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REE IN SOME TERTIARY VOLCANIC COMPLEXES IN THE REPUBLIC OF MACEDONIA

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A b s t r a c t: Petrological and geochemical features of the Tertiary magmatic rocks from the Republic of Macedonia were subject of study in this paper. The latest K-Ar, $^{87}Sr/^{86}Sr$, and REE data for samples from Kratovo–Zletovo, Sasa–Toranica and Damjan–Buchim ore districts are presented. Whole rock XRF analyses confirmed host rock composition as dacites, quartz-latites, trachyandesites, rhyolites and rhyodacites. Absolute age determinations by the K-Ar dating method have shown ages range from 31 to 14 Ma confirming Oligocene-Miocene age as previously determined by relative methods. Determinations of $^{87}Sr/^{86}Sr$ ratios (0.70504 to 0.71126) suggest material is sourced from the contact zone between the lower crust and upper mantle where contamination of primary melt occurred. New REE data including negative Eu anomalies along with previously determined La/Yb ratios ranging from 13.3 to 43.0 (Serafimovski 1990) confirm inferred material source. These new data reconfirm previous results, provide insight into the Tertiary magmatic history of the district, and suggest the exact origin of the material that produced the Tertiary magmatic rocks.

Key words: rare earth elements (REE); Sasa; Toranica; Kratovo; Zletovo; Damjan; Buchim; volcanic rocks; age; Tertiary

INTRODUCTION

Surface manifestations of the Tertiary magmatism within the Republic of Macedonia were determined almost at whole of its territory, but were of different intensities and scales. This magmatism/volcanism mainly occured as extrusive and efusive, which at certain regions, as Kratovo-Zletovo volcanic area is, reached surface of 1200 km^2 (Serafimovski, 1990, 1993; Stojanov and Serafimovski, 1990b) and represents one of the largest complexes at the Balkans and wider. The most common and the most important occurences of the Tertiary magmatism are located in the Eastern parts of the Republic of Macedonia, excluding Kožuf magmatism (Boev, 1988; Boev et al., 1997), which has been located in the southern parts of the Vardar zone, close to the Greece national border, continuing into the volcanic complex Aridea.

The basic characteristics of the Tertiary magmatism within the Republic of Macedonia were given by Karamata (1982), Karamata et al., (1992), Serafimovski (1993), Boev et al. (1995), and others, while certain petrological, geochemical and geochronological features of particular volcanic complex could be found in Boev (1988), Stojanov and Serafimovski (1990 a, b), Boev et al. (1992), etc. Geochronological data of studied rocks from certain localities, characterized by occurence of Tertiary magmatism, pointing out the existence of Oligo-Miocene magmatism, who's absolute age ranges from 33 Ma for the alkali trachyte dykes near the Mrdaja, Dojran (Stojanov and Sveshnikova, 1985) up to 1.8 Ma at Kožuf (Boev, 1988). Absolute age of Oligo-Miocene volcanics in the Eastern Macedonia (Kratovo–Zletovo, Damjan–Bučim, Osogovo) most often is within the range of 32–16 Ma (Serafimovski, 1990; Aleksandrov, 1992; Tasev, 2003). Intrusive facies of this magmatism have been studied in central parts of the Vardar zone and were defined as Cretaceous-Tertiary (Boev and Lepitkova, 2004). Certain facies of the Neogene volcanism within the Vardar zone have shown emphasized alkali character or they were grouped within the ultraalkaline rocks (Yanev et al., 2003).

The study of REE in Tertiary volcanic rocks at the territory of the Republic of Macedonia was not of any systematic programme. Certain data, explaining geochemical features of volcanic rocks, could be found in Karamata et al. (1992), Serafimovski (1990), Boev (1988) etc., or REE data were presented in papers related to particular localities in the Republic of Macedonia (Serafimovski, 1993; Serafimovski et al, 2003; Tasev et al., 2005; Serafimovski et al., 2006).

We have to point out that at the territory of the Republic of Macedonia with the Tertiary magmatism have been related numerous polymetalic deposits and occurences of lead, zinc, copper, gold, arsenic, iron, uranium, etc., while some of them are very productive (Serafimovski et al., 2003).

