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The rare earth elements in zircons as pathfinder of geological events

Редкоземните елементи в циркони като индикатор за разчитане на геоложки събития

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Abstract. The usual main purpose of the zircon investigation is to determine the precise age of particular rocks, applying the U-Pb isotope method. In this study we attempt to reveal the vast potential of zircons in understanding the magmatic and modification processes, as well as the structure of the deeper Earth's interior, using the analysis of the zircon population of the major volcanic variety in the Ruen tectono-magmatic zone, Kyustendil area, SW Bulgaria. The ascending magmas crosscut different rock types and units along their path to the Earth's surface. Using the zircon crystal analysis, we may make consideration about the age and chemical characteristics of these units. The trace and rare earth element (REE) content of the zircons brings insights for the rock formation time and discloses characteristics of the deeper parts of the Earth's crust.

Keywords: zircon population, REE composition, magmatism, orogeny, paleoenvironment.

Introduction

Zircon crystals are remarkably useful in geological studies, not only for age dating of magmatic or metamorphic rocks but they can bring significant information about the geological history of a particular region. The characteristics of their internal crystal structure, observed by cathodoluminescence (CL) images, reveal their evolution through the presence of autocrysts, antecrysts, xenocrysts or inherited old zircon cores (Miller et al., 2007). The chemical composition of zircons in terms of trace element and rare earth element (REE) incorporation has distinct signatures, resulting of magmatic, metamorphic or hydrothermal alteration processes. Using *in-situ* LA-ICP-MS U-Pb isotope age data we can link the established characteristic trace-element features with the corresponding geological process, e.g. linking the xenocrysts and inherited zircon cores with the source or host rocks, and autoante crysts with the zircon growth in either short- or long-lived magma chambers. The formation of the volcanic rocks results from magmas that are generated either in the subcontinental lithosphere or the Earth's crust; during their ascent, the magmas may evaluate through FC (fractional crystallization), AFC (assimilation and FC), mixing processes and may also "grab" and contain structurally and chemically diverse zircons. They might efficiently serve in a peculiar manner as a natural "drill hole" within the Earth's interior, bringing information about the structure of a particular terrain, bringing data from deeper levels in the crust. The analyses of the zircon population can be used also for paleoenvironmental reconstructions.

To demonstrate the effectiveness of the combined age and trace-element studies of the zircons, in the present study we apply the analysis of the zircon population on volcanic rocks from the Kopriva trachyrhyodacites in the Ruen tectono-magmatic zone, Kyustendil area, SW Bulgaria.

Analytical methods

Zircon crystals were separated from 63–250 μm size fractions using standard heavy liquid techniques. Single zircon crystals were then handpicked and mounted in epoxy resin and polished to the

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middle of the grains. To reveal the internal textures of the crystals we made cathodoluminescence (CL) and backscattered (BSE) images of the zircon grains using SEM-EDS (JEOL JSM-6610 LV) scanning electron microscope (SEM) at University of Belgrade (Faculty of Mining and Geology) and CamScan CS 4 scanning electron microscope (SEM) at ETH-Zurich – equipped with an ellipsoidal mirror. Zircon LA-ICP-MS U-Th-Pb isotope dating and analysis of the trace and REE were made at the Geological institute of BAS, using NW excimer laser with DRC-e PE system and the ETH-Zurich system of Geolas 193 nm laser connected with Elan 6100 PE. The software used for data reduction is Glitter for the U-Th-Pb dating of the zircons and SILLS (Signal Integration for Laboratory Laser Systems) for their composition. Isotope age calculations and plots are constructed by ISOPLOT and Microsoft EXCEL.

Geological setting

The general magmatic activity in SW Bulgaria, particularly in the Kyustendil area is genetically connected to the Ruen tectono-magmatic zone (Harkovska, 1984). It represents a major tectonic fracture with NW-SE (135–144°) orientation with a variable width from 5 to 12 km, extending from SE to NW on over 120 km within the territory of three countries: Bulgaria, RN Macedonia and Serbia. The dominant rock type in the zone is referred to as the Kopriva trachyrhyodacites with very characteristic porphyries of K-feldspar (Harkovska, 1974; Grozdev, 2014 and references therein). The latter form 1–2 to 5 cm pale pink sanidine crystals with perfect crystalographical shape, or twin crystals. The Oligocene (34–28 Ma) age of the magmatic activity in the zone is confirmed by precise U-Pb zircon dating (Grozdev, 2014).

