Article

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Posted Date: 12 March 2025

doi: 10.20944/preprints202503.0840.v1

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U-Pb Zircon Age Constraints on the Paleozoic Sedimentation, Magmatism and Metamorphism of the Sredogriv metamorphics, Western Balkan Zone, NW Bulgaria

Nikolay Bonev [1,2,*], Petyo Filipov [3], Tsvetomila Vladinova [3], Tanya Stoylkova [4], Hristiana Georgieva [3], Svetoslav Georgiev [3], Hristo Kiselinov [5] and Lyubomirka Macheva [6]

[1] Department of Geology, Paleontology and Fossil Fuels, Sofia University St. Kliment Ohridski, 15 Tzar Osvoboditel Bd., 1504 Sofia, Bulgaria; niki@gea.uni-sofia.bg
[2] Bulgarian Academy of Sciences, 1 November 15 Str., 1040 Sofia, Bulgaria; ngbonev@gmail.com
[3] Department of Geochemistry and Petrology, Geological Institute of the Bulgarian Academy of Sciences, 24 Acad. G. Boncev Str., 1113 Sofia, Bulgaria; p_philipov@geology.bas.bg
[4] Department of Mineralogy, Petrology and Economic Geology, Sofia University St. Kliment Ohridski, 15 Tzar Osvoboditel Bd., 1504 Sofia, Bulgaria; tstoylkova@gea-uni-sofia.bg
[5] Department of Regional Geology and Tectonics, Geological Institute of the Bulgarian Academy of Sciences, 24 Acad. G. Boncev Str., 1113 Sofia, Bulgaria; hristo_bk@geology.bas.bg
[6] Department of Mineralogy and Mineral Resources, Institute of Mineralogy and Crystallography of the Bulgarian Academy of Sciences; lu_macheva@dir.bg
* Correspondence: niki@gea.uni-sofia.bg

Abstract: The Sredogriv greenschist facies rocks belong to the Western Balkan Zone in northwestern Bulgaria. The low-grade rocks consist of clastic-tuffaceous precursors and presumably olistostromic magmatic bodies. We present U-Pb LA-ICP-MS zircon age constraints for the Sredogriv metaconglomerate, intruding metaalbitophyre and a breccia-conglomerate of the sedimentary cover. Detrital zircons in the Sredogriv metaconglomerate yielded a maximum depositional age of 523 Ma, with a prominent Neoproterozoic-Early Cambrian detrital zircon age clusters derived from igneous sources. The metaalbitophyre crystallized at 308 Ma and contains the same age clusters of inherited zircons. A maximum age of deposition is defined at 263 Ma for a breccia-conglomerate of the Smolyanovtsi Formation from the sedimentary cover that recycled material from the Sredogriv metamorphics and Carboniferous-Permian magmatic rocks. Proximity to Cadomian island arc sources and provenance from the northern periphery of Gondwana outline the depositional setting of the Sredogriv sedimentary succession. The timing of the Variscan greenschist facies metamorphism of the Sredogriv metamorphics is bracketed between 308 Ma and the depositional age of 272 Ma of another adjacent clastic formation. The results obtained allow us to identify the timing of the Cadomian sedimentary history and the Variscan magmatic and tectono-metamorphic evolution in part of the Western Balkan Zone

Keywords: U-Pb zircon geochronology; Sredogriv metamorphics; western balkan zone; Bulgaria

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1. Introduction

The Balkan Zone forms crucial part of the Alpine fold-and-thrust belt exposed in northwestern Bulgaria, and it is considered to represent Balkan terrane, together with other two large-scale Moesian and Thracian terranes on the territory of Bulgaria that have been linked to Gondwana geodynamic evolution [1–4] (Figure 1). This evolution involves oceanic crust formation, island arc development and collision of Gondwana-derived crustal blocks with the Laurasia continental margin during the Late Neoproterozic to Early Paleozoic times [2-6], which testifies for the presence of tectono-magmatic elements of the Avalonian-Cadomian orogeny [3,6–9], as well as the same elements of the Variscan orogeny [6,10,11] in the Balkan Zone. Hovever, despite that the Late Carboniferous-Early Permian crystallization ages of Variscan magmatism in the Balkan Zone is relatively well-known [e.g. 7,12–13], the reliable age constraints for pre-Variscan and Variscan sedimentation and Variscan metamorphism are generally scarce or still lacking in most parts of the Balkan Zone. Specifically, the clastic sedimentation of the Permian red beds is inferred only from the stratigraphic position to the underlying Lower Paleozoic strata for some of which biostratigraphic ages exist [10,14], while the knowledge of the Carboniferous high-grade metamorphism at 336.5±5.4 Ma is based only on a single zircon age [6] and its cooling derived by $^{40}Ar/^{39}Ar$ mica ages in the range of 306-317 Ma [15] in the Sredna Gora Zone south of the Balkan Zone.

