RESEARCH ARTICLE

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Variscan ultra-high-pressure eclogite in the Upper Allochthon of the Rhodope Metamorphic Complex (Bulgaria)

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Funding information

Slovak Research and Development Agency, Grant/Award Number: APVV-18-0107; University of Bonn; VEGA, Grant/Award Number: 2/0056/20

Abstract

The Rhodope Metamorphic Complex (RMC) in Bulgaria has been established as a Mesozoic ultra-high-pressure metamorphic province by findings of microdiamond in gneisses. Additionally, Variscan ultra-high-pressure metamorphism has been proposed for the Ograzhden/Vertiskos Unit in the Upper Allochthon of the RMC, based on findings of coesite, graphite pseudomorphs after diamond and indirect age constraints. We confirm ultra-high-pressure metamorphism of eclogites in this unit using thermobarometry, phase-equilibrium modelling and the Variscan age of metamorphism using Lu–Hf garnet–whole-rock dating. In Belica (southern Rila Mountains), kyanite- and phengite-bearing eclogite enclosed in high-grade gneisses records P-T conditions of 3.0–3.5 GPa and 700–750°C. Lu–Hf dating of eclogite samples from Belica and Gega (Ograzhden Mountain), where coesite was found, yielded ages of 334.1 \pm 1.8 and 334.0 \pm 2.2 Ma, respectively, interpreted as the age of garnet growth during post-collisional subduction of continental crust after closure of the Rheic Ocean.

1 | INTRODUCTION

Ultra-high-pressure (UHP) metamorphism records deep burial of crustal material during subduction and collision. UHP rocks have been identified in many Phanerozoic orogens, including the Rhodope Metamorphic Complex (RMC) in Bulgaria and Greece (Figure 1). In the Eastern, Central and Western Rhodopes, the UHP metamorphism is Mesozoic (Bauer et al., 2007; Liati et al., 2011; Petrík et al., 2016). However, Variscan UHP metamorphism has been suggested for structurally high tectonic units in the westernmost part of the RMC (Kostopoulos et al., 2000; Peytcheva et al., 2015; Zidarov et al., 1995) implying that Variscan and Early Alpine UHP metamorphism can be found in closely associated geological units. To clarify the existence of Variscan UHP metamorphism in the RMC, we

studied eclogites from the Ograzhden Unit in western Bulgaria using metamorphic petrology and Lu-Hf geochronology.

1.1 | Regional geological setting

The RMC is part of the Alpine-Mediterranean mountain belt in Southeast Europe, characterized by thrust sheets of metamorphic rocks, mostly gneisses and pierced by granitoid intrusions. As defined by Ricou et al. (1998), the RMC comprises the Eastern, Central and Western Rhodope Mountains, the Rila and Pirin Mountains and the southern part of the Serbo-Macedonian Massif (Figure 1). The RMC is subdivided into the Lower, Middle, Upper and Uppermost Allochthon (Janák et al., 2011). Although the allochthons were

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² WILEY- Terra originally stacked by thrusting, most of their present tectonic contacts are Eocene to Miocene extensional detachment faults (e.g. Brun & Sokoutis, 2018). Findings of microdiamond in metamorphic rocks established the RMC as an UHP metamorphic terrane (Collings et al., 2016; Mposkos & Kostopoulos, 2001; Perraki et al., 2006; Petrík et al., 2016; Schmidt et al., 2010). Evidence for UHP meta-

morphism was found in the Eastern, Central and Western Rhodopes (Figure 1) and is probably Jurassic, between 200 and 150 Ma (Bauer et al., 2007; Liati et al., 2011; Nagel et al., 2011; Petrík et al., 2016). It either reflects subduction of the European margin under an island arc (Bonev et al., 2015) or closure of the Palaeotethys (Petrík et al., 2016).

This study deals with the Ograzhden Unit, the structurally highest thrust sheet of the Upper Allochthon in the Bulgarian part of the western RMC, equivalent to the Vertiskos Unit in Greece. It comprises orthogneiss and to a minor extent paragneisses, marble and metamafic rocks. U-Pb zircon dating of orthogneisses yielded

Statement of Significance

The article for the first time demonstrates the existence of Variscan ultra-high-pressure metamorphism in southeast Europe by phase-equilibrium modelling and Lu-Hf garnet dating of eclogites. The dating yielded identical, highly precise results for two localities of 334.0 ± 2.2 and 334.1 ± 1.8 Ma. This is evidence for post-collisional subduction of continental crust south of the Rheic ocean suture. This result is highly significant for the reconstruction of Carboniferous tectonics in Europe.

