U-Pb zircon and titanite ages and Sr-Nd-Hf isotope constraints on the timing and evolution of the Petrohan-Mezdreyia pluton (Western Balkan Mts, Bulgaria)

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Abstract. A combination of methods is applied in the present study to define the exact age of the Petrohan and Mezdneya plutons and trace their magma evolution. Field, petrological, and geochemical studies of the Petrohan pluton revealed its complex evolution and emphasized the role of magma mingling and mixing, complementary to the normal assimilation and fractional crystallization (AFC) processes. Using high-precision conventional U-Pb (CA)-ID-TIMS zircon and titanite dating in combination with CA-LA-ICP-MS zircon dating and tracing, we suggest an incremental growth of a common Petrohan-Mezdneya pluton. It was assembled over minimum 4.5 Ma from 311.14±0.48 Ma to 307.54±0.54 Ma. The younger age of the gabbro (308.12±0.33 Ma), compared with the age of granodiorites (311.14±0.48 Ma), provides numerical proofs for magma replenishment during the assembling of the Petrohan pluton. Whole-rock strontium-neodymium (initial ⁸⁷Sr/⁸⁶Sr ratios of 0.70521–0.70527 to 0.70462 and ¹⁴³Nd/¹⁴⁴Nd of 0.51221 to 0.51210) and Hf-zircon isotope data (ε-Hf from –5.8 to +3.6) argue for interaction of mantle derived magma with crustal melts but also mixing and mingling and transfer of zircon grains between the gabbroic and granitic melts. Possible petrogenetic scenario includes melting of subcontinental mantle lithosphere and crust and evolution through AFC, FC and mingling/mixing processes. Considering the Petrohan-Mezdneya pluton as part of the Variscan orogeny in SE Europe, our new data support the accretion/collision of both the Balkan and Sredna Gora/Getic units with Moesia in the Early Carboniferous followed by syn- and post-collisional Carboniferous and Permian magmatism.

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INTRODUCTION

The Petrohan and Mezdneya plutons are part of the Variscan belt in SE Europe (e.g., Haydoutov and Yanev, 1997; Carrigan *et al.*, 2005). Traditionally, they are referred to the Stara Planina Calc-Alkaline Formation – Carboniferous-Permian calc-alkaline granitoids that crop out in the Balkan Terrane of Bulgaria (Dimitrov, 1932, 1958; Dimitrova, 1965; Voutov, 1970; Dimitrova and Arnaudova, 1977;

Haydoutov and Yanev, 1997). In recent publications, these granitoids were correlated with contemporary granitoids of the Sredna Gora Terrane (e.g., Carrigan *et al.*, 2005) and the Sakar-Strandzha Zone (SSZ) (Ivanov, 2017; Machev *et al.*, 2015; Natal'in *et al.*, 2016). The Carboniferous–Permian metagranitoids are exhumed in the cores of some metamorphic core complexes in the Rhodopes (e.g., Byala Reka and Central Rhodopean Dome; Liati and Gebauer, 1999; Cherneva and Georgieva, 2005;

Peytcheva *et al.*, 1998, 2004b) or are tectonically eroded in the metamorphic basement of the Sakar Unit of SSZ (Machev *et al.*, 2015; Peytcheva *et al.*, 2016; Bonev *et al.*, 2017). Few older granites of ~330 Ma crop out in western Bulgaria, namely, the Tran granite (Dyulgerov *et al.*, 2010; Peytcheva *et al.*, 2011) and Klissura granite (Malinov *et al.*, 2004; Peytcheva *et al.*, 2006). These studies revealed that the Variscan magmatism is widespread in Bulgaria between 330–290 Ma. The time window of 40 Ma is wide enough to suggest changing tectonic setting, which will be reflected in the chemical and mineral characteristics of the magmatic rocks. Combined with precise dating of the magmatic events, they will provide essential components to understand the orogenic processes and crustal evolution of the Balkans.

In order to constrain the magmatic evolution of the Petrohan-Mezdrea pluton and draw conclusions about the tectonic setting of the region, we applied a set of methods including U-Pb zircon and titanite age dating, analyses of zircon population and zircon thermometry, and combined them with whole-rock Sr-Nd isotope tracing and Hf-isotopes studies of zircons. Field and petrological-geochemical studies of the Petrohan pluton in the last decade have revealed a complex magmatic evolution and emphasized the role of magma mingling and mixing, complimentary to the normal AFC processes. They also raise the question whether we can find specific zircon fingerprints of the hybrid rocks and distinguish mingling-mixing events with geochronological methods. For answering these specific questions, we applied high-precision conventional U-Pb (CA)-ID-TIMS zircon and titanite dating and compiled it with CA-LA-ICP-MS zircon dating and tracing.

An important question regarding the Variscan orogeny in Southeastern Europe and Western Turkey is the closure and opening of oceans and the change from subduction to collision and post collision (*e.g.*, Finger *et al.*, 1997; Natal'in *et al.*, 2016). Although we are focusing on only one assembled pluton (Petrohan-Mezdrea), we will consider the results of its dating and geochemical tracing in the context of the Variscan orogeny of the region and try to put some constraints on the possible regional reconstructions.

GEOLOGICAL SETTING

The Petrohan and Mezdrea plutons (PP and MP) are intruded in the core of the Berkovitsa anticline SE-NE of the town of Berkovitsa in the Western Balkan Mts (Fig. 1). The exposed part of the Petro-

han pluton exceeds 180 km² and, together with the Mezdrea pluton (around 25 km²), it can be considered one of the biggest batholiths in Bulgaria. Both plutons are intruded in the low-grade metamorphic rocks of the Early Paleozoic Diabase-Phyllitoid Complex (DPC; Dimitrov, 1939). According to the lithostratigraphic scheme of Haydoutov *et al.* (1979, 1991), the host rocks are part of the Berkovitsa and Dalgi Dyal groups, corresponding to the middle and upper parts of DPC. The phyllites are contact-metamorphosed close to the plutons and the zone of thermal overprint exceeds 2 km (Haydoutov *et al.*, 1995). The contact of the Petrohan pluton with the Klissura granite (Malinov *et al.*, 2004; Peytcheva *et al.*, 2006) or with the metamorphic rocks of the Barziya Migmatite Complex (Haydoutov *et al.*, 1992) is intrusive or tectonic (Fig. 1).

Petrography and field relationships of the granitoids

The Petrohan pluton is a complex body, assembled by gabbroic to granitic rocks with a prevailing distribution of the intermediate and acid varieties. The pluton is metaluminous, with calc-alkaline and high-K calc-alkaline affinity. Most authors describe it as a multiphase intrusion to explain the wide range of exposed rocks (Dimitrov, 1932, 1958; Dimitrova, 1965; Dimitrova and Arnaudova, 1977; Haydoutov *et al.* 1979). Mafic magmatic enclaves (MME) are a characteristic feature of the Petrohan pluton in the outcrops south of Spanchevtsi Village (Fig. 1). They were considered gabbroic xenoliths in the granodioritic intrusions in earlier studies (Voutov, 1970).

The MME reveal transitional composition between the gabbroic and granitoid magma, sharing rock-forming minerals and chemical features of both varieties. The MMEs are part of the field and petrographic evidence of magma mingling and mixing processes. These were described in detail by Tacheva *et al.* (2006) and Tacheva (2013) and include: swarms of basic to intermediate enclaves, chilled margins and cauliflower structures along the contact of the mafic sheets/bodies with the granitoids; veins of leucogranite enveloping the basic to intermediate enclaves; patchy textures resulting from different degree of mixing; “pockets” of pegmatoid-like gabbro-diorites. Among the petrographic evidence, we will mention the similar mineral composition of granitoids and MMEs, hybrid gabbros or diorites. The main constituent minerals are plagioclase (Pl), amphibole (Amf), biotite (Bi), potassium feldspar (Kfs) and quartz (Q) in variable proportions. The shared composition is explained by interaction of the gabbroic magma with the gra-

nitic mush and the exchange of minerals and elements (e.g., Didier and Barbarin, 1991; Janoušek *et al.*, 2004). Consequently, the mixing results in approximation of the chemical composition, which is more enhanced in the gabbroic varieties as hybrid gabbros to gabbro-diorites and diorites.