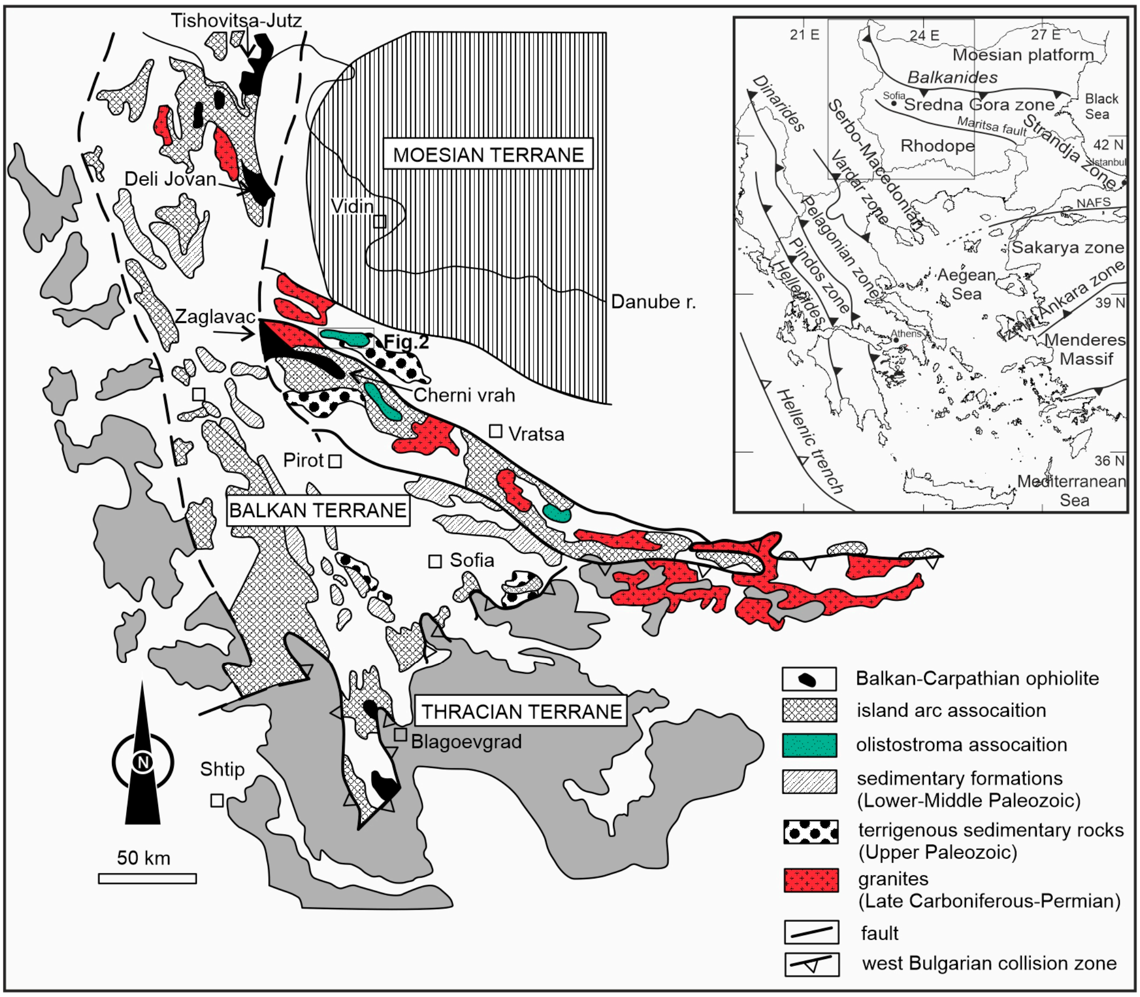

Figure 1. Tectonic scheme of the Moesian, Balkan and Thracian terranes on the territories of Bulgaria, Serbia and Romania, simplified after [3]. Inset: The Alpine belt in the Aegean region of the Eastern Mediterranean. Boxed area in the inset frames the tectonic scheme area, where the location the Sredogriv metamorphics is also shown.

In northwestern Bulgaria, the Balkan Zone consists of Forebalkan and Western Balkan units involved in the Alpine fold-and-thrust belt [16] (Figure 1). Other subdivision identifing the Western Balkan Zone includes Alpine thrust-imbricated Berkovitsa, Vratsa, Montana and Belogradchik units [17].

The Western Balkan Zone is built of Neoproterozoic-Cambrian crystalline basement and Late Paleozoic-Mesozoic cover rocks [3,4,8,16–18]. In the old Bulgarian geological literature, the low-grade crystalline basement of the Western Balkan Zone is reffered as to the Diabase-Phyllitoid formation [19] or complex [20], in which basalt lenses and blocks were interpreted as olistoliths [21]. The latter complex is inferred of latest Neoproterozoic-Early Paleozoic age based on finds of Lower and Upper Ordovician acritarchs [22] and the stratigraphic relationships with the underlying, presumably older magmatic units (see below). However, in the Diabase-Phyllitoid complex, a recent U-Pb zircon geochronology revealed crystallization of a pillow basalt at 519.9 ± 3.6 Ma [23] and a maximum depositional age of a metaconglomerate at 510 ± 6 Ma and a sandstone at 540 ± 5.9 Ma [4,18], which althogether rather consistently define a Cambrian age of this complex.

In the Diabase-Phyllitoid complex, three lithostratigraphic groups have been subdivided, namely Cherni Vrah, Berkovitsa and Dalgi Djal groups [24,25]. These groups differ among each other in their lithologic character and tectono-stratigraphic relationships.

The Cherni Vrah Group is ophiolitic, and it is traditionally regarded as representing an element of the Balkan-Carpathian complete ophiolite that includes N-MORB type cumulate, mafic inrusive and volcanic section of an oceanic lithosphere [5,26]. The age of the Cherni Vrah Group was defined as Neoproterozoic by a single U-Pb zircon crystallization age of a gabbro at 563±5 Ma [27]. The latter age was interpreted as detrital by Kiselinov et al. [28] that dated the Cherni Vrah gabbro as Devonian at 391.2±1.3 Ma by LA-ICP-MS method on multiple zircon grains. The counterparts of the Balkan-Carpathian ophiolite in Eastern Serbia and Romania demonstrate Devonian U-Pb zircon crystallization ages of Deli Jovan ophiolite gabbro at 405±2.6 Ma [29], an age of 388.1±5.1 Ma for the Zaglavac ophiolite gabbro [30], and 380-390 Ma Sm-Nd isochron ages for Tishovitsa-Jutz ophiolite gabbro [31] (see Figure 1 for location of the ophiolitic bodies).

The Berkovitsa Group is island arc-related, and consists of Ca-alkaline volcanic (metabasalt, metaandesite and metatrachyandesite) and plutonic counterparts and associated sedimentary successesions of an intra-oceanic arc system, for which is inferred pre-Ordovician (latest Neoproterozoic-Cambrian) age based on previously reported acritarchs in the Diabase-Phyllitoid complex [25]. An angular unconformity of the Berkovitsa Group island arc onto the Cherni Vrah Group ophiolite is reported by the latter author. Cambrian age of 493.0±6.6 Ma was defined for the Berkovitsa Group Pilatovo gabbro by U-Pb method on zircons [32]. Similarly, a tuffitic metasiltstone and a metasandstone from the Berkovitsa Group yielded maximum depositional ages of 494.5±5 Ma and 521±5 Ma, respectively [4].

The Dalgi Djal Group is olistostromic, in which alternating metasedimentary lithologies host olistoliths from the Cherni Vrah ophiolite and magmatic rocks of the Berkovitsa island arc system [25]. The inferred early Ordovician age of the Dalgi Djal Group is based on the acritarchs found in similar rock types to this group from other exposed areas of the Diabase-Phyllitoid complex in the Balkan terrane [25]. The Dalgi Djal Group overlies unconformable the Berkovitsa Group and it is interpreted as a sedimentary assemblage formed during the destruction and obduction of the Balkan-Carpathian ophiolite.

The investigated here Sredogriv low-grade metasedimentary rocks have been correlated with the Dalgi Djal Group [25], and for them critical age constraints on the sedimentary depositional history and magmatic components contained in the metasedimentary rocks, as well as for the timing of the experienced low-grade metamorphism are still lacking. This hampers establishing the earlier Paleozoic sedimentary and tectono-metamorphic evolution of some of the low-grade metamorphic units that constitute the important Cadomian and Variscan crustal elements subsequently implicated in the Alpine Balkan fold-and-thrust belt.

In this contribution, we present detrital zircon U-Pb geochronology for the depositional timing of the precursors of the Sredogriv low-grade metamorphic rocks, as well as on the clastic sedimentary rocks of its immediate cover (Figure 2). It is also complemented by U-Pb geochronology of the felsic magmatic rocks contained in these low-grade metamorphic rocks and whole-rock geochemistry of the latter. The aim of this study is to provide age constraints relative to the magmatic protolith and

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depositional history of the Sredogriv metamorphics as an important crustal element of the Western Balkan Zone, as well as to bracket the temporal frame of the experienced greenschist facies metamorphism using also the depositional history of the Late Paleozoic cover rocks.