METHODOLOGY

Samples were prepared and analyzed in a batch system. Each batch contained a method reagent blank, certified reference material and 17% replicates. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt was immediately poured into a solution of 5% nitric acid containing an internal standard, and mixed continuously until completely dissolved (~30 minutes). The samples were run for major oxides and selected trace elements on a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP and Varian Vista 735 ICP. Calibration was performed using 7 prepared USGS and CANMET certified reference materials. One of the 7 standards is used during the analysis for every group of ten samples. For REE determination the sample solution prepared as mentioned above was spiked with internal standards to cover the entire mass range, then further diluted and introduced into a Perkin Elmer SCIEX ELAN 6100 ICP/MS using a proprietary sample introduction methodology. Accuracy (assessed using an in-house standard) was better than 10% for most elements.

Some geological features of the Tertiary magmatism

The Cenozoic basins at the territory of the Republic of Macedonia are mainly filled in by volcanogene-sedimentary and sedimentary complexes (margine sediments – Eocene, and continental sediments in higher parts Oligocene-Miocene). The profile of Eocene sediments has been characterized by conglomerates, which interchange with flysch and terrigene-carbonaceous formations. In Oligocene dominate volcanics-quartzlatites and hornblende biotitic andesites. The Miocene volcanosedimentary complexes include ignimbrites. The Pliocene tuffaceous series interchange with lake clays, sands and andesite breccias. The Tertiary magmatism in this area occurred from Oligocene up to Pliocene. The existing geochronological data are pointing to a Lower Pliocene magmatism present in a wide area within the Kratovo–Zletovo volcanic area (32–25 Ma; Fig. 1) while certain andesite dykes near the Žguri locality have shown absolute age og 16 Ma (Serafimovski, 1993) as in Bučim–Damjan–Borov Dol region (32–23 Ma; Fig. 1). Pliocene magmatism occurred within the range of 7–1.8 Ma (Boev, 1988). The most common are latites of age 5–4.5 Ma. Volcanogene-intrusive complex composed of andesites, quartzlatites and rhyolites of Pliocene age has been localized in the southern parts of the Republic of Macedonia near to Alshar close to the Greek-Macedonian border (Boev, 1988; Janković, 1993). It can be stated that during the process of the Cenozoic activization at the territory of the Republic of Macedonia occured three stages of magmatic pulsations in Oligocene, Miocene and Pliocene. The processes of ore mineralization formation, spatially and timely, were closely related to the occurrence of the magmatism. For example, porhpyry copper mineralizations in the Bučim and Borov Dol are related to the Oligocene dykes and latite stocks. The Pliocene mineralizations in the Alshar area are closely related to the Pliocene volcanism in that area. The age of polymetallic mineralizations in the Sasa and Toranica are closely related to the latite and quartzlatite dykes intruded during the Miocene (24–17 Ma; Fig. 1). The Tertiary magmatism in the Eastern Macedonia has been located in the rim NE parts close to the border with Bulgaria in a belt wide 50–70 km. That belt has been controled by the fissure system, which is product of the Cenozoic activization oriented under steep angle versus the Mesozoic structures in the Vardar zone. The three main fissure systems of general NW–SE have controled the spatial distribution of volcanogene-intrusive rocks at that territory.

RESULTS AND DISCUSSION

The present results concerning the REE in the Tertiary volcanic rocks in the Republic of Macedonia represents the most representative volcanic complexes, Kratovo–Zletovo volcanic area, Osogovo volcanic area and Damjan–Bučim volcanic area, localized in Eastern Macedonia (Fig. 1).