The MMEs are composed of Pl (45–55%) and mafic minerals (40–50%). The proportion of Pl and Amf decreases in the granitoids to 35–45% and 5–20%, respectively, whereas the Q and KFs constitute 35–50%. In the granitoids, biotite is the main mafic mineral, while in the MME and inter-

Fig. 1. Simplified geological map of the region of the Petrohan and Mezhdreya plutons (modified after Haydoutov *et al.*, 1992, and Malinov *et al.*, 2004) with sample localities. The inset shows the tectonic units in Bulgaria (after Ivanov, 2017) and the position of study area.

mediate varieties (hybrid gabbros – diorites) Amf dominates. The latter forms idiomorphic to hypidiomorphic grains that often include Pl and Bi. The plagioclase composition is $An_{17.7-35}$ in the granodiorites and $An_{8.2-55.5}$ in diorites and hybrid gabbros. It varies from $An_{1.5}$ to $An_{99.2}$ in the MME, with a typical range of $An_{11.3-52}$. Its compositional zonation is either normal or reverse (Tacheva, 2013).

The accessory phases in the granitoids of the Petrohan pluton (in all rock varieties) include zircon (Zrn), apatite (Ap) and titanite (Ttn), as well as Fe-Ti oxides (magnetite and ilmenite). Allanite-(Ce) and thorite are observed in the granitoids, and garnet is sparse, found only in the leucogranites (mobilized granitic melts; Tacheva *et al.*, 2006).

The Mezdneya pluton is composed of quartz-monzonites to granites, with pink phenocrysts of K-feldspars (up to 2 cm). The magmatic rocks are calc-alkaline, meta- to peraluminous and often overprinted by K-silicate and propylitic hydrothermal alteration (Nedyalkov *et al.*, 2007). Main rock-forming minerals consist of Pl, KFs, Bi, Q and Amf, and the accessories are Zrn, Tnt, Ap, Mt and allanite-(Ce). This composition is similar to the acid and intermediate varieties of the Petrohan pluton, but Nedyalkov *et al.* (2007) outline some differences, such as the higher iron content of Bi, the distinct hornblende amphibole and the typical big pinkish microcline-porphyries.

The pre-Triassic age of the Petrohan and Mezdneya plutons is constrained by the transgressive position of Triassic sediments on top of the Petrohan diorites and granites. On the other hand, granitoids intrude the Early Paleozoic DPC. Consequently, derived from field relationships, the age of the magmatism is Late Paleozoic (Variscan). Absolute dating of the plutons was performed by Amov *et al.* (1981), using model Pb-Pb method, and an uranium isotope age of 280–260 Ma was obtained. Later, Carrigan *et al.* (2005) applied *in-situ* SIMS (secondary ion mass-spectrometry) U-Pb zircon dating and defined an age of 304 ± 4 Ma for the granites of the Petrohan pluton.

SAMPLES AND ANALYTICAL TECHNIQUES

Sampling of PMP (Fig. 1) for the present study comprises ten whole-rock samples. Seven samples from the Petrohan pluton (hybrid gabbro AvQ-171, MME E94-4, spessartitic dyke E94, diorite AvQ166, granodiorites AvQ-172, E94-3, and leucogranite E95-1), and one sample from the KFs-porphyry Mezdneya granite (E97) were used for U-Pb zircon and titanite dating and for LA-ICP-MS zircon tracing. Three of them (AvQ171, AvQ172 and E94-4) were chosen

for Hf-zircon isotope tracing. Whole rock (WR) Sr-Nd isotope studies include additional two samples from the Petrohan pluton – a “pegmatoid” diorite with idiomorphic needle Amf (E93), and a diorite E95-2.

Sample preparation

Sample crushing and powdering of an average whole-rock, as well as zircon and titanite separations, were made in the laboratories of the Institute of Mineralogy and Crystallography and the Geological Institute, Bulgarian Academy of Sciences. The zircon and titanite concentrates were collected, using heavy liquids and an in-laboratory designed electro-magnetic separator. The zircons and titanites were finally hand-picked under binocular microscope.

Pre-treatment of zircons for U-Pb analyses

Most of the analysed zircons were either air- (Krough, 1982) or chemically abraded (CA; Matinson, 2005). The leaching step for the CA treated zircons was mainly 8–9 hours and only for the AvQ171-12 grains the 12-hour leaching was applied. Details about the procedures and the effect of CA pre-treatment are given by von Quadt *et al.* (2014) and Peytcheva *et al.* (2015).

Cathodoluminescence (CL) and Back-Scattered-Electron (BSE) imaging

CL and BSE images were obtained from zircons and titanites embedded in an epoxy-resin pellet and then polished to the middle of the grains. The CL-images were taken from a split screen on a Cam-Scan CS 4 scanning electron microscope (SEM) at ETH Zurich (EMEZ) and the Lausanne University, Switzerland.

Laser Ablation ICPMS (LA-ICPMS) of zircon

Laser ablation ICP-MS spot analyses were done, using the New Wave Research (NWR) 193 nm Excimer laser UP-193FX attached to a Perkin-Elmer ELAN DRC-e quadrupole inductively coupled plasma mass spectrometer (LA-ICP-MS) at the Geological Institute, Bulgarian Academy of Sciences. GJ1 zircon was used as primary standard reference material (SRM), and Plesovice as secondary SRM (Jackson *et al.*, 2004; Slama *et al.*, 2008). We used spot diameters of 35 μ m with a laser pulse repetition rate of 8 Hz. The age-dating results were calculated offline, using GLITTER 4.0 (Macquarie University). For each sample, all concordant zircons were

used to calculate a mean $^{238}\text{U}/^{206}\text{Pb}$ age, or a concordia age. Concordia plots, ages, and averaging were processed, using ISOPLOT 3.0 (Ludwig, 2001) or ISOPLOT 4.15.

Isotope-dilution thermal ionisation mass-spectrometer (ID-TIMS) U-Pb isotope analyses of zircons and titanites

The abraded and non-abraded zircons were spiked, using the EARTHTIME ^{202}Pb - ^{205}Pb - ^{233}U - ^{235}U tracer solution and dissolved in HF + trace HNO_3 at 210 °C for ~60–70 h. The samples were dried down and re-dissolved in 6N HCl at 210 °C for 12 hours to convert the samples to chlorides. The solutions were dried again and re-dissolved in 3N HCl. Uranium and Pb were then separated using ion exchange chromatography, following procedures modified after Krogh (1973). Both U and Pb were loaded onto single Re filaments with one microdrop of a silica gel emitter. All measurements were performed at ETH Zurich on a Thermo-Scientific TRITONPLUS thermal ionisation mass spectrometer (TIMS). Pb was measured sequentially on a dynamic MassCom secondary electron multiplier and U was measured in static mode as U-oxide, using Faraday cups fitted with $10^{12} \Omega$ resistor amplifiers. Data reduction and error propagation of the U-Pb data was carried out, using Tripoli and U-Pb Redux software (Bowring *et al.*, 2011) and the U decay constants of Jaffey *et al.* (1971). All uncertainties are reported at the 2 σ level.

Hf isotope analyses of zircons

The *in-situ* Hf isotope data were acquired, using a 193 nm ArF laser connected to the NuII MC-ICP-MS. Ablation was conducted in He (flow rate ~0.95 l/min) and combined with argon (~0.9 l/min), using a spot size of 60 μm and a 5 Hz laser pulse repetition rate over a 60 s ablation period. The most critical factor in obtaining accurate $^{176}\text{Hf}/^{177}\text{Hf}$ ratios by laser ablation concerns the ability to correct for the isobaric interference of Lu and Yb on ^{176}Hf , depending on the REE content of the analysed zircon. The correction itself is performed by measuring an interference-free Yb isotope during the analysis, such as ^{171}Yb or ^{173}Yb , and then calculating the magnitude of the ^{176}Yb interference by using the recommended $^{176}\text{Yb}/^{171}\text{Yb}$ or $^{176}\text{Yb}/^{173}\text{Yb}$ ratios of Segal *et al.* (2003). The Lu correction is performed in the same fashion by monitoring ^{175}Lu and using $^{176}\text{Lu}/^{175}\text{Lu} = 0.02669$. To control and correct the measured Hf-ratios, we analysed two zircon standards with different REE contents (Mon-

astery and Mud Tank). For the calculation of the $\epsilon\text{-Hf}$ values, the following present-day ratios of the Chondritic Uniform Reservoir (CHUR) were used: $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{CH}} = 0.282769$ (Nowell *et al.*, 1998) and $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{CH}} = 0.0334$. For age correction of the Hf isotope ratios at 305 Ma, a $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of 0.0050 was used for all zircons.

