Zircon composition as an assessment tool of magma fertility: a case study of Paleogene igneous rocks in the western parts of the Morava-Rhodope Zone

Химичен състав на цирконите като средство за оценка на рудоносен магматизъм: примерно изследване на палеогенски магмени скали от западните части на Моравско-Родопската зона

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Keywords: zircon chemistry, trace elements, REE, fertile rocks, LA-ICP-MS.

Introduction. In the present study we provide data for the chemical composition of zircons from Paleogene igneous rocks of different magmatic and metallogenic regions in the western parts of the Morava-Rhodope Zone on the Balkan Peninsula, such as: Kratovo and Bajlovce areas (Macedonia), Surdulica region (SE Serbia) and Kyustendil area (SW Bulgaria). These regions are known for their Pb-Zn ore deposits of economic importance and some Cu (Au) ore mineralizations related to the Upper Paleogene magmatic rocks. We used previously dated (U-Pb LA-ICP-MS) zircons of volcanic origin mainly. The goal of the zircon tracing was to establish the amount of hydration and the oxidation state of the magmas, which are favourable for metal transport and ore precipitation (e.g., Richards et al., 2012).

Theoretical background and analytical methods. The hydrothermal ore-forming fluids are generally related to calc-alkaline rocks of granodiorite-granite composition (Hedenquist, Lowenstern, 1994). The ore-forming magmas have distinctive whole-rock chemical composition, such as high Sr/Y, V/Sc and Eu/Eu* ratios (Richards et al., 2012; Rohrlach, Loucks, 2005; Chiaradia et al., 2012; etc.). Unfortunately, these ratios (Sr/Y and Eu/Eu*) are easily affected by weathering or hydrothermal alteration processes of the rocks. On the other hand, zircon is very common in intermediate to felsic igneous rocks and can survive significant detrital transport or intensive hydrothermal alteration, preserving the signatures of the original magmatic environment (Rohrlach, Loucks, 2005; Lu et al., 2016).

The trace-element composition of zircon is easily obtained with LA-ICP-MS technique. For present study we used the equipment of the Geological Institute, Bulgarian Academy of Sciences. Because of the presence of small mineral inclusions, common for zircon crystals, we applied the proposed by Lu et al. (2016) approach. We excluded analyses with La >1 ppm, which indicate apatite contamination, leading to increased LREE concentration in the zircon grain; Ti >50 ppm revealing contamination with Ti-(Fe-) oxides; Ba >8 ppm representing contamination from fluid inclusions or cracks in the zircon. The Ce/Nd ratio is taken for estimation of the Ce/Ce* anomaly, because the low (often below the detection limit) La and Pr content.

Results and discussion. The “hidden” ore-potential of the investigated Paleogene magmatic rocks is shown on Figure 1. We plotted the data not only for the Paleogene zircons but also for inherited grains and cores. The chondrite normalized REE patterns of the zircons (Fig. 1A) reveal negligible to well pronounced negative Eu-anomaly. In fertile magmatic suits this patterns should be flatter, without or with weak Eu-anomaly and should reveal Eu/Eu* ratio higher than 0.3 (Lu et al., 2016). An obvious apatite contamination (blue triangles, age 205 Ma) for the inherited zircons from the basement of Kratovo area is observed. The weak negative Eu-anomaly is explained by higher water content of magma, which suppresses the plagioclase crystallization.

On the diagrams of Figures 1B and 1C almost all studied zircons from the Paleogene rocks fall into the field of the perspective fertile magmatic rocks. Only inherited zircons from the basement rocks show infertile compositions. The Surdulica area zircons data plot close to the fields borders and do not indicate clear magma fertility (Fig. 1B, C). In the other regions the majority of Paleogene zircons reveal Eu/Eu* ratio above 0.3 and (Ce/Nd)/Y above 0.01) pointing to magmatism with high magmatic water content or high oxidation state, or both. Using the Ce/Nd ratio (Figs. 1B, 1D) we may conclude that the majority of zircons crystallized at high oxygen fugacity conditions. The ratio (Eu/Eu*)/Y is consistent (Fig. 1D) with amphibole fractionation that depleted the melt in Y and was complementary to the water-suppressed plagioclase crystallization (Richards, 2011). For all fertile igneous rocks the Dy/Yb ratio should be less than 0.3 (Lu

