New K-Ar, $^{87}Sr/^{86}Sr$, REE, and XRF data for Tertiary volcanic rocks in the Sasa-Toranica ore district, Macedonia

G. Tasev, T. Serafimovski, P. Lazarov
Department of Mineral Deposits, Faculty of Mining and Geology, Goce Delcev 89, 2000 Stip, Macedonina

Abstract. The latest K-Ar, $^{87}Sr/^{86}Sr$, and REE data for samples from Sasa-Toranica ore district are presented. Whole rock XRF analyses confirm host rock composition as dacites, quartz-latites, trachyandesites and rhyolites. K-Ar absolute ages range from 31 to 14 Ma confirming Oligocene-Miocene age as previously determined by relative methods. $^{87}Sr/^{86}Sr$ ratios (0.70954 to 0.71126) suggest material is sourced from the contact zone between the lower crust and upper mantle where contamination of primary melt occured. 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.

Keywords. Sasa, Toranica, volcanic rocks, age, origin, contamination, Tertiary

1 Introduction

Tertiary volcanic rocks in the Osogovo-Besna Kobila (Sasa-Toranica ore district) area regionally strike NW-SE for 100 km on both sides of Macedonia-Bulgaria border. Volcanic rocks in the area occur as ~50 m thick elongate dykes oriented roughly east-west (260°). From the Osogovo Mountain to the Besna Kobila Mountain (Osogovo-Luke-Karamanica), volcanic rocks are present as pyroclastics (Deve Bair), volcanic domes, dykes, necks and veins. Volcanic rocks at the Osogovo-Besna Kobila mountains cut the Paleozoic and Riphean-Cambrian metamorphic and igneous rocks and overlie Upper Eocene sedimentary sequences. The volcanics are mainly dacitic tuffs (Deve Bair), dacites, quartzlatites, rhyolites, trachyandezites, andesite-latites and occasionally lamprophyre veins (Sasa and Toranica localities).

2 Methodology

After detailed sampling and preparation at the Faculty of Mining and Geology in Stip, samples were sent to the Geological Department, University of Padova, Italy for whole rock XRF analysis, Actlabs in Canada for ICP-MS and INAA REE analysis, the Geology Department, Royal Holloway University of London, U.K. for TIMS $^{87}Sr/^{86}Sr$ ratios, and the Geological Institute in Budapest, Hungary for K-Ar dating.

3 Results and discussion

The new K-Ar, Sr isotope, REE, and whole rock XRF data from Sasa-Toranica host rocks provide insight into the composition, timing, and sources of volcanic activity in the region.

Dacites in the Luke-Kiselica area occur from the Karamanica mountain to the southeast at the Osogovo mountain (Serafimovski and Alexandrov 1995). The dacites contain plagioclase (37% An), small amount of orthoclase, quartz, biotite and amphibole phenocrysts. Their matrix is holocrystaline to hypocrystaline with glassy domains. Apatite, sphene and zircon were identified as accessory minerals; while sericite, chlorite, kaolinite, carbonate and metallic minerals are present as secondary minerals.

Quartzlatites are found near the springs of Lucka River and Kuprina Padina as dykes and at Samar and Karamanica as dykes and volcanic flows (Samar and Crcorija) over the volcano-sedimentary rocks. They are characterized by a porphyritic coarse grained texture with sanidine and plagioclase (35-40% An) phenocrysts, with secondary amphibole and augite phenocrysts. Sphene and zircon are accessory minerals. These rocks also contain metallic secondary minerals.

Hialoandesites appear as necks and lava flows over the Upper Pliocene sediments at Gradeska Mountain. These rocks are porphyry-vitrophyric with phenocrysts of plagioclase (37% An), biotite, amphibole and augite; apatite and zircon occur as accessory minerals.

Hypoabyssal and subvolcanic dacites and quartzlatites dominate the Sasa-Toranica zone (Osogovo). All the dacites and quartzlatites in the Sasa-Toranica zone experienced hydrothermal alteration. Dacites are holocrystalline with ~ 30% phenocrystals of andesine (5-16%), quartz (2-3%) and smal amount of orthoclase and coloured minerals (13-20%), mainly replaced by epidote, chlorite and carbonates. Hydrothermal alteration of andesites result in various new mineral assemblages. Illitization, seritization and propylitization dominante andesite alteration. Apatite, zircon, sphene and magnetite are present as accesory minerals, while pyrite, chalcopyrite, sphalerite and galena represent economic mineralization.

Close

Table 1: Chemical composition of rocks in the Toranica-Sasa ore region (%).

