Analysis of the zircon population and Sr-isotope data of the Paleogene igneous rocks from Kyustendil area, SW Bulgaria

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Abstract. In the present study, we apply a combination of Sr-isotope whole-rock analyses and LA-ICP-MS U-Pb zircon dating to understand the magmatic evolution of the igneous rocks in the Ruen Zone, western Bulgaria, and bracket the time of their formation. This approach reveals a general interval of magmatic activity from 35.57 ± 0.27 Ma (Pishtilski volcanics) to 28.63 ± 0.58 Ma (cross-cutting dykes in the Osogovo Mountain). The volcanic rocks from the Prekolnitsa Graben are formed with significant (50%) crustal contamination/assimilation. Three major sources of crustal rocks can be outlined, with Triassic, Ordovician and Cambrian age, respectively. For the subvolcanic to plutonic magmatic rocks of the Osogovo Mountain, we suggest maturation and zircon crystallization over 2–4 Ma. The magma was generated dominantly in the continental crust and evolved through mainly fractional crystallization (FC) in the upper crustal chamber, whereas the evolution of the Osogovo dykes requires additional involvement of AFC (Assimilation and Fractional Crystallization) and contamination processes.


Keywords: Paleogene, volcanic rocks, zircon analysis, U-Pb dating, inheritance, assimilation.

INTRODUCTION

The Alpine evolution of southern Bulgaria is defined by Late Cretaceous subduction-related magmatism in the Srednogorie tectonic zone and post-subduction Cenozoic (mainly Paleogene) magmatic activity with migration of the magmatic front to paleosouth, in the Morava-Rhodope tectonic zone (e.g., Dabovski et al., 1991; von Quadt et al., 2005; Dabovski and Zagorchev, 2009). This magmatism has been studied extensively, and many aspects of its timing, general geochemical features or tectonic settings have been constrained. However, the development of new analytical techniques and accumulation of data give rise to new ideas or improvement of the existing models.

In the present work, we apply some of these techniques to the igneous rocks in the Kyustendil area, which is a part of the Ruen magmatotectonic zone (Harkovska, 1984). The latter crosscuts the bigger Morava-Rhodope tectonic zone (Dabovski and Zagorchev, 2009), being also a part of the Macedonian-Rhodope-North Aegean volcanic zone (Dabovski et al., 1991). Significant geological constraints on the petrology and geochemistry of the rocks have been provided (Arnaudova, 1973; Harkovska, 1974; Machev, 2001a, b; Grozdev et al., 2010). The age of these magmatic rocks is well constrained as latest Eocene and early Oligocene both by their interrelations with paleontologically dated sediments (Ivanov et al., 1971) and with isotopic dating (Harkovska and Pécskay, 1997; Graf, 2001; Kounov et al., 2004, 2012; Grozdev, 2011).

We apply U-(Th)-Pb “in situ” zircon dating of the Paleogene volcanic and plutonic rocks from the Kyustendil area, which give evidence not only for the final magmatic crystallization of zircons, but provide information for the magma sources as well. In this research, we used a more detailed approach, with special attention to all available zircon crystals in the samples (the zircon population) combining zircon internal morpho-
logy (from CL-images) with dating of magmatic rims/grains, inherited cores and crystals. Such approach brings insights into the processes of formation of igneous rocks: with crustal assimilation/contamination or without interaction with hosting rocks. We show that the obtained zircon ages reveal the interaction of the magma with exact terranes, shedding more light on the deeper crustal levels and the outcropped basement rocks. Finally, zircon analysis is complemented with whole-rock (WR) Sr isotope data to provide an accurate assumption about the petrogenetic paths of the magma that produced the variety of intrusive, shallow intrusive and volcanic rocks in the Ruen zone of the Morava-Rhodope tectonic zone.

GEOLOGICAL SETTING AND SAMPLING

The study region is situated about 10 km WSW of Kyustendil Town, SW Bulgaria (Fig. 1). The Cenozoic (Paleogene) magmatic rocks crop out in the Prekolnitsa Graben (Harkovska, 1974) and the Osogovo Mountain, forming an elongated strip with NW-SE direction defined as the Ruen magmatotectonic zone (Harkovska, 1984). They intrude or overlie high- and low-grade metamorphic rocks of the Lower and Vlasina units of the Serbo-Macedonian Massif (Antic et al., 2016, and references therein) corresponding to the Ograzhdene, Struma (including Osogovo-Lisets Complex: Kounov et al., 2004) and Morava units of the Morava-Rhodope tectonic zone (Dabovski and Zagorchev, 2009).