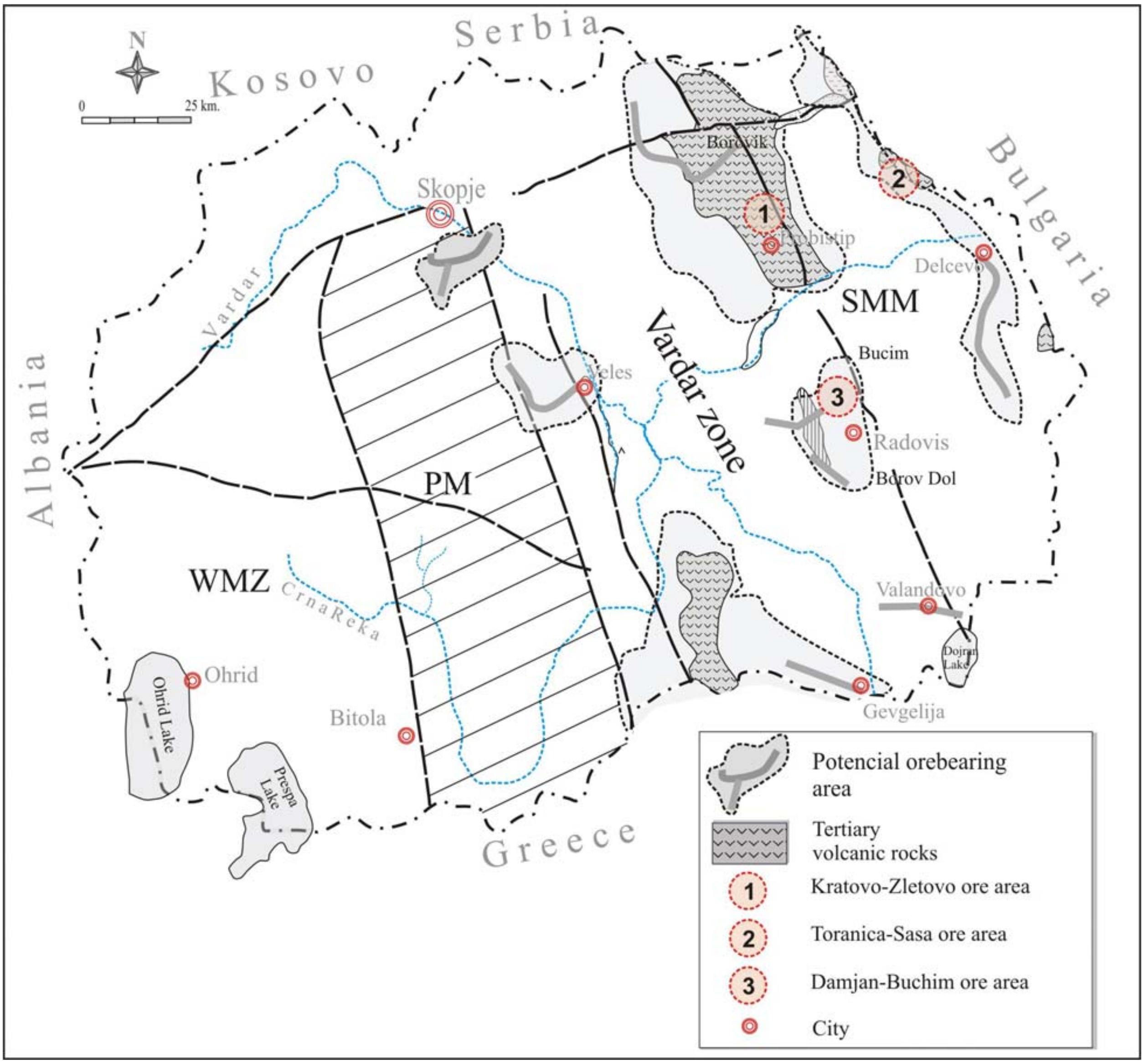

Fig. 1. Distribution of the Tertiary magmatism at the area of the Republic of Macedonia and position studied areas (Tasev et al., 2005; Serafimovski et al., 2006)

Within these volcanic complexes were localized even productive polymetallic mineralizations of Pb-Zn and Cu-Au. Quite often, mineralized areas were intensively hydrothermaly altered, which has been confirmed by analyses of different volcancic rocks. The review of the results from studied volcanic rocks and obtained REE data has been organized by the most important regions with Tertiary volcanic rocks, such as Kratovo–Zletovo, Osogovo and Damjan–Bučim.

Kratovo–Zletovo

Our first subject for this study was the Kratovo–Zletovo as the largest magmatic area in Macedonia with a surface of 1200 km^2. This are is also a very important mining area with significant Pb-Zn deposits. Many authors have studied this area and their studies can be found in Stojanov (1974), Stojanov and Denkovski (1974), Serafimovski (1990), Stojanov and Serafimovski (1990b), Serafimovski (1993), etc. Volcanic deposits predominate in the area, but plutonic rocks are also be found. Effusive volcanic products are represented by latites, andesites, andesite-dacite ignimbrites, dacite. Volcanic activity, which have produced magmatic rocks described above, migrated from NW to SE direction. Some intrusive bodies also occur in Kratovo–Zletovo area. One pluton is situated near Karlukovo village and one diorite-porphyrite dyke near Borovic village (Boev and Yanev, 2001). The Karlukovo pluton is of quartz-monzonitic to monzonitic composition.

