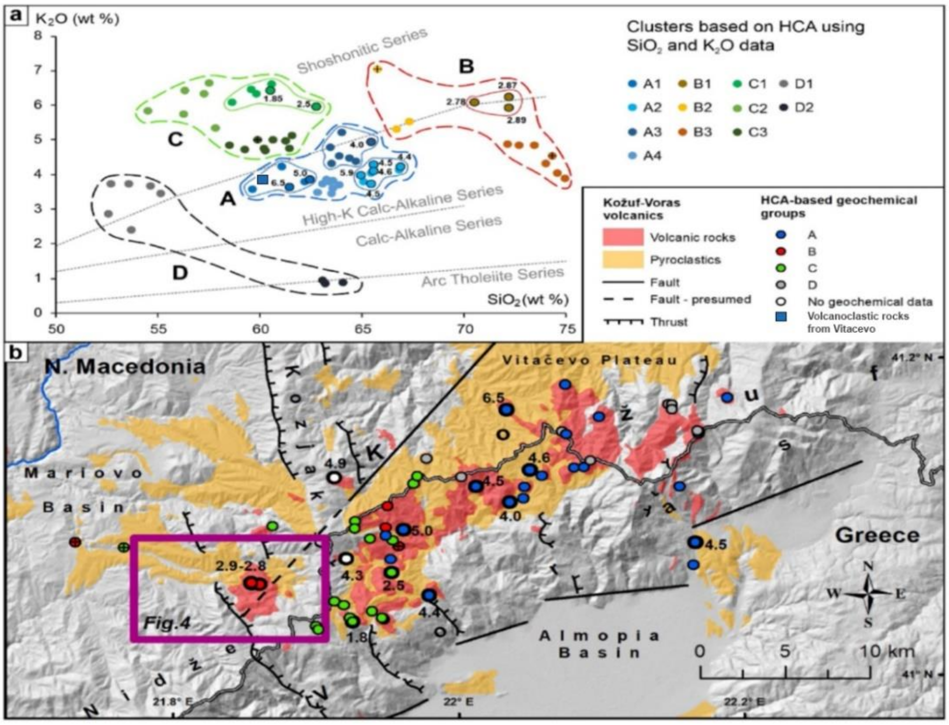


**Fig. 1**. Overview of the current data for the Kožuf volcanic area through cluster analysis of the geochemical composition (according to Molnar et al., 2021). a – Distribution by clusters according to $K_2O$-$SiO_2$ composition. b – Spatial distribution of the phenomena for which there is location data. In addition, the geochronological data for the dated localities are shown.

## MATERIALS AND METHODS

Samples of the volcanoclastic sedimentary rocks from Vitačevo were collected from the profile where the volcanoclastic rocks lie directly over the lake sediments of the Tikveš basin (Figure 2).

Five samples were collected and microscopic examinations (petrographic examinations), geochemical examinations, and isotopic examinations were performed on them.

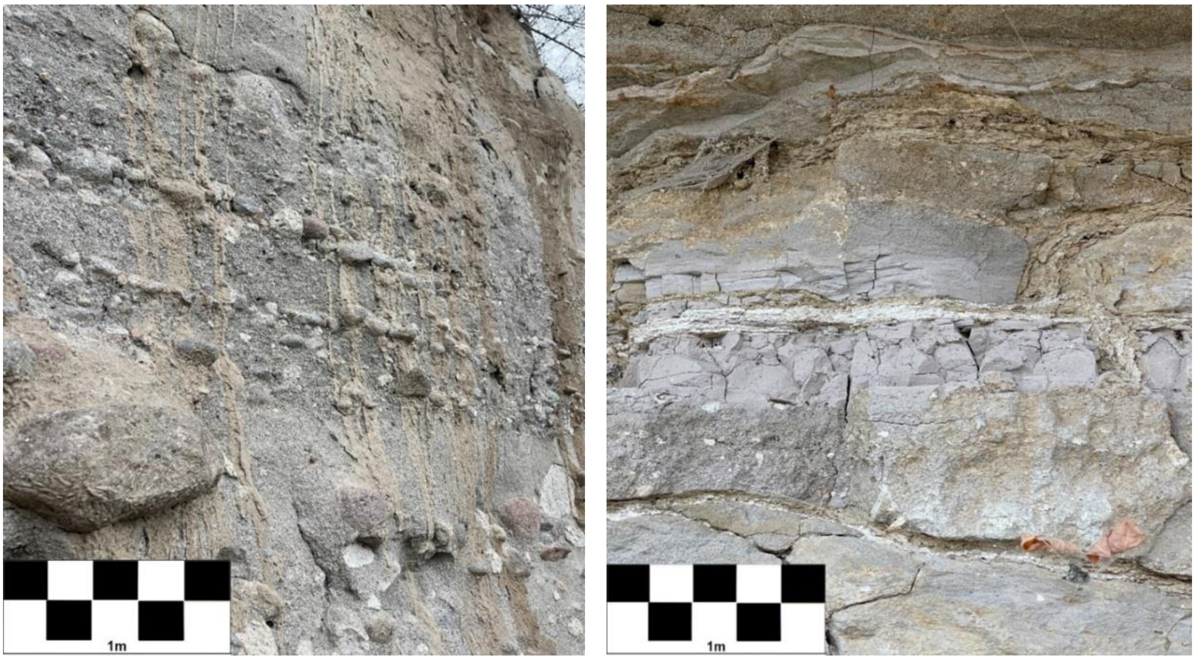


**Fig. 2.** Volcanoclastic sedimentary rocks of the Vitačevo volcanic plateau (photo I. Boev, 2024)

Figure 2 shows details of the volcanoclastic rocks of Vitačevo. It can be seen that they are built from pieces of volcanic fragments that have variable dimensions (from 2 cm to 20 cm, and in some cases there are larger blocks that have dimensions up to 1 m). These volcanic rocks lie in a bedrock that is represented by fine-grained volcanic material with grain sizes from 0.2 to 1 cm. Throughout the series of volcanoclastic rocks there is also the occurrence of volcanic glasses that occur in layers with a thickness of 2 cm to 50 cm. The material taken for examination is a volcanic piece with dimensions of about 10 cm.