Rb-Sr and Sm-Nd whole-rock isotope analyses

The isotopic composition of Sr and Nd were performed at IGP-ETH Zurich, using ID-TIMS techniques. Nd isotopic ratios were normalised to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Analytical reproducibility was estimated by periodically measuring the La Jolla standard (Nd) as well as the NBS 987 (Sr). Further details are given in Gallhofer *et al.* (2017).

RESULTS

Isotope-geochemical results

Sr-Nd whole rock isotope signatures

The strontium isotope data for the rocks of granitoid to diorite composition show wide range of measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7062–0.7099; Table 1) but are consistent in their initial $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.70521–0.70527 calculated for 305 Ma. The samples define an isochrone line (Fig. 2a) with an age of 304 ± 16 Ma (MSWD = 22; $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.70525 \pm 0.00013$). This isochrone reveals the characteristics of a typical mixing line on the $1/\text{Sr}^*1000$ vs $^{87}\text{Sr}/^{86}\text{Sr}$ diagram (Fig. 2b) where the points yield the same linearity as on the isochrone diagram. Below the lines is the point corresponding to the hybrid gabbro AvQ171 with slightly lower initial strontium isotope ratio (0.70462). All initial strontium isotope ratios are close to the enriched mantle array (Fig. 2d). In Fig. 2c, the position of the points suggests either AFC (assimilation and fractional crystallisation) or only FC.

The neodymium isotope data for three of the rock varieties reveal similar initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (≈ 0.51220 ; Fig. 2e, Table 1), corresponding to ϵNd of -0.7 to -0.9 . One diorite sample yields more crustal-influenced ϵNd of -2.9 . All samples lie in the enriched mantle array or point to negligible modification by a crustal component (Fig. 2d).

Hf-isotopes of zircons

Hafnium-isotope analyses are presented in Table 2. The $\epsilon\text{-Hf}$ zircon values of the granodiorite (AvQ172), hybrid gabbro (AvQ171) and MME (E94-4) (corrected for an age of 305 Ma; Table 2,

Table 1

Strontium and neodymium isotope data for samples of the Petrohan pluton

No.	Lab. No.	Sample No.	Pluton	Sample description	SiO ₂ wt%	Rb ppm	Sr ppm	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	2 σ error	(⁸⁷ Rb/ ⁸⁶ Sr) _i (305 Ma)
1	4088	E-93	Petrohan	diorite with needle Amf	54.4	57.3	757	0.21900	0.706223	0.000016	0.70527
2	4089	E-94-3	Petrohan	granodiorite	65.0	86.5	430	0.58200	0.707733	0.000014	0.70521
3	4090	E95-1	Petrohan	leucocratic granite	73.3	101.5	277	1.06040	0.709854	0.000008	0.70525
4	4091	E95-2	Petrohan	diorite	57.5	63.7	711	0.25920	0.706369	0.000011	0.70524
5	2959	AvQ171	Petrohan	hybrid gabbro	53.3	86.0	389	0.63932	0.707397	0.000014	0.70462

No.	Lab. No.	Sample No.	Sample description	Sm ppm	Nd ppm	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	2 σ error	εNd-today	(¹⁴³ Nd/ ¹⁴⁴ Nd) _i (305 Ma)	εNd at 305 Ma
1	4088	E-93	diorite with needle Amf	6.55	36.4	0.1133351	0.512427	0.000005	-4.12	0.5122007	-0.87
2	4089	E-94-3	granodiorite	3.78	23.0	0.1035115	0.512415	0.000005	-4.35	0.5122083	-0.72
3	4090	E95-1	leucocratic granite	2.91	20.9	0.0876943	0.512374	0.000005	-5.15	0.5121989	-0.90
4	4091	E95-2	diorite	5.70	31.2	0.1150654	0.512325	0.000007	-6.11	0.5120952	-2.93

Fig. 2. Sr-Nd isotope diagrams for the Petrohan pluton (for isotope data see Table 1): a) $^{87}\text{Rb}/^{86}\text{Sr}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ isochrone diagram; b) $1/\text{Sr} \times 10000$ vs $^{87}\text{Sr}/^{86}\text{Sr}$ of the same samples showing linearity that infers magma mixing; the white circle corresponds to sample AvQ171 and is not taken into account for age calculation; c) SiO_2 (wt%) vs $(^{87}\text{Sr}/^{86}\text{Sr})_i$ plot; d) $(^{87}\text{Sr}/^{86}\text{Sr})_i$ vs $(^{143}\text{Nd}/^{144}\text{Nd})_i$ evolutionary isotope diagram; e) SiO_2 (wt%) vs $(^{143}\text{Nd}/^{144}\text{Nd})_i$ plot. Abbreviations: DMM – depleted mantle magma; HIMU – high μ ($\mu = ^{238}\text{U}/^{204}\text{Pb}$) mantle magma; EM1 and EM2 – enriched mantle types with lower (I) and higher (II) $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Trends of source contamination (SC), fractional crystallization (FC) and assimilation + FC (AFC) are shown with arrows in c) and e).

Fig. 3) vary between -4.4 and $+0.4$ in the hybrid gabbro (mean value -2.1), from -5.8 to $+0.5$ in the granodiorite (mean value -1.6) and spread from -1.3 to $+3.6$ (mean value $+1.8$) in the MME. These data are informative for advanced interaction (mixing) of the gabbroic and granitic magma in the case of samples AvQ171 and AvQ172 and limited (mingling) modification of the gabbroic magma in the MME. The cores of the zircons are more crustal-influenced (more negative $\epsilon\text{-Hf}$ values), compared

to the rims (e.g., grains 3, 12 in AvQ171; grains 12, 17 in AvQ172; Table 2, Fig. 3).

Th and U composition of zircon

The Th/U ratios decrease from the basic to acid rocks (Table 3, Fig. 4), which is in line with a normal differentiation trend of magmas (e.g., Samper-ton *et al.*, 2015). Thorium content is high in most dioritic, hybrid gabbro and MME zircons (mainly

Table 2

Hafnium-in-zircon isotope data for samples of the Petrohan pluton

No.	Sample No.	$^{176}\text{Hf}/^{177}\text{Hf}$	2 σ error	Lu/Hf	Yb/Hf	$^{176}\text{Lu}/^{177}\text{Hf}$	ϵHf today	ϵHf T-305
<i>AvQ171 – Petrohan hybrid gabbro</i>								
1	AvQ171-7cr	0.282594	0.000022	0.019	0.1430	0.0027	−6.3	−0.3
2	AvQ171-8r	0.282552	0.000032	0.027	0.1470	0.0037	−7.7	−1.9
3	AvQ171-12c	0.282511	0.000030	0.061	0.3540	0.0085	−9.2	−4.4
4	AvQ171-12r	0.282620	0.000029	0.028	0.1440	0.0039	−5.3	0.4
5	AvQ171-3c	0.282554	0.000026	0.020	0.1100	0.0028	−7.7	−1.7
6	AvQ171-3r	0.282567	0.000035	0.035	0.1920	0.0048	−7.2	−1.6
<i>AvQ172 – Petrohan granodiorite</i>								
7	AvQ172-8r	0.282611	0.000029	0.015	0.0833	0.0021	−5.7	0.5
8	AvQ172-7r	0.282554	0.000027	0.014	0.0916	0.0020	−7.7	−1.5
9	AvQ172-12c	0.282422	0.000012	0.001	0.0100	0.0001	−12.3	−5.8
10	AvQ172-12r	0.282481	0.000016	0.007	0.0360	0.0009	−10.3	−3.9
11	AvQ172-17c	0.282555	0.000013	0.008	0.0666	0.0011	−7.6	−1.3
12	AvQ172-17r	0.282588	0.000027	0.016	0.0890	0.0022	−6.5	−0.4
<i>E94-4 – Petrohan MME</i>								
13	E94/4-16	0.282555	0.000034	0.007	0.0427	0.0010	−7.7	−1.3
14	E94/4-14	0.282672	0.000029	0.006	0.0342	0.0008	−3.5	2.9
15	E94/4-12c	0.282644	0.000015	0.010	0.0586	0.0014	−4.5	1.8
16	E94/4-10	0.282672	0.000023	0.009	0.0514	0.0012	−3.5	2.8
17	E94/4-7	0.282698	0.000049	0.014	0.0814	0.0019	−2.6	3.6
18	E94/4-4	0.282619	0.000033	0.009	0.0527	0.0013	−5.4	0.9

Abbreviations: c – core; r – rim; Remark: Zircons of samples AvQ171 and AvQ172 are chemically abraded.