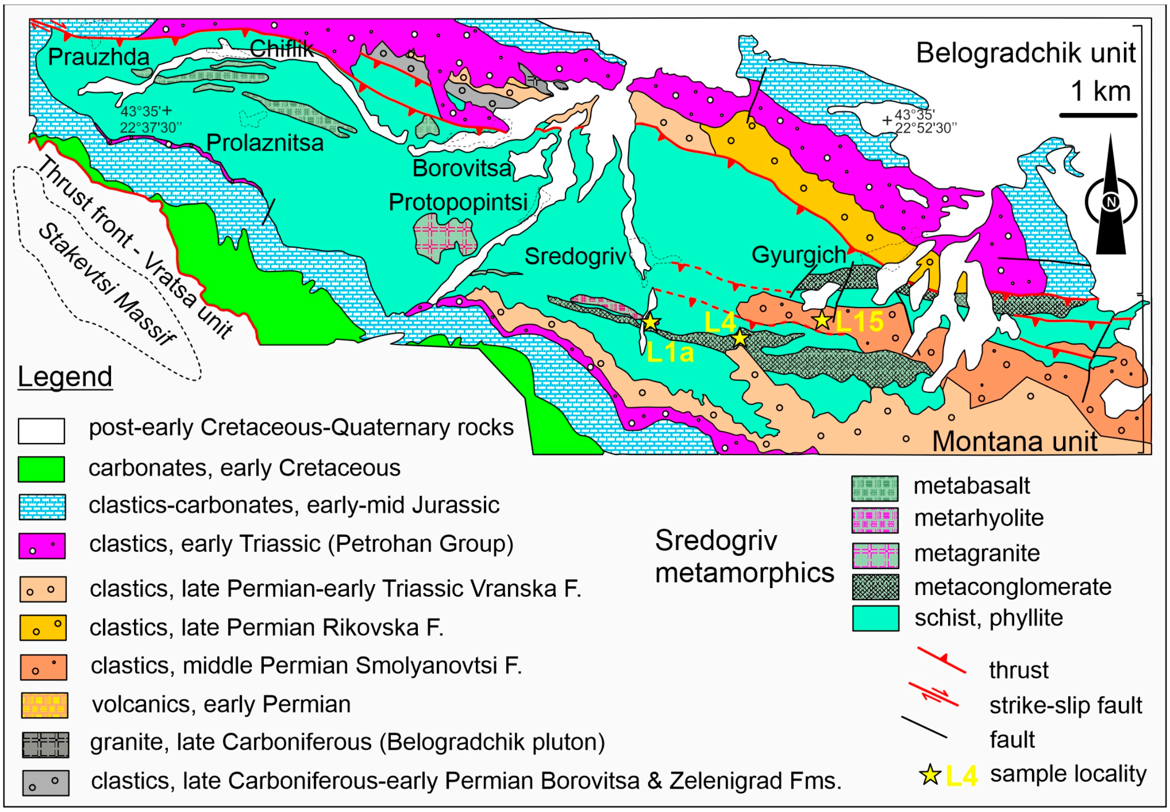

Figure 2. Simplified geological map of the Sredogriv metamorphics after [33,34] showing the locations and numbers of the studied samples.

2. Geological Setting and Field Observations

The Sredogriv metamorphics [33,34] belong to the Montana unit, which is a component of the large-scale Western Balkan Zone [17]. They represent NW-SE elongated strip of low-grade metamorphic rocks without exposed base, that appear below the unconformable latest Paleozoic-Mesozoic sedimentary cover rocks (Figure 2). Initially, they have been subdivided into the Sredogriv Formation [35], and later included into the Diabase-Phyllitoid complex [20,36]. The Sredogriv metamorphics, together with presumably Permain in age clastic and volcanic rocks, build up the basement of the Montana unit, which is covered by Lower Triassic and Middle Jurassic-Early Cretaceous clastic-carbonate successions showing internal unconformities among the distinct formations [33,34] (Figure 3). The Montana unit is thrusted over the Belogradchik unit along the late Alpine Vedernik thrust. The age of the Sredogriv metamorphics is inferred to be Silurian [37], Devonian-Early Carboniferous [20], pre-Devonian [35] and Ordovician by analogy with the Dalgi Djal Group [25]. According to Moskovski et al. [35], the Sredogriv Formation consists of a lower terrigenous member and an upper terrigenous-tuffaceous member. Haydoutov [38] unifies the Sredogriv Formation together with four other formations into the terrigenous-volcanogenic suite called “Stara Planina flyschoid Formation”. Intense deformation, greenschist facies metamorphism and modified primary stratification led Angelov et al. [33,34] to unify the parametamorphic rocks along with the allochthonous magmatic rocks into a single unit called the Sredogriv metamorphics. Kiselinov [39] has distinguished six deformational stages (assigned to Cadomian, Variscan and Alpine orogenies) of the Sredogriv metamorphics and obtained a Neoproterozoic U-Pb zircon protolith age of 618±10 Ma for the Protopopintsi metagranitoid, which is considered as an olistolith

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within these metamorphics. Kiselinov [39,40] studied the geochemical composition of several samples of metabasites, metagranites and metavolcanites included in the Sredogriv metamorphites and interpreted them as having formed in different tectonic settings. These results support the suggestion of an older peri-Gondwanan origin of the igneous olistoliths and olistoplaques that were tectonically included during the late Silurian and Devonian into an epicontinental basin. The obtained Ediacaran age (618 Ma) of the Protopopintsi granite (representing a large olistoplaque in the Sredogriv metamorphites) also testifies to the peri-Gondwanan origin of the basement of the Balkan assemblage [41,42].

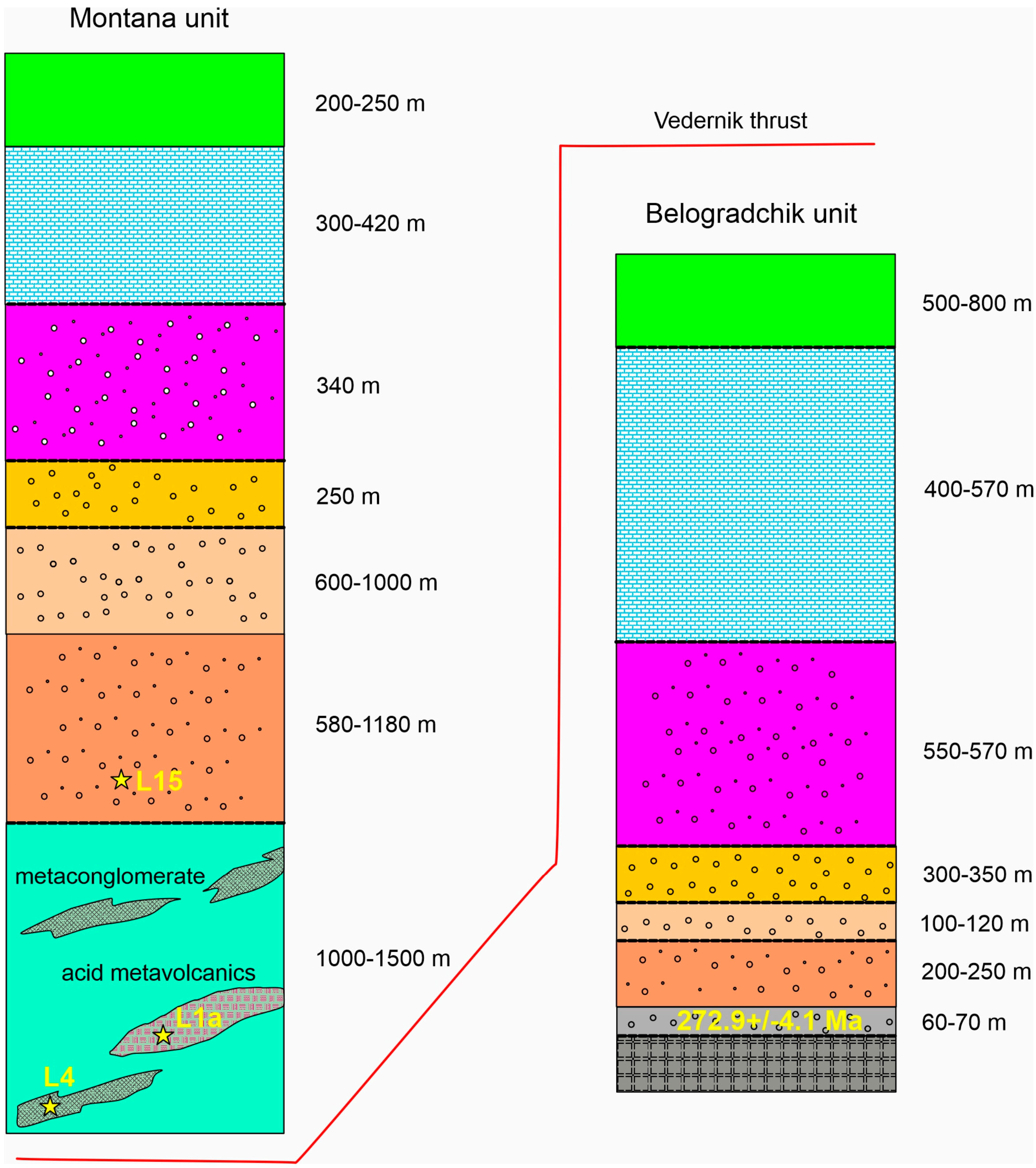

Figure 3. Simplified geological column of the Montana and Belogradchik units of the Western Balkan Zone [after 33] showing the locations and numbers of the studied samples. See Figure 2 for the ornaments. The maximum depositional age of Zelenigrad Formation is shown in Belogradchik unit column.