Petrographic investigations provide the following informations:

(i) petrographic rock classification;

(ii) microstructural description;

(iii) a table with the modal percentage and average grain size for each mineral;

(iv) description of the minerals in decreasing order of abundance.

Samples were cut and prepared as ~20 × 40 mm polished thin sections.

Euhedral phenocrysts of plagioclase are randomly oriented and, together with subordinate phenocrysts of amphibole and biotite, are immersed within a very fine-grained groundmass dominated by K-feldspar (Table 1). The isotropic nature of the porphyritic texture indicates that this magmatic rock ended its crystallization in a stress-free magmatic chamber.

Table 1

*Modal mineralogical analysis under the polarized microscope*

| Mineral | Alteration and weahetring mineral | Modal % | Size range (mm) |
|---|---|---|---|
| Phenocrysts | | | |
| Plagioclase | | 25 | 0.1–5 |
| Hornblende | | 5 | 0.5–7 |
| Biotite | | 1 | 0.4–5 |
| K-feldspar(?) | | tr | |
| Groundmass | | | |
| K-feldspar | | 69 | 0.001 |
| Magnetite | Hematite | 1 | 0.1 |
| | Epidote | tr | Up to 0.3 |

tr = trace

## RESULTS AND DISCUSSION

Plagioclase forms euhedral phenocrysts ranging from 0.1 mm to 5 mm long. The crystal size distribution of the plagioclase imparts a seriate texture to this porphyritic rock. The plagioclase phenocrysts are fresh and display albite and albite-Carlsbad twinnings associated with euhedral oscillatory growth zoning. In rare cases, the plagioclase forms glomerophenocrysts. Some phenocrysts comprise an irregular zone of very fine-grained and earthy material and a rim of albite (Figures 3 and 6). We interpret these textures as the evidence of an episode of destabilization of plagioclase within the magma.

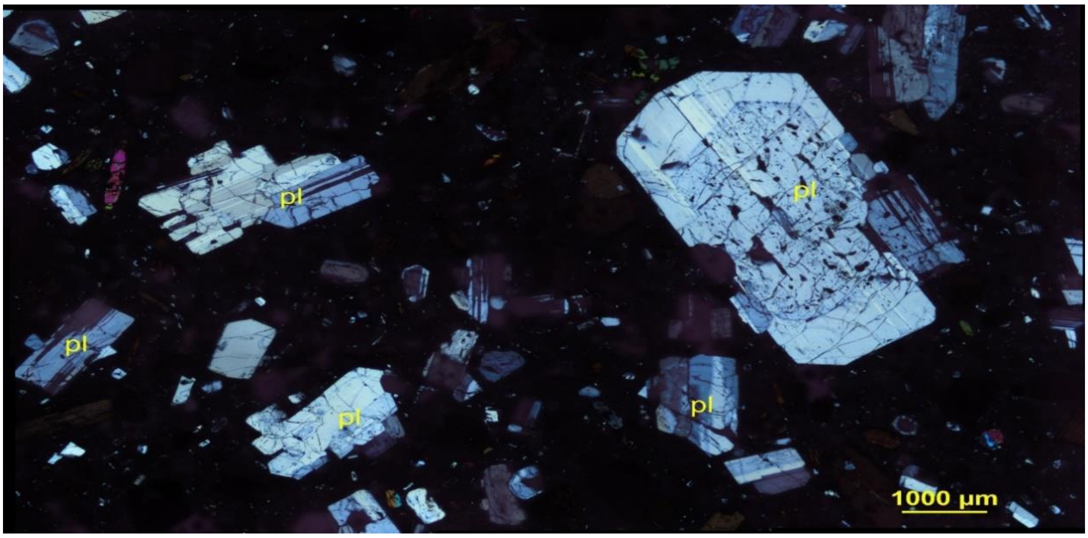


**Fig. 3**. Plagioclase phenocrysts (pl) are euhedral, seriate, and randomly oriented within the very fine-grained groundmass. Crossed polarizers transmitted light.

K-feldspar is very fine-grained and dominates the composition of the groundmass. Its homogeneous distribution can be observed in the stained offcut above. Rare euhedral phenocrysts of K-feldspar are observed in the offcut; however, no K-feldspar phenocryst is included in the polished thin section. Amphibole is the second most abundant phenocryst. Its euhedral crystals range from 0.5 mm to 7 mm long. Some of the fine- and medium-grained phenocrysts show a discontinuous and anhedral growth zoning with darker brown colours in the core of the crystals (Figure 4).

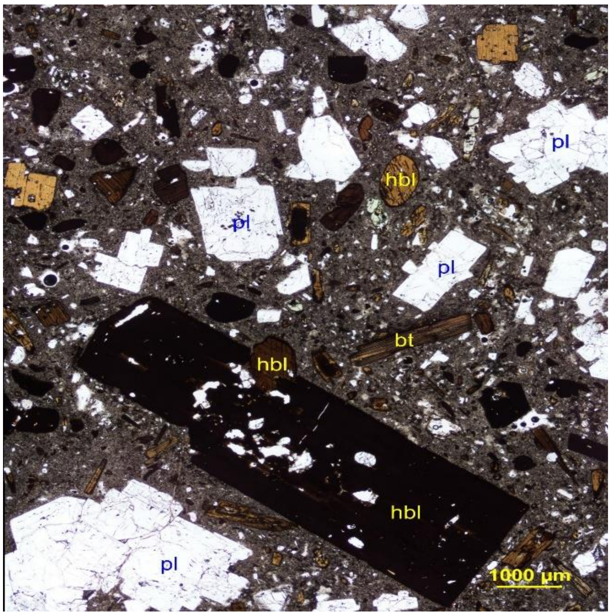


**Fig. 4**. Hornblende prevails among the ferromagnesian phenocrysts and occurs as mostly euhedral crystals (hbl). Biotite is subordinate (bt). Plane-polarized transmitted light.