>500 ppm, few exceptionally high values of >4000 ppm; Table 3). The U content is also very high in the zircons of the mafic rock varieties (2000 ppm to 5000 ppm, exceptionally >10,000 ppm), but also in zircons of the leucocratic granite (1000–3000 ppm).

Lower Th and U content is observed in some granodioritic zircons (Fig. 4) and is interpreted as normal magma differentiation and concurrent growth of accessory phases as titanite, thorite, uranorthorite, allanite, etc. Some zircons in the diorite and hybrid

Fig. 3. Hafnium isotope diagram for zircon samples AvQ172 (granodiorite), AvQ171 (hybrid gabbro) and E94-4 (MME). AvQ171 and E94-4 are considered contemporary but are shown with 0.5 Ma age difference for visibility. Abbreviations: c – core; r – rim.

Fig. 4. Th/U vs Ti (ppm) diagram for zircons from the Petrohan pluton (Table 3). The grey lines correspond to temperatures that are calculated using titanium-in-zircon thermometry (Watson and Harrison, 2005; Ferry and Watson, 2007). Used abbreviations: HbGb – hybrid gabbro; MME – mafic magmatic enclave; D – diorite; Grd – granodiorite; LGr – leucocratic granite.

Table 3

LA-ICP-MS tracing data for zircons of the Petrohan pluton

Sample	Zircon	Ti, ppm	Th, ppm	U, ppm	Th/U
E96_2HGb	3	7.7	523	5361	0.10
E96_2HGb	4	7.0	1851	10523	0.18
E93D	14R	9.9	4530	3020	1.50
E93D	10	7.1	2820	2260	1.25
E93D	8	10.3	4790	3100	1.55
AvQ166D	7	9.9	147	2820	0.05
AvQ166D	8	6.7	265	3100	0.09
AvQ166D	9	10.3	149	1680	0.09
AvQ166D	10	8.8	111	1710	0.06
AvQ166D	12	9.6	99	2790	0.04
AvQ166D	3	4.5	3473	8638	0.40
E96_3MME	4	6.1	929	413	2.25
E96_3MME	9	10.3	782	296	2.64
E94_4MME	9C	6.4	482	600	0.8
E94_4MME	10C	4.3	316	409	0.77
E94_4MME	12C	5.3	451	421	1.07
E94_4MME	14C	4.5	202	279	0.72
E94_4MME	16R	6.7	264	349	0.76
E94_3Grd	1R	4.6	316	473	0.67
E94_3Grd	5R	5.2	322	437	0.74
E94_3Grd	5C-40	6.0	184	254	0.72
E94_3Grd	6R	6.2	179	261	0.69
E94_3Grd	3R	5.3	290	459	0.63
E94_3Grd	3C-40	5.2	247	283	0.87
E94_3Grd	7	3.9	205	331	0.62
E94_3Grd	9C	8.6	151	161	0.94
E94_3Grd	10R	8.0	2160	1820	1.19
E94_3Grd	13R	2.7	309	481	0.64
E94_3Grd	13C-40	3.1	227	315	0.72
E94_3Grd	14C-40	8.4	98	127	0.77
E94_3Grd	10c	3.7	217	1388	0.16
E96_4Mob	11r	4.6	539	3111	0.17
E96_4Mob	12r	7.5	276	1936	0.14
E96_4Mob	13c	5.9	150	1108	0.14
E96_4Mob	14r	3.4	322	2441	0.13
E96_4Mob	15c	3.8	295	1889	0.16
E96_4Mob	16c1	5.9	237	1600	0.15
E96_4Mob	17c2	4.8	445	2466	0.18
E96_4Mob	18c	2.6	230	1668	0.14

Abbreviations: c – core; r – rim

gabbro samples reveal a distinctive drop in Th/U (from 1.2–1.5 to 0.1), which suggests zircon recrystallisation and Th gain in other mineral phases.

Zircon thermometry

Titanium-in-zircon thermometry (Watson and Harrison, 2005; Ferry and Watson, 2007) permits the determination of the temperatures at which zircons crystallise in evolving magmas (Claiborne *et al.*, 2010; Reid *et al.*, 2011). The presence of magmatic

quartz in most rock varieties suggests that the silica activity (a_{SiO_2}) was ~ 1 . Based on the presence of magmatic titanite, we apply an a_{TiO_2} of 0.7 (Chelle-Michou *et al.*, 2014; Buret *et al.*, 2016). Temperatures calculated for all hybrid gabbros, MME, diorites and granites are shown in Fig. 4 vs. Th/U ratio of the same zircons. The highest temperatures 780–790 °C are estimated for the diorites, the lowest (650–680 °C) for granodiorites and leucogranites. Most granite and MME zircons crystallise at 700–740 °C (Fig. 4); hybrid gabbros are in the up-

per part of this range. We cannot observe a clear trend of decreasing temperatures from core to rim.

Age data

Zircon population

All studied samples from the Petrohan and Mezdreya granitoids and associated hybrid rocks contain abundant zircon populations. The zircons reveal oscillatory magmatic zoning. The oscillatory bands are usually fine in the granitic rocks, indicating high zirconium saturation, and wide in the hybrid gabbro (AvQ171) and MME as an evidence of generally low/lower zirconium saturation. In some zircons, a recrystallised core is observed, but further analyses defined them as antecrysts – zircons that crystallised from an earlier magma batch (in the sense of Miller *et al.*, 2007). Zircon crystals are mainly intermediate prismatic. They are beige to brownish-purple, transparent to semi-transparent. Typically, hybrid-gabbroic zircons are dark (brownish), indicating high U content. Zircon morphology is defined by two main bi-pyramids {101} and {211} in combination with the prisms {101} > {100}. These are characteristic for calc-alkaline magmas with crust-mantle origin (Pupin, 1980).

ID-TIMS and CA-ID-TIMS U-Pb zircon and titanite dating

The ID-TIMS U-Pb zircon age data are done for both non-abraded and chemically abraded zircons (Table 4, Fig. 5). Most non-abraded zircons reveal Pb-loss and lie on the discordia with poorly constrained lower intercept age (*e.g.*, Fig. 5a). CA-treated zircons of the Petrohan granitoids and the diorite E95-2 (Fig. 5a–d) yield ages mainly in the range of 310–312 Ma, whereas, for the sample E95-1 (leucocratic granite), a concordia age of 311.14 ± 0.48 Ma can be calculated (Fig. 5c). CA treated zircons of the hybrid gabbro are slightly younger 305–308 Ma, whereas the two grains that were leached for 12 h define a concordia age of 308.12 ± 0.33 Ma (all reported ages are with 2σ uncertainties). Mezdreya granite zircons behave similarly to the one of the Petrohan pluton and reveal Pb-loss of the non-abraded grains. Concordant CA-treated crystals yield and age of 307.54 ± 0.54 Ma (Fig. 5d).

Zircon U-Pb age data are compiled with dating of the titanites in granitoids to gabbros, including MME and one lamprophyric (spessartitic) dyke (Table 5, Fig. 6). Generally, the 2σ uncertainties (see the error ellipses in Fig. 6) of the titanites are

a bit larger due to uncertainties in the common Pb composition, as Pb is typically higher in titanites compared to zircons (Tables 4, 5). Lower uranium content is seen in some analysed titanites of E94-4 (MME) and all grains of E-97 (Mezdreya granite; Table 5) and results in their higher age data uncertainty. Precise ages are defined for titanites with higher U content, such as those of the hybrid gabbro (AvQ171), the granodiorite (E94-3) and two grains from the E94-4 MME. They spread between 305 Ma and 309 Ma, with a peak of ages at ~ 305 Ma (Fig. 6).

