Chemical composition of sanidine crystals from the Kopriva trachyrhyodacites, Prekolnitsa graben, SW Bulgaria

Химичен състав на санидинови кристали от Копривският тип трахириодацити, Преколнишки грабен, ЮЗ България

Valentin Grozdev, Rossitsa D. Vassileva
Валентин Гроздев, Росица Д. Василева

Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 24, 1113 Sofia, Bulgaria;
E-mail: val.grozdev@abv.bg

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Introduction

A distinctive mineralogical feature of the Paleogene volcanic rocks from Prekolnitsa graben, SW Bulgaria, are the big (from 1 to 5, rarely up to 10 cm) sanidine crystals in the Kopriva volcanics (named after Harkovska, 1974). The host rocks are characterized petrologically and geochemically as trachyrhyodacites (Grozdev et al., 2012). The optical and chemical properties of the sanidine single crystals and Karlsbad twins were investigated by Arnaudova et al. (1971), Arnaudova and Raynov (1971), Arnaudova et al. (1980), etc. Here we present new data about the chemical composition in terms of major and trace elements of the sanidine crystals.

Analytical approach

The major and trace elements of the whole-rock and of the sanidine crystals were analyzed using LA-ICP-MS at GI–BAS. The used analytical system consists of a 193 nm ArF excimer laser coupled with an ELAN DRC-e ICP quadrupole mass spectrometer. An energy density of above 10 J/cm^2 on the sample and a laser pulse frequency of 10 Hz, wit beam diameter of 75 μm were used. External standardization with NIST-610 glass standard provides relative element concentrations, transformed into true values by internal EPMA standardization and SILLS software program. For the purpose of the study representative single crystals were oriented, cut, polished and analyzed on a profile from the core to the rims.

Geological setting and petrography

The volcanic rocks westwards of Kyustendil, SW Bulgaria, are part of the Ruen zone (Harkovska, 1984), in which can be distinguished several igneous types: Kopriva, Gyueshevo and Pishtilski volcanics, Osogovo granite and granite-porphyry dykes. The Kopriva volcanics (Harkovska, 1974), constituting nearly 85% of the igneous rocks in the zone, and are the most representative rock type there. The Osogovo granite is the only pluton in the zone. The Gyueshevo volcanics and the granite-porphyry dykes from the Osogovo blok are in subvolcanic facies, whereas the Kopriva and Pishtilski igneous type are in volcanic facies.

Besides the large sanidine crystals of the Kopriva volcanics, in the porphyry generation can be seen plagioclase, quartz, biotite and amphibole as well. The plagioclase phenocrysts are zonal, often showing albite twins. Together with plagioclase from the groundmass they suffer alteration by secondary minerals. Quartz in the porphyric generation has typical rounded forms (2–6 mm), or irregular bay-like resorbed shape. Biotite prevails over amphibole. Both mafic minerals are altered. The amphibole phenocrysts (magnesiohornblende, defined by EPMA) have idiomorphic shape and are often almost completely replaced by opaque minerals. The accessory minerals are presented by apatite, magnetite, zircon and titanite in the ground mass or as inclusions in sanidine, biotite and amphibole phenocrysts. The structure of the groundmass is microlithic (individual microliths from plagioclase and biotite) to cryptocrystalline (felsitic).

Results and discussion

The mean chemical composition of the studied crystals is $Or_{74.86}Ab_{22.02}Cn_{2.26}An_{0.85}$. Besides the major elements of the sanidines (K_2O 12.7–13; Al_2O_3 19.41–20.06; Na_2O 2.44–2.58; CaO 0.15–0.21; FeO ~0.07 wt.%) in this study were analysed 39 elements (LILE, transition metals, HFSE and REE) the majority of which

contents are below the detection limit of the analytical method. Only 13 trace elements (in order of decreasing content: Ba, Sr, Rb, Pb, Ga, Li, Sc, Zn, Cu, Tl, Sn, Cs, Y) are presented in significant amount. From the REE, though in low concentration, are presented only the LREE (from La to Gd, except Nd) with concentrations from 2.1 to 0.1 ppm.

However, in considerable abundance are the alkali and alkaline earth elements: Ba 12698; Sr 1406; Rb 235; Li 10.54 ppm (average contents). Apart from them lead and gallium incorporation (Pb 76.12, Ga 12.68 ppm) is considerable. Rubidium content remains almost constant in the crystals (229–243 ppm). The values of Ba, Sr and Rb are in good agreement with those reported by Arnaudova et al. (1980). The Ba/Rb ratio ranges from 74.08 to 38.92, while Sr/Rb shows slight variation from 6.74 to 5.21, both elements Ba and Sr have concordant behaviour.

The crystal growth have some particular chemical variation expressed in the following manner: the values of the major constituents K and Na and the trace elements with low content (Ga 12.6; Li 10.53; Zn 3.23; Tl 1.93; Cs 0.35 ppm) reveal constant concentration in the different crystal zones. On the other hand the concentration of Ba, Sr, Pb, Sc and Cu shows significant decrease from core to rims, defining trace element zonal distribution (from core to rim: Ba 17597–9112; Sr 1601–1232; Pb 87.18–66.08; Sc 5.93–4.56; Cu 2.35–0.99 ppm, respectively). From the LREE only La (2.11–1.19 ppm) and Eu (1.89–1.22 ppm) show decreasing pattern of distribution from the central parts of the crystals to their rims.

The determined increased content of Ba and Sr in the central parts of the large crystals indicate initial crystallization of sanidine in relatively deeper levels of the crust (Smith, 1983). The strong accommodation of Ba and Sr in the large sanidine crystals compared to potassic feldspars from the groundmass (data from Arnaudova et al., 1980), suggest that the examined sanidines are formed in different time and conditions, before the eruptive appearance on the surface of the Kopriva trachyrhyodacites.

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