Ordovician (~462-452 Ma) and Silurian protolith ages (~443-426 Ma: Himmerkus et al., 2009a: Macheva et al., 2006). Svn- to post-tectonic granite intrusions, which crosscut the main foliation



FIGURE 1 Tectonic map of the Rhodope Metamorphic Complex modified after Bonev et al. (2006), Burg et al. (1996), Dixon and Dimitriadis (1984), Janák et al. (2011), and Ricou et al. (1998) with localities of the investigated eclogites from Belica and Gega and early alpine UHP localities (*Liati et al., 2011; Petrík et al., 2016)

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but are affected by late shear zones, yielded Triassic ages of ~249–222 Ma (Himmerkus et al., 2009b; Peytcheva, et al., 2009; Zidarov et al., 2007).

An outlier of the Ograzhden Unit occurs at Obidim on the eastern slopes of the Pirin Mountains (Figure 1). Zircons from two metagranites in this area yielded Ordovician protolith ages of 456.1 ± 1.8 and 452 ± 14 Ma and zircons from a metagabbro 454.1 ± 8.3 Ma (Peytcheva et al., 2009). Another Ograzhden outlier occurs near Belica (Figure 1) at the northern end of the Mesta Graben, on the southern slopes of the Rila Mountains.

Eclogites and other HP/UHP rocks occur at several localities in the Vertiskos/Ograzhden and related units. At Gega (Ograzhden; Figure 1), Zidarov et al. (1995) described a kyanite-eclogite containing coesite. Metamorphic zircon rims with ages around 330 Ma, in amphibolite-facies country rocks of the eclogite, suggest a Variscan age for metamorphism (Peytcheva et al., 2015). Thermobarometry of a kyanite eclogite from Obidim (Pirin Mountains) yielded UHP conditions of ~3 GPa/700-750°C (Janák et al., 2011). The nearby occurrence of a 321 \pm 19 Ma migmatite (Peytcheva, et al., 2009) again suggests a Variscan age. Scattered relics of eclogite have also been described from the Vertiskos Unit in Greece (e.g. Dimitriadis & Godelitsas, 1991). Kydonakis et al. (2015) studied garnet-kyanite mica schists from the Vertiskos Unit and demonstrated eclogite-facies conditions. They suggested the schists to originally represent the Mesozoic cover of the Vertiskos basement and that therefore the eclogite-facies metamorphism is Mesozoic in age. Kostopoulos et al. (2000) described graphite pseudomorphs after diamond in an amphibolite xenolith within the Triassic Arnea granite intruding the Vertiskos Unit (Figure 1) and argued that the diamond-forming UHP metamorphism must have been pre-Triassic, probably Carboniferous.

In summary, the age of HP/UHP metamorphism in the Vertiskos/ Ograzhden basement and related units is still unclear: In the Bulgarian part, a Variscan age appears more likely; in Greece, both Alpine and Variscan ages have been suggested. In order to clarify the age of this HP/UHP metamorphism, we determined age and metamorphic conditions of eclogites from the Ograzhden Unit, with two samples from Belica (BEL-1 used for thermobarometry and BEL-2 for geochronology) and one sample from Gega (NF17-5 for geochronology).

FIGURE 2 Eclogite texture (BSE) and compositional profile across a garnet grain in sample BEL-1. (a, b) Garnet porphyroblasts with inclusions of omphacite (Omp), phengite (Ph) and kyanite (Ky), symplectitic texture of diopside (Di) + plagioclase (PI), and amphibole (Amp) in the matrix. (c) Garnet partly replaced by orthopyroxene (Opx) and plagioclase. (d) Kyanite mantled by sapphirine (Spr), spinel (Spl), corundum (Crn) and anorthite-rich plagioclase (Pl). (e) Garnet with line of analysed profile. (f) Compositional profile of garnet with variations in mole fractions (find microprobe data in Table S1).



2 | METHODS

The methods are specified in Supplementary Information (Methods S1).

2.1 | Eclogite texture and P-T conditions

The investigated eclogites come from Belica (southern Rila Mountains, 1 km NW of Belica town, 41.9575 °N/ 23.5436 °E) and Gega (southern Ograzhden Mountains, SE periphery of Gega village, 41.4481°N/23.0067°E). The samples from Belica (BEL-1, BEL-2) were taken from the same outcrop, less than a metre apart and could also be treated as one sample. We consider it unlikely that these samples experienced different P-T-t histories. The reason for taking different pieces was that different laboratories collaborated, Bonn/Cologne doing the dating and Bratislava doing the petrology.