CA-LA-ICP-MS U-Pb zircon data

U-Pb dating (Table 6) of 12-hour CA treated zircons are in good agreement with the CA-ID-TIMS data of zircons and titanites. Although some grains reveal still negligible (AvQ171) or substantial (AvQ172) Pb loss, most of the grains are concordant at 307.8 ± 2.7 Ma (hybrid gabbro) and 311.9 ± 1.9 Ma (granodiorite) (Fig. 7a, b).

DISCUSSION

Age of the pluton assembly and time scales of processes

The new geochronological data are in good agreement with field data for magma mixing and mingling. The PMP was assembled over at least 4.5 Ma from 311.14 ± 0.48 Ma to 308.12 ± 0.33 Ma (CA-ID-TIMS U-Pb concordia ages of granitoids and hybrid varieties) or 307.54 ± 0.54 Ma (Mezdreya granites). They suggest incremental growth of the PMP, although presented data provide convincing evidence only for the intrusions at distinct periods around 311 Ma, 310 Ma, 308 Ma and 307.5 Ma. The presence of auto- and antecrysts hampers very precise dating of the successive intrusion of magma batches that may originate in the crust and mantle (see discussion below). Although the Palaeozoic rocks reveal higher absolute uncertainties of the concordia ages, compared with younger magmatic suites that are dated with the same precision of 0.1–0.3%, the CA-ID-TIMS U-Pb zircon method yields data that help distinguishing at least some of the magma intrusions. Based on the precise data, we are also able to distinguish the later gabbro intrusion, providing additional numerical proofs for the magma mingling/mixing processes in the generation of the PMP.

Growth of plutons over few Ma is documented in the Variscan and Alpine belts, *e.g.*, the Adamello and Bergell plutons in the Alps (Schaltegger *et al.*,

Table 4

ID-TIMS U-Pb data for zircons of the Petrohan-Mezdreyia pluton

Fractions	Weight (mg)	Concentrations				Ratios (errors 2-sigma)						Age (Ma)					
		U (ppm)	Pb (ppm)	206 Pb* 204 Pb	206 Pb 238 U	% err	207 Pb 235 U	% err	207 Pb 206 Pb	% err	corr. coef.	206 Pb 238 U	2 sigma abs.	207 Pb 235 U	2 sigma abs.		
AvQ171 hybrid gabbro																	
1	0.0301	233	12	6901	0.04801	0.47	0.3479	0.48	0.0526	0.10	0.98	302.30	1.42	303.20	2.97	309.90	0.31
2	0.0035	250	15	597	0.04824	0.50	0.3511	0.60	0.0528	0.31	0.86	303.70	1.52	305.50	2.63	319.40	0.99
9	0.0051	557	37	162	0.04858	0.18	0.3515	1.24	0.0525	1.16	0.52	305.81	0.54	305.84	1.58	306.10	3.54
12_1	0.0065	640	36	4085	0.05259	0.17	0.3549	0.19	0.0489	0.09	0.41	308.06	0.28	308.43	0.50	311.16	3.92
12_2	0.0131	1421	87	38506	0.05262	0.10	0.3549	0.13	0.0489	0.10	0.69	307.83	0.29	308.37	0.35	312.44	2.18
AvQ172 granodiorite																	
1	0.0035	247	11	476	0.03948	0.46	0.2862	0.48	0.0526	0.14	0.96	249.60	1.15	255.60	2.45	310.70	0.43
2	0.0071	124	7	331	0.04469	0.46	0.3246	0.49	0.0527	0.17	0.94	281.80	1.30	285.40	2.68	314.70	0.53
4	0.0026	882	43	3609	0.04416	0.53	0.3205	1.61	0.0526	0.33	0.33	278.56	1.47	282.28	0.93	313.27	1.03
8	0.0026	1186	67	5498	0.04779	0.13	0.3468	0.29	0.0526	0.26	0.44	300.93	0.39	302.35	1.34	313.27	0.83
7	0.0078	95	6	491	0.04871	0.46	0.3506	0.52	0.0522	0.24	0.89	306.60	1.41	305.20	2.72	294.20	0.71
6	0.0032	415	23	1686	0.04928	0.24	0.3593	0.82	0.0529	0.75	0.41	310.08	0.74	311.67	1.28	323.59	2.43
E95_1 leucocratic (remobilized) granite																	
5F	0.0073	5395	336	11976	0.04895	0.11	0.3546	0.13	0.0525	0.53	0.91	308.07	0.35	308.17	2.80	308.89	1.63
1F	0.0047	67	3	598	0.04938	0.16	0.3584	0.74	0.0526	0.69	0.46	310.73	0.48	311.02	1.42	313.20	2.15
3	0.0095	351	23	230	0.04762	0.12	0.3426	0.42	0.0522	0.38	0.44	299.91	0.35	299.11	1.33	292.88	1.11
6	0.0097	151	9	1430	0.04962	0.46	0.3582	1.20	0.0524	1.08	0.45	312.16	1.43	310.87	1.41	301.15	3.24
7	0.0161	371	20	11721	0.04952	0.18	0.3590	1.43	0.0526	1.42	0.13	311.58	0.55	311.45	0.39	310.47	4.41
E95_2 diorite																	
1	0.0696	136	8	653	0.04975	0.16	0.3610	0.51	0.0526	0.48	0.36	312.99	0.50	312.95	1.13	312.62	1.49
7	0.0273	264	15	7051	0.04922	0.47	0.3550	0.60	0.0523	0.38	0.78	309.72	1.44	308.50	2.39	299.27	1.13
6	0.0082	329	18	5871	0.04938	0.23	0.3580	0.67	0.0526	0.63	0.34	310.70	0.71	310.70	1.06	310.69	1.96
E97 Mezdreyia granite																	
1	0.0043	298	16	2816	0.04796	0.83	0.3477	0.90	0.0526	0.33	0.93	302.0	2.51	303.0	2.81	311.2	1.04
2	0.0036	211	12	1435	0.04838	0.56	0.3509	0.85	0.0526	0.61	0.69	304.6	1.71	305.4	2.12	311.5	1.91
3	0.0043	256	12	1216	0.04321	0.34	0.3130	0.81	0.0525	0.70	0.51	272.7	0.93	276.5	1.41	308.6	2.17
4	0.0026	41	3	182	0.04885	0.50	0.35455	3.27	0.05264	3.07	0.47	307.5	1.54	308.1	1.45	313.2	9.62
5	0.0035	23	1	368	0.04919	1.10	0.35765	5.52	0.05273	5.26	0.33	309.5	3.39	310.5	1.02	317.4	16.71
6	0.0042	57	3	749	0.04887	0.21	0.35682	0.57	0.05295	0.50	0.49	307.6	0.65	309.8	1.53	326.8	1.64
7	0.0026	128	7	931	0.04880	0.31	0.3518	1.03	0.0523	0.98	0.31	307.2	0.96	306.1	0.94	297.6	2.91
8	0.0037	130	7	1705	0.04876	0.30	0.3543	0.79	0.0527	0.70	0.46	306.9	0.93	308.0	1.41	316.1	2.21

Remark: bold italic – CA treated zircons; zircons AvQ171 12-1 and 12-2 ale leached 12 hours, all other CA treated grains 8-9 hours.

2009; Samperton *et al.*, 2015), the St-Jean-du-Doigt intrusion in Brittany, France (Barboni *et al.*, 2013), the Meghri-Ordubad pluton in the Lesser Caucasus

(Rezeau *et al.*, 2016), or the Late Mesozoic Heyu and Taishanmiao batholiths in Central China (Bao *et al.*, 2017, and references therein). The assembly

Fig. 5. Concordia diagrams for ID-TIMS dated zircons of samples from the Petrohan-Mezdreyia pluton: a) AvQ171 (hybrid gabbro); b) AvQ172 (granodiorite); c) E95-1 (leucocratic granite – mobilized melt); d) E95-2 (diorite); e) E97 (granite Mezdreya pluton), and f) summary of the CA-treated U-Pb zircon age data. Mark the spread of concordant zircons in the granitoids from 309 to 312 Ma and the peak of zircon ages in the hybrid gabbro and in the granitoids at ~308 Ma.