Results

The zircon population from the representative Kopriva volcanics in the Ruen zone is characterized by crystals with complex internal structures (Grozdev, 2011). The Paleogene magmatic age is recorded mostly on the rims that overgrew older zircon cores. In the zircon population only ~ 1/3 of the studied crystals are autocrysts and the rest of the obtained Paleogene ages are acquired from zircon rims (Fig. 1A, B). The age of Kopriva volcanics is defined at 31.1±1.3 Ma (Grozdev, 2014), while the core ages are predominantly in the interval of 220–256 Ma (Fig. 1A) with a secondary weak age peak at 400–460 Ma. The results with 220–256 Ma suggest some magmatic activity during the late Paleozoic and early Mesozoic time in the region of study, whereas the plutonic body was trapped in the deeper crustal levels as suggested by the age of the older cores. The CL-images (Fig. 1B) clearly reveal the older zircon cores (brighter in CL), are overgrown by younger Paleogene zircon rims (darker in CL).

The geochemical comparison of the Paleogene and Permian–Triassic zircons reveals similar rare-earth element composition (Fig. 1C–D) and REE chondrite-normalized patterns. They latter are depleted in LREE, showing very high M-HREE and pronounced positive Ce-anomaly with some Eu depletion. The vast majority of the investigated zircons (Fig. 1D) both from Paleogene rims and Permian–Triassic zircon cores demonstrate a magmatic origin of their formation (Zhu et al., 2022) according to the HREE content and the Lu/Dy ratio in the zircons.

Discussion and some conclusions

The majority (more than half) of the inherited cores of older zircons observed in several samples from the Kopriva trachyrhyodacites clearly suggest crustal assimilation (Grozdev et al., 2017). Apparently, the Paleogene magma assimilated crustal materials in deep lower-middle crust magma chamber before their appearance on the Earth's surface by later processes (Grozdev, 2014). It is supposed however that zircon saturation and overgrowth start in an upper-crustal magma chamber after the plagioclase fractionation, which is indicated by the negative Eu-anomaly and high M-HREE content in the Paleogene zircons. If the studied trachyrhyodacites were developed in the middle or lower crust, this would be evidenced by the depletion of MREE and HREE, corresponding to amphibole and garnet formation, respectively. For the P-T zircon cores we suggest identical evolution and magmatic origin because of the similar REE-patterns and the magmatic oscillatory zonation of the older inherited (Permian–Triassic) and Paleogene rims.

The zircon core ages point to a magmatic event on the boundary of the Paleozoic–Mesozoic eras. Early–Middle Triassic age is determined for the Krupnik granite (Zagorchev et al., 2017), for the granitic Igralishte pluton (Peytcheva et al., 2009) and Skrut granite (Zidarov et al., 2007) in the Ograzhden and Belassitsa Mts, and for the Kerkini-Arnea granites in Greece 243–248 Ma (Poli et al., 2008), as well as the Berovo granitic pluton (252±2Ma) in RN Macedonia (Georgiev et al., 2012). These granitoid plutons are intruded into the metamorphic rocks of the Variscan basement, represented by the Struma Unit in the study area (Dabovski, Zagorchev, 2009). Our zircon data support the idea that in the Kyustendil region, terrains like Struma Unit are presented in