**Biotite** forms euhedral phenocrysts ranging from 0.4 mm to 5 mm long (Figure 5). The biotite is relatively fresh and, like the other phenocrysts, shows a seriate grain size distribution.

Fine grained **magnetite** is disseminated within the groundmass. Some crystals are replaced by hematite; however, most of the crystals are fresh and impart a magmatic susceptibility of 2.05 (Figure 5).

Very rare crystals of epidote are dispersed within the groundmass and, in some cases, define irregular crystal clusters.

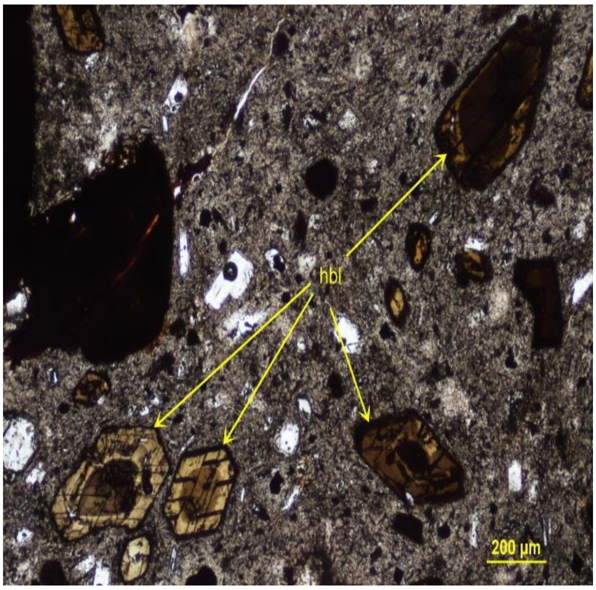


**Fig. 5**. Some hornblende crystals show growth zoning characterized by darker brown colours in the core of the crystals. Plane-polarized transmitted light.

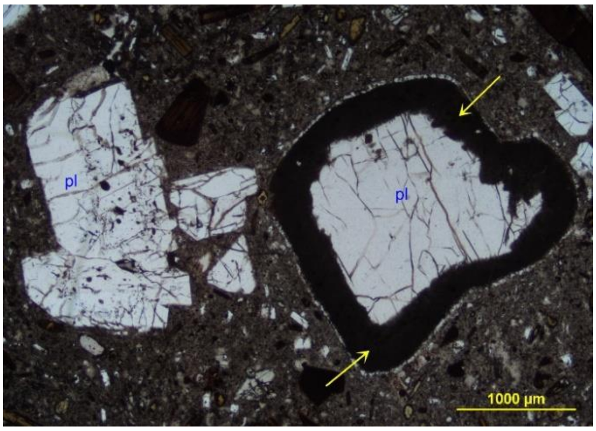


**Fig. 6.** Some plagioclase phenocrysts comprise a strongly altered and earthy zone (yellow arrow) surrounded by albitic rim. Plane-polarized transmitted light.

## GEOCHEMICAL INVESTIGATIONS

### *Lithogeochemistry and whole rock analyses and isotope investigations*

The most aggressive fusion technique employs a lithium metaborate/tetraborate fusion. Fusion is performed by a robot at Actlabs, Canada, which provides a fast fusion of the highest quality in the industry. The resulting molten bead is rapidly digested in a weak nitric acid solution. The fusion ensures that the entire sample is dissolved. It is only with this attack that major oxides including $SiO_2$, refractory minerals (i.e., zircon, sphene, monazite, chromite, gahnite, etc.), REE, and other high field strength elements are put into solution. High sulphide-bearing rocks may require different treatment but can still be adequately analyzed. Analysis is by ICP-OES and ICP-MS.

The quality of the data is exceptional and can be used for the most exacting applications.

*Methodology of Sr and Nd isotope analyses*

The rock powder was dissolved in Hf+$HNO_3$ at 150 ºC for 5 days, and chemical separation procedures for Sr follow the methodology of Creaser et al. (2004) and Holmden et al. (1997). Isotopic analysis for Sr used MC-ICPMS methods. All analyses are presented relative to a value of 0.710245 for the SRM9 $^{87}$Sr isotopic standard.

The powder was accurately weighed and dissolved in mixed 24N Hf + 16N $HNO_3$ media in sealed PFA teflon vessels at 160°C for 6 days. The fluoride residue is converted to chloride with HCl, and Nd separated by conventional cation and HDEHP-based chromatography. Chemical processing blanks are < 200 picograms of Nd, and are insignificant relative to the amount of Sm or Nd analyzed for any rock sample. Further details can be found in Creaser et al. (1997) and Unterschutz et al. (2002). The isotopic composition of Nd is determined in static mode by Multi-Collector ICP-Mass Spectrometry (Schmidberger et al., 2007). All isotope ratios are normalized for variable mass fractionation to a value of $^{146}$Nd / $^{144}$Nd = 0.7219 using the exponential fractionation law. The $^{143}$Nd / $^{144}$Nd ratio of samples is presented here relative to a value of 0.511850 for the LaJolla Nd isotopic standard, monitored by use of an in-house Alfa Nd isotopic standard for each analytical session. Using the same isotopic analysis and normalization procedures above, we analyzed the Geological Survey of Japan Nd isotope standard "Shin Etsu: J-Ndi-1" (Garcon et al., 2018) which has a $^{143}$Nd / $^{144}$Nd value of 0.512099 relative to a LaJolla $^{143}$Nd / $^{144}$Nd value of 0.511850, when normalized to $^{146}$Nd / $^{144}$Nd = 0.7219. The value of $^{143}$Nd / $^{144}$Nd determined for the JNdi-1 standard conducted during the analysis of the samples reported here was 0.512093 ± 11 (2 SE). The analyses were carried out in the laboratories of Actlab, Canada.