Both sampled eclogite bodies are hosted by high-grade basement rocks within the Ograzhden Unit. The eclogites are composed of garnet, omphacite, kyanite and phengite, considered to be the primary eclogite-facies minerals, which are variably overprinted by lower-pressure assemblages (Figure 2). Garnet porphyroblasts (Figure 2a,b) contain numerous inclusions of omphacite, phengite, kyanite, quartz, pargasitic amphibole, zoisite and rutile. Omphacite with jadeite content of up to 42-45 mol% occurs as inclusions in garnet. Matrix omphacite is partly replaced by symplectites of diopside + plagioclase. Kyanite is present as subhedral porphyroblasts in the matrix and as inclusions of 10-20 µm size in garnet. Matrix kyanite contains inclusions of omphacite and quartz, and is mostly mantled by sapphirine, Alspinel, corundum and plagioclase (Figure 2d). Inclusions of quartz in garnet and kyanite rarely show a polycrystalline texture with undulose extinction and radial cracks indicating breakdown of coesite, however, no remnants of coesite were found by Raman spectroscopy. The lack of mineralogical evidence for UHP conditions is hard to explain but could be related to HP overprinting. Phengite with up to 3.5 atoms per formula unit (a.p.f.u.) Si occurs as inclusions in garnet. Poikiloblastic garnet is partly replaced by orthopyroxene, plagioclase and amphibole forming a kelyphitic texture. Matrix amphibole forms dark-green to brown-green porphyroblasts. The garnet in sample BEL-1 is zoned with increasing Mg ($X_{Prp} = 0.31-0.37$) and decreasing Ca ($X_{Grs} = 0.23-0.18$) and Mn ($X_{Sns} = 0.03 - 0.01$) from the core to the rim (Figure 2). Further descriptions of the garnets of the samples Bel-2 and NF17-5 follow below.

Peak metamorphic P-T conditions have been calculated for sample BEL-1 using thermodynamic modelling, and "conventional" geothermobarometry. We used the Perple_X thermodynamic software (Connolly, 2005: version 6.8.6) with the internally consistent thermodynamic database of Holland and Powell (2011). Solid-solution models for garnet, white mica (White et al., 2014), omphacite (Green et al., 2007), plagioclase (Holland & Powell, 2003) and amphibole (Dale et al., 2005) were used, as available from the Perple_X datafile (solution_model.dat). The bulk rock composition was determined from whole-rock analysis.

The calculated phase diagram (Figure 3) shows that compositional isopleths of garnet (X_{Mg}^{Grt}), omphacite (X_{Na}^{Omp}) and phengite (Si a.p.f.u.) matching the measured compositions (Table 1) intersect in the stability field of garnet + phengite + omphacite + kyanite + rutile + coesite, i.e. the peak-pressure metamorphic assemblage, constraining P-T conditions of 3.0-3.5 GPa and 700-750°C. At these conditions, amphibole and zoisite are not stable which suggests that inclusions of amphibole and zoisite in garnet are remnants from a prograde, lower P-T stage. The P-T results obtained by conventional geothermobarometry (Ravna & Terry, 2004) from the garnet with the highest grossular content, omphacite with the highest jadeite content and phengite with the highest Si content (Table 1) yield pressure values of 2.7–3.2 GPa at a temperature of 648–724°C. The uncertainty limits of this thermobarometer are $\pm 65^{\circ}$ C and ± 0.32 GPa (Ravna & Terry, 2004). The oxidation state of iron can be the main problem concerning the calculated temperature. Therefore, we additionally used zirconium-in-rutile geothermometer (Tomkins et al., 2007) for calculating the temperature from Zr contents in rutile inclusions in garnet. The measured Zr concentration (259–311 ppm; 276 average) yields temperatures of 725-736°C at 3-3.5 GPa. These results are in line with those obtained from thermodynamic modelling and are interpreted to be representative of peak equilibration conditions for the investigated eclogite.