Our field observations confirmed previous data that the Sredogriv metamorphics are strongly deformed in greenschist facies metamorphic conditions (Figure 4a). These metamorphics consist of

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alternating quartz-sericite schist, sericite-chlorite schist, calc-schist, phyllite, metaaleurolite, metasandstone and metaconglomerate. Basic and acidic metaigneous bodies within this metasedimentary succession are considered allochthonous, representing various olistostromic bodies [33,34]. In the field, it is hardly to identify the olistostomic nature of the magmatic rocks because some demonstrate features of mafic dykes (thin elongated bodies) or felsic sill (foliation/stratification-parallel thin bodies) within the metamorphic succession that shows typical greenschist facies mineral assemblages. Moreover, the mafic dykes shows rather consistent E-W to ESE-WNW strike that implies they represent a conjugate network of mafic igneous bodies (see Figure 2).

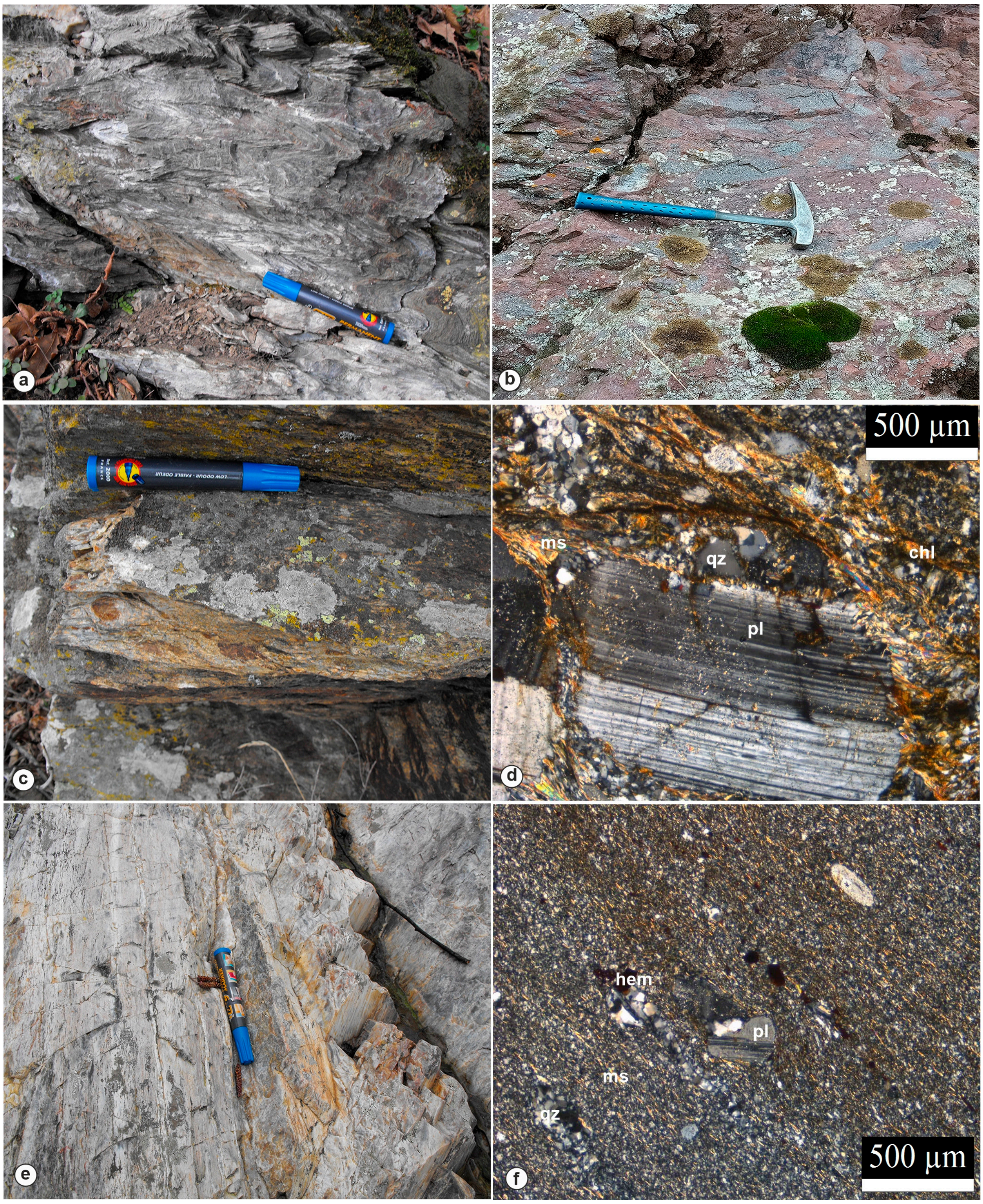

Figure 4. Field photographs and microphotographs of the studied metamorphic and non-metamorphic rock samples of the Sredogriv metamorphics and its immediate sedimentary cover: (**a**) field aspect of folded quartz-chlorite-sericite schist; (**b**) field aspect of breccia-conglomerate sample L15; (**c**) field aspect of metaconglomerate sample L4; (**d**) a microphotograph of sample L4; (**e**) field aspect of metaalbitophyre sample

L1a; (**f**) a microphotograph of sample L1a. Mineral abbreviations: qz, quartz; pl, plagioclase; chl, chlorite; ms, muscovite (sericite); hem, hematite.

3. Materials and Methods

Our investigation focuses on key metamagmatic body and metaclastic rock horizon of the Sredogriv metamorphics and the first sedimentary cover of unconformably overlying Smolyanovtsi Formation built of clastic rocks. The sample numbers mentioned below refer to those shown in Figures 2 and 3. These samples were used for U-Pb zircon geochronology.

A single sample L4 (N43°52945° E22°80330°) is collected from a metaconglomerate from the Sredogriv low-grade metamorphics, which form discontinuous distinct horizon of variable thickness. This polymictic metaconglomerate consists of quartz, gneiss, phyllite, schist, granitoid clasts that range in size from 2 to 6 cm, all set in a medium- to coarse-grained supporting matrix of similar compositon to that of the clasts (Figure 4c). The metaconglomerate demonstrates a well-developed greenschist facies foliation delineated by chlorite-muscovite (sericite) aggregates and recrystallized quartz grains (Figure 4d).

Another sample L1a (N43°533514° E22°784586°) from the Sredogriv low-grade metamorphics comes from a felsic sill-like and foliation parallel metaigneous body reaching thickness up to 20 m that is intercalated within the metamorphic succession (Figure 4e). In thin section, this felsic body represent metaalbitophyre consisting of plagioclase and quartz phenocrysts set in a fine-grained recrystallized groundmass that contains foliation-delineating quartz and sericite, together with altered magnetite to hematite (Figure 4f).