Table 5

ID-TIMS U-Pb data for titanites of the Petrohan-Mezdrevya pluton

Sample	Concentrations			Isotope Ratios (with 2-sigma errors)							Age (Ma)		
	Wt. mg	U ppm	Pb ppm	^{206}Pb ^{206}Pb	^{206}Pb ^{206}Pb	^{206}Pb ^{238}U	% err	^{207}Pb ^{235}U	% err	^{207}Pb ^{206}Pb	% err	^{207}Pb ^{235}U	^{207}Pb ^{206}Pb
<i>AvQ171 Hybrid gabbro</i>													
Tit-AvQ171-1	0.021	337	29	410	0.770	0.04849	0.212	0.3498	0.498	0.0523	0.435	304.60	1.31
Tit-AvQ171-2	0.011	161	13	259	0.485	0.04849	0.209	0.3507	0.645	0.0525	0.610	305.25	1.70
Tit-AvQ171-3	0.013	486	35	560	0.520	0.04884	0.163	0.3535	0.345	0.0525	0.282	307.37	0.92
Tit-AvQ171-4	0.011	500	39	587	0.660	0.04911	0.115	0.3546	0.192	0.0524	0.171	308.19	0.51
Tit-AvQ171-5	0.009	341	28	417	0.697	0.04905	0.166	0.3560	0.293	0.0526	0.257	309.22	0.78
Tit-AvQ171-6	0.010	134	12	204	0.750	0.04904	0.174	0.3570	0.389	0.0528	0.400	309.97	1.04
<i>E94_3 Granitodiorite</i>													
Tit-E94-3-2	0.013	178	12	325	0.253	0.04880	0.185	0.3532	0.551	0.0525	0.508	307.15	1.46
Tit-E94-3-1	0.012	481	34	254	0.232	0.04845	0.463	0.3505	0.671	0.0525	0.671	305.08	2.16
Tit-E94-3-3	0.017	759	45	468	0.166	0.04883	0.456	0.3534	0.599	0.0525	0.370	307.30	1.59
<i>E94_4 Mafic magmatic enclave (MME)</i>													
Tit-E94-4-1	0.016	289	22	328	0.456	0.04889	1.128	0.3539	1.277	0.0525	0.587	307.69	3.39
Tit-E94-4-2	0.012	168	14	277	0.663	0.04854	0.204	0.3511	0.756	0.0525	0.717	305.56	1.99
Tit-E94-4-3	0.016	1075	64	689	0.188	0.04872	0.575	0.3512	0.696	0.0523	0.375	305.65	1.84
<i>E94 Spessartitic dyke</i>													
Tit-E94-7-2	0.014	251	17	435	0.394	0.04883	0.178	0.3533	0.394	0.0525	0.330	307.21	1.04
Tit-E94-7-3	0.018	106	13	155	1.706	0.04360	0.254	0.3149	0.853	0.0524	0.818	277.98	2.07
<i>E97 Mezdevya granite</i>													
Tit-E97-4	0.020	47	6	145		0.04933	0.32	0.3562	1.87	0.0524	1.74	309.4	5.784
Tit-E97-5	0.015	35	5	104		0.04788	0.39	0.3503	2.62	0.0531	2.45	305.0	7.976
Tit-E97-6	0.012	46	5	99.0		0.05007	0.42	0.3696	4.20	0.0535	3.97	319.3	13.4
Tit-E97-4	0.020	47	6	145		0.04933	0.32	0.3562	1.87	0.0524	1.74	309.4	5.784
Tit-E97-5	0.015	35	5	104		0.04788	0.39	0.3503	2.62	0.0531	2.45	305.0	7.976
Tit-E97-6	0.012	46	5	99.0		0.05007	0.42	0.3696	4.20	0.0535	3.97	319.3	13.4

Fig. 6. Concordia diagram for ID-TIMS dated titanites of samples from the Petrohan-Mezhdreya pluton.

of one pluton might be separated in time as revealed on the Meghri-Ordubad pluton in the Lesser Caucasus (Eocene to Miocene; Rezeau *et al.*, 2016), or the West Rhodope batholith in Bulgaria (*e.g.*, Peytcheva *et al.*, 2007, and references therein). In the PMP, we can suggest stacking of the pluton in crustal chambers with magma replenishment over 4–5 Ma, which requires a specific tectonic setting for certain period (see discussion below). The pluton was exhumed in the Late Carboniferous–Permian and is now overlain by Permian volcanics and Lower Triassic terrigenous sediments (Fig. 1).

The titanite U-Pb dating overlaps mainly with weakly CA-treated zircon data (305–308 Ma). Age data are generally slightly younger than the ones for the penetrative chemically abraded zircons but older than those of the not pre-treated zircon grains. Titanite growth at the end of the magmatic crystallisation is inferred from the hypidi(?)omorphic and xenomorphic forms of grains in the interstices of the major rock-forming minerals (Tacheva, 2013) and from the sectoral zonation of the crystals (Paterson and Stephens, 1992). There is a substantial peak of titanite ages in MME, hybrid gabbro and even granodiorites of PP at 305–307 Ma, which we may explain with a combination of lower closing temperature of the U-Pb isotope system in titanites and possible diffusional Pb loss (higher rates of Pb diffusion in titanites, compared with zircon; Cherniak, 1993; Cherniak and Watson, 2001). Remarkable is the higher U content in the titanites from the outcrops with mixing/mingling of magma, which possibly results from the fast growth of titanite after the mixing with water-rich and oxidised gabbroic mag-

ma. Consequently, these titanites are measured with higher precision (2 σ uncertainty of 0.12–0.20% in the $^{206}\text{Pb}/^{238}\text{U}$ ratio; Table 5), which is comparable with the precision of the zircon ages.

It should also be mentioned that the age of 300.93 ± 0.4 Ma to 306.6 ± 1.4 Ma of weakly CA-treated zircons of the Petrohan granodiorite (AvQ172) overlaps with published SIMS age of 304 ± 4 Ma (Carrigan *et al.*, 2005) within error. Furthermore, the model Pb-Pb age of Amov *et al.* (1981) is similar to the apparent age of the discordant not treated zircons in the Petrohan granodiorite of 250–280 Ma (Table 4). Consequently, we can use data from all applied dating techniques but should be careful with their interpretations. For correlation, we should have in mind that most of the age data result from either (i) *in-situ* U-Pb LA-ICP-MS and SIMS dating and may be slightly younger than the real age; or (ii) conventional ID-TIMS of not abraded zircons, which may yield discordant and substantially younger apparent ages.

Magma generation and evolution: the constraints from the Hf-zircon and whole-rock Sr-Nd isotopes

Whole rock strontium and neodymium isotope data, combined with Hf-zircon isotope results, indicate interaction of mantle derived magma with a crustal melt. The isotope-geochemical data argue for a primary quite primitive basic (gabbroic) magma (hybrid gabbro with initial strontium isotope ratio of $^{87}\text{Sr}/^{86}\text{Sr} = 0.70462$) that is sourced in the enriched mantle or the depleted mantle but afterwards slightly modified by the crust. The initial strontium ratio of the hybrid varieties and granodiorites/granites of ~ 0.70525 and ϵNd of -0.7 to -0.9 can be explained with AFC in lower-middle crustal chamber and /or mixing/mingling and FC in middle/upper crustal chamber. The mixing process is especially supported by the wide range of $\epsilon\text{-Hf}$ zircon values of the granodiorite (AvQ172) and hybrid gabbro (AvQ171) between -5.8 to $+0.5$ that suggest transfer of zircon crystals between the contrasting magma (mantle- and crustal derived) and further growth in the mash. Magma replenishment with later intrusion of basic/gabbroic magma is evident from the more negative $\epsilon\text{-Hf}$ values of the zircon cores, compared to the rims.