FIGURE 3 P-T section for the kyanite eclogite (sample BEL-1) from Belica, the same locality as the dated sample (BEL-2), in the system NCKFMASH (Na₂O = 2.79, CaO = 14.14, K₂O = 0.19, FeO = 5.93, MgO = 12.84, Al₂O₃ = 11.34, SiO₂ = 52.25, H₂O = saturated phase) with compositional isopleths of garnet (XMgGrt = Mg/(Mg + Ca + Fe)), omphacite (XNaOmp = Na/ (Na + Ca)), and phengite (SiPh a.p.f.u.).

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TABLE 1 Representative compositions of garnet, omphacite and phengite from sample BEL-1 measured by WDS (wavelength-dispersive spectrometer) analysis used for P-T calculations.

Mineral	Grt core	Grt rim	Omp	Omp	Omp	Omp	Ph	Ph	Ph	Ph
SiO ₂	39.68	39.48	55.81	54.25	55.00	55.00	53.50	50.61	53.88	50.27
TiO ₂	0.12	0.01	0.16	0.27	0.19	0.15	0.02	0.15	0.02	0.27
Al ₂ O ₃	22.19	22.31	11.08	11.49	10.90	11.78	26.18	28.18	25.62	29.54
FeO ^t	20.33	19.58	4.59	4.15	3.81	3.69	3.97	3.37	4.18	2.21
MnO	0.99	0.7	0.09	0.07	0.05	0.03	0.08	0.07	0.01	0.04
MgO	8.83	9.68	9.19	8.68	10.05	9.86	4.24	3.66	4.26	2.68
CaO	8.45	7.47	14.61	14.07	15.67	14.64	0.35	0.26	0.52	0.31
Na ₂ O			6.23	6.04	5.46	5.79	0.13	0.15	0.17	0.05
K ₂ O							8.91	9.29	8.85	9.44
Total	100.59	99.23	101.76	99.02	101.13	100.93	97.48	95.74	97.50	94.80
0	12	12	6	6	6	6	11	11	11	11
Si	3.00	3.00	1.96	1.95	1.94	1.94	3.48	3.35	3.50	3.34
Ті	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00
AI	1.98	2.00	0.46	0.49	0.45	0.49	2.01	2.20	1.96	2.31
Fe	1.28	1.24	0.13	0.12	0.11	0.11	0.22	0.19	0.23	0.12
Mn	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.99	1.10	0.48	0.47	0.53	0.52	0.41	0.36	0.41	0.27
Ca	0.68	0.61	0.55	0.54	0.59	0.55	0.02	0.02	0.04	0.02
Na			0.42	0.42	0.37	0.40	0.02	0.02	0.02	0.01
К							0.74	0.79	0.73	0.80
Total	8.01	8.00	4.00	4.01	4.01	4.01	6.90	6.94	6.90	6.88
X _{Alm}	0.42	0.42								
X _{Sps}	0.02	0.02								
X _{Prp}	0.33	0.37								
X _{Grs}	0.23	0.20								
X _{Na}			0.43	0.44	0.39	0.42				

TABLE 2X-Ray Fluorescence (XRF) whole-rock analyses ofmajor elements of dated eclogite samples BEL-2 and NF17-5(bdl = below detection limit).

	BEL-2	NF17- 5
SiO ₂ (%)	49.8	50.7
TiO ₂ (%)	0.65	0.37
Al ₂ O ₃ (%)	17.6	18.5
Fe ₂ O ₃ (%)	7.66	7.99
MnO (%)	0.14	0.17
MgO (%)	8.49	7.76
CaO (%)	10.4	10.5
Na ₂ O (%)	3.42	3.04
K ₂ O (%)	0.17	0.06
P ₂ O ₅ (%)	bdl	bdl
LOI (%)	0.42	0.06
Total sum (%)	98.9	99.0

2.2 | Major-element and Lu distribution in garnet of the dated samples BEL-2 and NF17-5

For the two dated samples, major element chemistry and the Lu distribution in garnets were analysed because of its importance for the interpretation of dating results. XRF whole-rock analyses of major elements are given in table 2. The major-element composition of garnet is AIm_{45-48} - Prp_{25-30} - Grs_{20-27} - $Sps_{0.9-1.4}$ in sample BEL-2, and AIm_{40-50} - Prp_{26-37} - Grs_{18-26} - $Sps_{0.5-1.2}$ in sample NF17-5 (Figures 4 and 5). In both samples, the partly irregular outlines of the garnet crystals indicate some resorption. Both samples show slight, local enrichments in Fe and Mn content directly at the rims, indicating back-diffusion during resorption.