*K-Ar methodology*

An aliquot of the sample was weighed into an Al container, loaded into the sample system of extraction unit, and degassed at ~100°C over 2 d to remove the surface gases. Ar was extracted from the sample in a double vacuum furnace, at 1700°C. The determination of radiogenic Ar content was performed twice on an MI-1201 IG mass spectrometer by the isotope dilution method, with $^{38}$Ar as a spike, which is introduced to the sample system prior to each extraction.

The extracted gases were cleaned using a two-step purification system. Then, pure Ar was introduced into a custom-built magnetic sector mass spectrometer (Reynolds-type). It shall be noted that the test was done twice per sample, in order to ensure the consistency of the results. Two globally accepted standards (Bern-4M Muscovite and 1/65 "Asia" rhyolite matrix) were measured for $^{38}$Ar spike calibration. For age calculations, the international values for constants were used, as follows: $\lambda_K = 0.581 \times 10^{-10}$ y$^{-1}$, $\lambda_{\beta^-} = 4.962 \times 10^{-10}$ y$^{-1}$, $^{40}$K = 0.01167 (at. %).

*Results obtained and comment*

The results of the specific chemical composition of the main elements as well as trace elements and elements from the rare earth group are shown in Table 2. The chemical analysis shows that these are inter-medium volcanic rocks with a $SiO_2$ content around of 60 % and a large amount of alkali ($K_2O$ + $Na_2O$) of 8.2%, of which $K_2O$ itself ranges from 3.48 to 3.85%, so that these rocks have a pronounced alkaline character. These results of the chemical analysis show that these rocks can be classified as trachyandesites (Figure 7). Microscopic examinations indicate the presence of modal plagioclase of 25 %, hornblende of 5 % and biotite of 1 % and K-feldspar in groundmass in 69 %.

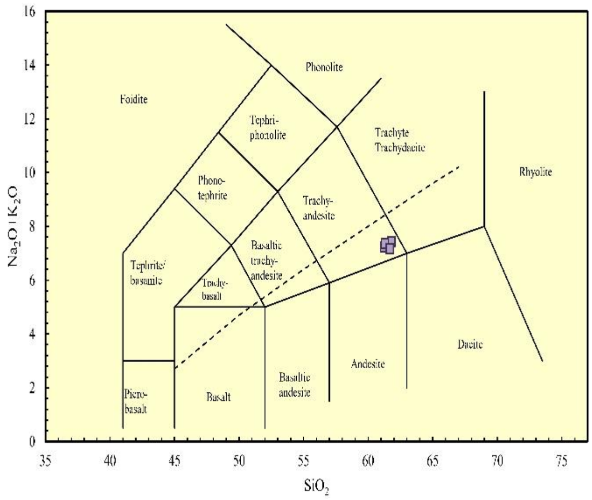


**Fig. 7**. TAS diagram (Le Maitre, 1989) for the Lower Pliocene volcanoclastic rocks from the Vitačevo volcanic plateau

Table 2

*Chemical and geochemical characteristic of the Lower Pliocene volcanoclastic rocks from the Vitačevo volcanic plateau*