In the Prekolnitsa Graben, five stages of Cenozoic magmatic activity can be distinguished (from base to top, Fig. 1): 1) volcaniclastic and tuff material (mainly acid in composition) of the basal conglomerate formation (Harkovska, 1974); 2) Pishitski volcanics, classified as trachyryodacites (Grozdev et al., 2012); 3) Gyueshevo volcanics, represented by sub-volcanic bodies and flows (?) of fine to coarse porphyritic dacite to rhyolite; 4) Kopriva body, being large NW elongated coarse sanidine-phryic trachyryodacite; and 5) felsic rhyolite dykes, which crosscut the Kopriva body and represent the final magmatic activity in the Graben.

The Pishitski trachyryodacites are extruded in the sediments of the Dolno Selo Formation. The latter are built up predominantly of sandstones (alternation of sandstones, siltstones and polymict conglomerates). These sediments are intersected and overlain by the Gyueshevo volcanics.

Field relationships show...
that the Kopriva body crosscuts both the sedimentary succession (including the Pishtilski volcanics) and the Gyueshevo volcanics.

The Cenozoic magmatic activity in the southwestern slopes of the Osogovo block (Zagорчев and Russeva, 1982) is expressed by the Osogovo granite intrusion (Fig. 1) and numerous dykes. The Osogovo granite is a relatively large plutonic body (about 150 km$^2$), elongated in NW-SE direction and intruded in predominantly high-grade metamorphic rocks. Swarms of coarse sanidine-porphyry rhyolitic to granite-porphyry dykes intersect both the metamorphic basement and the Osogovo granite with the same NW-SE orientation.

The Paleogene igneous rocks of the Ruen zone are volcanic, subvolcanic and plutonic, with predominantly acid composition (Harkovska et al., 1984; see also Table 1). They are determined (Grozdev et al., 2010) as rhyodacites (Gyueshevo volcanics V11, V35), trachryhyodacites (Kopriva volcanics, V13, V154, and Pishtilski volcanics V47, V186) and granites (Osogovo V20, V172) to granite-porphries (dyke sample V18). On the SiO$_2$ versus K$_2$O diagram, they plot in the field of the high-K calc-alkaline magmatic series.

In the present study, we discuss the Pishtilski trachryhyodacites (V47, V186), Gyueshevo rhyodacites (V11, V35), Kopriva trachryhyodacites (V13, V154 – not shown on the map), as well as the Osogovo granite (V20, V172) and granite-porphyry dykes (V18, V24; Fig. 1).

### ANALYTICAL METHODS

The sample preparation and zircon separation were performed at the Geological Institute of the Bulgarian Academy of Sciences (GI-BAS) in Sofia. Zircon crystals for LA-ICP-MS U-Pb dating were embedded in epoxy-resin and the mounts (pellets) were polished to the middle of the grains prior to CL and BSE images, which were taken on a CamScan CS 4 scanning electron microscope (SEM) at ETH-Zurich equipped with an ellipsoidal mirror. The “in situ” LA-ICP-MS (U-Th-Pb) analyses were performed, using both the Geolas 193 nm laser with Elan 6100 PE system at ETH-Zurich and the NW UP193FX excimer laser with DRC-e PE system at the Geological Institute of BAS. Energy density on sample ca 7–7.2 J × cm$^{-2}$, repetition rate of 8 Hz and ablation craters of 35–40 mm were the common analytical conditions.

The GJ1 zircon standard (Jackson et al., 2004) was used as primary standard reference material (SRM) and Plesovice (Slama et al., 2008) as secondary SRM for internal control. The results were calculated offline, using GLITTER 4.0 (Macquarie University). A Th-disequilibrium correction was applied to all analyses. For each sample, all discordant zircons were used to calculate a Concordia age, or a mean $^{238}$U/$^{206}$Pb age, and probability density was plotted with the application of ISOPLOT 3.0 (Ludwig, 2003).

The whole-rock $^{87}$Sr/$^{86}$Sr and $^{143}$Nd/$^{144}$Nd ratios were obtained after digestion of whole-rock powder in HF and HNO$_3$ and chromatographic cleaning procedure. Sr and Nd isotopes were analyzed on Thermo TRITONPLUS TIMS at ETH Zurich. The measured $^{87}$Sr/$^{86}$Sr ratios were normalized to $^{87}$Sr/$^{86}$Sr value of 0.11944. The measured $^{143}$Nd/$^{144}$Nd value of the NBS 987 standard obtained during the period of measurements was 0.512637±12.