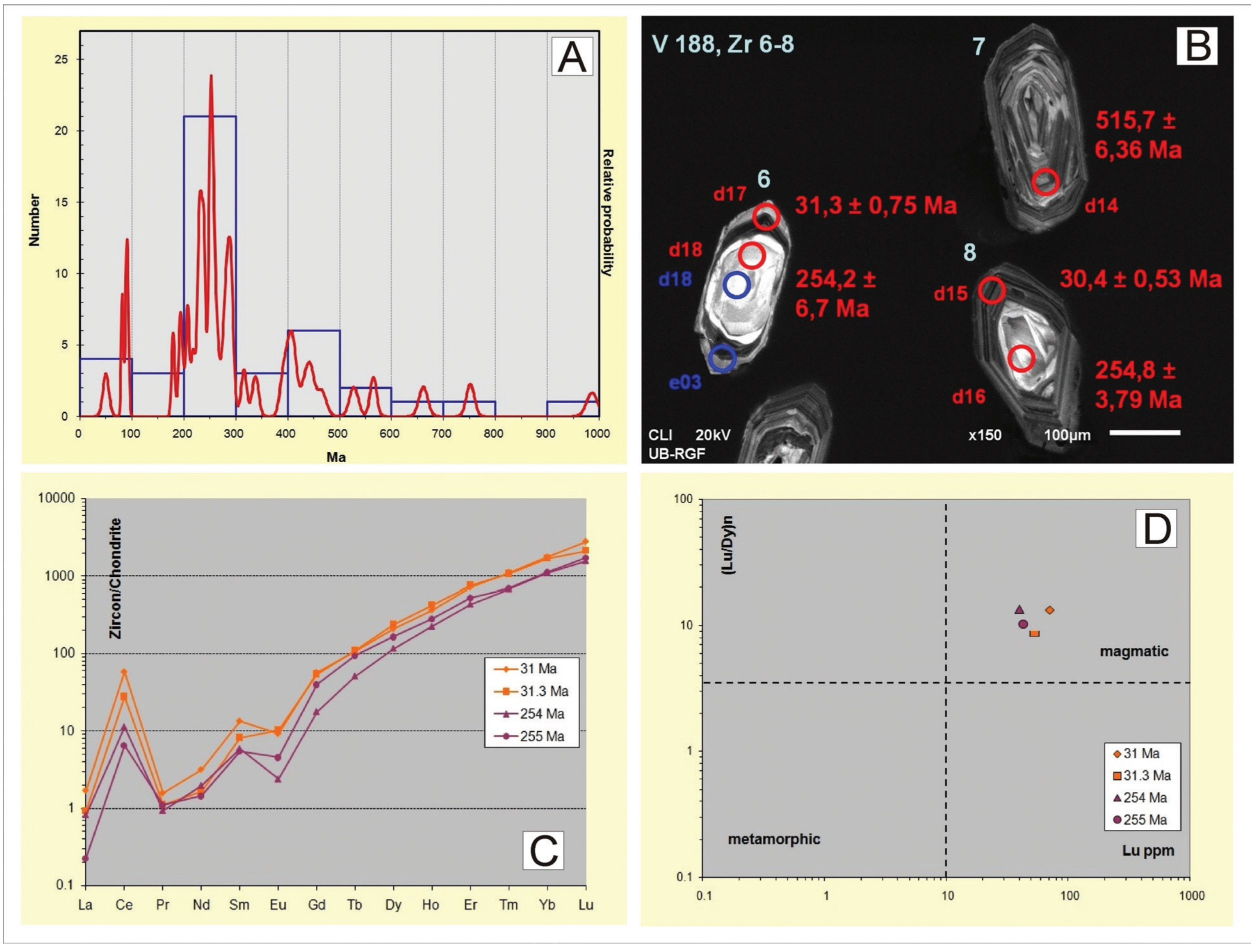

Fig. 1. *A*) Probability density plot of zircons; *B*) CL-images of zircons with ablation craters for ages (red) and composition (blue); *C*) REE-normalized pattern for zircons; *D*) Chondrite-normalized (Lu/Dy)n vs. Lu in ppm, for zircons

depth and include similar granitic plutonic bodies, overthrusted by the Morava Unit.

The presence of inherited zircons in the volcanics of the Prekolnitsa Graben is an important source of information about the structure of the deeper part of the crust. Using the data for early Mesozoic protolithic age (around 250 Ma), we conclude that the Early–Middle Triassic magmatism is contemporary with another geological event at that time – the deposition of the red-colored continental conglomerates and sandstones from the Permian and Lower Triassic formation in Bulgaria. By analogy with the so-called “Old Red Sandstone” with Devonian age, widely cropping out on the British Island as more than 10 km thick unit, we may interprete as a product of erosion of greater paleo-orogen with dimensions like the Himalayas (Pimpirev, 2019). Therefore, we may speculate that magmatic intrusion at that time and intensive erosion/deposition in continental dry environment operated together, driven by the buoyancy uplift of the ancient paleo-orogen, namely the Variscan orogen.

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