REE analyses of magmatic rocks from the Kratovo–Zletovo area were performed at the *Active Labs, Canada*. Obtained results are given in Table 1.

Table 1

Rare earth elements content in rocks from the Kratovo–Zletovo ore area (ppm)

Element	MAK-15 III	MAK-18 II	MAK-20 I	MAK-21 IV
La	58.4	32.7	50.7	28.6
Ce	106	61.1	90.4	53.9
Pr	12.1	7.35	9.98	6.25
Nd	43.6	27.5	35.2	22.8
Sm	7.7	5.4	5.9	4.3
Eu	1.79	1.40	1.34	1.13
Gd	6.1	5.0	5.0	4.1
Tb	0.8	0.8	0.7	0.7
Dy	4.2	4.5	3.7	3.8
Ho	0.8	0.9	0.7	0.7
Er	2.2	2.7	2.1	2.2
Tm	0.33	0.42	0.33	0.34
Yb	2.1	2.7	2.1	2.2
Lu	0.32	0.41	0.31	0.35

In accordance with data from Table 1, was preformed normalization of REE values versus chondrite ones, plot was constructed and illustrated on Figure 2.

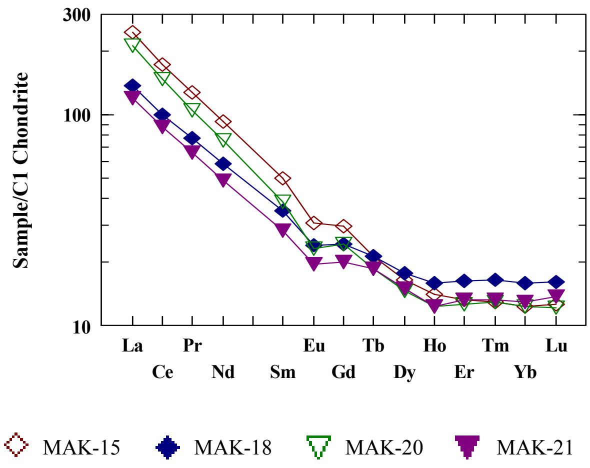

Fig. 2. Plot of normalized values of rare earth elements in comparison to those in chondrites, for rock samples from the Kratovo–Zletovo ore region

From the Figure 2 can be seen that the REE in the Kratovo–Zletovo ore area, going from left to right, exhibits a decreasing trend. Analyzing the left and right side of the plot, can be concluded that there is a decrease (right part) of heavy rare earth elements (HREE, with an atomic number higher than those of Eu or atomic number higher than 63) in comparison with ligh rare earth elements (LREE, with an atomic number lower than those of Eu or lower than 63). Such values are product of fractionation of light rare earth elements and their increase in comparison to the chondritic values. That fractionation occured as a direct consequence of partial melting, which according to the angle of the line in the diagrame was not of higher intensity. Analyzing the midle part of the plot can be seen that there is a slight negative Eu anomaly, which shows decreasing of Eu values compared to the "ideal" line between the Sm and Gd. Calculations of such an anomaly (using the formula given by Taylor and McLennan,1985) are given in Table 2.

Table 2

Values of Eu anomaly in samples from the Kratovo–Zletovo ore region

Samples	Value of Eu anomaly
MAK-15 III	0.797654
MAK-18 II	0.822415
MAK-20 I	0.755663
MAK-21 IV	0.820559

From the Table 2 can be seen that Eu anomaly values are within the range from 0.755662705 to 0.822415183 or smaler than 1 confirming negative anomaly (Rollinson, 1992). Eu anomalies are mainly controled by feldspars. Eu^{2+} is compatible in plagioclase and K-feldspar in comparison to Eu^{3+}, which is incompatible. Removal of feldspar from the melt by fractional crystallization or partial melting of rock that contained feldspar can lead to increase of negative Eu anomaly. The variations of Ba content vs. constant Rb content confirmed that fractionation of K-feldspar and amphibole is the predominant differentiation process and the Eu anomaly – the limited participation of the plagioclase in this process (Boev and Yanev, 2001).

