СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,
год. 83, кн. 3, 2022, с. 109–112

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,
vol. 83, part 3, 2022, p. 109–112

Национална конференция с международно участие „ГЕОНАУКИ 2022“
National Conference with International Participation "GEOSCIENCES 2022"

Late Permian high-pressure metamorphism in the Devesil Unit, East Rhodopes (SE Bulgaria) – Single or multiple metamorphic events

Къснопермски високобаричен метаморфизъм в Девесилската единица, И. Родопи (ЮИ България) – еднократно или многократни метаморфни събития

Lyubomirka Macheva[1], Philip Machev[2], Irena Peytcheva[3], Marcel Guillong[4], Julia Plotkina[5], Ekaterina Salnikova[5], Marina Koreshkova[6]

Любомирка Мачева[1], Филип Мачев[2], Ирена Пейчева[3], Марсел Гийонг[4], Юлия Плоткина[5], Екатерина Салникова[5], Марина Корешкова[6]

[1] Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", BAS, Sofia; E-mail: lu_macheva@dir.bg
[2] Sofia University „St. Kliment Ohridski", Sofia; E-mail: machev@gea.uni-sofia.bg
[3] Geological Institute "Acad. Strashimir Dimitrov", BAS, Sofia; E-mail: ipeytcheva@geology.bas.bg
[4] Department of Earth Sciences, ETH Zürich, Switzerland; E-mail: marcel.guillong@erdw.ethz.ch
[5] Institute of Precambrian Geology and Geochronology, Saint Petersburg; E-mails: plotkina@yandex.ru, katesalnikova@yandex.ru
[6] St. Petersburg State University, Saint Petersburg; E-mail: m.koreshkova@spbu.ru

Abstract. Metaeclogites from the Devesil Unit, East Rhodopes are studied. Well preserved eclogite paragenesis is presented by omphacite+garnet+rutile and is obliterated by still high temperature retrograde assemblage of newly formed garnet, diopside, amphibole, plagioclase, titanite, and quartz. The P-T conditions of the high pressure metamorphism are in the range 620–665 °C and 1.8–2.0 GPa, whereas the retrograde stage occurs at temperature 600–650 °C and pressure 0.6–0,8 GPa. Cathodoluminescence images and LA-ICP-MS dating of zircon grains point to multiple metamorphic origin of the mineral the earliest with Late Permian–Early Triassic age, followed by Early Jurassic and Early Cretaceous metamorphic events.

Keywords: East Rhodopes, metamorphism, eclogites, zircon.

Introduction

The Rhodopes region comprises a complex assembly of allochthonous continental terranes with different composition, age, and metamorphic evolution, which were derived from successive Alpine stages of nappe-stacking and post-collisional extension. Numerous eclogitic boudins and slivers are scattered throughout these terranes being exhumed to the Earth's surface from deep crustal levels or mantle depths and representing important witnesses of subduction-collision processes. In the last two decades plenty of geochronological data have been collected for high- and ultrahigh pressure rock cropping out in the Rhodopes area, some of which controversial. The use in recent years of microscale dating of distinct zircon domains containing relics of multiple metamorphic events is a key tool to characterize the polyphase evolution of complex metamorphic terranes.

In this study, we describe the petrological characteristics of HP mafic rocks from Devesil lithotectonic Unit in the East Rhodopes, zircon U-Pb geochronological data, and P-T conditions of metamorphism using conventional geothermobarometry.

Geological setting and petrography

The eclogitic rocks under study are part of the Devesil Lithotectonic Unit (DLU) (Sarov et al., 2008), which is located in the Eastern Rhodopes (Bulgaria). It is built of metagabbro associated with meta-

https://doi.org/10.52215/rev.bgs.2022.83.3.109

plagiogranites, marbles, metapelites with sporadic thin intercalations of metaquartzites, and lenses of amphibolized eclogites. The unit is limited at the bottom and top by ductile shear zones – Kesebir and Devesil zones, separating it from Kesebir and Krumovitsa Units, respectively.