| Elements | No | | | | | Elements | No | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | | 1 | 2 | 3 | 4 | 5 |
| $SiO_2$ | 60.04 | 60.09 | 60.5 | 60.21 | 60.11 | Mo | 1 | 1 | 1 | 1 | 1 |
| $TiO_2$ | 0.662 | 0.587 | 0.632 | 0.642 | 0.675 | Ag | 0.2 | 0.1 | 0.3 | 0.4 | 0.3 |
| $Al_2O_3$ | 16.76 | 16.87 | 16.32 | 16.98 | 16.48 | In | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| $Fe_2O_3$ | 5.23 | 5.46 | 5.42 | 5.65 | 5.38 | Sn | 1 | 1 | 1 | 1 | 1 |
| MnO | 0.096 | 0.087 | 0.076 | 0.089 | 0.094 | Sb | 0.3 | 0.3 | 0.2 | 0.2 | 0.2 |
| MgO | 2.54 | 2.67 | 2.65 | 2.45 | 2.63 | Cs | 6.2 | 6.4 | 6.6 | 6.7 | 6.3 |
| CaO | 4.75 | 4.87 | 4.62 | 4.53 | 4.75 | Ba | 1671 | 1687 | 1898 | 1700 | 1692 |
| $Na_2O$ | 3.46 | 3.54 | 3.43 | 3.57 | 3.51 | La | 78.6 | 78.2 | 78.3 | 79.1 | 79.2 |
| $K_2O$ | 3.66 | 3.57 | 3.85 | 3.67 | 3.48 | Ce | 147 | 149 | 148 | 148 | 147 |
| $P_2O_5$ | 0.38 | 0.41 | 0.39 | 0.42 | 0.34 | Pr | 16.1 | 16.5 | 16.8 | 16.3 | 16.9 |
| LOI | 1.93 | 1.89 | 1.97 | 1.85 | 1.83 | Nd | 56.2 | 56.7 | 56.4 | 56.9 | 56.5 |
| **Total** | **99.508** | **100.044** | **99.858** | **100.061** | **99.279** | Sm | 8.16 | 8.24 | 8.32 | 8.29 | 8.23 |
| Sc | 12 | 1 | 14 | 12 | 13 | Eu | 1.79 | 1.82 | 1.85 | 1.77 | 1.81 |
| Be | 3 | 2 | 3 | 4 | 3 | Gd | 4.72 | 4.76 | 4.81 | 4.79 | 4.8 |
| V | 107 | 108 | 109 | 108 | 107 | Tb | 0.65 | 0.61 | 0.63 | 0.64 | 0.66 |
| Cr | 70 | 75 | 78 | 81 | 72 | Dy | 3.1 | 3.2 | 3.3 | 3.2 | 3.1 |
| Co | 14 | 15 | 13 | 14 | 14 | Ho | 0.58 | 0.6 | 0.61 | 0.59 | 0.59 |
| Ni | 15 | 12 | 12 | 11 | 14 | Er | 1.63 | 1.65 | 1.66 | 1.64 | 1.62 |
| Cu | 20 | 22 | 21 | 24 | 25 | Tm | 0.247 | 0.251 | 0.252 | 0.249 | 0.248 |
| Zn | 60 | 56 | 58 | 61 | 62 | Yb | 1.63 | 1.65 | 1.64 | 1.62 | 1.63 |
| Ga | 20 | 18 | 21 | 19 | 22 | Lu | 0.258 | 0.262 | 0.261 | 0.263 | 0.259 |
| Ge | 1.3 | 1.5 | 1.2 | 1.5 | 1.1 | Hf | 4.9 | 4.7 | 4.9 | 4.8 | 4.9 |
| As | 2 | 3 | 2 | 4 | 2 | Ta | 0.87 | 0.91 | 0.94 | 0.88 | 0.98 |
| Rb | 129 | 125 | 132 | 121 | 124 | W | 1.1 | 1.2 | 1.4 | 1.2 | 1.3 |
| Sr | 1250 | 1260 | 1280 | 1230 | 1240 | Tl | 0.82 | 0.85 | 0.83 | 0.81 | 0.84 |
| Y | 16.4 | 16.2 | 17.1 | 17.3 | 16.9 | Pb | 67 | 68 | 69 | 66 | 68 |
| Zr | 200 | 210 | 220 | 200 | 200 | Bi | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Nb | 11.2 | 11.3 | 11.5 | 11.2 | 11.9 | Th | 28.4 | 27.9 | 28.6 | 29.3 | 29.1 |
| | | | | | | U | 7.8 | 8.1 | 8.2 | 8.1 | 8.3 |

## GEOCHEMICAL CHARACTERISTICS

Figure 8 shows the diagram of the normalized values of REE in the volcanoclastic rocks of the Vitačevo volcanic plateau in terms of chondrite values (Boynton, 1984) that is characterized by significant values of enrichment LREE and MREE, relatively low HREE concentration and a low negative anomaly of Eu and Gd.

Figure 9 shows the diagram of the normalized values of REE in the volcanoclastic rocks of the Vitačevo volcanic plateau area relative to the values of the primitive mantle (Sun and McDonough, 1989). From the diagram it can be seen that in all examined samples there is a significant negative anomaly of Nb, Ta, and a pronounced positive anomaly of Ce.

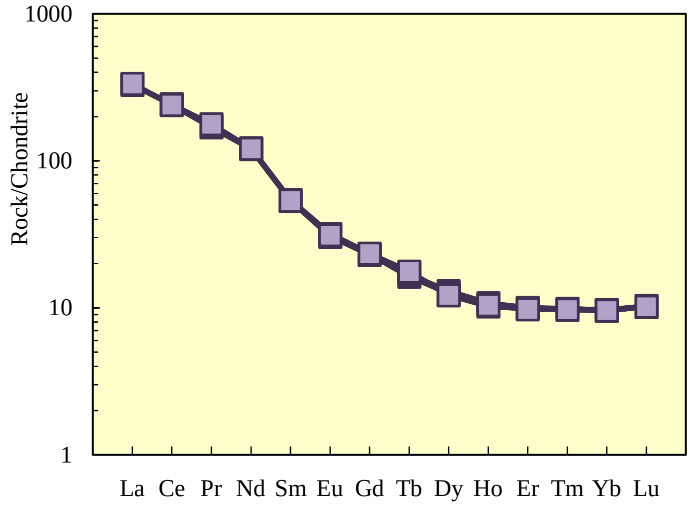


**Fig. 8.** Chondrite normalized REE patterns for the Lower Pliocene volcanoclastic rocks from the Vitačevo volcanic plateau. Chondrite values after Boynton (1984)

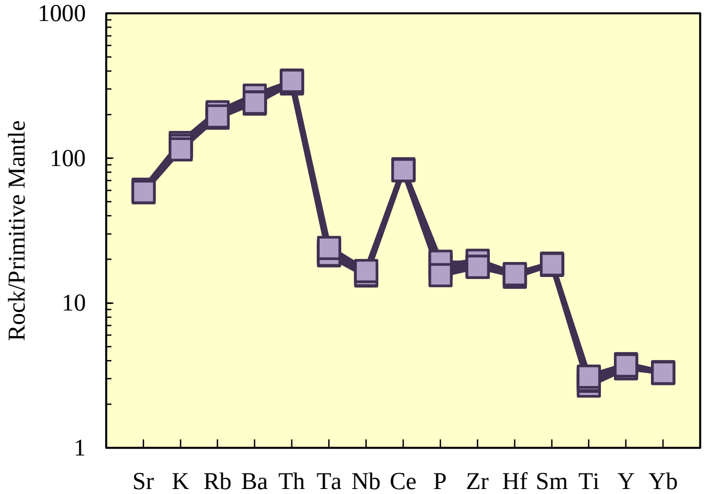


**Fig. 9.** Primitive mantle normalized trace element diagram for the Lower Pliocene volcanoclastic rocks from the Vitačevo volcanic plateau. Normalization factors after Sun and McDonough (1989)

*Sr-Nd isotope geochemistry*

For geochemical investigations of strontium and neodymium isotopes, two samples are given and the obtained results are shown in Table 3. The presented results show that the isotopes of strontium $^{87}Sr/^{86}Sr$ range from 0.708421 to 0.709579, while the isotopes of the neodymium $^{143}Nd/^{144}Nd$ move in the interval of 0.512441 – 0.512472.