Constraints on the tectonic setting

The Variscan orogeny of Europe marks the final amalgamation of Laurasia and Gondwana to form the supercontinent Pangea (*e.g.*, Matte, 1986; von

Table 6

CA-LA-ICP-MS data for pervasively chemically abraded zircons of samples AvQ171 (hybrid gabbro) and AvQ172 (granodiorite) of the Petrohan pluton

N	Zircon	Isotope ratios					Rho	Age, Ma			Concentrations		Ratio				
		²⁰⁶ Pb/ ²³⁸ U	1 SE	²⁰⁷ Pb/ ²³⁵ U	1 SE	²⁰⁸ Pb/ ²³² Th		1 SE	²⁰⁷ Pb/ ²⁰⁶ Pb	1 SE	²⁰⁶ Pb/ ²³⁸ U	2S		²⁰⁷ Pb/ ²³⁵ U	2S	Th, ppm	U, ppm
AvQ171-CA																	
1	1r	0.04534	0.00056	0.3288	0.0092	0.0144	0.0005	0.0526	0.0013	0.62	285.9	14	289	14	436	972	0.45
2	2r	0.04170	0.00050	0.3108	0.0068	0.0128	0.0005	0.0540	0.0010	0.65	263.4	11	275	11	2263	3755	0.60
3	2c	0.04673	0.00062	0.3343	0.0111	0.0146	0.0006	0.0488	0.0015	0.61	294.4	17	290	17	591	885	0.67
4	3r	0.04838	0.00058	0.3599	0.0083	0.0151	0.0006	0.0540	0.0010	0.64	304.6	12	312	12	1805	2611	0.69
5	3c	0.04609	0.00059	0.3444	0.0106	0.0147	0.0006	0.0542	0.0014	0.62	290.5	16	300	16	947	1374	0.69
6	4c	0.03493	0.00042	0.2782	0.0066	0.0103	0.0004	0.0578	0.0012	0.64	221.3	10	249	10	6110	4045	1.51
7	5r	0.04935	0.00068	0.3456	0.0139	0.0153	0.0008	0.0508	0.0018	0.61	310.6	8.4	301	21	242	499	0.48
8	5c	0.04924	0.00061	0.3471	0.0093	0.0151	0.0007	0.0511	0.0012	0.64	309.9	7.5	303	14	1555	1799	0.86
9	7r	0.04772	0.00060	0.3407	0.0097	0.0146	0.0007	0.0518	0.0013	0.63	300.5	7.4	298	15	2518	2574	0.98
10	7c	0.04903	0.00068	0.3372	0.0138	0.0145	0.0008	0.0499	0.0018	0.61	308.5	8.4	295	21	246	578	0.43
11	8r	0.04853	0.00070	0.3518	0.0158	0.0142	0.0008	0.0526	0.0020	0.60	305.5	8.6	306	24	507	970	0.52
12	12c	0.04880	0.00065	0.3567	0.0126	0.0146	0.0008	0.0530	0.0016	0.62	307.2	8.0	310	19	1114	1303	0.86
13	12r	0.05001	0.00064	0.3637	0.0112	0.0147	0.0008	0.0527	0.0014	0.63	314.6	7.9	315	17	1331	1381	0.96
AvQ172-CA																	
1	7c	0.04936	0.00065	0.3634	0.0125	0.0152	0.0006	0.0534	0.0016	0.61	310.6	18	315	18	402	649	0.62
2	7r	0.04946	0.00064	0.3489	0.0114	0.0150	0.0006	0.0512	0.0015	0.62	311.2	7.9	304	17	385	533	0.72
3	8r	0.04937	0.00068	0.3588	0.0138	0.0141	0.0006	0.0527	0.0018	0.61	310.7	8.4	311	20	238	432	0.55
4	8c	0.04954	0.00076	0.3648	0.0184	0.0163	0.0008	0.0534	0.0024	0.60	311.7	9.3	316	27	230	427	0.54
5	9c	0.05003	0.00080	0.3464	0.0198	0.0149	0.0007	0.0502	0.0027	0.59	314.7	9.8	302	30	100	187	0.54
6	10r	0.04762	0.00062	0.3329	0.0110	0.0149	0.0006	0.0507	0.0015	0.62	299.9	7.6	292	17	296	505	0.59
7	12r	0.04634	0.00058	0.3320	0.0090	0.0143	0.0007	0.0520	0.0012	0.63	292.0	7.1	291	14	163	906	0.18
8	12c	0.03940	0.00084	0.3511	0.0344	0.0128	0.0008	0.0646	0.0053	0.57	249.1	10.4	306	51	33	46	0.72
9	13r	0.04749	0.00068	0.3397	0.0148	0.0148	0.0008	0.0519	0.0020	0.60	299.1	8.4	297	22	166	323	0.51
10	13c	0.04941	0.00068	0.3597	0.0143	0.0169	0.0009	0.0528	0.0018	0.61	310.9	8.4	312	21	220	411	0.54
11	14r	0.04940	0.00069	0.3468	0.0140	0.0158	0.0009	0.0509	0.0018	0.61	310.9	8.5	302	21	260	507	0.51
12	15r	0.04949	0.00066	0.3573	0.0127	0.0157	0.0009	0.0524	0.0016	0.62	311.4	8.1	310	19	248	462	0.54
13	15c	0.04952	0.00069	0.3557	0.0148	0.0161	0.0010	0.0521	0.0019	0.61	311.6	8.5	309	22	219	303	0.72
14	17r	0.05060	0.00078	0.3589	0.0189	0.0157	0.0011	0.0514	0.0024	0.60	318.2	9.6	311	28	120	244	0.49
15	19r	0.04972	0.00069	0.3405	0.0139	0.0165	0.0011	0.0497	0.0018	0.61	312.8	8.5	298	21	162	274	0.59

Abbreviations: c – core; r – rim.

Fig. 7. CA-LA-ICP-MS Concordia diagrams for pervasively chemically abraded zircons of samples AvQ171 – hybrid gabbro (a) and AvQ172 – granodiorite (b). Concordant ages are calculated for the concordant zircons and shown on the right side (filled symbols correspond to the CA-ID-TIMS data and are shown for comparison but not taken for calculation).

Raumer *et al.*, 2003). Based on tectonic reconstruction of the European Variscides, Devonian spreading and subduction were followed by Carboniferous collision and Carboniferous–Permian extension (*e.g.*, Finger, 1997; Schulmann *et al.*, 2014; Plissart *et al.*, 2017). The geochronological evidence for the Variscan orogeny on the Carpathian-Balkans is in agreement with the data for Central and Western Europe, although there are a few specifics. Gabbros of the Cherni Vrah ophiolitic complex in the Western Balkan (Haydoutov *et al.*, 1989), representing the easternmost outcrop of the dismembered Carpathian-Balkan ophiolites (CBO), were recently dated as Devonian (Kiselinov *et al.*, 2017). The newly obtained LA-ICP-MS U-Pb zircon age of

391.2 ± 1.3 Ma fits well with published age data for the other CBO segments, all dated between 405 ± 3 Ma (Deli Jovan, East Serbia; SHRIMP U-Pb zircon dating, Zakariadze *et al.*, 2012) and 388.1 ± 5.1 Ma to 383.9 ± 4.2 Ma (Zaglavak, East Serbia; LA-ICP-MS U-Pb zircon ages, Balica *et al.*, 2014). Tectonic reconstructions in the Carpathian-Balkan sector of the Variscides suggest obduction (not subduction) of the oceanic crust to the north (*e.g.*, Plissart *et al.*, 2017), so we should not expect voluminous granitoid magmatism in the Balkan Mts area during the Devonian. Following these reconstruction remnants of Devonian eclogites and possible subduction, related magmatism might be found in the units south of the CB suture.