The Mn distribution map from sample BEL-2 (Figure 4b) shows the highest Mn content directly at the rim of the resorbed garnet. The Lu line profiles through this garnet grain (Figure 4b), however, show maxima close to but not directly at the rim of the garnet, and not coinciding with the Mn increase. One of the garnet grains from sample



FIGURE 4 Major element and Lu distribution in garnet grains from sample BEL-2 (Belica). (a) Mn concentration map and major-element profile of the garnet composition (find microprobe data in Table S2). (b) Mn concentration map with laser spots and Lu concentration profile.

FIGURE 5 Major element and Lu distribution in garnet grains from sample NF17-5 (Gega). (a) Mn concentration map and major-element profile of the garnet composition (find microprobe data in Table S3). (b) Mn concentration map with laser spots and Lu concentration profile.

NF 17-5 has been disintegrated into three pieces by fracturing and resorption (Figure 5). Abundance of Mn in this garnet is rather uniform but shows a slight increase at the resorbed rims of disrupted garnet fragments. Lutetium increases towards the rims of the original grain and does not correspond to the Mn distribution. There is almost no increase in Lu at the rims between the garnet fragments.

2.3 | Lu-Hf geochronology

The Lu–Hf isotopic compositions of the mineral separates and whole rock powders are shown in Table 3. In sample NF17-5, absolute Hf contents in the whole rock vary between 0.526 and 0.556 ppm and $^{176}{\rm Lu}/^{177}{\rm Hf}$ ratios between 0.05993 and 0.07443. In the garnet

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TABLE 3 Lu-Hf isotopic compositions of the whole rocks (WR; b = bombed digestion, tt = tabletop) and garnet separates (Grt) of the sample NF17-5 and BEL-2.

Sample	Туре	Lu (ppm)	Hf (ppm)	¹⁷⁶ Lu/ ¹⁷⁷ Hf	Error	¹⁷⁶ Hf/ ¹⁷⁷ Hf	Error
NF17-5	Grt 1	0.526	0.0503	1.493	0.003	0.292294	0.000078
NF17-5	Grt 2	0.556	0.0511	1.548	0.003	0.292587	0.000090
NF17-5	Grt 3	0.550	0.0499	1.567	0.003	0.292812	0.000020
NF17-5	WR b 1	0.157	0.378	0.05993	0.00012	0.283316	0.000023
NF17-5	WR tt 1	0.156	0.301	0.07443	0.00015	0.283396	0.000032
NF17-5	WR b 2	0.159	0.366	0.06052	0.00012	0.283341	0.000088
NF17-5	WR tt 2	0.156	0.298	0.07428	0.00015	0.283404	0.000034
BEL-2	Grt 1	1.05	0.176	0.8450	0.0017	0.288076	0.000027
BEL-2	Grt 2	0.975	0.174	0.7956	0.0016	0.287721	0.000057
BEL-2	Grt 3	0.981	0.168	0.8281	0.0017	0.287975	0.000103
BEL-2	WR b 1	0.191	0.756	0.03591	0.00007	0.283003	0.000012
BEL-2	WR tt 1	0.187	0.524	0.05083	0.00011	0.283101	0.000039
BEL-2	WR b 2	0.188	0.790	0.03378	0.00007	0.282995	0.000025
BEL-2	WR tt 2	0.188	0.508	0.05226	0.00011	0.283123	0.000028



FIGURE 6 Lu-Hf isochrons for the two eclogite samples BEL-2 and NF17-5. Uncertainties are 2σ . The decay constant $\lambda 176Lu = 1.865 \times 10^{-11} a^{-1}$ was used (Scherer et al., 2001). WR b = bomb-digested whole rock, WR tt = tabletop-digested whole rock, Grt = garnet separate

separates of sample NF17-5, the absolute Hf contents range between 0.156 and 0.159 ppm and the $^{176}\rm{Lu}/^{177}\rm{Hf}$ ratios between 1.493 and 1.567.

In sample BEL-2, absolute Hf contents in the whole rock vary between 0.508 and 0.790 ppm and $^{176}Lu/^{177}Hf$ ratios between 0.03378 and 0.05226. In the garnet separates of sample BEL-2, the absolute Hf contents range between 0.168 and 0.176 ppm and the $^{176}Lu/^{177}Hf$ ratios between 0.7956 and 0.8450.

The isochrons (Figure 6) yield identical ages of 334.0 ± 2.2 Ma (Mean Square Weighted Deviation (MSWD) 0.36, n = 7) for Gega (NF17-5) and 334.1 ± 1.8 Ma (MSWD 0.63, n = 7) for Belica (BEL-2).

