Trace element distribution in coexisting rock-forming minerals of the Smilyan granite

Разпределение на елементи-следи в съсъществуващи скалообразуващи минерали от Смилянския гранит

Emiliya Raeva[1], Zlatka Cherneva[2]
Емилия Раева[1], Златка Чернева[2]

[1] University of Mining and Geology “St. Ivan Rilski”, 1700 Sofia, Prof. B. Kamenov Str.; E-mail: rapakiviedr@gmail.com
[2] Sofia University “St. Kliment Ohridski”, 1504 Sofia, 15 Tsar Osvoboditel Blvd.; E-mail: cherneva@gea.uni-sofia.bg

Key words: geochemistry, LILE, REE, plagioclase, K-feldspar, biotite, LA-ICP-MS.

Introduction

The distribution of trace elements between minerals in igneous rocks supplies significant evidence for the evolution of magmas and helps for determination of mineral/melt partition coefficients. Measurement of this distribution therefore provides direct information on trace element behavior during crystallization and related differentiation processes (Gromet, Silver, 1983). Trace elements determination depends on analytical techniques advances. The LA-ICP-MS spot analyses of selected small portions of mineral grains in thin-sections make possible in situ chemical quantification of trace elements in coexisting rock-forming minerals. We present LA-ICP-MS results on the distribution of trace elements between K-feldspar, plagioclase and biotite in the Smilyan granite pluton, Central Rhodopes.

Materials and methods

Three samples selected represent the Smilyan pluton compositional variation from mesocratic (E227: N41°27′42″/E24°44′04″) to widespread leucocratic granite (E179: N41°27′39″/E24°42′38″; and E160: N41°26′18″/E24°46′32″). Previous studies on Smilyan granite (Belmustakova, 1995; Raeva, 2009) reveal relatively monotonous trace elements geochemistry (high Ba contents, uniform REE patterns, missing Eu-anomaly) with poorly expressed differentiation trends (increasing Rb/Sr and Rb/Ba). The modal proportions of the above samples show considerable K-feldspar increase (8.1→18.1→26.5%), and decrease of plagioclase (53.1→47.3→36.1%) and biotite (8.5→4.1→3.7%). The variation of modal composition at relatively uniform whole rocks geochemistry suggests that trace elements distribution between coexisting minerals keep record of magma differentiation during Smilyan pluton crystallization.

LA-ICP-MS analyses were performed in the Geological Institute of the Bulgarian Academy of Sciences using NIST-610 glass as external standard and SiO_2 as internal one, previously determined by electron microprobe on the same minerals. According to methodical recommendations (available elsewhere) and our own experiments we got the best results at laser frequency of 10 Hz, a spot diameter of 150 μm and a thickness of sample of 60 μm.

Geochemical results

LIL elements exhibit preferential concentration of Sr in plagioclase, Ba in K-feldspar and Rb in biotite. Large variation of individual contents refers to compositional zonation (feldspars), modal mineral proportions, and whole rock contents.

Plagioclase normal zonation (cores $An_{15–18}$, rims and small grains $An_{09–14}$, Raeva, 2009) corresponds to higher Sr (>1800 ppm) and Ba contents (>350 ppm) in large grain cores, and lower contents in the rims and small grains. Both elements reach the highest contents (Sr 3000 ppm and Ba 600 ppm) in plagioclase cores of mesocratic granite E227. Average contents calculated form rims and small grains correlate positively with modal proportion of plagioclase and decrease from mesocratic towards leucocratic granites (Sr: 1693→1361→546 ppm; Ba: 243→235→58 ppm). The coefficients of concentration (CC=mineral/rock) follow the same trend keeping CC^{Sr} >1 and CC^{Ba} <1, thus supporting compatible behavior of Sr and incompatible one of Ba in all plagioclases. The contents of Rb (≤2 ppm) and CC^{Rb} values (<0.01) emphasize incompatible behaviour during plagioclase crystallization.

K-feldspars show decreasing Ab and increasing Or component from large grains cores ($Ab_{14–19}Or_{79–86}$) towards rims ($Ab_{08–17}Or_{81–91}$) and small crystals

($Ab_{06–15}Or_{85–92}$) (Raeva, 2009). Ba and Sr are distinguished with the highest contents in large grains cores (up to 14170 ppm and 1662 ppm resp.), while Rb is concentrated in the rims and small grains (up to 449 ppm). Average Ba and Sr contents corelate negatively with modal K-feldspar proportion and decrease towards more leucocratic granite (Ba: 9250→7735→2640 ppm; Sr: 1430→1046→446 ppm). Rb deviates from the above trend with the highest average contents in K-feldspar from the most felsic granite (327→274→391 ppm). Ba and Rb keep CC values >1, while CC^{Sr} is close to 1 in all cases. CC^{Rb}/CC^{Ba} ratio increases gradually in the above sequence revealing general Rb-enrichment during magma evolution and increasing compatibility of Rb in K-feldspar.