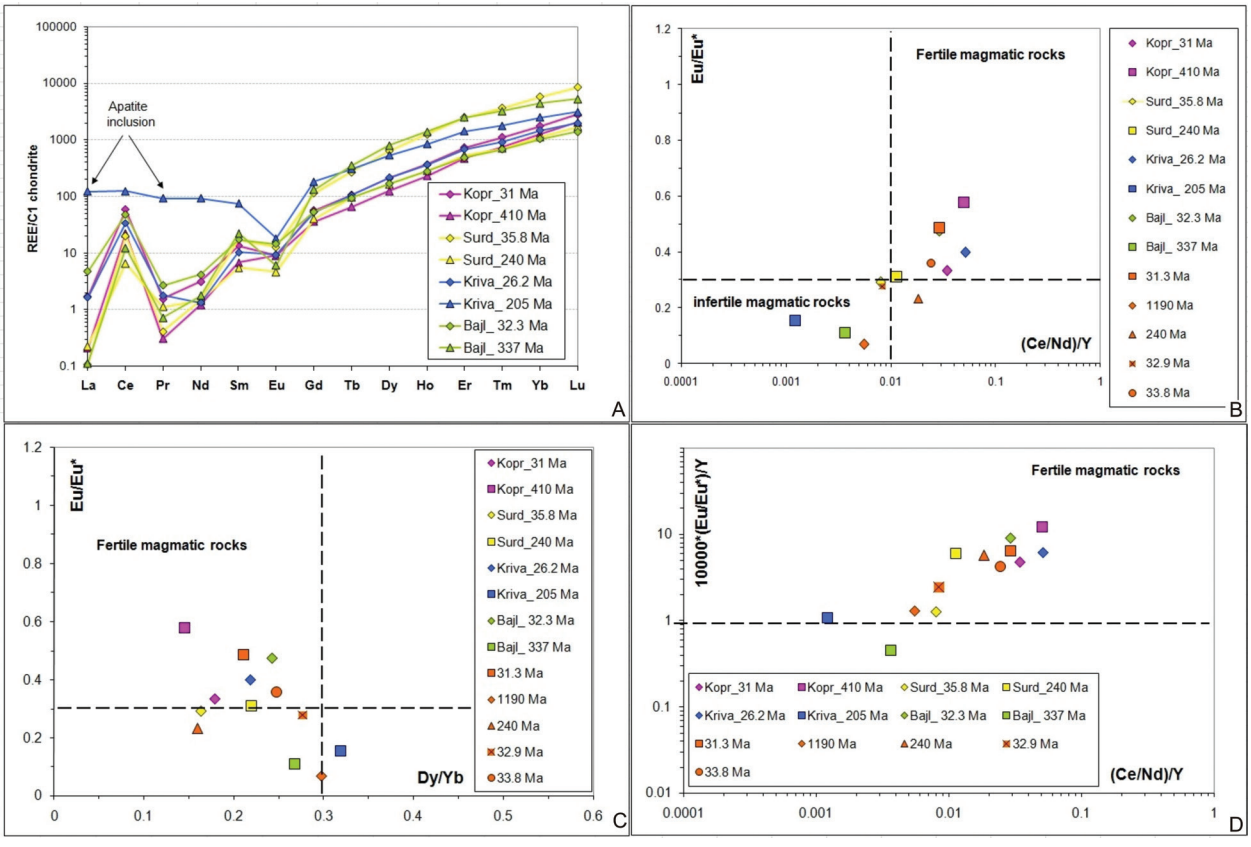

Fig. 1. Chemical composition of zircons: *A*, C1 chondrite normalized REE pattern, values after Sun and McDonough (1989); *B*, zircon Eu/Eu* vs. (Ce/Nd)/Y plot; *C*, zircon Eu/Eu* vs. Dy/Yb plot; *D*, zircon 10 000*(Eu/Eu*)/Y vs. (Ce/Nd)/Y plot. The used colors refer to: Kopriva trachyrhyodacites (pink), altered Kopriva type (orange); Surdulica granodiorites (yellow); Kratovo latites (blue); Bajlovce trachytes (green).

et al., 2016 and reference therein) as a proxy of amphibole fractionation with MREE incorporation; as a consequence, amphibole fractionation in hydrous melts should decrease the Dy/Yb ratio (Davidson et al., 2007).

Generally, the indicative ratios in the zircons, which were proposed by Lu et al. (2016; see also references therein) may discriminate unperspective A-, S-type and some I-type dry and reduced granitoids, from potentially mineralizing I-type granitoids.

Conclusions. Based on the zircon trace-element composition of the Paleogene zircons in the studied rocks we may conclude a generally fertile magmatism, sourced probably in the subduction enriched subcontinental mantle lithosphere and substantially modified in the crust through early amphibole fractionation (lower Dy/Yb ratio) and late plagioclase fractionation (Eu/Eu* ratio >0.3). The oxidation state of magma (estimated by the positive Ce-anomaly in zircons – Ce/Nd and (Ce/Nd)/Y ratios) was also in favour of ore precipitation. Consequently, the data is in agreement with the presence of ore deposits (mainly Pb-Zn ± Cu) in the studied regions in Macedonia, Serbia and Bulgaria. They show the potential of the zircon chemistry as an exploration tool.

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