Carboniferous–Permian granitoids occur in different tectonic units of Bulgaria and the results from their age dating are summarised in Fig. 8. We used only the most reliable age data from U-Pb ID-TIMS, SIMS, SHRIMP and LA-ICP-MS isotope methods, with only one Ar/Ar dating of the Svidnya pluton where the zircon dating failed. The granitoid Variscan magmatism (Fig. 8) starts in the western Balkan in the Early Carboniferous with the potassic alkaline Svidnya granite that is dated at ~338 Ma by Ar/Ar (Buzzy *et al.*, 2017). Close after, at around 330 Ma (332±6 Ma; Peytcheva *et al.*, 2006) formed the Klissura granite, which is contemporary with the granites in the Tran region 332.57±0.60 Ma (Peytcheva *et al.*, 2011) intruding the Getic Unit (including Sredna Gora, according to Schmid *et al.*, 2008). As the Klissura and Tran granites reveal crustal affinity influenced by the varying composition of the Pre-Variscan basement, and high-grade metamorphism in the Sredna Gora basement occurred at 336.5±5.4 Ma (Carrigan *et al.*, 2006), we can suggest collision-related magmatism at that time. The latter lasted at least 15 Ma until around 315 Ma and was marked by voluminous gra-

nitic magmatism in the Balkans (Ravno Bučje-San Nikola or Sveti Nikola pluton 320 Ma – Carrigan *et al.*, 2005; Jovanović *et al.*, 2018; Stakevtsi granite ~320 Ma – S. Georgiev, pers. comm.) and in Sredna Gora (Koprivshitsa 312.0±5.4 Ma – Carrigan *et al.*, 2005; Lesitchovo granite 316.5±3.5 Ma – Peytcheva *et al.*, 2004). During this time, there is no reason to separate the Variscan magmatism in the Balkan tectonic unit from that in the Getic /Sredna Gora units, no matter which tectonic scenario we assume – collisional or subductional (Carrigan *et al.*, 2005; Okay *et al.*, 2017). Considering the mainly granitic magmatism (S- and I-type) and the closure of the Devonian ocean, we prefer the interpretation with collisional magmatism. For the subduction scenario, there should be evidence for a migration of the subducting slab to the south in time or spreading in an ocean (Palaeotethys) south of the Getic and Rhodope units. Such data are still missing from the Balkan sector of the Variscides.

The tectonic setting changed at around 305 Ma, when gabbroic magmas generated and intruded both main tectonic units – the Balkan and Sredna Gora/Getic units, but also the Sakar-Strandzha

Fig. 8. Summary of the time intervals of granitoid magmatism in the different tectonic units of Bulgaria (after Ivanov, 2017 and Schmid *et al.*, 2008) during the Variscan orogeny, defined by U-Pb isotope methods (ID-TIMS, SIMS, SHRIMP and LA-ICP-MS), with only one Ar/Ar dating of the Svidnya pluton. Devonian ophiolites and transitional Permian–Triassic magmatic rocks are excluded. Data from: 1) Buzzi *et al.* (2010); 2) Dyulgerov *et al.* (2017); 3) Peytcheva *et al.* (2006); 4) S. Georgiev, pers. comm.; 5) S. Georgiev (2016); 6) Carrigan *et al.* (2005); 7) Nedialkov *et al.* (2007); 8) Nedialkov *et al.* (2015); 9) Dyulgerov *et al.* (2010); 10) Peytcheva *et al.* (2011); 11) Peytcheva and von Quadt (2004); 12) Bonev *et al.* (2017); 13) Machev *et al.* (2002); 14) Peytcheva *et al.* (2016); 15) Georgiev *et al.* (2012); 16) Peytcheva and von Quadt (1995); 17) Cherneva *et al.* (2002); 18) Ovtcharova *et al.* (2002); 19) Carrigan *et al.* (2003); 20) Georgiev *et al.* (2016); 21) Peytcheva *et al.* (2004b); 22) Liati and Gebauer (1999); 23) Turpaud and Reischmann (2010); 24) this study. The abbreviation CRD is used for the Central Rhodopean Dome.

Zone. Granitoid to dioritic and gabbroic plutons in the Balkan unit are PMP (311.14 ± 0.48 Ma to 307.54 ± 0.54 Ma, this study) and the Vezhen Pluton (new well-constrained LA-ICP-MS U-Pb zircon dating from 307 Ma to 302 Ma – Georgiev *et al.*, 2016; former upper intercept age of Kamenov *et al.*, 2002, at 314 ± 6 Ma is interpreted to reflect negligible lead inheritance). Both plutons give evidence for magma mingling and mixing (Kamenov *et al.*, 2002; Tacheva *et al.*, 2006; Georgiev *et al.*, 2016). In the Sredna Gora Unit, the Smilovene I type granodiorite (304.1 ± 5.5 Ma – Carrigan *et al.*, 2005), Medet gabbro (305.55 ± 0.50 Ma – Peytcheva *et al.*, 2004) and the I-type Hisariya granite (303.5 ± 3.3 Ma – Carrigan *et al.*, 2005) provide evidence for the interaction of a primary mantle gabbroic magma with the continental crust to produce hybrid, intermediate and acid rocks. With the same group of granitoids, we should correlate the Sakar and Strandzha granitoids that are dated at 305–301 Ma (Sakar granite at 301.9 ± 1.1 Ma or 305 ± 5.5 Ma – Machev *et al.*, 2015; Peytcheva *et al.*, 2016; Bonev *et al.*, 2017; and Zhelyazkovo gabbro at 302.1 ± 1.5 Ma – Peytcheva *et al.*, 2016).

Our new data for the Petrohan pluton suggest stacking of the mantle and hybrid magma in the middle-upper crustal chamber, with magma replenishment over 4–5 Ma, which requires a compressional/transpressional setting, followed by transtensional? tectonic setting for a certain period. Furthermore, the following Permian magmatism was not within-plate/extension related. Consequently, we would suggest mantle delamination or mantle underplating that led to melting of subcontinental mantle lithosphere or to influx of asthenosphere magma, melting and assimilation of crustal materials and further evolution through AFC and mingling/mixing processes.

The Variscan magmatism in the Balkans and Carpathians continues in the Carboniferous–Permian (Fig. 8) and Permian–Triassic and is reported for all three units. One peak of granitoid magmatism occurred at around 295–285 Ma (Carrigan *et al.*, 2005; Georgiev *et al.*, 2012; Machev *et al.*, 2015; Nedialkov *et al.*, 2015; Bonev *et al.*, 2017) and is generally interpreted to mark further melting of crustal materials due to thermal flux. Unfortunately, petrological and geochemical data for this magmatism are still sparse to draw well-constrained conclusions about the tectonic setting. In the region of PMP, the Permian magmatism is expressed as volcanics and dykes with intermediate to basic composition and its age is not precisely defined. Late Permian to Triassic granitoid magmatism is described mainly in the SSZ and the Serbo-Macedonian Massif and its

interpretation is controversial. The subduction-related setting is supported by Natal'in *et al.* (2016, and references therein), suggesting long-lived Cambrian–Triassic Silk Road magmatic arc, which evolved on the northern side of the Palaeotethys. The Early Triassic granitoids in the Serbo-Macedonian Massif (Ograzhden Unit or Vertiskos Unit), on the other hand, are interpreted as post-collisional (Zidarov *et al.*, 2006; Peytcheva *et al.*, 2009, 2015; Antić *et al.*, 2016) and rift-related (within-plate granites, *e.g.*, Himmerkus *et al.*, 2009). As we discussed above, tectonic reconstructions in the Balkan-Carpathians support the accretion/collision of the Balkan with the Moesian and Sredna Gora/Getic units in the Early Carboniferous. Consequently, subduction-related magmatism at distinct periods from the Cambrian to the Silurian and possibly in the Devonian is related to various palaeo-oceans or parts of the Palaeotethys.

CONCLUSIONS

- 1) The Petrohan-Mezdrea pluton was assembled from 311.14 ± 0.48 Ma to 307.54 ± 0.54 Ma;
- 2) Stacking of mantle and hybrid magma in lower-middle and upper crustal chambers over at least 4.5 Ma is assumed to explain the incremental growth of PMP;
- 3) The new CA-ID-TIMS U-Pb zircon data provide numerical proofs for the magma mingling/mixing processes in the generation of the PMP. The precision of the CA-ID-TIMS U-Pb zircon dating ($\sim 0.1\%$) allows the distinction of magma replenishment – intrusion of younger gabbro (308.12 ± 0.33 Ma) in the older granodiorites (311.14 ± 0.48 Ma);
- 4) Whole-rock strontium-neodymium and Hf-zircon isotope data infer interaction of mantle derived magma with crustal melts. Possible petrogenetic processes are AFC in a lower-middle crustal chamber and mixing/mingling and FC in a middle/upper crustal chamber;
- 5) The comparison of our new data with numerous published studies on the petrology, geochemistry and timing of C-P granitoids and metagranitoids in Bulgaria supports the accretion/collision of the Balkan with the Moesian and Sredna Gora/Getic units in the Early Carboniferous, and syn- to post-collisional setting of magmatism in the Middle–Late Carboniferous and Permian.

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