Biotite (#Mg 0.30–0.55; Al^{IV} 2.33–2.66, Raeva, 2009) concentrates Rb as show high CC^{Rb} values (7–12) and individual contents in the range 600–1100 ppm. The contents of Ba however are usually higher (Rb/Ba <1) except for biotite in the most felsic sample E160 where Rb/Ba is >1. CC^{Ba} and CC^{Rb} values decrease (from average 1.9 to 0.7 and from 9.9 to 7.9 resp.) with increasing modal proportion of K-feldspar. Low contents are typical for Sr (3–53 ppm) with CC^{Sr} <0.1.

REE contents are low in feldspars, with HREE below detection limits usually, and LREE sum in the range 1.6–11.1 ppm for plagioclase, and 0.5–3 ppm for K-feldspar. All CC values are low (≤0.1) except for Eu (Kfs: 0.4 to 2.5; Pl: 0.3 to 1.1). Plagioclase and K-feldspar show similar chondrite normalized patterns with strong positive Eu-anomaly and noticeable LREE fractionation (La_N/Yb_N >1). The sum of LREE in coexisting feldspars increases slightly from meso- to leucogranites. Biotites are distinguished with variable REE contents. The majority of them have low REE sum (0.2–4.4 ppm), low CC values <1 (with $CC^{LREE} < CC^{HREE}$). Both chondrite- and wholerock-normalized patterns display positive Eu anomaly and negative Ce-anomaly. Biotite in the most felsic sample E160 differs with higher REE contents (REE sum 15–19 ppm), higher LREE/HREE ratio and negligible Eu anomaly. CC^{La}/CC^{Lu} and La_N/Lu_N ratio values show positive correlation with REE sum and negative correlation with biotite modal proportion.

Discussion and conclusions

Part of the geochemical features considered above support magma evolution trends corresponding to whole rock geochemistry, namely: normal zonation of Sr and Ba in both feldspars as well as increasing Rb compatibility in K-feldspar rims; low REE contents, similar normalized patterns with strong positive Eu-anomaly in feldspars; increasing of LREE in coexisting feldspars and biotite from meso- to leucogranites. Some results suggest high level of Sr, Ba and Eu saturation in the magma. The negative correlation of Sr and Ba contents in plagioclase, and Ba and Rb contents in biotite with K-feldspar modal proportion emphasizes that individual contents depend mostly on liquid saturation of LILE despite variation in modal proportions of minerals. The positive Eu-anomaly in biotite supports an interpretation of Eu-saturated liquid. The negative Ce-anomaly of biotite is a peculiar feature which interpretation needs special attention in future studies.

The geochemical balance gives quantitative estimate of trace elements distribution between the rock-forming minerals. Plagioclase carries the major part of Sr with decreasing balance proportion from mesocratic to leucocratic samples from 72 to 47% of Sr available. K-feldspar is the major reservoir of Ba with increasing balance proportion from 48 to 65% of Ba available in the same sequence of samples. Biotite and K-feldspar are competitors for Rb with leading role of biotite in mesocratic sample (63% of Rb available) and K-feldspar in leucocratic samples (60–80% of Rb available). REE balance show that feldspars carry up to 30% of Eu available and less than 5% of every one of LREE. The role of biotite in REE balance distribution is insignificant.

Acknowledgments: The National Science Fund of the Ministry of Education and Science in Bulgaria have supported this work financially, grant MY03-262–2011.

References

Belmustakova, H. 1995. Petrology of the Smilyan pluton (Central Rhodope) and its metamorphic frame. – *Rev. Bulg. Geol. Soc.*, *56*, 1, 75–91 (in Bulgarian with English abstract).

Gromet, L. P., L. T. Silver. 1983. Rare earth element distributions among minerals in a granodiorite and their petrogenetic implications. – *Geochim. Cosmochim. Acta*, *47*, 925–939.

Raeva, E. 2009. *Geochemistry of Granites and Metagranites from Upper Arda River Valley, Central Rhodopes, Bulgaria*. PhD thesis, Sofia University "St. Kliment Ohridski", 216 p. (in Bulgarian).