Strontium isotopes ($^{87}Sr/^{86}Sr$) clearly indicate the origin of the primary magma from which these volcanic rocks differentiated. The source of the magma is unambiguously in the upper mantle and therefore these rocks not differ from the Pliocene volcanism on Kožuf Mountain where the strontium isotopes are in the interval of 0.7080 to 0.7090.

T a b l e 3

*$^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotope ration in volcanoclastic rocks from the Vitačevo plateau*

| | $^{87}Sr/^{86}Sr$ | ± 2 SE | $^{143}Nd/^{144}Nd$ | ±2 SE* | εNd0 |
|---|---|---|---|---|---|
| V1 | 0.708752 | 0.000015 | 0.512304 | 0.000008 | –6.5 |
| V2 | 0.708787 | 0.000016 | 0.512372 | 0.000008 | –6.5 |

* Uncertainty in Sr and Nd isotopic composition is ± 2 standard error.
ε Nd0 is the epsilon $^{143}Nd$ value calculated present day.

The examined volcanic rocks from the volcanoclastic complex of the Vitačevo volcanic plateau are characterized by low values of isotopes of $^{87}Sr/^{86}Sr$ and low isotope values of $^{143}Nd/^{144}Nd$

(Figure 10, V1–V2 group), which clearly indicates the greater similarity of these volcanic rocks with the volcanic rocks of Kožuf Mountain of Pliocene age.

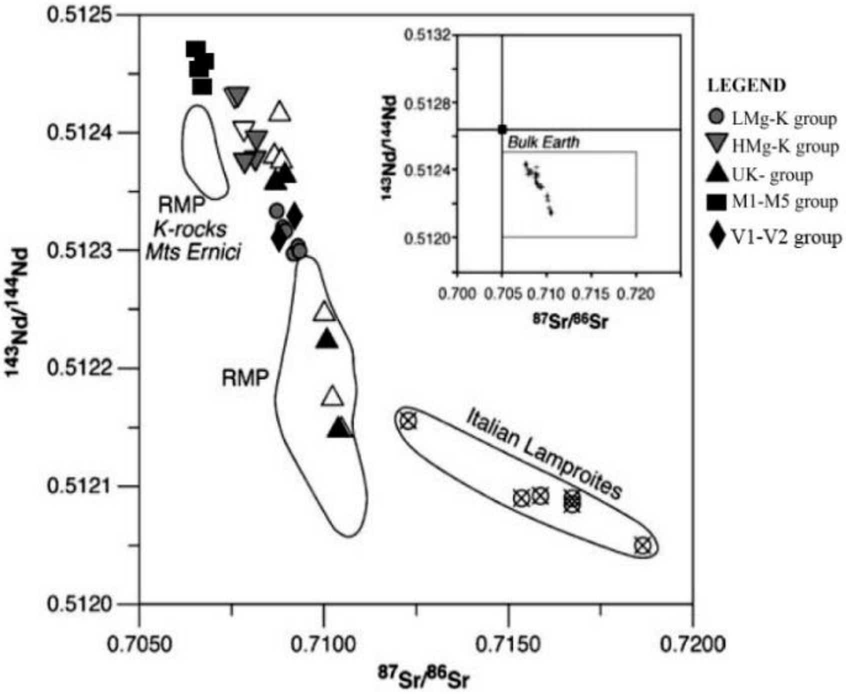


**Fig. 10.** $^{143}Nd/^{144}Nd$ vs $^{87}Sr/^{86}Sr$ plot for the studied samples. The data for the Roman Magmatic Province (RMP; Conticelli et al., 2002) and for the Tuscan lamproites (Conticelli et al., 2002; Peccerillo and Martinotti, 2006) are also plotted for comparison

*K-Ar geochronology*

The isotopic age of the volcanoclastic rocks from Vitačevo was determined by the K/Ar method and the results shown in the Table 4 were obtained.

The presented data show that the age of these rocks is Lower Pliocene (5.8 Ma) and that these are very similar rocks to the volcanic rocks of Kožuf Mountain (6.5–1.8 Ma).

Age values were calculated from the analytical data using the decay constants for $^{40}K$ and the isotopic abundances for terrestrial K and atmospheric Ar listed by Steiger and Jäger (1977), and the assumptions of conventional K-Ar dating (Dalrymple and Lanphere, 1969). The uncertainties for the age values are based on the effects of analytical error only, at the 95% confidence level (2σ).

T a b l e 4

*K/Ar age determination of volcanoclastic rocks from the Vitačevo plateau*

| | K, % | $^{40}Ar$ rad, (nmol kg$^{-1}$) | $^{40}Ar$ rad % | Age, Ma | Error 2σ |
|---|---|---|---|---|---|
| V1 | 3.00 | 30.3 | 47 | 5.8 | ±c0.7 |
| V2 | 3.03 | 30 | 57 | 5.8 | ±0.7 |

## CONCLUSION

The volcanoclastic rocks found within the Vitačevo volcanic plateau primarily consist of lacustrine tuffs containing rounded fragments of stratified volcanic rocks. These fragments exhibit characteristics typical of intermediate rocks, falling within the latites and trachytes group. Structurally, these rocks exhibit a porphyritic texture, with phenocrysts composed of plagioclase, hornblende, and biotite, embedded within a groundmass consisting of feldspar and magnetite. Isotopic dating indicates an age of 5.8 million years corresponding to the Lower Pliocene period.