Metaeclogites are found as sporadic small blocks and interlayers within garnet-two mica schists in several localities of the lower section of the Devesil Unit. They are dark green in color with massive structure. In the strongly deformed parts monomineralic stripes of fine grained garnet are observed. The protoliths of metaeclogites are basic magmatic rocks with MORB characteristics (SiO_2=44.8–48.9% and MgO = 5.7–6.7%).

The high-pressure (HP) mineral assemblage garnet (Grt1)+omphacite (Omp)+rutile (Rt) is preserved only in the least retrogressed rocks. Apatite and zircon are accessory phases. Grt1 grains form small partially rounded porphyroblasts up to 0.2 cm in diameters, which are rich in numerous inclusions of omphacite, quartz, rutile and needle-like clusters of oriented rutile exolutions. Grt1 shows prograde zoning with increase of almandine and pyrope components from core towards margins up to 66.4% and 21.3%, respectively and decreasing of grossular in the same direction from 28.9 to 12.1%. Spessartine remains relatively constant rapidly increasing at the rims. In the scarce samples of minor retrogression, omphacite is by far the dominant eclogite facies mineral preserved as pale green subhedral grains both in the garnet porphyroblast and as main matrix constituent. However, in the more intensively retrogressed domains the mineral is partly or completely replaced by albite-clinopyroxene (diopside) symplectites which are a common decompression feature in HP and UHP eclogites. The Jadeite-component of clinopyroxene varies in the range 42.8–56.70%. Rutile occurs as numerous small grains in garnet porphyroblasts or in symplectitized matrix rimmed by sphene and ilmenite. The calculated P-T conditions of the HP metamorphic stage correspond to 620–665 °C and 1.8–2.0 GPa.

The retrograde mineral assemblage in more amphibolitized domains consists of Grt2+diopside-plagioclase symplectites+amphibole+plagioclase. Grt2 forms small idioblastic recrystallized inclusion-free grains. Sometimes Grt2 porphyroblasts are arranged in monomineralic bands up to 1–2 cm thick, consisting of anastomousing large monocrystaline grains up to 6 mm in length armored by fine-grained idioblastic individuals. The mineral is almost unzoned being rich in spessartine component (up to 23%) and depleted in pyrope (max 11%), the grossular minal is in the range 6.2–17.4%. The symplectitic pyroxene is nearly pure diopside with Jd component 2.4–3.3%, while plagioclase is albitic in composition ($An_{4–10.7}$). Amphibole is common mineral at advanced stages of retrogression. During this high-temperature amphibolite facies overprint poikilitic porphyroblasts of large green-yellow Mg-hornblende are formed containing inclusions of garnet, clinopyroxene-albite symplectites, quartz and rutile. The intensely amphibolitized metaeclogite domains consist mainly of atoll-shaped garnet relics, large amphibole poikiloblasts, plagioclase and quartz. Calculated P-T conditions of this retrograde metamorphic stage are highly limited to 0.6–0.8 GPa and 620–640 °C.

Zircon internal structure, chemistry, and U-Pb geochronology

We separated about 90 zircon grains from which only the half are used for U-Pb LA-ICP-MS dating and trace element analysis, the others are used for inclusions study.