Sample L15 (N43°534928° E22°850475°) is collected from a red-brown clast-supported breccia-conglomerate that belongs to the inferred Lower Permian in age Smolyanovtsi Formation from the first unconformable sedimentary cover of the Sredogriv metamorphics (see Figure 3). The clast-supported breccia-conglomerate consists of quartz, gneiss, phyllite, schist, granitoid and mostly of angular volcanic clasts that range in size up to 20 cm, all set in a coarse-grained matrix of similar compositon to that of the clasts (Figure 4b).

For U-Pb dating zircons were recovered from jaw crushed and milled rock samples using a Wilfley shaker table, followed by magnetic and heavy liquid ($CHBr_3$ and CH_2I_2) separation at the Geological Institute of the Bulgarian Academy of Sciences. Zircon grains were hand-picked under binocular microscope and thermally annealed at 900° C for 48 h in a muffle and afterwards mounted in epoxy resin and polished. Optical cathodoluminescence (CL) imaging was carried out for identifying inherited cores, cracks and inclusions inside the crystals using motorized optical system Cathodyne NewTec Scientific attached to microscope Leica 2700 at the Geological Institute of the Bulgarian Academy of Sciences. U-Pb in-situ zircon dating was performed at the laser ablation mass-spectrometry (LA-ICP-MS) laboratory of the Geological Institute using a New Wave UP193FX LA coupled to a Perkin Elmer ELAN DRC-e quadrupole ICP-MS. Ablation parameters were set up to diameter of 35 μm, frequency of 8 Hz and detection time within 0.002-0.003 s. Analyses were calibrated with the GEMOC-GJ1 zircon [43] as an external standard for fractionation correction. Plešovice [44] and 91500 [45] zircons were used as unknowns and used to correct systematic errors. Data reduction was processed using Iolite v. 2.5 [46], applying down-hole fractionation correction. Diagram plots and concordia ages were obtained using Isoplot 4.15 [47]. Analytical data derived from the U-Pb zircon geochronology are provided in Table S1 of the Supplementary material.

The Sredogiv metamorphites were sampled with a few samples including metaconglomerate, quartz-chlorite, sericite-chlorite and black schists. The selected for whole-rock geochemistry five samples were crushed to a fine powder following standard procedures. Whole-rock major element analyses by X-ray fluorescence (XRF) were performed on PANalytical (EDXRF, Epsilon 3XLE, Omnian 3SW) instrument at the University of Sofia St. Kliment Ohridski, Bulgaria. XRF analyses were conducted on fused beads of powdered material from the samples of mafic rocks. The fused beads were prepared by mixing approximately 1 g of sample with 3 g of lithium metaborate ($LiBO_2$) and 6 g of lithium tetraborate ($Li_2B_4O_7$) flux. The melting process was realized using a Claisse LeNeo Fused

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Bead maker, in 5% Au–95% Pt casting bowls at 1065 °C. The loss of ignition (LOI) at 1000 ºC was expressed as a percentage of sample weight dried in an oven at 110 ºC overnight. Analytical errors for major oxides are within the range of 1%. The trace elements and the rare-earth elements (REE) were measured in fused beads using LA-ICP-MS at the Geological Institute of the Bulgarian Academy of Sciences, using the whole-rock SiO_2 content as an internal standard and NIST 610 as an external standard. Whole-rock chemical analyses are given in Table S2 of the Supplementary material.

4. Results

4.1. U-Pb Geochronology

The dated zircons in the metaconglomerate sample L4 vary in size from 150 μm to 350 μm, with an average aspect ratio of 2. They display semi-rounded shapes and preserved mostly oscillatory- and rarely sector zoning patterns, which both are characteristic for a magmatic origin (Figure 5a).

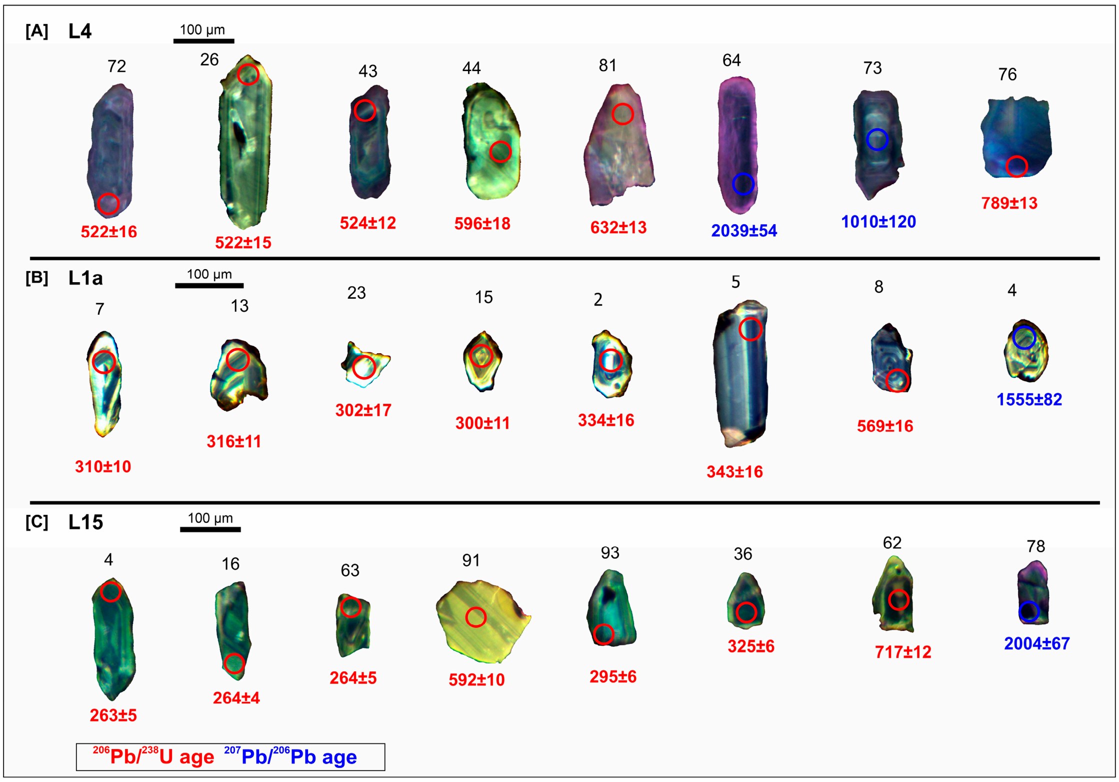

Figure 5. Selected cathodeluminescence images of dated zircons in the studied samples: (**a**) sample L4; (**b**) sample L1a; (**c**) sample L15.

In sample L4, the $^{206}Pb/^{238}U$ ages obtained from 105 analyses range from 1996 Ma to 516 Ma (Figure 6a, Table S1). From seventy-seven concordant zircons a series of clusters were established with different density and various ages. The main age cluster of twenty-three zircons yielded a concordia age of 597.1±3.3 Ma, followed by a cluster of seventeen zircons that gave a concordia age of 587.5±3.5 Ma, and a cluster of fourteen zircons with a concordia age of 640.8±5.8 Ma (Figure 6a). Eight concordant zircons cluster at 555.5±0.36 Ma, five concordant zircons cluster at 611.3±4.7 Ma and three concordant zircon cluster at 624.6±6.2 Ma. Two zircon pairs gave concordant ages, respectively, at 687±49 Ma and at 1996±12 Ma. Single zircons yielded concordant ages at 944±21 Ma and at 791±12 Ma. The five youngest concordant zircons provided an age of 523±6.5 Ma, and hence, define an early Cambrian maximum depositional age (Figure 6a). The Th/U ratios of the dated zircons of this sample range from 0.14 to 1.77, which is typical for magmatic zircons [e.g. 48,49].