Chemically, these rocks can be categorized as intermediate rocks, specifically trachy-andesite-latites. Geochemically, analysis of rare earth elements (REE) content and isotopic ratios such as $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ suggests an origin from the metasomatized upper part of the upper mantle with notable contributions from rocks in the lower continental crust.

## REFERENCES


Боев, Б. (1988): *Пеӣролошки, īеохемиски и вулканолошки каракӣерисӣики на вулканскиӣе карӣи од Кожуф Планина.* Докторска дисертација, Рударско-геолошки факултет – Штип, Универзитет „Св. Кирил и Методиј“, Скопје, 195 стр.

Boev, B., Yanev, Y. (2001): Tertiary magmatism within the Republic of Macedonia: Review. *Acta vulcanologica* **13**, 57–72.

Boynton, W. V. (1984): Geochemistry of the rare earth elements: meteorite studies. In: Henderson P. (ed.): *Rare Earth Element Geochemistry*. Elsevier, Amsterdam, pp. 63–114.

Conticelli, S., D’Antonio, M., Pinarelli, L., Civetta, L. (2002): Source contamination and mantle heterogeneity in the genesis of Italian potassic and ultrapotassic rocks: Sr–Nd–Pb isotope data from Roman Province and Southern Tuscany. *Mineralogy and Petrology* **74** (2),189–222. DOI:10.1007/s007100200004

Creaser, R. A., Grutter, H. S., Carlson, J., Crawford, B. (2004): Macrocrystal phlogopite Rb-Sr dates for the Ekati property kimberlites, Slave Province, Canada. Evidence for multiple intrusive episodes in the Paleocene and Eocene. *Lithos* **76** (1), 399–414.

Dalrymple, G. B., Lamphere, M. A. (1969): *Potassium-Argon Dating. Principles, Techniques, and Applications to Geochronology*, 258 p. San Francisco, W. H. Freeman Co. (A series of books in geology).

Думурџанов, Н. Христов, С., Павловски, Б., Иванова, В. (1981): Толкувач за листовите Витолиште и Кајмакчалан, *Основна īеолошка карӣа (1:100 000) на СФРЈ,* Сојузен геолошки завод, Белград, 61 стр.

Dumurdžanov, N., Krstić, N., Mihajlović, D., Ognjanova-Rumenova, N., Petrov, G. (2003): New data on stratigraphy of the Neogene and Pleistocene in Mariovo, Macedonia. *Geologica Macedonica* **17**, 43–52

Dumurdžanov, N., Serafimovski, T., Burchfiel, B. C. (2004): Evolution of the Neogene-Pleistocene basins of Macedonia. Geological Society of America, *Digital Map and Chart Series 1 (Accompanying Notes)*, 20 p.

Dumurdžanov, N., Serafimovski, T., Burchfiel, B. C. (2005): Cenozoic tectonics of Macedonia and its relation to the South Balkan extensional regime. *Geosphere* **1**, 1–22.

Eleftheriadis, G., Castorina, F., Soldatos, T., Masi, U. (2003): Geochemical and Sr–Nd isotopic evidence for the genesis of the Late Cainozoic Almopia volcanic rocks (Central Macedonia, Greece). *Mineralogy and Petrology* **78**, 21–36. https://doi.org/10.1007/s00710-002-0217-0

Eleftheriadis, G., Vougioukalakis, G. (2006): Geological overview of Almopia – Volcanism. In: Tsoukala, E. (ed.): *A Guide to Speleopark of Almopia. Geology-Paleontology-Speleology*. Aridea, Greece, p. 108.

Goldstein, S. L., O’Nions, R. K., Hamilton, P. J. (1984): A Sm-Nd isotopic study of atmospheric dusts and particulates from major river systems. *Earth and Planetary Science Letters* **70**, 221–236.

Holmden, C., Creaser, R. A., Muehlenbachs, K. (1997): Paleosalinities in brackish water environments: A method based on the isotopic paleohydrology of strontium. *Geochimica et Cosmochimica Acta* **61**, 2105–2118.

Христов, С., Карајовановиќ, М., Страчков М. (1973): Толкувач за листот Кавадарци, *Основна īеолошка карӣа (1:100 000) на СФРЈ*, Сојузен геолошки завод, 63 стр.

Институт за истражување на минерали и суровини (1978): *Завршен извешӣај за исӣражување на јаīлен во Мариово во ӣериод 1974–1977*, Геолошки завод, Скопје.

Janković, S., Boev, B., Serafimovski, T. (1997): *Magmatism and Tertiary Mineralization of the Kožuf Metallogenetic District, the Republic of Macedonia, with Particular Reference to the Alshar deposit*. Faculty of Mining and Geology. Štip, Special Publications, 5. 262 p.

Karamata, S., Stojanov, R., Serafimovski, T., Boev, B., Aleksandrov, M. (1992): Tertiary magmatism in the Dinarides and the Serbo-Macedonian massif. *Geologica Macedonica* **6** (2), 127–186.

Kolios, N., Innocenti, F., Manetti, P., Peccerillo, A., Giuliani, O. (1980): The Pliocene volcanism of the Voras Mts (Central Macedonia, Greece). *Bulletin Volcanologique* **43**, 553–568. https://doi.org/10.1007/BF02597692

Le Maitre, R. W. (1989): *A Classification of Igneous Rocks and Glossary of Terms: Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Igneous Rocks*, Blackwell, Oxford, 193 p.