Zircon crystals are colorless to pile-yellowish and transparent with a size of 80–120 μm. The grains are mainly short prismatic to partially rounded or oval in shape with aspect ratio of 1:2 to 1.5:2. CL images reveal their complex internal structure with a broad dark internal parts and thin (up to 10 μm) bright irregular rims (Fig.1a). Sector and in particular fir-tree zoning, typical for formation in eclogite/granulite facies (Schaltegger et al., 1999; Corfu et al., 2003) is very common feature for dark central domains of the studied zircons. Some crystals show partially dissolved or resorbed irregular outlines around which thin dark shells are formed. The internal structural features and the smoothed outlines of zircon crystals suggest high grade metamorphic origin (Rubatto, Hermann 2003; Bingen et al., 2004) supported also by their low Th and U contents: 0.3–2.9 ppm for Th and 7.5–68.7 ppm for U, and thus very low Th/U ratio (0.02–0.08), being much lower than in igneous rocks (usually >0.1) (Rowley et al., 1997; Rubatto, 2002; Bingen et al., 2004; Wu, Zheng, 2004; Yakymchuk et al., 2018). Low REE contents and chondrite-normalized REE patterns without negative Eu anomaly (Rubatto, 2002) is in accordance with their metamorphic origin too. Moreover, it can also be concluded that zircons are formed in the presence of garnet and rutile but in the absence of plagioclase (Hermann et al., 2001; Rubatto, 2002; Rubatto, Hermann, 2003) that is under eclogite (or granulite?) facies conditions. No difference are observed in Th and U contents, Th/U ratio, and chondrite-normalized REE patterns between different CL zones (cores, rims, and shells) of zircon grains, i.e. they are chemically homogenous.

To understand the metamorphic conditions at which zircons (re)crystallized, we calculated Ti-in-

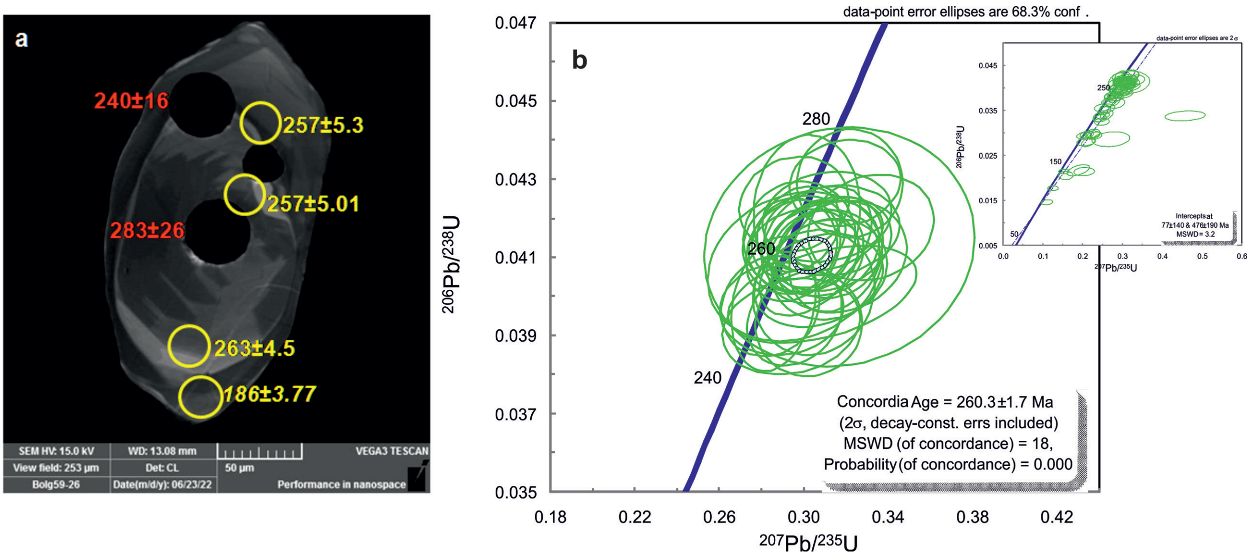

Fig. 1. *a*) CL image of zircon crystal from Devesil metaeclogites with different growth zones. Yellow circles and numbers are analyses made at Department of Earth Sciences, ETH-Zurich; red numbers are analyses from the Isotope Laboratory at the Geological Institute BAS), Sofia; *b*) Concordia diagram of zircon dark domains cluster at ca. 260 Ma. The small Concordia diagram at the top right shows various amounts of Pb-loss after ca. 260 Ma. Data plotted below ca. 260 Ma cluster are from rims and shells of old grains, and newly formed grains.

zircon temperatures, which vary in broad limits from 568 to 683 °C. This means that mineral forms in a protracted temperature interval, mainly at the decompression stage of the metamorphism as predicted by Kohn et al. (2015) for most zircons from HP/UHP eclogites.