### RESULTS

The initial $^{87}$Sr/$^{86}$Sr data of the studied igneous rocks (calculated for an age of 30 Ma) are in the interval of 0.708 to 0.712. On the diagram SiO$_2$ versus K$_2$O, two fields are clearly distinguishable: one group includes the volcanic rocks from the Pre-
kolnitsa Graben, and another group is defined by the rocks of the Osogovo block.

The subvolcanic to plutonic group has similar silica content but different, more evolved initial Sr-isotopes ratios. Minor increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ in the Kopriva volcanics infers assimilation and fractional crystallization (AFC) trend.

The position of the Osogovo granite and its dykes on the diagram gives evidence for either different crustal source (older crustal rocks with higher Rb content) or further assimilation of crustal material in the source. According to the diagram (Fig. 2), in the middle-upper crustal chamber the Osogovo granite (V 20, V 172) evolved through mainly FC and was less contaminated with crustal material than the granite-porphry dykes (V18, V 24). For the latter, we may assume involvement of AFC as well. The similarity between the strontium isotope characteristics of the Osogovo intrusive and the Gyueshevo shallow intrusive rocks and volcanics is remarkable.

LA-ICP-MS zircon age data are provided in the Appendix. In the text below, we present only concordant U-Pb zircon ages, excluding the mixed or discordant ages.

The zircon population of the Pishtilski volcanics is represented by equal amounts of Paleogene grains as autocrysts (own magmatic) zircons (Miller et al., 2007) and as Paleogene rims on older zircon grains. The calculated Concordia age of 35.57±0.27 Ma is shown on the Concordia diagram (Fig. 3a). The older zircon cores (about 50%) are mainly in the range of 470–550 Ma, or rarely Carboniferous (Fig. 3b).

The zircon population of the Gyueshevo volcanics is represented by 2/3 Paleogene grains with significant amount of antecrysts (Fig. 3c, d). Only 1/3 of all analyzed crystals are older zircon cores and grains, which represent inherited xenocrysts. The determined concordant age is 30.78±0.49 Ma. The measured older zircon ages in cores or xenocrysts define two peaks of mean $^{206}\text{Pb}/^{238}\text{U}$ ages at around 200 Ma and 250 Ma. Some single grains/cores were dated at 300–350 Ma and 530 Ma.

In the Kopriva volcanics (Fig. 3e, f), the Paleogene own magmatic zircons (autocrysts) without old cores represent 1/3 of the analyzed grains. The majority of the Palaeogene ages were recorded as zircon rims on inherited zircon crystals, which are 50% of all grains. The measured older ages belong only to old zircon cores, and xenocrysts were not observed. Two pronounced time intervals (Fig. 3f) are characteristic there: around 205 Ma and 250 Ma, correspondingly. An obviously vast amount of antecrysts reveal several well-expressed peaks for 33–34 Ma, 36 Ma and 40 Ma (Fig. 3e). The youngest zircon crystallization at 29.29±0.77 Ma is determined by two concordant zircon crystals.

The zircon populations from the Osogovo granite are dominated by own magmatic zirconcs, and only two older zircon cores occur with ages of 474 Ma and 1,803 Ma, respectively. The majority of measured ages are discordant. Only four grains reveal concordant but different ages (Fig. 4a, b). Some intervals resulting from antecrysts’ ages can be outlined at around 31 Ma, 33 Ma and 34 Ma. The youngest zircon age

![Fig. 2. SiO$_2$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ plot, informative for the magma evolution trends. Abbreviations: AFC – assimilation and fractional crystallization, SC – source contamination, FC/M – fractional crystallization/melting.](image-url)
Fig. 3. U/Pb age data and probability density plot (PDP) diagrams of the volcanic rocks from the Prekolinitsa Graben: a) Concordia diagram of the Pishtilski type; b) PDP diagram of the Pishtilski type; c) Concordia diagram of the Gyueshevo type; d) PDP diagram of the Gyueshevo type; e) data for Paleogene zircons of the Kopriva type; f) ages of inherited older zircons in the Kopriva type.
zircon dating of sample V 18. The age of the dyke is defined by five concordant grains at 28.63±0.58 Ma (206Pb/238U mean age; Fig. 4c). They represent the final magmatic activity in this region.