No.	SiO_2	TiO_2	Al_2O_3	Fe_t	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
MK1	63.93	0.65	14.35	4.34	0.11	3.15	3.91	2.56	6.32	0.6	3.96
MK2	69.1	0.43	14.92	3.04	0.08	1.38	2.78	3.38	4.58	0.24	3.43
MK3	60.48	0.54	16.43	3.18	0.1	2.86	6.85	3.67	5.57	0.28	3.05
MK4	68.46	0.44	15.47	3.15	0.08	1.24	2.69	2.66	5.47	0.23	4.03
MK5	69.09	0.44	15.0	3.02	0.1	1.4	2.89	3.4	4.37	0.24	4.06
MK6	67.62	0.46	15.53	3.11	0.07	1.42	3.27	3.24	4.98	0.24	3.87
MK7	65.73	0.63	14.94	3.98	0.09	2.86	3.14	2.88	5.19	0.49	3.69
MK8	69.19	0.4	14.72	3.16	0.31	1.87	2.51	1.58	5.93	0.27	2.77
MK9	68.35	0.41	15.15	3.35	0.34	1.46	3.7	1.46	5.37	0.25	5.31
MK10	68.59	0.42	15.29	3.22	0.3	1.38	2.85	1.95	5.66	0.24	4.33
MK11	68.65	0.4	15.29	3.02	0.24	1.32	2.55	2.85	5.35	0.24	3.56
MK12	63.0	0.52	16.24	5.12	0.1	2.0	4.04	3.28	5.36	0.28	4.96
MK13	66.83	0.56	15.52	4.14	0.4	2.58	2.47	2.43	4.66	0.21	4.93

Note: 1. MK-1 Trachydacite; 2. MK-2 Trachyte-rhyolite-dacite; 3. MK-3 Trachyandesite-trachydacite; 4. MK-4 Trachydacite; 5. MK-5 Dacite; 6. MK-6 Trachydacite; 7. MK-7 Trachydacite; 8. MK-8 Dacite; 9. MK-9 Dacite; 10. MK-10 Dacite; 11. MK-11 Trachydacite; 12. MK-12 Trachydacite; 13. MK-13 Dacite.

Quartzlaties are the most common rocks in the zone mentioned above. They occur as elongated dykes a few kilometers in length. These rocks are characterized by large phenocrysts of sanidine, andezine and femic minerals biotite, amphibole and rarely augite. Sanidine crystals are fresh and quite large (up to 5-6 cm). Quartzlatites were intensively hydrothermaly altered.

Transition rocks from quartzlatites to rhyolites are found at a few locations at Osogovo Mountain. Rocks with increased SiO_2 content occur near the Sekirica Tower close to the Macedonian-Bulgarian state border. These rocks were intensly propylitized and hydrothermaly altered.

The volcanic rocks from the Kozja River and Svinja River (Sasa Mine area) are dominantly dacites and quartzlatites. The volcanic rocks from this area are intensly propylitized and hydrothermaly altered. In addtion to previously mentioned secondary minerals, these rocks also contain ore minerals including pyrite, galena, sphalerite, sometimes chalcopyrite and occasionally traces of ceruzite, anglezite and malachite.Trachyandesites occur as small bodies at subvolcanic-volcanic levels in the Sasa-Toranica zone and its western borders. They are characterized by porphyry structure (fine grained porphyry) and crystalized microlitic or microtrachytic matrix. Phenocrystals of large, around 2 to 3 mm, andezine, sanidine, biotite, augite and hornblende are present. Apatite, sphene, and zircon occurs as accessory minerals. In comparison to the quartzlatites, the trachyandesites are characterized by lower SiO_2 concentrations. Similar rocks were identified in Pecovska Maala on the Osogovo Mountain on the Bulgarian side of the Bulgaria-Macedonian border.

Lamprophyres occur as small dykes near Sredno Brdo and Toranica. They are dark grey to brown rocks with a fine-grained porphyrtic texture and glassy matrix. Pyroxene, amphibole and biotite pheocrysts are identified. Accessory minerals are apatite, sphene and zircon.

Data obtained after geochemical analyses were entered into the computer software IGPET 2000 and Microsoft Excel; results are displayed in Table 1.

Use of IGPET 2000 software facilitated determination of rock types by the Total Alkali Silica (TAS) classification scheme, their classification under the calk-alkaline or tholeiitic series of rocks (Fig. 1, 2), and subsequent interpretations based on the classifications.

Graphical view of those determinations is presented in Figure 1.