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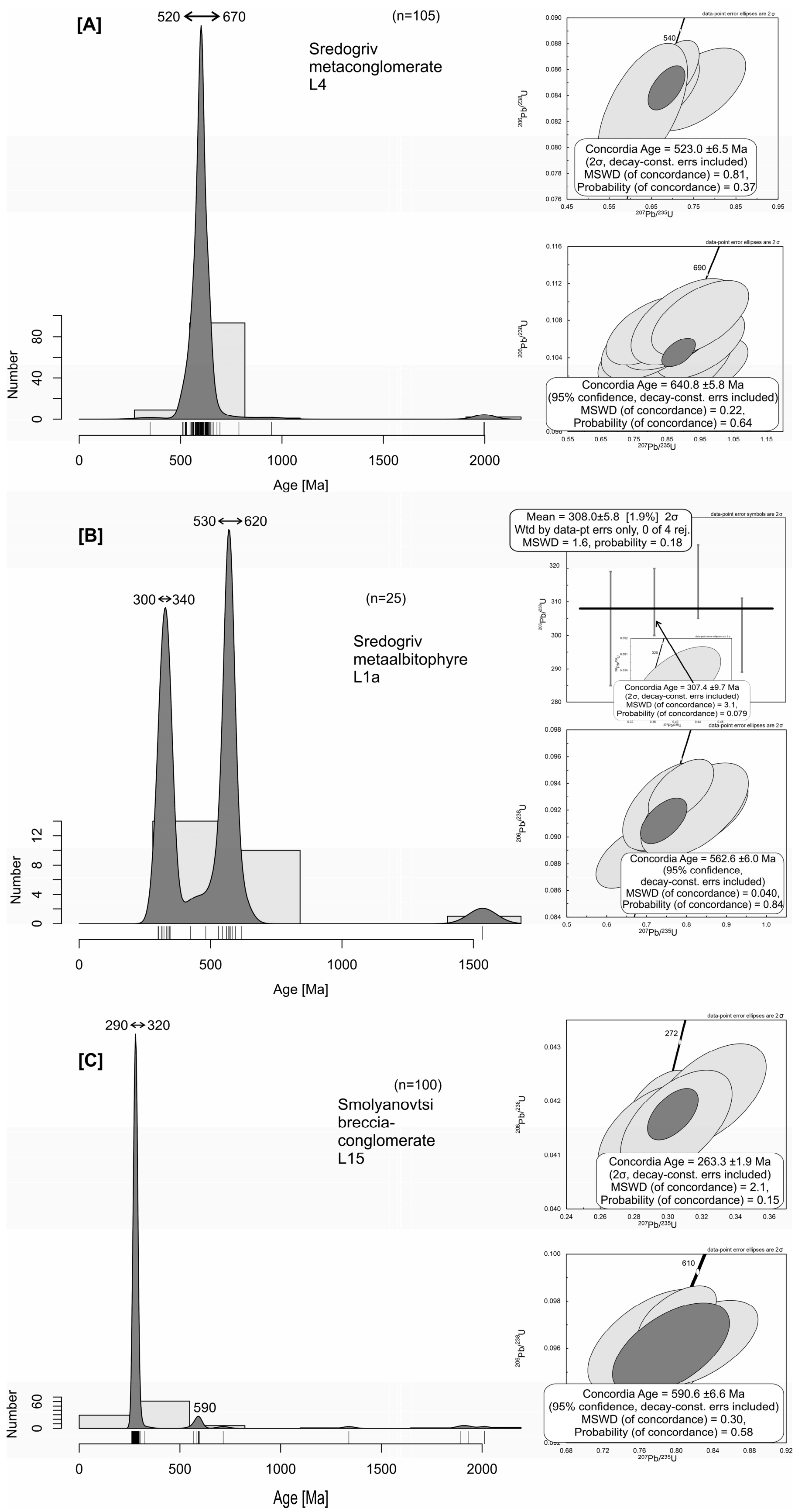

Figure 6. Diagrams of U-Pb zircon analyses of the dated samples: (**a**) Kernel Density Estimation (KDE) and concordia diagrams of zircons from sample L4; (**b**) KDE and concordia diagrams of zircons from sample L1a; (**c**) KDE and concordia diagrams of zircons from sample L15.

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Zircons from the metaalbitophyre sample L1a show mainly prismatic and rarely pyramidal crystals varying in size from 70 μm to 250 μm, which have magmatic oscillatory- and sector zoning patterns (Figure 5b). In sample L1a, the $^{206}Pb/^{238}U$ ages obtained from 25 analyses range from 1532 Ma to 302 Ma (Figure 6b, Table S1). Four youngest zircons yielded a weighted mean age of 308±5.8 Ma (Figure 6b). One out of all four is concordant at 307.4±9.7 Ma confirming the weighted mean age of the youngest population, which is interpreted to date magmatic crystallization of the albitophyre. Inherited zircons gave concordant ages, respectively, at 562.6±6.0 Ma by seven grains (Figure 6b), and single zircon crystals are concordant at 337.5±3.7 Ma, 479±16 Ma, 529±13 Ma, 619±6.0 Ma and 1532±22 Ma (see Table S1). The Th/U ratios of the dated concordant zircons of sample L1a range from 0.36 to 1.22, which is typical for magmatic zircons.

The dated zircons in breccia-conglomerate sample L15 vary in size from 80 μm to 300 μm. They display semi-rounded shapes and preserved mostly oscillatory-zoned pattern, which is characteristic for a magmatic origin (Figure 5c). In this sample, the $^{206}Pb/^{238}U$ ages obtained from 100 analyses range from 2009 Ma to 261 Ma (Figure 6c). From eighty-three concordant zircons, a series of clusters were established with different density and various ages. The main age cluster of twenty zircons yielded a concordia age of 279.5±1.5 Ma, followed by a cluster of thirteen zircons that gave a concordia age of 285±1.6 Ma, and a cluster of twelve zircons with a concordia age of 271.5±1.6 Ma. Eleven concordant zircons cluster at 292.5±1.7 Ma, seven concordant zircons cluster at 267.4±1.8 Ma, five concordant zircons cluster at 264±2.5 Ma, four concordant zircons cluster at 590.6±6.6 Ma (Figure 6c) and three concordant zircons cluster at 276.1±2.6 Ma. Single zircons yielded concordant ages at 2009±25 Ma, at 720±12 Ma and at 323.5±5.8 Ma (see Table S1). The five youngest concordant zircons delivered an age of 263.3±1.9 Ma, and hence, define a latest middle Permian maximum depositional age (Figure 6c). The Th/U ratios of the dated zircons in this sample range from 0.23 to 0.96 testifying to a magmatic origin.

4.2. Whole-Rock Geochemistry

The selected five samples for whole-rock geochemistry represent different types of clastic metasedimentary rocks that include metaconglomerate, metasandstone, metaleurolite and phyllite.

The content of major oxides SiO_2 (55.36 – 73.27 wt%), Al_2O_3 (13.12 – 24.03 wt%), and $Fe_2O_3^t$ (2.66 – 6.57 wt%), MgO (0.64 – 2.28 wt%) is similar to the average upper continental crust composition of Taylor and MacLennan [50]. The higher value of Na_2O/Al_2O (0.06 – 0.34) compared to K_2O/Al_2O_3 (0.07 – 0.19) confirms the plagioclase predominance over the K-feldspar. The strong negative correlation between SiO_2 and Al_2O_3 (-0.98), and the contents of TiO_2 (-0.93) and $Fe_2O_3^t$ (-0.82) could be related to quartz predominance and sorting of the precursory sedimentary rocks. The major minerals (muscovite, chlorite, and plagioclase) induce a pronounced positive dependence between the oxides of Al with K (0.70) and Fe^t (0.71). The logarithmic values of SiO_2/Al_2O_3 and Na_2O/K_2O on the classification diagram [after 51] comprise greywacke protolith composition (Figure 7a).