Lippolt, H. J., Fuhrmann, U. (1986): K-Ar age determination on volcanics of Alsar mine/Yugoslavia. In: Nolte, E. (ed.): *Proceed. Workshop on the Feasibility of Solar Neutrino Detection with $^{206}$Pb by Geochemical and Mass Spectroscopical Measurements*. Report GSI-86-9, Technische Universität, München.

Molnár, K., Lahitte, P., Dibacto, S., Benkó, Z., Agostini, S., Döncző, B., Ionescu, A., Milevski, I., Szikszai, Z., Kertész, Z., Temovski, M. (2022): The westernmost Late Miocene-Pliocene volcanic activity in the Vardar zone (North Macedonia). *International Journal of Earth Science* **111**, pp. 749–766 (Geol Rundsch). https://doi.org/10.1007/s00531-021-02153-2

Neubauer, F., Pavićević, M. K., Genser, J., Jelenković, R., Boev, B., Amthauer, G. (2009): $^{40}Ar/^{39}Ar$ dating of geological events of the Allchar deposit and its host rocks. *Goldschmidt Conference* A938.

Peccerillo, A., Martinotti, G. (2006): The Western Mediterranean lamproitic magmatism: origin and geodynamic significance. *Terra Nova* **18** (2), 109–117.

Ракичевиќ, Т., Пенцерковски, Ј. (1970): Толкувач за листот Кожуф, *Основна геолошка карта (1:100 000) на СФРЈ*, Сојузен геолошки завод, 47 стр.

Ракичевиќ, Т., Стојанов, Р., Арсовски, М. (1973): Толкувач за листот Прилеп, *Основна геолошка карта (1:100 000) на СФРЈ*, Сојузен геолошки завод, 65 стр.

Schmidberger, S. S., Heaman, L. M., Simonetti, A, Creaser, R. A., Whiteford, S. (2007): Lu-Hf, in-situ Sr and Pb isotope and trace element systematics for mantle eclogites from the Diavik diamond mine: Evidence for Paleoproterozoic subduction beneath the Slave craton, Canada. *Earth and Planetary Science Letters* **254**, 55–68.

Steiger, R.H. and Jäger, E. (1997): Subcommission on Geochronology. Convention on the use of decay constants in geo- and cosmochronology. *Earth and Planetary Science Letters* **36**, 359–362.

Sun, S. S., McDonough, W. F. (1989): Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders A. D., Norry, M. J. (eds.): *Magmatism in the Ocean Basins. J Geol Soc London*, Spec Publ **42**, 313–345.

Tanaka, T., et al. (2000): JNdi-1: A neodymium isotopic refrence in consistency with LaJolla neodymium. *Chemical Geology* **168**, 279–281.

Unterschutz, J. L. E., Creaser, R. A., Erdmer, P., Thompson, R. I., Daughtry, K. L. (2002): North American margin origin of Quesnel terrane strata in the southern Canadian Cordillera: Inferences from geochemical and Nd isotopic characteristics of Triassic metasedimentary rocks. *Geological Society of America Bulletin*, **114** (4), 462–475. DOI: 10.1130/0016-7606(2002)114<0462:NAMOOQ>2.0.CO;2

Vougioukalakis, G. (2002): *Petrological, Geochemical and Volcanological Study of the Almopias Pliocene Volcanic Formations and Their Correlation with the Geothermal Manifestations in the Area*. PhD Thesis. Aristotle University of Thessaloniki, p. 303 (in Greek).

Yanev, Y., Boev, B., Doglioni, C., Innocenti, F., Manetti, P., Pécskay, Z., Tonarini, S., D'Orazio, M. (2008a): Late Miocene to Pleistocene potassic volcanism in the Republic of Macedonia. *Mineralogy and Petrology* **94**, 45–60. https://doi.org/10.1007/s00710-008-0009-2

Yanev, Y., Boev. B., Manetti, P., Ivanova, R., D'Orazio, M., Innocenti, F. (2008b): Mineralogy of the Plio-Pleistocene potassic and ultrapotassic volcanic rocks from the Republic of Macedonia. *Geochemistry, Mineralogy and Petrology*, **46** Sofia, 35–67.

## Р е з и м е

## СТАРОСТ НА ВУЛКАНОКЛАСТИЧНИТЕ СЕДИМЕНТНИ КАРПИ ОД ВУЛКАНСКОТО ПЛАТО ВИТАЧЕВО (КОЖУФ ПЛАНИНА), СЕВЕРНА МАКЕДОНИЈА

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**Клучни зборови:** вулканокластични седиментни карпи; латити-трахити

Вулканокластичните карпи пронајдени во вулканската висорамнина Витачево првенствено се состојат од езерски туфови кои содржат заоблени фрагменти од стратифицирани вулкански карпи. Овие фрагменти покажуваат карактеристики типични за средни карпи, кои спаѓаат во групата на латити и трахити. Структурно, овие карпи покажуваат порфиритна текстура, со фенокристали составени од плагиокласт, хорнбленда и биотит, вградени во земјена маса составена од фелдспат и магнетит. Изотопското датирање укажува на старост од 5,8 милиони години, што одговара на периодот на долниот плиоцен. Хемиски, овие карпи можат да се категоризираат како средни карпи, конкретно трахи-андезит-латити. Сепак, микроскопските испитувања сугерираат класификација во групата на алкални базалти. Геохемиски, анализата на содржината на ретките земјени елементи (REE) и изотопските соодноси како што се $^{87}Sr/^{86}Sr$ и $^{143}Nd/^{144}Nd$ сугерираат потекло од метасоматизираниот горен дел на горната обвивка со забележителен придонес од карпите во долната континентална кора.