TAS classification indicate that the rocks of interest mostly plot in the areas that define dacites, trachydacites, trachyandesites and rhyolites. All analyzed rocks plot in the area of calk-alkali series. Selected samples were analyzed for rare earth element (REE) concentrations. The analyses were performed at the *Active Labs, Canada*. REE concentration data for four samples are presented in Table 2 and plotted in a chondrite-normalized spider diagram in Figure 2.

From the spider diagram (Fig. 2) it can be seen that the rare earth elements in the Sasa-Toranica ore region have a decreasing trend. Comparing the left and right side of the diagram suggests there is a decrease in heavy rare earth elements, HREE with an atomic number higher than 63 (Eu), in comparison with light rare earth elements, LREE with an atomic number lower than 63 (Eu). The trend is typical as the product of fractionation of light

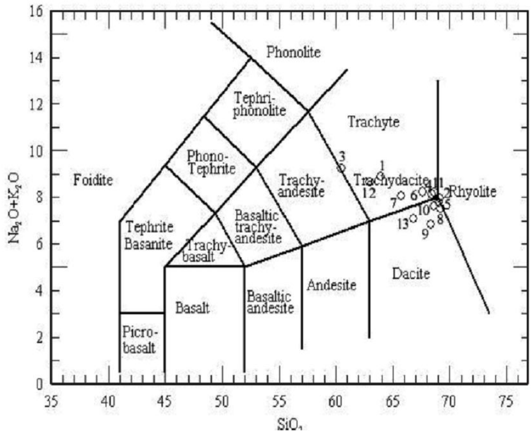

Figure I: Chemical classification and nomenclature of volcanic rocks in the Sasa-Toranica ore region, using diagram total alkalias vs. silica (Le Maitre et al. 1989).

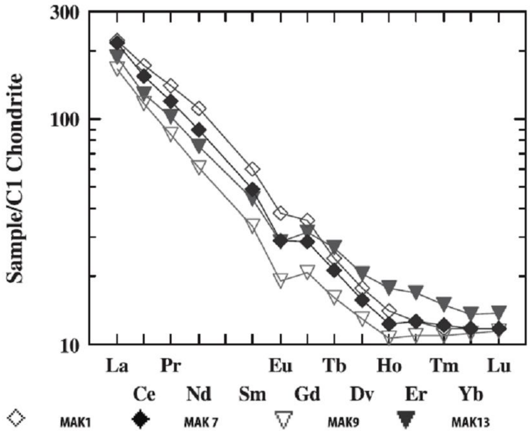

Figure 2: Diagram of normalized values of rare earth elements in comparison to those in chondrites, for rock samples from the Sasa-Toranica ore region.

Table 2: Rare earth elements content in rocks from the Sasa-Toranica ore region (ppm).

Element	MAK-1 I	MAK-7 I	MAK-9 II	MAK-13 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

Table 3: Values of Eu anomaly in samples from the Sasa-Toranica deposit.

Samples	Value of Eu anomaly
MAK-1 I	0.8289057
MAK-7 I	0.7740283
MAK-9 II	0.7276697
MAK-13 II	0.759748

rare earth elements and their increase in comparison to the chondritic values. Fractionation occurred as a direct consequence of partial melting, which according to the angle of the line in the diagram was not of high intensity.

Looking at the middle part of the diagram the value of Eu is slightly and negatively displaced from the "ideal" linear line between Sm and Gd defining a distinct negative Eu anomaly. A chondrite normalized, geometric mean calculation of the Eu anomaly is shown in Table 3.

From the table it can be seen that Eu anomaly values are in range from 0.727669702 up to 0.828905716, and all are less than 1, which implies a negative Eu anomaly (Rollinson 1992). Eu anomalies are controled by presence of feldspars. Eu^{2+} is compatible in plagioclase and K-feldspar, in contrast to the Eu^{3+} which is incompatible. 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 result in a negative Eu anomaly in the melt.

Accordingly, 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+}, by the processes of crystal fractionation or partial melting.

With the analyses of strontium isotopes (Table 4) was performed to construct a general model of formation for rock complexes at the Osogovo Mountain (Sasa-Toranica ore field). Strontium isotope analyses of rock samples from the volcanic rocks from the Sasa-Toranica ore field results in strontium ratios that range from 0.70954 up to 0.71125. The results suggest the magma forming Neogene magmatic complexes at the Osogovo Mountain is a product of primary magmatic melt originating from the border zone between upper mantle and continental crust where mixing and contamination of primary magma occurred.

The new data complies with previous $^{87}Sr/^{86}Sr$ data for Upper Tertiary calk-alkaline complexes formed in the Serb-Macedonian metallogenic province. $^{87}Sr/^{86}Sr$ ratios

Table 4: $^{87}Sr/^{86}Sr$ ratios in volcanic rocks from the Osogovo Mountain.