Such character of the Eu anomalies and HREE and LREE trends in the Tertiary volcanic rocks mostly are related to the oceanic and continental arcs of Cenozoic age (Titley and Beane, 1981; Richards, 2003; Cooke et al., 2005), and ocassionaly to old and folded belts, while both settings are characterized by compression tectonic areas and thined continetal crust (Titley and Beane, 1981).

Sasa–Toranica

Volcanic and volcano-intrusive rocks in the Sasa–Toranica ore area belong to one bigger metallogenic unit, in literature known as metallogenic zone Besna Kobila–Osogovo–Tasos, with northwest direction with total length of a 100 km, on both sides of Macedonia-Bulgaria interstate border (Serafimovski, 1990; Serafimovski, 1993; Alexandrov, 1992; Janković et al., 1995). Volcanic rocks in that zone have similar morphological, petrological and geochemical features and all of them are of Tertiary age. At the territory of the Republic of Macedonia they were determined in their marginal north-eastern parts on the state border with Republic of Bulgaria (Fig. 1). It should be mentioned that similar rocks were determined in Bulgaria also. Volcanic rocks in the area occur as elongated dykes with north-western direction, with thickness of around 50 m and azimuth of 260°. Composition of these rocks is mainly dacitic tuffs, dacites, quartzlatites, rhyolites, trachyandezites, andesitelatites and occasionally lamprophyre veins (Sasa and Toranica localities).

Certain samples from the Sasa–Toranica ore area were analyzed for contents of rare earth elements (REE). This type of analyses were performed in *Active Labs, Canada*. Results obtained from this analysis are given in Table 3.

Table 3

Rare earth elements content in rocks from the Sasa–Toranica ore region (ppm)

Element	MAK1 I	MAK7 I	MAK9 II	MAK13 II
La	53.10	52.00	39.60	44.90
Ce	106.00	95.40	72.10	79.30
Pr	13.30	11.40	8.08	9.72
Nd	52.50	42.10	28.30	35.20
Sm	9.20	7.50	5.10	6.80
Eu	2.22	1.68	1.11	1.65
Gd	7.30	5.90	4.30	6.50
Tb	0.90	0.80	0.60	1.00
Dy	4.50	4.00	3.30	5.20
Ho	0.80	0.70	0.60	1.00
Er	2.10	2.10	1.80	2.80
Tm	0.30	0.31	0.28	0.38
Yb	2.00	2.00	1.90	2.30
Lu	0.30	0.30	0.29	0.35

In accordance with data from the table above was performed normalization of values in comparison with chondritic values and it was ploted a diagrame of normalized values (Figure 3).

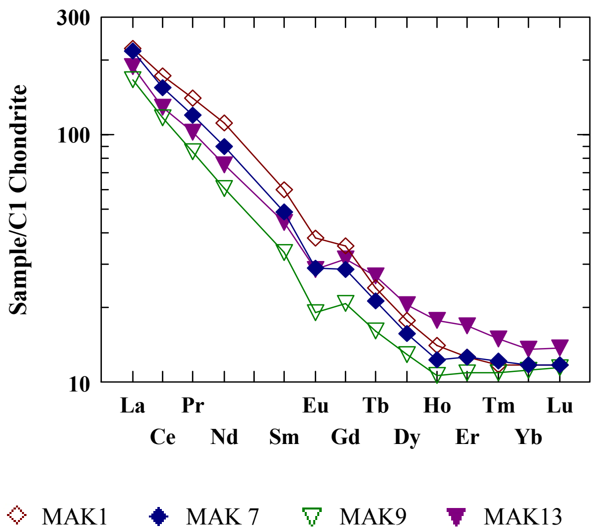

Fig. 3. Plot of normalized values of rare earth elements in comparison to those in chondrites, for rock samples from the Sasa–Toranica ore region

From the Figure 3 can be seen that the REE in the Sasa–Toranica ore region have decreasing trend. Analyzing the left and right side of the digrame can be concluded that there is a decrease (right part) of heavy rare earth elements (HREE, with an atomic number higher than those of Eu or atomic number higher than 63) in comparison with ligh rare earth elements (LREE, with an atomic number lower than those of Eu or lower than 63). Such values are product of fractionation of light rare earth elements and their increase in comparison to the chondritic values. That fractionation occured as a direct consequence of partial melting, which according to the angle of the line in the digrame was not of higher intensity.