**DISCUSSION**

The combination of WR Sr-isotope tracing and U-Pb dating provided information about the time of the magmatism and magma evolution during its ascent through the crust and storage in middle- to upper-crustal chambers. The crystallization age of the zircons, defined by the in-situ U-Pb LA-ICP-MS method, revealed a general interval of magmatic activity from 35.57±0.27 Ma (Pishtilski volcanics) to 28.63±0.58 Ma (cross-cutting dykes in the Osogovo Mountain). We did not apply pretreatment of the zircons (annealing or chemical abrasion: Mattinson, 2005; von Quadt et al., 2014), and thus we consider these ages as minimum time of crystallization. Our dating (including the error uncertainties) is in good agreement with field relationships (see above) and previous publications on the stratigraphy of the Ruen Zone (Harkovska, 1974).

The zircon population analyses and age data for all studied rocks show longer zircon growth, which is documented by the vast amount of antecrysts (Fig. 3e) with ages 33–34 Ma, 36 Ma and 38 Ma (Figs 3, 4). This zircon characteristic suggests possible magma replenishment or reheating of the magma chamber or chambers with rejuvenation of the volcanic activity.

Evidence for magma modification processes through assimilation and contamination is provided by the analysis of the zircon population in the studied rocks. The zircon population of the Pishtilski volcanics show significant amount (about 50%) of inherited zircons (rimms and grains) from crustal rocks (units) with Early Paleozoic to Neoproterozoic age (470–550 Ma; summary in Fig. 5). This is in good agreement with the nowadays surface geology that is
defined by high- and low-grade metamorphic rocks of the Lower and Vlasina Units of the Serbo-Macedonian Massif (Antic et al., 2016, and reference therein), corresponding to the Ograzhden, Struma and Morava units of the Morava-Rhodope tectonic zone (Dabovski and Zagorchev, 2009). The volcanic and subvolcanic rocks of the Gyueshevo and Kopri-va, and partly the Osogovo, dykes (unpublished CA- ID-TIMS data) show that the inheritance (more than 50% of zircon population) is dominated by zircons of Triassic age. Triassic granitoids are mainly out- cropped in the Ograzhden Unit/Vertiskos (Ograzhden batholith, Igralishte and Nikudim plutons, Skrut granite in Bulgaria and FYROM: Zidarov et al., 2007; Peytcheva et al., 2009; Georgiev et al., 2012). Evidence of Triassic magmatism in the basement was also published by Zagorchev et al. (2017). We may suggest the existence of buried (not outcropped) Triassic plutons in the deeper parts of the crust. Other sparse inherited zircons mark also Carboniferous and early-middle Proterozoic sources that may be related particularly to the high-grade rocks of the Ograzhden Unit (Peytcheva et al., 2015).

We suggest mainly AFC and SC processes in the source, and interaction of the “primary” magma with the local continental crust in the middle to up- per crustal chambers, based on the strontium isotope characteristics. $\text{Sr}^{87}/\text{Sr}^{86}$ initial ratio increases slightly with crustal assimilation (Fig. 2) in the case of the Kopriva volcanics (0.7088–0.7094). The very close strontium isotope characteristics argue for a common upper crustal source chamber for both the Kopriva and Pishtilski volcanics.

The considerably higher initial strontium ratio in the Gyueshevo volcanics, Osogovo granite and related dykes (0.7112–0.7122) requires involvement of older crustal material with higher Rb content. Assimilation/ contamination of crustal rocks is supported by the zir- con population analyses for the Gyueshevo volcanics, but not for the Osogovo granite, at least in the studied samples. This fact could be explained if we consider the Osogovo pluton as explored part of an upper crustal chamber, where the central parts are less contaminated and homogenized; there the magma evolved through fractional crystallization with very small changes in chemical (and mineral) composition, although the life of the chamber is estimated as 2–4 Ma (anti- and auto-cryptic zircons). The Gyueshevo volcanics and shallow intrusives may have been fed by the same cham- ber (as evident from the Sr-isotope ratios), but they intruded from the marginal upper parts of the chamber and were, therefore, more contaminated with zircons from host rocks.

**CONCLUSIONS**

(1) The Paleogene volcanic/subvolcanic rocks in the Ruen Zone, the greater part of which are actually the Kopriva trachyryhodacites from the Prekolinitsa Gra- ben, are formed through crustal assimilation and frac- tional crystallisation (AFC-process).
(2) According to zircon population analysis, the amount of crustal input in the Kopriva volcanics is at least 50%, and points to assimilation of Triassic basement rocks.

(3) The subvolcanic to plutonic acid rocks from the Osogovo Mountain and the Gyueshevo volcanics are products of one evolving, long-lived upper crustal magma chamber.

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