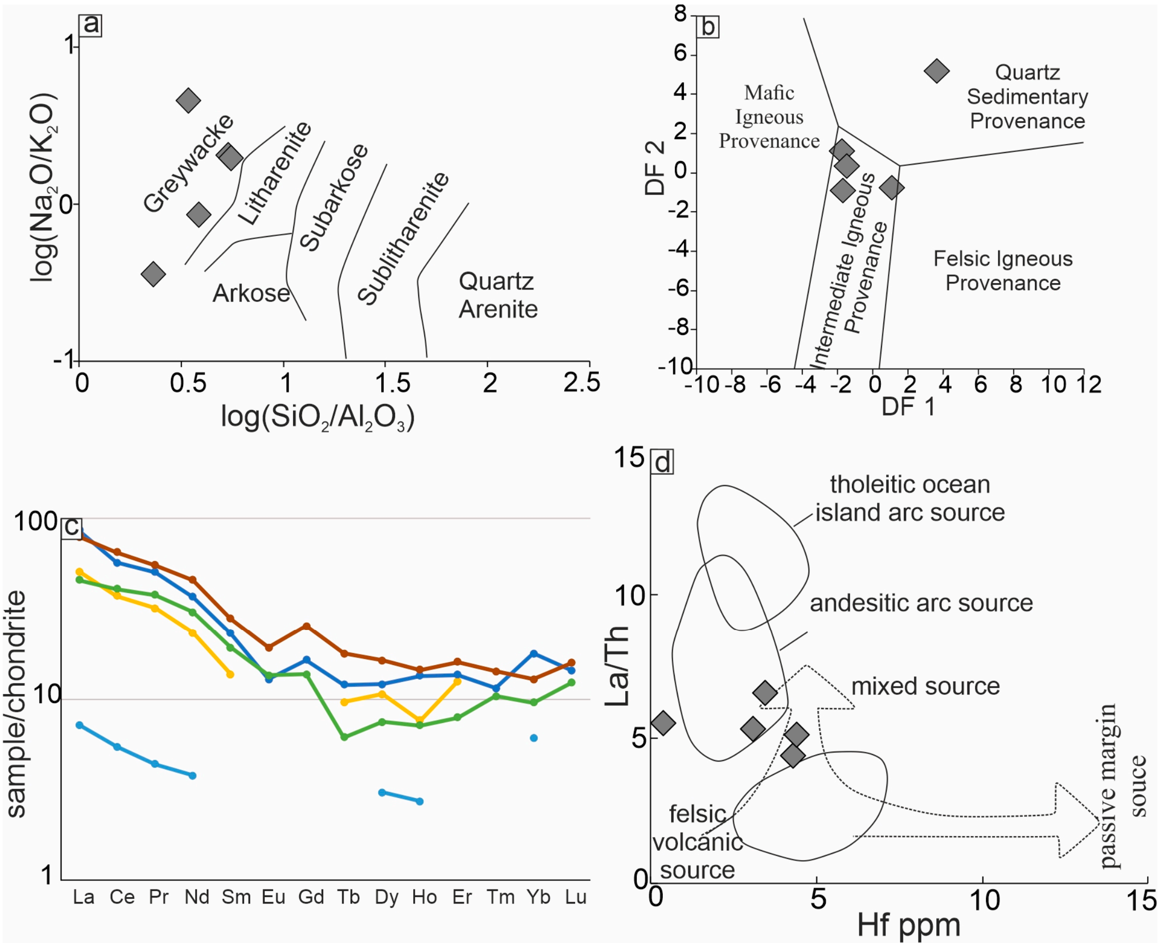

Figure 7. (**a**) log SiO_2/Al_2O_3 vs. Na_2O/K_2O classification diagram [after 51]; (**b**) Discriminant function diagram [after 52] of major elements for evaluating the provenance; (**c**) chondrite-normalized REE diagram (chondrite values after [50]); (**d**) La/Th vs. Hf diagram to discriminate the source rocks [after 53].

The dominance of intermediate igneous input is determined by discrimination functions (DF) used by the diagram of Roser and Korsch [52] (Figure 7b). The moderate degree of alteration corresponds to the Chemical Index of Alteration (CIA = 69 – 80, [after 54]).

The trace elements could clarify the provenance origin, depositional settings, and heavy sorting because of their low mobility during diagenesis and metamorphism. Most of them (e.g. V, Rb, Ta, U, Th, and REE) are incorporated into rock-forming minerals (micas) evidenced by positive correlation with major oxides (Al_2O_3, Fe_2O_3, K_2O, and MgO). The Th/Sc (0.24 – 0.43) and Zr/Sc (6.65 – 12.98) ratios indicate compositional variation consistent with the upper continental crust [55]. The chondrite-normalized REE patterns (Figure 7c) confirm continental crust composition with light REE enrichment (La_N/Sm_N = 2.37 – 3.71) and heavy REE depletion (Gd_N/Lu_N = 1.11 – 1.60) and negative Eu-anomaly (0.66 – 0.83). In the La/Th vs. Hf classification diagram [53] based on the composition of low-mobility elements (La, Th, Hf) assigns a predominance of andesitic arc source (La/Th ~ 5, Hf < 5 ppm, Figure 7d). The high-field strength elements (HFSE) (La, Th, Sc, Zr, Ti) used for discrimination of the tectonic regimes [56] suggest continental island arc tectonic setting.

5. Discussion

The Sredogriv metaconglomerate has an early Cambrian maximum depositional age of 523 Ma. The high Th/U ratios of the detrital zircons reflect a magmatic source, and the documented predominant age clusters of detrital zircons testify for the similar age as the detrital zircon age of 563 Ma for the Cherni Vrah gabbro from the Berkovitsa Group [27] and the age of 618 Ma for the

 doi:10.20944/preprints202503.0840.v1

Protopopintsi metagranite [39]. The latter is not hosted by the Sredogriv sedimentary succession, but underlies this succession, and the Protopopintsi metagranite obviously supplied detrital crustal material for the sedimentation of the future Sredogriv siliciclastic succession. This interpretation is further supported by the U-Pb zircon ages of nearby volcanic arc affinity Neoproterozoic gneisses ca. 651-601 Ma hosting 517 Ma-old felsic intrusion [8] in the Stakevtsi metamorphic complex located immediately southwest of the study area, which complex belongs to the Berkovitsa Group of the Vratsa unit (see Figure 2 for the location). Proximity to volcanic arc edifice of the basin that accumulated the Sredogriv sedimentary rocks is indicated by established tuffaceous material in the upper part of the succession [35] that resulted in omnipresent chlorite within this succession (see Figure 4a), as well as substantiated by the geochemical data of the metasedimentary rocks.