Looking closely into the middle part of the diagram it can be seen that the value of Eu, slightly and negatively, discloses from the "ideal" line between Sm and Gd or more precisely there is a negative Eu anomaly. In that direction was performed calculation of Eu anomaly, as a geometric mean value (Rollinson, 1992). Calculated values are shown in Table 4.

Table 4

Values of Eu anomaly in samples from the Sasa–Toranica ore region

Samples	Value of Eu anomaly
MAK-1 I	0.82891
MAK-7 I	0.77403
MAK-9 II	0.72767
MAK-13 II	0.75975

From the Table 4 it can be seen that Eu anomaly values are in range from 0.727669702 up to 0.828905716, or they are smaller than 1, which implies to the small negative Eu anomaly (Tasev, 2003; Tasev et al., 2005; Serafimovski et al., 2006). Eu anomalies, mainly, are controled by presence of feldspars. Eu^{2+} is compatible in plagioclase and K-feldspar, in contrast to the Eu^{3+} which is uncompatible. Thus the removal of feldspar from a felsic melt by crystal fractionation or the partial melting of a rock in which feldspar is retained in the source will give rise to a negative Eu anomaly in the melt.

According the data for Eu in analyzed samples and its negative anomaly it can be concluded that Eu has been removed from the melt as a compatible Eu^{2+}, in frame of processes of crystal fractionation or partial melting.

Damjan–Bučim

The Damjan–Bučim is a small volcanic area, but it is of high metallogenic importance because it contains the large Bučim porphyry copper deposit. Many authors have studied this area (Djordjevic and Karamata, 1976; Djordjević and Knežević, 1980; Serafimovski, 1990; Čifliganec, 1993) and more of the area can be found in their investigations. SiO_2 contents in volcanic rocks within the area vary from 57 to 71% and contents of all major elements gradually decrease. According to the chemical composition, the volcanic rocks vary from latites, through trachydacites-trachytes to trachyrhyolites. The latites and trachytes rocks form necks and subvolcanic bodies (e.g. the Bučim copper deposit) and lava flows associated with the central volcanoes. The trachyrhyolites form dykes. With regard to petrochemistry, unlike the Kratovo–Zletovo area, the volcanic rocks of Bučim–Borov Dol area belong to the shoshonite series only.

On certain samples from volcanic rocks sampled from the Damjan-Bučim ore area were performed analyses of rare earth elements. The results from this analysis are given in Table 5.

Table 5

Rare earth elements content in rocks from the Damjan–Bučim ore region (ppm)

Element	MAK-27 I	MAK-30 I	MAK-31 II	MAK-31 II rep	MAK-32 II
La	32.8	68.3	44.9	43.7	67.5
Ce	59.5	119	86.7	84.5	118
Pr	7.12	13.6	10.5	10.2	13.0
Nd	27.1	48.2	38.8	37.5	45.9
Sm	5.1	8.3	7.0	6.8	7.7
Eu	1.45	2.00	1.52	1.49	1.86
Gd	4.7	6.8	5.6	5.5	6.1
Tb	0.7	0.9	0.8	0.7	0.8
Dy	3.9	4.5	3.8	3.7	4.3
Ho	0.8	0.8	0.7	0.7	0.8
Er	2.3	2.3	1.9	1.8	2.3
Tm	0.34	0.33	0.28	0.28	0.33
Yb	2.3	2.3	1.9	1.8	2.3
Lu	0.33	0.34	0.28	0.28	0.34

Values from Table 5 were normalized versus chondritic values. In accordance with that was constructed a plot of normalized values as shown on Figure 4.

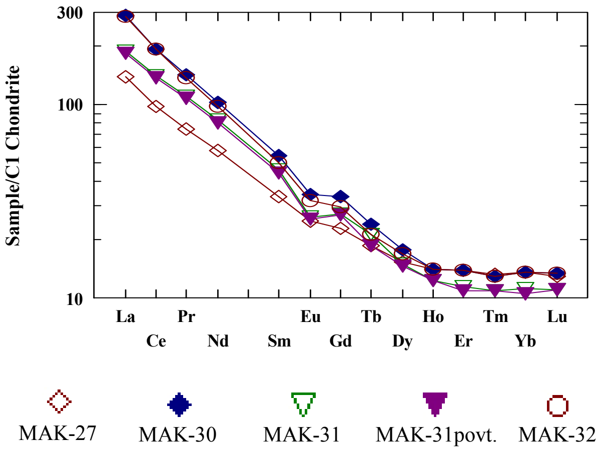

Fig. 4. Plot of normalized values of rare earth elements in comparison to those in chondrites, for rock samples from the Damjan–Buchim ore region