3 | DISCUSSION AND CONCLUSIONS

3.1 | Garnet composition patterns and age interpretation

Major-element maps and profiles of BEL-2 and NF17-5 show homogeneous distribution, reflecting diffusional re-equilibration. A slight increase in Mn at resorbed garnet rims can be explained by backdiffusion during resorption (Figures 4 and 5).

Distribution of Lu in the dated samples does not show the typical bell-shaped concentration profiles with a central peak as often

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observed and interpreted to result from Lu fractionation into garnet (e.g. Otamendi et al., 2002; Skora et al., 2006). Instead, the profile of BEL-2 (Figure 4) is saddle-shaped with peaks in the outer parts of the garnet crystals. We interpret the marginal peaks as not being due to resorption and back-diffusion (which could lead to a "younging" of the ages; Kelly, Carlson, & Connelly 2011) because (a) they are not directly at the rims but inside the garnet; and (b) they do not correspond with the most resorbed rims. Such secondary peaks are explained by an increase in diffusion rate during garnet crystallization when the temperature increases (Skora et al., 2006). In NF17-5, the Lu contents increases from core to rim with the highest values in the outermost measured spots. Nevertheless, we interpret these profiles as showing growth zoning with rim peaks, where the outermost points were not measured close enough to the rim to see if the Lu content decreases again (Figure 5). Remnants of a central Lu peak, if they exist, may have been missed by the sections.

3.2 | Variscan UHP metamorphism

Ultra-high-pressure metamorphism of eclogite in the Ograzhden Unit has now been demonstrated at three localities, Gega (Zidarov et al., 1995; coesite), Obidim (~3 GPa/700-750°C; Janák et al., 2011) and Belica (3.0-3.5 GPa/700-750°C; this study). The Variscan Orogeny in the Balkan Peninsula comprised the northward subduction of the Rheic Ocean, separating the Sredna Gora Terrane (of which the Ograzhden unit was a part, see Gorinova et al., 2019) from the Balkan Terrane (Figure 1; Carrigan et al., 2005; Haydoutov, 1989; Haydoutov & Yanev, 1997; Plissart et al., 2017).

Sm-Nd ages of 409 ± 38 Ma for oceanic crust formation of the Balkan-Carpathian Ophiolites along the suture between Balkan and Sredna Gora terranes (Plissart et al., 2017), as well as ages of ~336 Ma for high-grade metamorphism in the Sredna Gora Zone (Carrigan et al., 2006) and 340–350 Ma for HP metamorphism of structurally equivalent units in the Southern Carpathians (Medaris et al., 2003) fit such a scenario. An older (~400 Ma) ⁴⁰Ar/³⁹Ar age for retrogression of eclogite in the Sredna Gora Zone (Gaggero et al., 2009) may be related to an earlier metamorphic cycle or result from excess Ar.

The terranes collided at 350 to 340 Ma, with Sredna Gora forming the lower plate in the collision (Plissart et al., 2017). UHP metamorphism in the Ograzhden Unit at ~334 Ma could be explained by continuing, post-collisional subduction of continental crust.

The RMC, therefore, experienced UHP metamorphism twice, during the Variscan and Early Alpine Orogeny. This reflects the tendency of continents to break apart and re-collide along earlier collisional orogenic belts, a process known as the Wilson cycle (Wilson, 1966).

ACKNOWLEDGEMENTS

This is contribution no. 63 of the DFG-funded LA-ICP-MS Laboratory at the IOG, University of Bonn, Germany. This work was supported by the Slovak Research and Development Agency under grant project APVV-18-0107 to M.J., and Scientific grant agency VEGA project 2/0056/20 to M.J. We thank Jaroslaw Majka and two anonymous reviewers for constructive review and Klaus Mezger for editorial work. Special thanks to Irena Miladinova and Ina Martinet for support with measurements and data treatment. Open access funding enabled and organized by ProjektDEAL.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the main text and the Supporting Information of this article.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

Methods and Supplementary Microprobe Data

How to cite this article: Trapp S, Janák M, Fassmer K, Froitzheim N, Münker C, Georgiev N. Variscan ultra-highpressure eclogite in the Upper Allochthon of the Rhodope Metamorphic Complex (Bulgaria). *Terra Nova*. 2020;00:1–10. https://doi.org/10.1111/ter.12503