Mineral and fluid inclusions identified in the central parts of the zircon grains (e.g. titanite, rutile, quartz, omphacite, sodium alumina augite, albite, high-density CO_2-rich fluid inclusions), indicate that at least part of the host mineral was formed under HP conditions. In addition, linearly arranged fluid inclusion formed across the grains at the later more low pressure and low temperature stage of the metamorphism.

U-Pb dating of zircons from Devesil eclogites was done at first at the Geological Institute (BAS) in Sofia using quadrupole-based LA-ICP-MS. Because of the very low U and Th contents of zircons additional measurements were made at the Department of Earth Sciences, ETH-Zürich using high resolution mass spectrometer. The latter analyses at smaller spot diameter allowed collecting signal even from the thin outer shells of the zircon grains. A total of 85 spot analyses were measured on 42 grains, which are scattered along the Concordia diagram from ca. 270 to 93 Ma (Fig. 1b). A large cluster of 42 spot analyses is formed around 260 Ma and several smaller clusters – at 170–180 and at 113–93 Ma. The first one comprises analyses from the CL-dark domains of the grains including sector and fir-tree zones. $^{206}Pb/^{238}U$ age for this group is 260.3±1.7 Ma (Fig. 1b). The other two clusters consists of 5 to 10 spots and represent analyses in the rims and the shells of the grains, respectively as well as in the new formed grains. We interpret the age of 260.3±1.7 Ma as time of the HP/HT metamorphism. The second cluster may be attributed to the important for the Rhodopes Jurassic subduction event and the other scattered spots may be linked to the opening of the isotope system by subsequent thermal events during Cretaceous–Paleogene time.

Conclusions

Investigations of metaeclogites from Devesil Lithotectonic Unit, East Rhodopes provide new petrological and geochronological data for the involvement of these rocks in Late Permian 260.3±1.7 Ma HP/HT metamorphic event at 620–665 °C and 1.8–2.0 GPa, followed by exhumation by near isothermal decompression at temperature 600–640 °C and 0.6–0.8 GPa pressure. Partial dissolution of old and formation of new zircon grains suggests that Jurassic–Early Cretaceous subduction at 170–130 Ma has had a significant impact on Devesil eclogites. Additional U-Pb mineral ages of garnet, rutile, and titanite will help to bring more reliability in the geological meaning of the calculated ages.

So far, there are no records of Permian eclogites in the Rhodopes and neighboring areas, but structural and chemical features of studied zircons as well as the composition of fluid and mineral inclusions allow us to assume their metamorphic high pressure origin. Liati (2005) and Bauer et al. (2007) reported Permian ages of zircons from West and East Rhodopes eclogites, respectively 246±4 Ma and 288±6 Ma, measured in oscillatory zoned cores of the grains and therefore interpreted as protolith ages. Miladinova et al. (2013) published data for Triassic in age eclogites (ca. 243 Ma) from Rila Mt. associating their formation with the southward subduction of Palaeotethys during Triassic time and contemporaneous opening of Neotethys to the south, assuming the subsequent collision processes responsible for the incorporation of these eclogites in the Upper Allochthon of the Rhodopes nappe stack.

Acknowledgements: The investigations were supported by the bilateral project Bulgaria-Russia – KP-06-Russia-32 (Bulgarian part) and 20-55-18017 (Russian part).

References

Bingen, B., H. Austrheim, M. J. Whitehouse, W. J. Davis. 2004. Trace element signature and U-Pb geochronology of eclogite-facies zircon, Bergen Arcs, Caledonides of W. Norway. – *Contrib. Mineral. Petrol*., *147*, 671–683; https://doi.org/10.1007/s00410-004-0585-z.