From the plot above it is obvious that REE's have shown decreasing trend going from left to right. Comparing left and right side of the plate we can notice that there is depletion of LREE (right side) in comparison to the HREE (left side. Analyzing the central part of the plot we have noticed that there is a slight negative Eu anomaly. In an attempt to determine an absolute value of the Eu anomaly we have calculated it, as it is shown in Table 6.

Table 6

Values of Eu anomaly in samples from the Damjan–Bučim ore area

Sample	Value of Eu anomaly
MAK-27 I	0.90361
MAK-30 I	0.81331
MAK-31 II	0.74419
MAK-31 II rep	0.74089
MAK-32 II	0.82746

From the Table 6 it can be concluded that values of the Eu anomaly are in range 0.74089 to 0.90361 or they are slightly lower than 1, which point out to a negative Eu anomaly (Rollinson, 1992). As well as for previously mention ore areas, Kratovo–Zletovo and Sasa–Toranica, we may conclude that removal of feldspar from a felsic melt by crystal fractionation or eventual partial melting of a rock in which feldspar was contained could give rise to a negative Eu.

The igneous rocks of Kratovo–Zletovo and Buchim–Borov Dol areas using available trace elements data can be classified as subduction-related volcanic arc magmatic rocks (Serafimovski, 1990; Boev and Yanev, 2001). The similarity with the trace elements contents of the Buchim-Borov Dol rocks with the rocks of the active continental margins is indicated by Boev et al. (1992).

CONCLUSION

From the results of the REE of the Tertiary volcanic rocks in the Republic of Macedonia, discussed above, can be seen that within all samples was pronounced negative Eu anomaly, which is mainly controled by feldspars. Namely, Eu^{2+} has been compatible in plagioclase and K-feldspar in comparison to Eu^{3+}, which is incompatible. Removal of feldspar from the melt by fractional crystallization or partial melting of rock that contained feldspar led to increase of negative Eu anomaly. The variations of Ba content vs. constant Rb content confirmed that fractionation of K-feldspar and amphibole is the predominant differentiation process and the Eu anomaly – the limited participation of the plagioclase in this process.

Such character of the Eu anomalies and HREE and LREE trends in the Tertiary volcanic rocks mostly are related to the oceanic and continental arcs of Cenozoic age, and ocassionaly to old and folded belts, while both settings are characterized by compression tectonic areas and thined continetal crust.

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Р е з и м е

REE ВО НЕКОИ ТЕРЦИЕРНИ ВУЛКАНСКИ КОМПЛЕКСИ ВО РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: елементи на ретки земји (REE); Саса; Тораница; Картово; Злетово; Дамјан; Бучим; вулкански карпи; старост; терциерни

Предмет на проучување во овој труд се петролошките и геохемиските карактеристики на терциерните магматски карпи од Република Македонија, Презентирани се најновите податоци за K-Ar, $^{87}Sr/^{86}Sr$, и REE во примероци од рудните области Кратово–Злетово, Саса–Тораница и Дамјан–Бучим. Рендгенските анализи на цели карпи ги потврдија составите на карпите како дацити, кварц-латити, трахиандезити, риолити и риодацити. Одредувањето на апсолутната старост со методот K-Ar покажа дека таа се движи од 31 до 14 Ma, потврдувајќи ја така олигоценско-миоценската старост, претходно одредена преку релативните методи. Утврдените односи $^{87}Sr/^{86}Sr$ (0,70504 до 0,71126) сугерираат дека материјалот потекнува од контактната зона помеѓу горната мантија и долната кора, каде што се одвивала контаминација на примарниот растоп. Новите податоци за REE, вклучувајќи ги негативните аномалии на Eu, покрај претходно утврдените односи La/Yb кои се во распон од 13.3 до 43.0 (Серафимовски, 1990), ги потврдуваат заклучоците за изворот на материјалот. Овие нови податоци ги потвдуваат претходните резултати, овозможуваат увид во терциерната магматска историја на областа и го сугерира точното потекло на материјалот кој ги создал терциерните магматски карпи.