The Ediacaran-Early Cambrian major age cluster of detrital zircons (670-520 Ma), together with a single Cryogenian (791 Ma) and Thonian (944 Ma) zircons, and the two Paleoproterozoic (1996 Ma) in the Sredogriv metaconglomerate (Figure 6a), are indistinguishable from the reported detrital zircon age clusters at 496 Ma, 519 Ma, 533 Ma, 568 Ma, 577 Ma, 586 Ma, 601 Ma, 630 Ma, 1.9 Ga and 2.0 Ga in the clastic metasedimentary rocks from the Berkovitsa Group and the Diabase-Phylitoid complex [4]. Moreover, the maximum depositional age of the Sredogriv metaconglomerate is very close or even indistinguishable from the maximum depositional ages of 521±5 Ma and 494±5 Ma of tuffitic metasiltstone and metasandstone of the Berkovitsa Group, respectively, and the maximum depositional age of 510±6 Ma of a metaconglomerate in the Diabase-Phyllitoid complex [4]. Based on statistical analysis of the detrital zircons from the Moesian and Balkan terranes and other Avalonian-Cadomian terranes worldwide Žák et al. [4] defined a provenance of the detrital sedimentary material from trans-Saharan belt and/or Saharan metacraton igneous sources at the northern periphery of Gondwana for the Berkovitsa Group and Diabase-Phyllitoid complex, and for other units in the western and central Balkan zone i.e. the Balkan terrane. These igneous sources and provenance area fully correspond to those recovered by the detrital zircons in the Sredogriv siliciclastic rocks.

To sum up, the Sredogriv siliciclastic rocks were deposited in a basin proximal (e.g. fore-arc/back-arc) to Cadomian arc system (Berkovitsa island arc sensu [25]) during the early Cambrian, where they received rather unimodal major Ediacaran-Early Cambrian crustal material input from adjacent igneous sources at the northern periphery of Gondwana. We therefore correlate the Sredogriv metasiliciclastic rocks with the sedimentary section of the Berkovitsa Group based on their lithologic context and Early Cambrian depositional age.

The Sredogriv metaalbitophyre demonstrates magmatic crystallization in Late Carboniferous around 308 Ma, when it emplaced into the Sredogriv sedimentary succession, and this igneous age is fully comparable to the ages of many others Late Carboniferous magmatic bodies known in the Western Balkan Zone [e.g. 7,13 and references therein]. In this sense, the metaalbitophyre represents a manifestation of the region-wide Late Carboniferous magmatism linked to the late Variscan tectono-magmatic evolution recorded in this zone. The inherited Ediacaran-Early Cambrian zircons (620-530 Ma, Figure 6b) in the metaalbitophyre are obviously xenocrysts sampled “en route” to the surface from the host Sredogriv sedimentary succession that demonstrates the same major Ediacaran-Early Cambrian detrital zircon age cluster. The inherited in the metaalbitophyre Mesoproterozoic zircons that cluster at 1.5 Ga might well correspond to the reported by Žák et al. [8] zircon peaks at 1.5 Ga and 1.6 Ga in the Ediacaran gneisses of the Stakevtsi Massif.

In turn, the Smolyanovtsi Formation has a latest middle Permian maximum depositional age of 263 Ma as derived from the conglomerate sample L15. This unconformably lying formation contains well-defined crustal components from a Paleo- to Neoproterozoic magmatic sources, the Early Cambrian Sredogriv metasiliciclastic rocks, as well as a detrital material from the Late Carboniferous to Middle Permian intrusive and extrusive bodies well-known in the region and the Western Balkan Zone as a whole (see Figure 3). Thus, the red beds of the Smolyanovtsi Formation recycled the crustal material from all underlying units and unequivocally support their detrital and magmatic crystallization zircon age determinations.

 doi:10.20944/preprints202503.0840.v1

The stratigraphic position and the maximum depositional age of the Smolyanovtsi Formation clearly define the upper age limit of the greenschist facies metamorphism and associated deformation experienced by the Sredogriv metamorphics as pre-middle Permian ca. 263 Ma. On the other side, the magmatic crystallization age of the Sredogriv metaalbitophyre unequvocally provides the lower age limit of the greenschist facies metamorphism and deformation postdating intrusion at 308 Ma. However, the inferred Late Carboniferous in age Zelenigrad Formation of the Belogradchik unit demonstrates a maximum depositional age of 272 Ma and recycles the crustal material of the same Neoproterozoic-Cambrian and Carboniferous and Permian igneous sources [57, see Figure 3]. These newly obtained U-Pb zircon age constraints imply that the greenschist facies metamorphism and associated deformation experienced by the Sredogriv metamorphics is temporarily bracketed between 308 Ma and 272 Ma. This ca. 36 Ma-lasting time interval corresponds to the Late Carboniferous-Early Permian tectono-metamorphic phase of the late Variscan orogeny, which is well-known in the Variscan belt of Western and Central Europe [e.g. 58-63] and to the east in the Black Sea region [64,65]. This Late Carboniferous-Early Permian tectono-metamorphic time interval recorded by the Sredogriv metamorphics adds a new insight into the Variscan collisional evolution and the accretion of the Balkan terrane to the Moesian terrane as suggested by several authors [3,4,10,25,64].

6. Conclusions

Our study allows us to draw the following conclusions regarding the sedimentary and magmatic history and tectono-metamorphic evolution of the Sredogriv low-grade metamorphics as an important crustal element that forms part of the crystalline basement of the Western Balkan Zone.

1. The sedimentation of the Sredogriv siliciclastic succession took place in Early Cambrian around ca. 523 Ma when crustal materials were recycled from limited Paleoproterozoic, and mostly Neoproterozoic-Early Cambrian igneous sources from located nearby volcanic arc, which have a provenance from the Saharan Metacraton at the northern periphery of Gondwana. In terms of the lithology and depositional age, the Sredogriv sedimentary succession can be correlated to the sedimentary section of the Neoproterozoic-Early Cambrian (Cadomian) island arc system of the Berkovitsa Group in the Western Balkan Zone.

2. Intrusion of acidic sill of metaalbitophyre in the Sredogriv sedimentary succession occurred in Late Carboniferous at 308 Ma, as well as the magmatic emplacement of the mafic dykes in this succession possibly occurred at the same time. The metaalbitophyre represents a manifestation of Late Carboniferous magmatism in the Western Balkan Zone. The inherited Neoproterozic-Cambrian zircons recovered in the metaalbitophyre are sampled from the Sredogriv sedimentary succession. The magmatic crystallization age of the albitophyre provides a lower age limit for the greenschist facies metamorphism of the Sredogriv metamorphics.

3. The first unconformable clastic sedimentary cover onto the Sredogriv metamorphics of the Smolyanovtsi Formation deposited in latest middle Permian at 263 Ma. The Smolyanovtsi Formation recycled the crustal material from the underlying Sredogriv metasiliciclastic rocks, Late Carboniferous albitophyre, and the regionally present Late Carboniferous-Middle Permian plutonic and volcanic bodies as derived from the contained detrital zircon populations. The depositional age of the Smolyanovtsi Formation provides an upper age limit for the greenschist facies metamorphism of the Sredogriv siliciclastic rocks.

4. The deposition of the unconformable clastic rocks of the immediately adjacent Zelenigrad Formation at 272 Ma, in turn, further makes lower the upper age limit of the greenschist facies metamorphism of the Sredogriv metasiliciclastic rocks. Thus, the greenschist facies metamorphism of the Sredogriv metamorphics is bracketed between 308 Ma and 272 Ma. This metamorphism spans the late phase of the Variscan tectono-metamorphic evolution, and the obtained age data represent the first evidence for the timing of the Variscan low-grade metamorphism in the Western Balkan Zone.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Table S1: U-Pb LA-ICP-MS zircon analyses of the dated samples; Table S2: Whole-rock geochemistry data table.

Author Contributions: Conceptualization, visualization, investigation, validation, writing—original draft preparation N.B.; funding acquisition, formal analysis, visualization, data curation, P.F.; formal analysis, T.V., H.G. and T.S.; writing—review and editing, S.G. and H.K.; investigation, L.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by NATIONAL SCIENCE FUND, BULGARIA, grant number KP-06-N74/4.

Data Availability Statement: The data collected during the field work are available on request from the first author.

Conflicts of Interest: The authors declare no conflicts of interest.

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