Bauer, C., D. Rubatto, K. Krenn, A. Proyer, G. Hoinkes. 2007. A zircon study from the Rhodope metamorphic complex, N. Greece: Time record of a multistage evolution. – *Lithos*, *99*, 207–228; https://doi.org/10.1016/j.lithos.2007.05.003.

Corfu, F., J. M. Hanchar, P. W. O. Hoskin, P. Kinny. 2003. Atlas of zircon textures. – In: *Reviews in Mineralogy and Geochemistry*, 53 (1), 469–500; https://doi.org/10.2113/0530469.

Hermann, J. R., D. Rubatto, A. Korsakov, V. S. Shatsky. 2001. Multiple zircon growth during fast exhumation of diamondiferous deeply subducted continental crust (Kokchetav Massif, Kazakhstan). – *Contrib. Mineral. Petrol*., *141*, 66–82; https://doi.org/10.1007/s004100000218.

Kohn, M. J., S. L. Corrie, C. Markley. 2015. The fall and rise of metamorphic zircon. – *Am. Mineral*., *100,* 897–908; https://doi.org/ 10.2138/am-2015-5064.

Liati, A. 2005. Identification of repeated Alpine (ultra) high-pressure metamorphic events by U–Pb SHRIMP geochronology and REE geochemistry of zircon: the Rhodope zone of Northern Greece. – *Contrib. Mineral. Petrol*., *150*, 608–630; https://doi.org/10.1007/s00410-005-0038-3.

Miladinova, I., N. Froitzheim, S. Sandman, T. J. Nagel, N. Georgiev, C. Münker. 2013. Middle Triassic eclogite in the Rila Mountains (Rhodope Upper Allochthon, Bulgaria): A vestige of Palaeotethys subduction? – *Berichte Geol. B.-A.*, *99*, p. 65.

Rowley, D., B. F. Xue, R. D. Tucker, Z. X. Peng, J. Baker, A. Davis. 1997. Ages of ultrahigh pressure metamorphism and protolith orthogneisses from the eastern Dabie Shan: U/Pb zircon geochronology. – *Earth Planet. Sci. Lett*., *151*, 191–203; https://doi.org/10.1016/S0012-821X(97)81848-1.

Rubatto, D. 2002. Zircon trace element geochemistry: partitioning with garnet and the link between U–Pb ages and metamorphism. – *Chem. Geology*, *184*, 123–138; https://doi.org/10.1016/S0009-2541(01)00355-2.

Rubatto, D., J. Hermann. 2003. Zircon formation during fluid circulation in eclogites (Monviso Western Alps): implications for Zr and Hf budget in subduction zones. – *Geochim. et Cosmochim. Acta*, *67*, 2173–2187; https://doi.org/10.1016/S0016-7037(02)01321-2.

Sarov, S., B. Yordanov, S. Georgiev, V. Valkov, E. Balkanska, V. Grozdev, R. Marinova, N. Markov. 2008. *Explanatory Note to the Geological Map of the Republic of Bulgaria. Scale 1:50000. Map sheet K-35-88-V (Krumovgrad) and K-35-100-A (Egrek)*. Sofia, Ministry of Environment and Water, Bulgarian Geological Survey, 124 p.

Schaltegger, U., C. Fanning, D. Günther, J. C. Maurin, K. Schulmann, D. Gebauer. 1999. Growth, annealing and recrystallization of zircon and preservation of monazite in high-grade metamorphism: conventional and in-situ U-Pb isotope, cathodoluminescence and microchemical evidence. – *Contrib. Mineral. Petrol*., *134*, 186–201; https://doi.org/10.1007/s004100050478.

Wu, Y. B., Y. F. Zheng. 2004. Genesis of zircon and its constraints on interpretation of U-Pb age. – *Chin. Sci. Bull*., *49*, 1554–1569; https://doi.org/10.1007/BF03184122.

Yakymchuk, C., C. L. Kirkland, C. Clark. 2018. Th/U ratios in metamorphic zircon. – *J. Metam. Geology*, *36*, 715–737; https://doi.org/10.1111/jmg.12307.