No.	Locality	Rock type	$^{87}Sr/^{86}Sr$
1	Golema R.950, Sasa	Quartzlatite	0.71051
2	Kozja R. IV_0, Sasa	Quartzlatite	0.70994
3	Svinja R. IV_0, Sasa	Quartzlatite	0.71126
4	Toranica – 2	Quartzlatite	0.71016
5	Toranica, TO-1	/	0.70979
6	Sasa	Andesite-latite	0.71064
7	Sasa	Quartzlatite	0.71024
8	Sasa, SA-2	/	0.70954
9	Toranica, MK-1	Trahydacite	0.71055
10	Sasa, MK-9	Dacite	0.71096

Table 5: Absolute age determination of volcanic rocks in the Sasa-Toranica ore region by the K/Ar method (Tasev 2003).

No.	Locality	Rock type	K-Ar age (m.y.)
1	Mal Ruen	Quartzlatite	28.38±1.09
2	Toranica-I	Quartzlatite	28.36±1.09
3	Sasa (Kozja R.)	Quartzlatite	30.72±1.19
4	Sasa (Kozja R.)	Andesite	29.25±1.13
5	Sasa (Crvena R.)	Granodiorite	31.16±1.40
6	Sasa	Andesite-latite	14.0±3.0
7	Sasa	Quartzlatite	24.0±3.0

of samples from Kozuf Mountain range from 0.7088 to 0.7090 and those for volcanic rocks from the Rogozna range between 0.7074 and 0.7085 (Serafimovski 1990).

Osogovo Tertiary igneous rocks are characterized by interesting distributions of Pb, Ba, Sr, Rb, Li, Cs and Be. Compared to Clark standard values Pb, Ba, Sr and Be are enriched while Li, Rb and Cs are similar to Clark standard values. Also, in magmatic processes it was noticed trend of increasing Li, Pb, Cs, Be, Rb and Ba concentrations going from fine-grained porphyry quartzlatites to coarse-grained porphyry quartzlatites (Serafimovski 1993a; Serafimovski et al. 2003). Tendencies in concentration distribution of elements show that the magmatic rocks originated from one magmatic chamber but during different time intervals producing different rock types. K-Ar isotopic age data give Tertiary magmatic ages in the study area. Results of this study are shown in Table 5.

The range of ages (Oligocene-Miocene) confirms the age determined by the relative methods.

4 Conclusion

This study of the volcanic rocks in the Sasa-Toranica ore region identified the distinct and uniform chemical composition of these rocks. The rocks are characterized as dacites, trachydacites, trachyandesites and rhyolites based on the TAS scheme. New K-Ar ages range from 31.16 ± 1.40 to 14.0±3.0 Ma confirming Oligocene-Miocene ages. Strontium isotope ratios and REE analyses identify magmatic material originated from the contact zone between the upper mantle and lower continental crust where certain contamination of primary melts occurred.

References

Rollinson H (1992) Using Geochemistry Data: evaluation, presentation, interpretation. pp. 352. Prentice Hall, an imprint of Pearson Education, Harlow, England.

Serafimovski T (1990) Metallogeny of the Lece-Halkidiki zone. Doctoral thesis, Faculty of Mining and Geology, Stip, p. 390 (in Macedonian)

Serafimovski T (1993a) Structural - Metalogenic features of the Lece-Halkidiki zone: Types of Mineral Deposit and Distribution. Faculty of Mining and Geology. Stip, Special Issue N. 2, 325 p, Stip.

Serafimovski T, Aleksandrov M (1995) Lead-zinc deposits and occurrences in the Republic of Macedonia. Faculty of Mining and Geology, Stip, Special Issue 4, p. 387 (in Macedonian)

Serafimovski T, Jelenkovic R, Tasev G (2003) Geodynamic Evolution and Metallogeny in the Southern Parts of the Balkan Peninsula. Geodynamics and Ore Deposit Evolution of the Alpine-Balkan-Carpathian-Dinaride Province. Final GEODE-ABCD Workshop. Programme and Abstracts. pp. 50. Seggauberg, Austria.

Serafimovski T, Jelenkovic R, Tasev G, Lazarov P (2003) Mineral Deposits Related to Tertiary Magmatism in the Southern Part of the Balkan Peninsula. Geologica Macedonica, Volume 17, pp. 19-23, Stip.

Tasev G (2003) Polymetalic mineralizations related to the Tertiary magmatism in the Republic of Macedonia. Faculty of Mining and Geology, Stip. Master thesis, p. 176. (in Macedonian)

Close